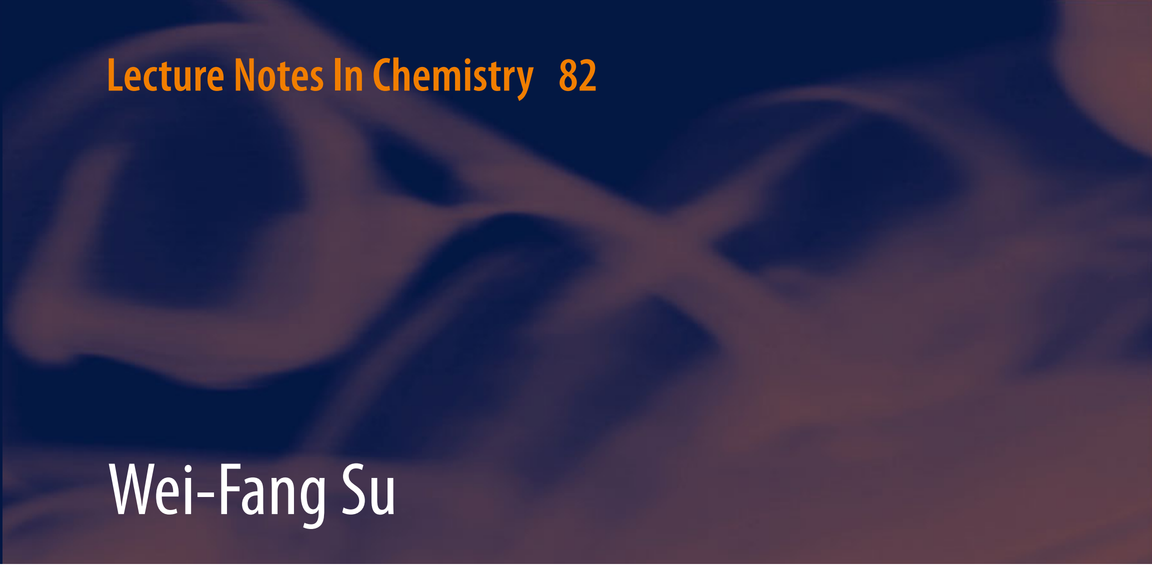
Lecture Notes In Chemistry 82



Wei-Fang Su

Principles of Polymer Design and Synthesis

Springer

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Volume 82

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Wei-Fang Su

Principles of Polymer Design and Synthesis

Springer

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Foreword

While the ubiquity of polymers might imply that this field forms a significant portion of undergraduate and graduate courses, students typically leave their studies with only rudimentary knowledge of this important subject. This is perhaps particularly surprising given that many of these new graduates will enter careers in the consumer goods, pharmaceutical, materials, electronics, or other industries where polymers hold the key to the performance of the final product. With this in mind, it is critical that we better prepare our students for their ultimate careers. For this reason, Principles of Polymer Design and Synthesis is a welcome addition to the toolkit for young scientists and engineers, providing a solid base for learning about the incredible influence of polymers to modern life. The logical format of the book and its combination of breadth and depth will also allow it to serve as a very useful text for established professionals who are entering the broad field of polymer chemistry or researchers who want to freshen up their knowledge with some of the latest directions in polymer design and synthesis.

The book introduces polymers to chemists, material scientists, and engineers with no prior experience of the area in a straightforward, rigorous, and logical manner. Intended for students who have completed undergraduate courses in organic and physical chemistry, the chapters cover the properties, synthesis, and characterization of polymeric materials. Readers will gain an appreciation for the diversity of polymers with examples ranging from natural proteins, rubber, and cellulose to the huge variety of synthetic materials that are used to produce fibers, plastics, and elastomers.

The aim is to equip scientists and engineers with a deeper understanding of how the structure of polymers dictates their function and potential applications—whether that may be in cheap polyethylene bags or sophisticated light emitting materials for flexible displays. Not only will readers learn how to synthesize common polymers, they will also gather greater knowledge of the principles for designing materials and an appreciation for the state of the art. The value in Principles of Polymer Design and Synthesis is in giving students and researchers a flavor of the breadth of polymer science and inspiring them to delve deeper into the field and develop materials for the next great advances to impact our lives.

Craig J. Hawker

Preface

Synthetic polymers are vital materials used in modern daily life from packaging, electronics, medical devices, clothing, vehicles, buildings, etc. How can a scientist or engineer synthesize and utilize polymers to solve the problems of daily life? This is the objective of this textbook to provide students with fundamental knowledge in the design and synthesis of polymers to achieve specific properties required in the applications. To have the ability to design a polymer, one has to understand the chemical structure effects on the physical and chemical characteristics of polymer first. Therefore, in this book, the first five chapters discuss the properties and characterization of polymers. Then, six chapters are followed to discuss the principles of polymerization reactions including step, radical chain, ionic chain, chain copolymerization, coordination, and ring opening. They cover the descriptions of how commonly known polymers are synthesized.

This book is intended as an introductory textbook for one semester course in polymer chemistry or polymer synthesis at the advanced undergraduate or beginning graduate level of students in chemistry, chemical engineering, and material science and engineering with no prior training in polymer. The students who uses this book should have completed undergraduate courses in organic chemistry and physical chemistry. After going through the lectures or reading the text of this book, they will have the capability to synthesize common known polymers and comprehend the advanced polymerization reactions reported in the literature to further design and synthesize new polymers.

Finally, I would like to thank the encouragement and patience obtained from my husband Cheng-Hong Su during the course of this work and the inspiration, chemical formula drawing, and proof reading from my students Chun-Chih Ho, Shih-Hsiang Lin, Tzu-Chia Huang, Shang-jung Wu, Shih-Chieh Wang, Jhin-Fong Lin, and Hsueh-Chung Liao. Thanks are also due to typing and organization of the manuscript done by Shiow-Wei Wang and drawing of figures done by Yin-Hsi Lin.

Contents

Chapter 1
Introduction

Synthetic polymers [1] are vital materials used in modern daily life from packaging, electronics, medical devices, clothing, vehicles, buildings, etc., due to their ease of processing and light weight. The first synthetic polymer, a phenol-formaldehyde resin, was invented in the early 1900s by Leo Baekeland [2]. It was a commercial success invention although most of scientists had no clear concept of polymer structure at that time. Wallace Carothers invented very important polymers of neoprene rubber and Nylon in 1930s which shaped the leadership of DuPont in polymer industry. Hermann Staudinger developed theoretical explanations of remarkable properties of polymers by ordinary intermolecular forces between molecules of very high molecular weight. He was awarded the Nobel Prize in Chemistry in 1953 for this outstanding contribution. World War II led to significant advances in polymer chemistry with the development of synthetic rubber as natural rubber was not accessible to the Allies. Karl Ziegler and Giulio Natta won the Nobel Prize in Chemistry in 1963, jointly for the development of coordination polymerization to have controlled stereochemistry of polymers using coordination catalysts. Their work has revolutionized the polymer industry to synthesize stereoregular polymers that have mechanical properties superior than that of non-stereoregular polymers. Equally significant work was done by Paul Flory 1974, Nobel laureate on the quantitative investigations of polymer behaviors in solution or in bulk.

Most of polymers are insulators, so they have passive functions and used as a bulk material for structure or as thin layer for coating barrier. In 1977, Alan Heeger, Alan MacDiarmid, and Hideki Shirakawa reported high conductivity in iodine-doped polyacetylene. This research earned them the 2000 Nobel Prize in Chemistry. Since then, the application of polymer has expanded into active functional area such as light emitting diode, sensor, solar cell, etc. Polymers can be tailor made to meet the requirements of specific application through molecular design and synthesis. Therefore, they have become the material of choice to face the ever fast changing world from electronics to medical applications.

The physical properties of polymers are mainly determined by their chemical structures. Chemical structures of polymers affect their flow and morphology that results in different physical properties. The processability of polymers is controlled

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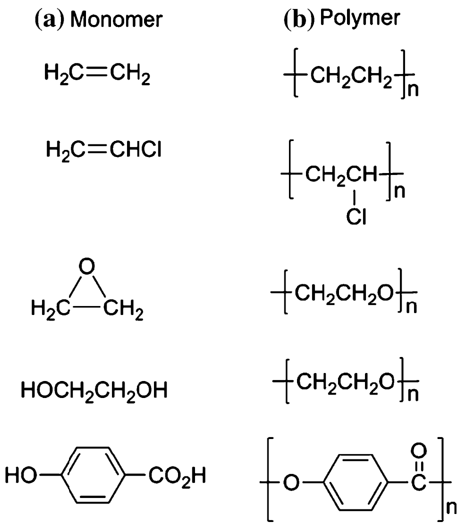


Fig. 1.1 Chemical structures of (**a**) monomers and (**b**) their corresponding polymers

by their flow characteristics in neat form or in solution which affects by their molecular weight.

Polymers are built up by linking together of large number of “monomers.” Monomers are small molecules with functional groups (organic compounds) and they can react with each other to form a large molecule. Figure 1.1 shows some commonly used polymers with their chemical structures of monomers and their corresponding polymers. The polymers have to have molecular weight larger than 10,000 to exhibit good mechanical properties for structural use. Oligomer is a molecule that has molecular weight between 1,000 and 10,000. The oligomer has been widely used in coating applications. End group is the chemical structure at the end of the polymer chains. When the polymer is ended with a functional group, such as $CH_3CH_2–[CH_2CH_2]_n–CH=CH_2$, the polymer is called telechelic polymer. In the same way, reactive oligomer is oligomer that contains end groups and capable to undergo polymerization.

The size of polymer is determined by the degree of polymerization (DP). It is a total number of structural units, including end groups, and is related to both chain length and molecular weight. For example, the molecular weight of polymethacrylate with DP = 500 is 500 multiplying by 74 (weight of unit) = 37,000. Because polymer chains within a given polymer sample are always of varying lengths, we need to use average value, such as number-average molecular weight ($\bar{M}_n$), weight-average molecular weight ($\bar{M}_w$), etc. The molecular weight distribution (PDI) is defined as dividing $\bar{M}_w$ over $\bar{M}_n$.

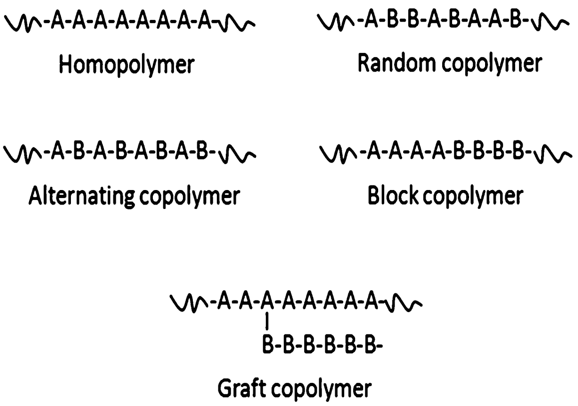


Fig. 1.2 Possible arrangements of repeating units to form different type polymers

1.1 Types of Polymers

There are many different types of polymers that can be differentiated from the arrangement of repeating units, and the different arrangements of molecular segment [3]. A polymer prepared from one kind of monomer is called homopolymer. A polymer prepared from more than one kind of monomer is called copolymer, including random copolymer, alternating copolymer, block copolymer, and graft copolymer (Fig. 1.2). These homopolymer and copolymers also can be prepared into polymers with different arrangement of molecular segment, such as star polymer, comb polymer, ladder polymer, dendrimer, and so on. (Fig. 1.3).

1.2 Types of Polymerization

The types of polymerizations are generally classified into chain polymerization and step polymerization according to chemical reactions in the polymerization [4]. The molecular weight of polymers can be built either gradually by step reactions or simultaneously by chain reaction depending on the chemical structure of the monomer. For the step polymerization, the monomers need to have bifunctional groups to link 1 molecule at one time. If the bifunctional groups are the same such as ethylene glycol ($OH–CH_2CH_2–OH$), one will need different type of bifunctional monomer such as terephthalic acid ($COOH–C_6H_4–COOH$) to synthesize polyester $[–CH_2–CH_2–O–C(=O)C_6H_4C(=O)O–]_n$ at relative high temperature to remove water. This type of polymerization is also called polycondensation polymerization due to the loss of molecule during the polymerization.

The monomers containing double bond can be polymerized by chain reaction. The polymerization proceeds by three steps of initiation, propagation, and termination. Depending on the type of initiation, the chain polymerization can be classified into free radical chain polymerization, ionic chain polymerization, and

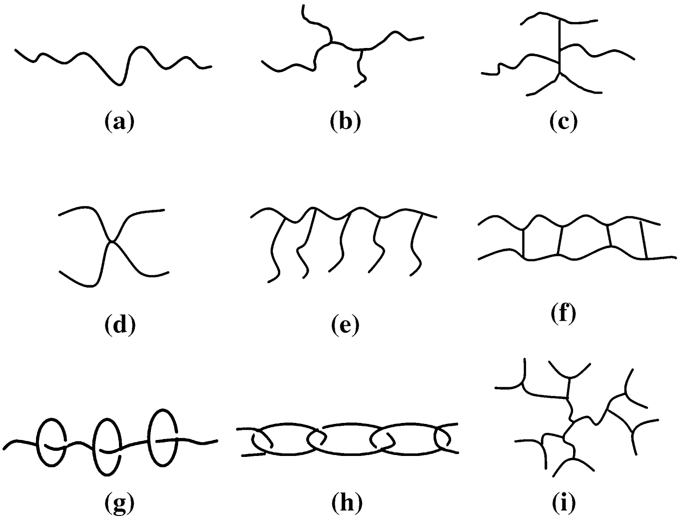


Fig. 1.3 Possible arrangements of molecular segment to form different type polymers: (**a**) linear polymer, (**b**) branched polymer, (**c**) crosslinked polymer, (**d**) star polymer, (**e**) comb polymer, (**f**) ladder polymer, (**g**) polyrotaxane, (**h**) polycatenane, (**i**) dendrimer

coordinating chain polymerization. Their principles will be addressed in the subsequent chapters. Copolymers are made from more than one kind of monomer to meet balanced properties required in many different applications. The differences in the reactivity of different monomer and growing polymer chain need to be considered in the synthesis of copolymer. We will also discuss this subject in the later chapter.

Ring opening polymerization has been extensively used in synthesis of polyether, polyamide, polysiloxane, and the curing of the epoxy resin. The reaction mechanism of ring opening polymerization is unique in its own way which shows a combination behavior of step polymerization and chain polymerization. The detailed reaction mechanism will be present in the last chapter of this book.

1.3 Nomenclature of Polymers

The nomenclature of polymers [1, 3] is usually based on the source of monomer, for example, poly(vinyl chloride) $–(CH_2CHCl)_n–$ is made from vinyl chloride monomer, and poly(ε-caprolacton) $–[NH–CO–(CH_2)_5]_n–$, that is the same as poly (6-aminocaproic acid), is made from ε-caprolacton. Many polymers commonly are named basis on their structures such as poly (hexamethylene sebacamide) $–[HN–(CH_2)_6–NHCO–(CH_2)_8–CO]_n–$, poly(ethylene terephthalate) $–[O–CH_2CH_2–O–CO–C_6H_5–CO]_n–$, and poly(trimethylene ethylene urethane) $–[O–CH_2CH_2CH_2–O–CO–NH–CH_2–CH_2–NH–CO]_n–$.

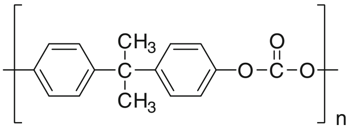
Table 1.1 Comparison between common name and IUPAC name of polymers

Structure	Common name	IUPAC name
$–(CH_2–CH_2)–$	polyethylene	poly(methylene)
$–(CH(CH_3)–CH_2)–$	polypropylene	poly(propylene)
$–(CH(C_6H_5)–CH_2)–$	polystyrene	poly(1-phenyl ethylene)

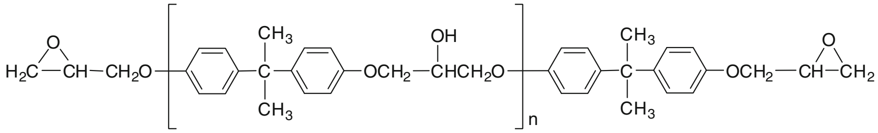
The International Union of Pure and Applied Chemistry (IUPAC) polymer nomenclature system is a more systematic approach. The basis of the IUPAC polymer nomenclature system is the selection of a preferred CRU (constitutional repeating unit), i.e., structural repeating unit, as tabulated in Table 1.1. The name is made according to the seniority among the atoms or subunits making up the CRU. The steps including (1) CRU is identified, (2) substituent groups on the backbone are assigned the lowest possible number, and (3) the name is placed in parentheses and prefixed with *poly*.

For the copolymers, they are named according to the arrangements of the repeating units in copolymers. For example, for a copolymer that consists of polystyrene and poly(methyl methacrylate), this copolymer can be abbreviated as either poly[styrene-co-(methyl methacrylate)] or copoly(styrene/methyl methacrylate). For an alternating copolymer, an abbreviation of *alt* can be placed between these two homopolymers, as poly[styrene-alt-(methyl methacrylate)]. Therefore, the *alt* is replaced by *block* and *graft* that can represent the block copolymer [polystyrene-block-poly(methyl methacrylate)] and graft copolymer [polystyrene-graft-poly(methyl methacrylate)], respectively.

The source-based nomenclature system is still one of choices in the polymer community, although the important reference sources such as Chemical Abstracts and Polymer Handbook have adopted the IUPAC system. Polymers used in business for long time usually have their own trade name, due to sometimes a polymer named by IUPAC name is not read easily and too long to use



Polycarbonate



Epoxy Resin

Fig. 1.4 Chemical structures of polycarbonate and epoxy resin

Table 1.2 Representative polymers used in modern society

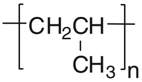
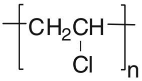
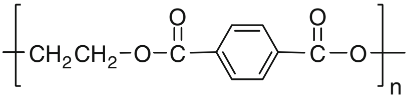
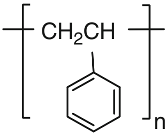
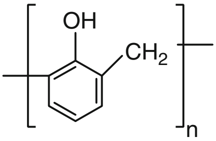
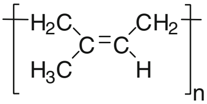
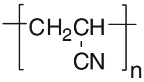
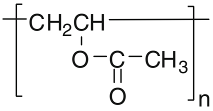
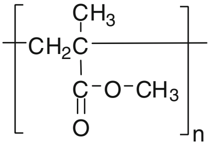
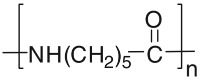
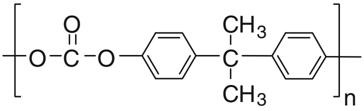
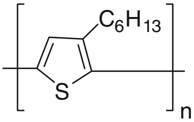
Common name	Abbreviation	Chemical structure
Polyethylene	PE	$-[CH_2CH_2]_n-$
Polypropylene	PP	 $-[CH_2CH(CH_3)]_n-$
Poly(vinyl chloride)	PVC	 $-[CH_2CH(Cl)]_n-$
Poly(ethylene terephthalate)	PET	
Polystyrene	PS	
Phenol–formaldehyde	none	
Polyisoprene	PI	
Polyacrylonitrile	PAN	 $-[CH_2CH(CN)]_n-$
Poly(vinyl acetate)	PVA	 $-[CH_2CH(O-C(=O)-CH_3)]_n-$
Poly(methyl methacrylate)	PMMA	 $-[CH_2C(CH_3)(C(=O)-O-CH_3)]_n-$
Polycaprolactam	Nylon 6	 $-[NH(CH_2)_5-C(=O)]_n-$
Polycarbonate	PC	
Poly(3-hexyl thiophene)	P3HT	

Table 1.3 Recycling codes of plastics [3]

Number	Letters	Plastic
1	PET	Poly(ethylene terephthalate)
2	HDPE	High density polyethylene
3	V *or* PVC	Poly(vinyl chloride)
4	LDPE	Low density polyethylene
5	PP	Polypropylene
6	PS	Polystyrene
7	OTHER	Others or mixed plastics

conveniently. For example, IUPAC name for polycarbonate is poly(oxy carbonyl oxy -1,4-phenylene-isopropylidene -1,4-phenylene) and the repeating unit is $–[O–CO–O–C_6H_4–C(CH_3)_2–C_6H_4]_n–$. Bisphenol A epoxy resin has an IUPAC name of 4,4′-dimethoxy oxirane -2,2-diphenyl propane. Figure 1.4 shows the chemical structures of polycarbonate and bisphenol A epoxy resin.

Table 1.2 organizes some representative polymers in modern society with their common name, abbreviation, and chemical structure according to the amount of usage. Their synthesis and properties will be discussed throughout this text book. The abbreviated name of polymer has been adapted for subsequent chapter for simplicity.

1.4 Polymer Recycling

Polymer recycling [3] is an important matter being carried out worldwide to reduce pollution and conserve material. Poly(ethylene terephthalate) (PET) and high density polyethylene (HDPE) share more than 70 % of the demand for recycled plastics. The recycling industry sometime encounters economic difficulties because most “virgin” plastics are not only of better quality than their recycled counterparts, but are often less expensive. In Taiwan, the majority of used plastics are burned as fuel or pyrolyzed to make fuel. The Society of the Plastics Industry (SPI) of USA has adopted plastic recycling codes to be used internationally as shown in Table 1.3, so the recycled polymers can be sorted according to their code before they are used as raw materials for specific applications.

1.5 Problems

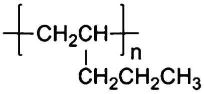
1. Write a concise definition of each term listed below, using examples as appropriate, (a) polymer, (b) monomer, (c) functional group, (d) oligomer, (e) telechelic polymer, (f) degree of polymerization, (g) molecular weight distribution, (o) copolymer, (p) chain polymerization, (q) step polymerization.

2. Write the name and structure of the monomers that are required to synthesize the following polymers. Please write the IUPAC name of each polymer.
3. Please discuss the importance of plastic recycling.

(a)

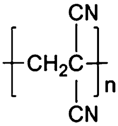
$\left[CH_2CHF \right]_n$

(b)



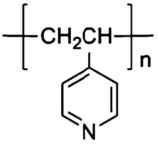
$\left[CH_2CH(CH_2CH_2CH_3) \right]_n$

(c)

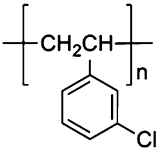


$\left[CH_2C(CN)_2 \right]_n$

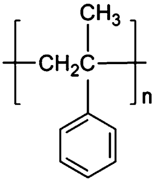
(d)



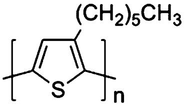
(e)



(f)



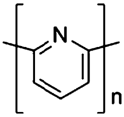
(g)



(h)

$\left[CH{=}CH \right]_n$

(i)



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Chapter 2
Polymer Size and Polymer Solutions

The size of single polymer chain is dependent on its molecular weight and morphology. The morphology of a single polymer chain is determined by its chemical structure and its environment. The polymer chain can be fully extended in a very dilute solution when a good solvent is used to dissolve the polymer. However, the single polymer chain is usually in coil form in solution due to the balanced interactions with solvent and polymer itself. We will discuss the size of polymer first, and then go to the coil formation in the polymer solution.

2.1 The Molecular Weight of Polymer

The molecular weight of polymer determines the mechanical properties of polymers. To have strong durable mechanical properties, the polymer has to have molecular weight much larger than 10,000 for structural applications. However, for thin film or other special application, low molecular weight polymer or oligomer sometime is adequate. As shown in Fig. 2.1, above (A), strength increases rapidly with molecular weight until a critical point (B) is reached. Mechanical strength increases more slowly above (B) and eventually reaches a limiting value (C). High molecular weight polymer has high viscosity and poor processability. The control of molecular weight and molecular weight distribution (MWD) is often used to obtain and improve certain desired physical properties in a polymer product.

Polymers, in their purest form, are mixtures of molecules of different molecular weights. The reason for the polydispersity of polymers lies in the statistical variations present in the polymerization processes. The above statement is true for common polymerization reaction such as free radical chain polymerization, step polymerization, etc. However, cationic or anionic chain polymerization as so called living polymerization has small MWD. Low dispersity can also be obtained from emulsion polymerization, and new polymerization techniques such as living free radical polymerization including nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible addition–fragmentation chain

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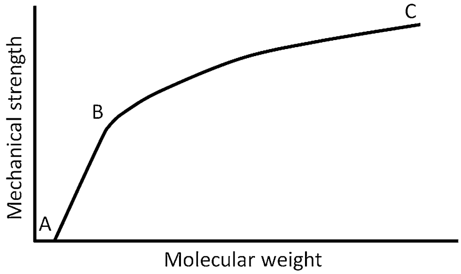


Fig. 2.1 Dependence of mechanical strength on polymer molecular weight [1]

transfer polymerization (RAFT). The chemistry of different polymerization reactions will be discussed in detail in the subsequent chapters.

Number-average molecular weight $(\bar{M}_n)$ is total weight (W) of all the molecules in a polymer sample divided by the total number of molecule present, as shown in Eq. 2.1, where N_x is the number of molecules of size M_x, $\underline{N}_x$ is number (mole) fraction of size M_x

$$\bar{M}_n = W/\Sigma N_x = \Sigma\, N_x M_x/\Sigma N_x = \Sigma\, \underline{N}_x M_x \tag{2.1}$$

Analytical methods used to determine $\bar{M}_n$ include (1) $\bar{M}_n < 25{,}000$ by vapor pressure osmometry, (2) $\bar{M}_n$ 50,000–2 million by membrane osmometry, and (3) $\bar{M}_n < 50{,}000$ by end group analysis, such as NMR for –C=C; titration for carboxylic acid ending group of polyester. They measure the colligative properties of polymer solutions. The colligative properties are the same for small and large molecules when comparing solutions at the same mole fraction concentration. Therefore, the $\bar{M}_n$ is biased toward smaller sized molecules. The detailed measurement methods of molecular weight will be discussed in Sect. 2.3. Weight-average molecular weight is defined as Eq. 2.2, where W_x is the weight fraction of M_x molecules, C_x is the weight concentration of M_x molecules, and C is the total weight concentration of all of the polymer molecules, and defined by Eqs. 2.3–2.5.

$$\bar{M}_w = \Sigma\, W_x M_x = \Sigma\, C_x M_x/\Sigma C_x \tag{2.2}$$

$$W_x = C_x/C \tag{2.3}$$

$$C_x = N_x M_x \tag{2.4}$$

$$C = \Sigma\, C_x = \Sigma\, N_x M_x \tag{2.5}$$

Light scattering is an analytical method to determine the $\bar{M}_w$ in the range of 10,000–10,000,000. It unlike colligative properties shows a greater number for larger sized molecules than for small-sized molecules. Viscosity-average molecular weight $(\bar{M}_v)$ is defined as Eq. 2.6, where a is a constant. The viscosity and weight average molecular weights are equal when a is unity. $\bar{M}_v$ is like $\bar{M}_w$, it is greater for the larger sized polymer molecules than for smaller ones.

$$\bar{M}_v = \left[\Sigma M_x^a W_x\right]^{1/a} = \left[\Sigma N_x M_x^{a+1} / \Sigma N_x M_x\right]^{1/a} \tag{2.6}$$

A measure of the polydispersity in a polymer is defined as $\bar{M}_w$ divided over $\bar{M}_n$ $(\bar{M}_w/\bar{M}_n)$. For a polydispersed polymer, $\bar{M}_w > \bar{M}_v > \bar{M}_n$ with the differences between the various average molecular weights increasing as the molecular-weight distribution (MWD) broadens, as shown in Fig. 2.2.

For example, consider a hypothetical mixture containing 95 % by weight of molecules of molecular weight 10,000, and 5 % of molecules of molecular weight 100. The $\bar{M}_n$ and $\bar{M}_w$ are calculated from Eqs. 2.1 and 2.2 as 1,680 and 9,505, respectively. The use of the $\bar{M}_n$ value of 1,680 gives an inaccurate indication of the properties of this polymer. The properties of the polymer are determined primarily by the molecules with a molecular weight of 10,000 that makes up 95 % of the weight of the mixture. The highest % fraction of molecular weight of molecule will contribute the most toward the bulk property. It is desirable to know the molecular weight distribution, then to predict the polymer properties. At present, the gel permeation chromatography (GPC) technique has been advanced to be able to easily measure $\bar{M}_n$, $\bar{M}_v$, $\bar{M}_w$, simultaneously and calculate PDI using only one sample. All the measurements of molecular weight of polymers are carried out using polymer solutions. Therefore, the accuracy of molecular weight measurement is dependent on the behavior of polymer solution. Usually, a calibration curve is established first using a specific polymer dissolving in a specific solvent. Polystyrene standard dissolved in tetrahydrofuran (THF) is the most popular calibration curve used in GPC. If the measured polymer exhibits different behavior in THF from that of polystyrene, then a deviation from the actual molecular weight is occurred. For example, a conducting polymer, poly (phenylene vinylene), containing rigid rod molecular structure shows a higher molecular weight when the standard of coil structured polystyrene is used. More detailed discussion of GPC is in Sect. 2.3.

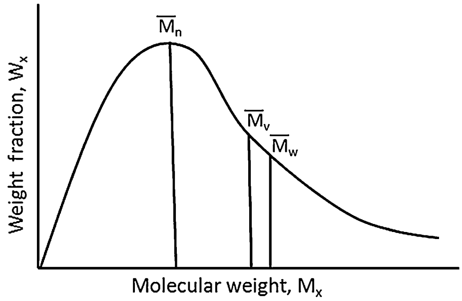


Fig. 2.2 Distribution of molecular weights in a typical polymer sample [1]

2.2 Polymer Solutions

Polymer solutions occur in two stages. Initially, the solvent molecules diffuse through the polymer matrix to form a swollen, solvated mass called a gel. In the second stage, the gel breaks up and the molecules are dispersed into a true solution. Not all polymers can form true solution in solvent.

Detailed studies of polymer solubility using thermodynamic principles have led to semi-empirical relationships for predicting the solubility [2]. Any solution process is governed by the free-energy relationship of Eq. 2.7:

$$\Delta G = \Delta H - T\Delta S \tag{2.7}$$

When a polymer dissolves spontaneously, the free energy of solution, ΔG, is negative. The entropy of solution, ΔS, has a positive value arising from increased conformational mobility of the polymer chains. Therefore, the magnitude of the enthalpy of solution, ΔH, determines the sign of ΔG. It has been proposed that the heat of mixing, ΔH_{mix}, for a binary system is related to concentration and energy parameters by Eq. 2.8:

$$\Delta H_{mix} = V_{mix}\left[\left(\frac{\Delta E_1}{V_1}\right)^{1/2} - \left(\frac{\Delta E_2}{V_2}\right)^{1/2}\right]^2 \emptyset_1 \emptyset_2 \tag{2.8}$$

where V_{mix} is the total volume of the mixture, V_1 and V_2 are molar volumes (molecular weight/density) of the two components, $\emptyset_1$ and $\emptyset_2$ are their volume fractions, and ΔE_1 and ΔE_2 are the energies of vaporization. The terms $\Delta E_1/V_1$ and $\Delta E_2/V_2$ are called the *cohesive energy densities.* If $(\Delta E/V)^{1/2}$ is replaced by the symbol δ, the equation can be simplified into Eq. 2.9:

$$\Delta H_{mix} = V_{mix}(\delta_1 - \delta_2)^2 \emptyset_1 \emptyset_2 \tag{2.9}$$

The interaction parameter between polymer and solvent can be estimated from ΔH_{mix} as:

$$\chi_{12} = \frac{V_1}{RT}(\delta_1 - \delta_2)^2 \tag{2.10}$$

The symbol δ is called the solubility parameter. Clearly, for the polymer to dissolve (negative ΔG), ΔH_{mix} must be small; therefore, $(\delta_1 - \delta_2)^2$ must also be small. In other words, δ_1 and δ_2 should be of about equal magnitude where $\delta_1 = \delta_2$, solubility is governed solely by entropy effects. Predictions of solubility are therefore based on finding solvents and polymers with similar solubility parameters, which requires a means of determining cohesive energy densities.

Cohesive energy density is the energy needed to remove a molecule from its nearest neighbors, thus is analogous to the heat of vaporization per volume for a volatile compound. For the solvent, δ_1 can be calculated directly from the latent heat of vaporization $\left(\Delta H_{vap}\right)$ using the relationship of Eq. 2.11:

$$\Delta E = \Delta H_{vap} - RT \tag{2.11}$$

R is the gas constant, and T is the temperature in kelvins. Thus, the cohesive energy of solvent is shown in Eq. 2.12:

$$\delta_1 = \left(\frac{\Delta H_{vap} - RT}{V}\right)^{1/2} \tag{2.12}$$

Since polymers have negligible vapor pressure, the most convenient method of determining δ_2 is to use group molar attraction constants. These are constants derived from studies of low-molecular-weight compounds that lead to numerical values for various molecular groupings on the basis of intermolecular forces. Two sets of values (designated G) have been suggested, one by Small [3], derived from heats of vaporization and the other by Hoy [4], based on vapor pressure measurements. Typical G values are given in Table 2.1. Clearly there are significant differences between the Small and Hoy values. The use of which set is normally determined by the method used to determine δ_1 for the solvent.

G values are additive for a given structure, and are related to δ by

$$\delta = \frac{d\Sigma G}{M} \tag{2.13}$$

where d is density and M is molecular weight. For polystyrene –[CH_2–$CH(C_6H_5)$]$_n$–, for example, which has a density of 1.05, a repeating unit mass of 104, and δ is calculated, using Small's G values, as

Table 2.1 Representative group molar attraction constants [3, 4]

Chemical group	G[(cal cm^3)$^{1/2}$mol^{-1}]	
	Small	Hoy
H_3C-	214	147.3
$-CH_2-$	133	131.5
$>CH-$	28	86.0
$>C<$	–93	32.0
$=CH_2$	190	126.0
$=CH-$	19	84.5
$-C_6H_5$ (phenyl)	735	–
$-CH=$ (aromatic)	–	117.1
$>C=O$ (ketone)	275	262.7
$-CO_2-$ (ester)	310	326.6

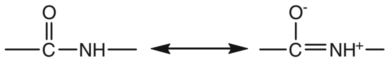
$$\delta = \frac{1.05(133 + 28 + 735)}{104} = 9.0$$

or using Hoy's data,

$$\delta = \frac{1.05[131.5 + 85.99 + 6(117.1)]}{104} = 9.3$$

Both data give similar solubility parameter. However, there is limitation of solubility parameter. They do not consider the strong dipolar forces such as hydrogen bonding, dipole–dipole attraction, etc. Modifications have been done by many researchers and available in literature [5, 6].

Once a polymer–solvent system has been selected, another consideration is how the polymer molecules behave in that solvent. Particularly important from the standpoint of molecular weight determinations is the resultant size, or *hydrodynamic volume*, of the polymer molecules in solution. Assuming polymer molecules of a given molecular weight are fully separated from one another by solvent, the hydrodynamic volume will depend on a variety of factors, including interactions between solvent and polymer molecules, chain branching, conformational effects arising from the polarity, and steric bulkiness of the substituent groups, and restricted rotation caused by resonance, for example, polyamide can exhibit resonance structure between neutral molecule and ionic molecule.



$$-\overset{\overset{\displaystyle O}{\|}}{C}-NH- \longleftrightarrow -\overset{\overset{\displaystyle O^-}{|}}{C}=NH^+-$$

Because of Brownian motion, molecules are changing shape continuously. Hence, the prediction of molecular size must base on statistical considerations and average dimensions. If a molecule was fully extended, its size could easily be computed from the knowledge of bond lengths and bond angles. Such is not the case, however, with most common polymers; therefore, size is generally expressed

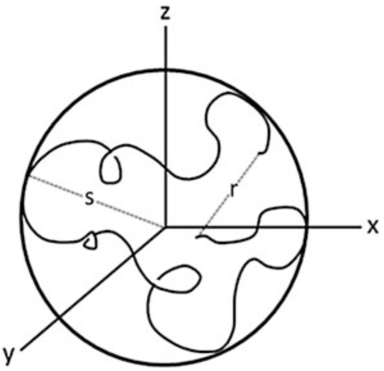


Fig. 2.3 Schematic representation of a molecular coil, r = end to end distance, s = radius of gyration [2]

in terms of the mean-square average distance between chain ends, $\bar{r}^2$, for a linear polymer, or the square average radius of gyration about the center of gravity, $\bar{s}^2$, for a branched polymer. Figure 2.3 illustrates the meaning of r and s from the perspective of a coiled structure of an individual polymer molecule having its center of gravity at the origin.

The average shape of the coiled molecule is spherical. The greater the affinity of solvent for polymer, the larger will be the sphere, that is, the hydrodynamic volume. As the solvent–polymer interaction decreases, intramolecular interactions become more important, leading to a contraction of the hydrodynamic volume. It is convenient to express r and s in terms of two factors: an unperturbed dimension (r_0 or s_0) and an expansion factor (α). Thus,

$$\bar{r}^2 = r_0^2\alpha^2 \tag{2.14}$$

$$\bar{s}^2 = s_0^2\alpha^2 \tag{2.15}$$

$$\alpha = \frac{\left(\bar{r}^2\right)^{1/2}}{\left(\bar{r}_0^2\right)^{1/2}} \tag{2.16}$$

The unperturbed dimension refers to the size of the macromolecule exclusive of solvent effects. It arises from a combination of free rotation and intramolecular interactions such as steric and polar interactions. The expansion factor, on the other hand, arises from interactions between solvent and polymer. For a linear polymer, $\bar{r}^2 = 6\bar{s}^2$. The α will be greater than unity in a "good" solvent, thus the actual (perturbed) dimensions will exceed the unperturbed dimensions. The greater the value of α is, the "better" the solvent is. For the special case where $\alpha = 1$, the polymer assumes its unperturbed dimensions and behaves as an "ideal" statistical coil.

Because solubility properties vary with temperature in a given solvent, α is temperature dependent. For a given polymer in a given solvent, the lowest temperature at which $\alpha = 1$ is called the theta (θ) temperature (or Flory temperature), and the solvent is then called a theta solvent. Additionally, the polymer is said to be in a theta state. In the theta state, the polymer is on the brink of becoming insoluble; in other words, the solvent is having a minimal solvation effect on the dissolved molecules. Any further diminish of this effect causes the attractive forces among polymer molecules to predominate, and the polymer precipitates.

From the standpoint of molecular weight determinations, the significance of solution viscosity is expressed according to the Flory-Fox equation [7],

$$[\eta] = \frac{\Phi\left(\bar{r}^2\right)^{3/2}}{\bar{M}} \tag{2.17}$$

where $[\eta]$ is the intrinsic viscosity (to be defined later), $\bar{M}$ is the average molecular weight, and Φ is a proportionality constant (called the Flory constant) equal to approximately 3 × 10^{24}. Substituting $\bar{r}_0^2 \cdot \alpha^2$ for $\bar{r}^2$, we obtain Mark-Houwink-Sakurada equation:

$$[\eta] = \frac{\Phi\left(\bar{r}_0^2\alpha^2\right)^{3/2}}{\bar{M}} \tag{2.18}$$

Equation 2.18 can be rearranged to

$$[\eta] = \Phi\left(\bar{r}_0^2\bar{M}^{-1}\right)^{3/2}\bar{M}^{1/2}\alpha^3 \tag{2.19}$$

Since $\bar{r}_0$ and $\bar{M}$ are constants, we can set $K = \Phi\left(\bar{r}_0^2\bar{M}^{-1}\right)^{3/2}$, then

$$[\eta] = K\bar{M}^{1/2}\alpha^3 \tag{2.20}$$

At the theta temperature, $\alpha = 1$ and

$$[\eta] = K\bar{M}^{1/2} \tag{2.21}$$

For conditions other than the theta temperature, the equation is expressed by

$$[\eta] = K\bar{M}^a \tag{2.22}$$

Apart from molecular weight determinations, many important practical considerations are arisen from solubility effects. For instance, one moves in the direction of "good" solvent to "poor", and intramolecular forces become more important, the polymer molecules shrink in volume. This increasing compactness leads to reduced "drag" and hence a lower viscosity which has been used to control the viscosity of polymer for ease of processing.

2.3 Measurement of Molecular Weight

Many techniques have been developed to determine the molecular weight of polymer [8]. Which technique to use is dependent on many factors such as the size of the polymer, the ease of access and operation of the equipment, the cost of the analysis, and so on.

For polymer molecular weight is less than 50,000, its molecular weight can be determined by the end group analysis. The methods for end group analysis include titration, elemental analysis, radio active tagging, and spectroscopy. Infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR), and mass spectroscopy (MS) are commonly used spectroscopic technique. The IR and NMR are usually less sensitive than that of MS due to the detection limit.

Rules of end group analysis for $\bar{M}_n$ are: (1) the method cannot be applied to branched polymers unless the number of branches is known with certainty; thus it is practically limited to linear polymers, (2) in a linear polymer there are twice as many end groups as polymer molecules, (3) if the polymer contains different groups at each end of the chain and only one characteristic end group is being measured, the number of this type is equal to the number of polymer molecules, (4) measurement of molecular weight by end-group analysis is only meaningful when the mechanisms of initiation and termination are well understood. To determine the number average molecular weight of the linear polyester before cross-linking, one can titrate the carboxyl and hydroxyl end groups by standard acid–base titration methods. In the case of carboxyl, a weighed sample of polymer is dissolved in an appropriate solvent such as acetone and titrated with standard base to a phenolphthalein end point. For hydroxyl, a sample is acetylated with excess acetic anhydride, and liberated acetic acid, together with carboxyl end groups, is similarly titrated. From the two titrations, one obtains the number of mini-equivalents of carboxyl and hydroxyl in the sample. The number average molecular weight (i.e., the number of grams per mole) is then given by Eq. 2.23:

$$\bar{M}_n = \frac{2 \times 1000 \times \text{sample wt.}}{\text{meq}COOH + \text{meq}OH} \tag{2.23}$$

The 2 in the numerator takes into account that two end groups are being counted per molecule. The *acid number* is defined as the number of milligrams of base required to neutralize 1 g of polyester which is used to monitor the progress of polyester synthesis in industry.

Of the various methods of number average molecular weight determination based on colligative properties, membrane osmometry is most useful. When pure solvent is

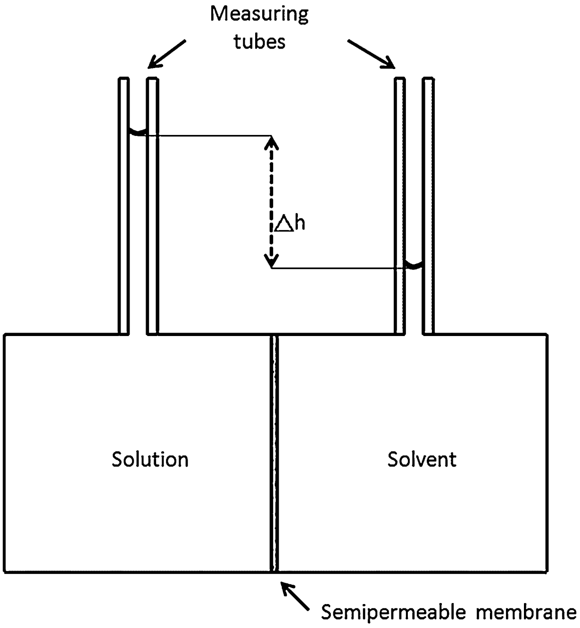


Fig. 2.4 Schematic representation of a membrane osmometer [2]

separated from a solution by a semi-permeable membrane that allows passage of solvent but not solute molecules, solvent will flow through the membrane into the solution. As the liquid level rises in the solution compartment, the hydrostatic pressure increases until it prevents further passage of solvent or, more exactly, until solvent flow is equal in both directions. The pressure at equilibrium is the osmotic pressure. A schematic representation of an osmometer is given in Fig. 2.4.

Osmotic pressure is related to molecular weight by the van't Hoff equation extrapolated to zero concentration:

$$\left(\frac{\pi}{C}\right)_{c=0} = \frac{RT}{\bar{M}_n} + A_2 C \tag{2.24}$$

where π, the osmotic pressure, is given by

$$\pi = \rho g \Delta h \tag{2.25}$$

where R is the gas constant, 0.082 L atm $\text{mol}^{-1}\text{K}^{-1}$ (CGS) or 8.314 J $\text{mol}^{-1}\text{K}^{-1}$ (SI); T is the temperature in kelvins; C is the concentration in grams per liter; ρ is the solvent density in grams per cubic centimeter, g is the acceleration due to gravity, 9.81 m/s^2; Δh is the difference in heights of solvent and solution in centimeters; and A_2 is the second virial coefficient (a measure of the interaction between solvent and polymer). A plot of *reduced osmotic pressure,* π/C, versus concentration (Fig. 2.5) is linear with the intercept equal to $RT/\bar{M}_n$ and the slope equal to A_2, units for π/C are dyn $\text{Lg}^{-1}\text{cm}^{-1}$ (CGS) or Jkg^{-1} (SI). Because A_2 is a measure of solvent–polymer interaction, the slope is zero at the theta temperature. Thus osmotic pressure measurements may be used to determine theta conditions.

Matrix assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF MS) is developed recently to determine the absolute molecular weight of large molecule. The polymer sample is imbedded in a low molecular weight organic compound that absorbs strongly at the wavelength of a UV laser. Upon UV radiation, organic compound absorbs energy, then energy transfer to polymer to form ions. Finally, the ions are detected. At higher molecular weight, the signal to noise ratio is reduced. From the integrated peak areas, reflecting the number of ions (N_j) and the average molecular weight (M_i), both $\bar{M}_n$ and $\bar{M}_w$ can be calculated. Figure 2.6 shows that a low molecular weight $(\bar{M}_w \sim 3{,}000)$ poly(3-

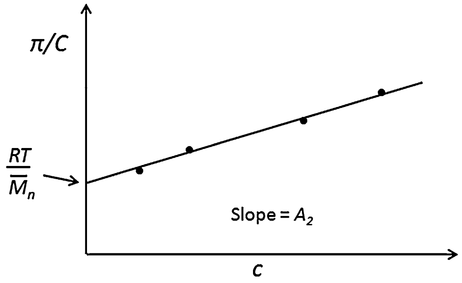


Fig. 2.5 Plot of reduced osmotic pressure versus concentration [2]

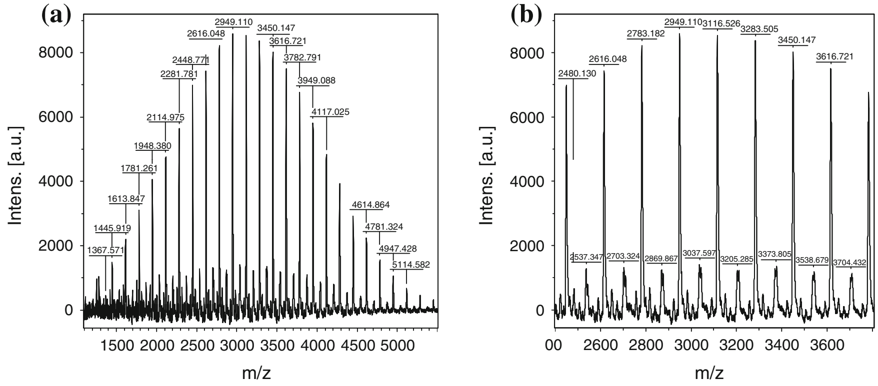


Fig. 2.6 MALDI mass spectrum of low molecular weight poly(3-hexyl thiophene) (**a**) whole spectrum, (**b**) magnified area between m/z 2,400 and 3,800

hexyl thiophene) was measured by MALDI-TOF MS. The spectrum shows the molecular weight distribution and the difference between every peak is equal to the repeating unit 3-hexyl thiophene of 167.

The absolute weight average molecular weight $(\bar{M}_w)$ can also be measured by light scattering method. The light passes through the solution, loses energy by absorption, conversion to heat, and scattering. The intensity of scattered light depends on concentration, size, polarizability of the scattering molecules. To evaluate the turbidity arising from scattering, one combines equations derived from scattering and index of refraction measurements. Turbidity, τ, is related to concentration, c, by the expression

$$\tau = Hc\bar{M}_w \tag{2.26}$$

where H is

$$H = \frac{32\pi^3}{3} \frac{n_0^2 (dn/dc)^2}{\lambda^4 N_0} \tag{2.27}$$

and n_0 is the refractive index of the solvent, λ is the wavelength of the incident light, and N_0 is Avogadro's number. The expression dn/dc, referred to as the *specific refractive increment*, is obtained by measuring the slope of the refractive index as a function of concentration, and it is constant for a given polymer, solvent, and temperature. As molecular size approaches the magnitude of light wavelength, corrections must be made for interference between scattered light coming from different parts of the molecules. To determine molecular weight, the expression for turbidity is rewritten as

$$\frac{Hc}{\tau} = \frac{1}{\bar{M}_w P(\theta)} + 2A_2 C \tag{2.28}$$

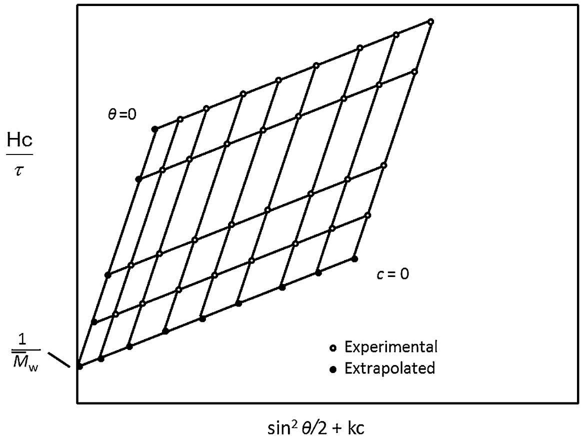


Fig. 2.7 Zimm plot of light-scattering data of polymer [2]

where $P(\theta)$ is a function of the angle, θ, at which τ is measured, a function that depends on the shape of the molecules in solution. A_2 is the second virial coefficient. Turbidity is then measured at different concentrations as well as at different angles, the latter to compensate for variations in molecular shape. The experimental data are then extrapolated to both zero concentration and zero angle, where $P(\theta)$ is equal to 1. Such double extrapolations, shown in Fig. 2.7, are called *Zimm plots*. The factor k on the abscissa is an arbitrary constant. The intercept corresponds to $1/\bar{M}_w$.

A major problem in light scattering is to obtain perfectly clear, dust-free solutions. This is usually accomplished by ultra centrifugation or careful filtration. Despite such difficulties, the light-scattering method is widely used for obtaining weight average molecular weights between 10,000 and 10,000,000. A schematic of a laser light-scattering photometer is given in Fig. 2.8.

Intrinsic viscosity is the most useful of the various viscosity designations because it can be related to molecular weight by the Mark-Houwink-Sakurada equation:

$$[\eta] = K\bar{M}_v^a \tag{2.29}$$

where $\bar{M}_v$, is the *viscosity average molecular weight*, defined as

$$\bar{M}_v = \left(\frac{\Sigma N_i M_i^{1+a}}{\Sigma N_i M_i}\right)^{1/a} \tag{2.30}$$

Log K and a are the intercept and slope, respectively, of a plot of log $[\eta]$ versus log $\bar{M}_w$ or log $\bar{M}_n$ of a series of fractionated polymer samples. Such plots are linear (except at low molecular weights) for linear polymers, thus

$$\log[\eta] = \log K + a\log\bar{M} \tag{2.31}$$

Fig. 2.8 Schematic of a laser light scattering photometer [2]

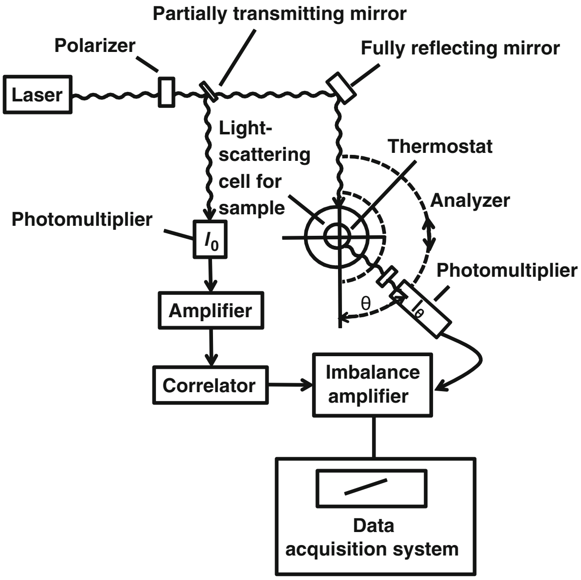
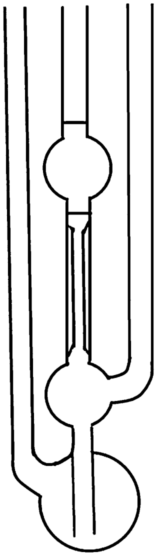


Fig. 2.9 A modified Ubbelohde viscometer with improved dilution characteristics



Factors that may complicate the application of the Mark-Houwink-Sakurada relationship are chain branching, too broad of molecular weight distribution in the samples used to determine K and a, solvation of polymer molecules, and the presence of alternating or block sequences in the polymer backbone. Chain entanglement is not usually a problem at high dilution except for extremely high molecular weights polymer. Ubbelohde type viscometer is more convenient to use

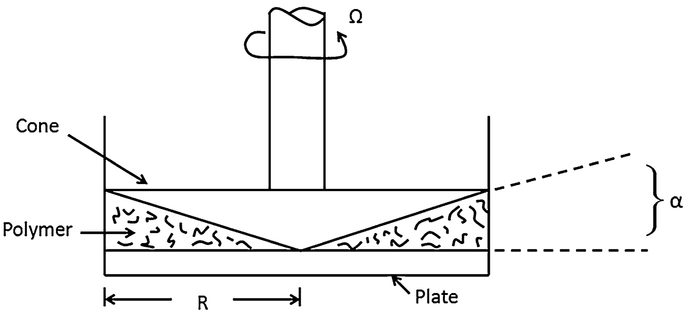


Fig. 2.10 Schematic of cone-plate rotational viscometer [2]

for the measurement of polymer viscosity, because it is not necessary to have exact volumes of solution to obtain reproducible results. Furthermore, additional solvent can be added (assuming the reservoir is large enough); thus concentration can be reduced without having to empty and refill the viscometer. A schematic of the Ubbelohde type viscometer is given in Fig. 2.9.

The viscosity of polymer can also be measured by the cone-plate rotational viscometer as shown in Fig. 2.10. The molten polymer or polymer solution is contained between the bottom plate and the cone, which is rotated at a constant velocity (Ω). Shear stress (τ) is defined as

$$\tau = \frac{3M}{2\pi R^3} \tag{2.32}$$

where M is the torque in dynes per centimeter (CGS) or in newtons per meter (SI), and R is the cone radius in centimeters. Shear rate ($\dot{r}$) is given by

$$\dot{r} = \frac{\Omega}{\alpha} \tag{2.33}$$

where Ω is the angular velocity in degrees per second (CGS) or in radians per second (SI) and α is the cone angle in degrees or radians. Viscosity is then

$$\eta = \frac{\tau}{\dot{r}} = \frac{3\alpha M}{2\pi R^3 \Omega} = \frac{kM}{\Omega} \tag{2.34}$$

where k is

$$k = \frac{3\alpha}{2\pi R^3} \tag{2.35}$$

Gel permeation chromatography (GPC) involves the permeation of a polymer solution through a column packed with microporous beads of cross-linked polystyrene. The column is packed from beads of different sized pore diameters, as shown in Fig. 2.11. The large size molecules go through the column faster than the small size molecule. Therefore, the largest molecules will be detected first. The

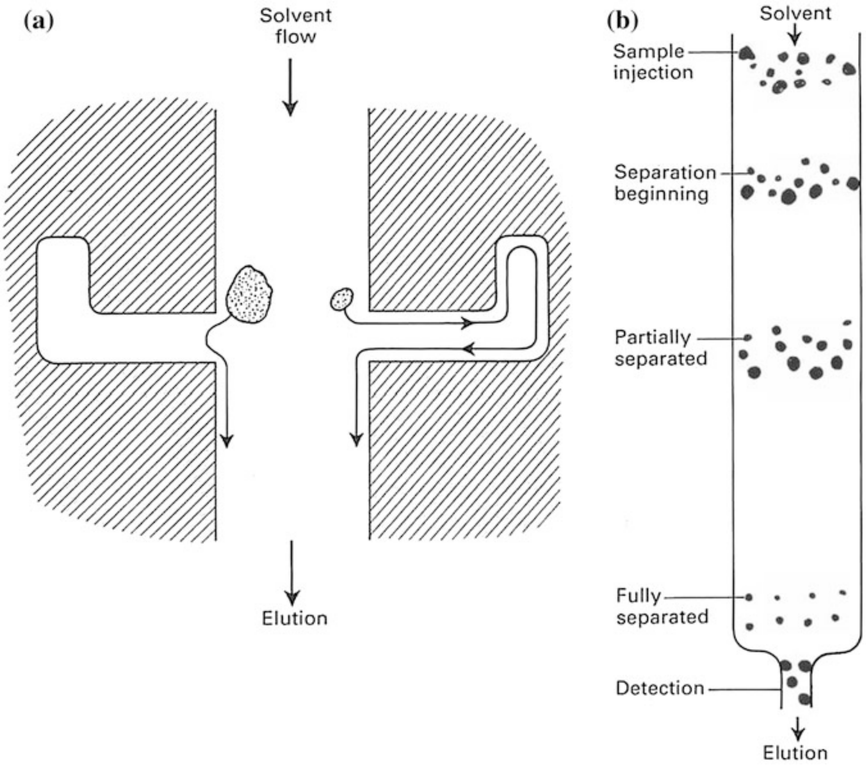


Fig. 2.11 Simple illustrations of the principle of gel permeation chromatography (GPC) [9]. (Adapted from I.M. Campbell, Introduction to Synthetic Polymers, Oxford, 1994, p. 26 with permission)

smallest size molecules will be detected last. From the elution time of different size molecule, the molecular weight of the polymer can be calculated through the calibration curves obtained from polystyrene standard.

For example, the synthesis of diblock copolymer: poly(styrene)-b-poly(2-vinylpyridine) (PS-b-P2VP) can be monitored by the GPC. Styrene is initiated by sec-butyl lithium first and then the polystyrene anion formed until the styrene monomer is completely consumed. Followed by introducing the 2-vinyl pyridine, a PS-b-P2VP block copolymer is finally prepared (Fig. 2.12). As shown in Fig. 2.13, the GPC results show that the PS anion was prepared first with low PDI (1.08). After adding the 2-VP, the PS-b-P2VP block copolymer was analyzed by GPC again, the PDI remained low, but the molecular weight has been doubled. More detailed discussions of anionic polymerizations will be present in Chap. 8.

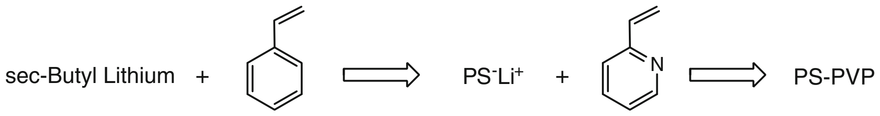
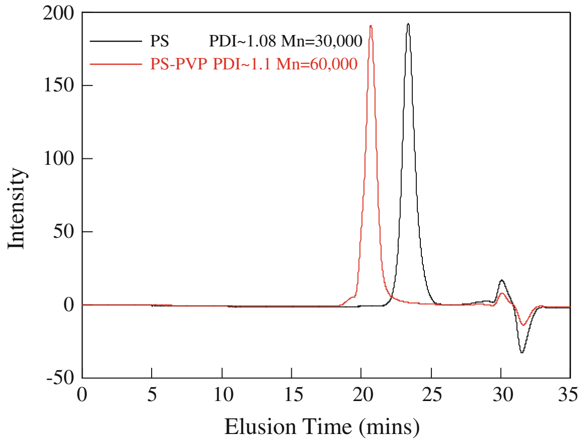


Fig. 2.12 Synthesis of PS-b-P2VP via anionic polymerization

Fig. 2.13 GPC traces of PS homo polymer and PS-b-P2VP block copolymer. The *right* peak is PS. The peak of copolymer is shifted to the *left* due to the addition of P2VP



2.4 Problems

1. A “model” of a linear polyethylene having a molecular weight of about 200,000 is being made by using a paper clip to represent one repeating unit. How many paper clips does one need to string together?
2. In general, the viscosity of polymer is reduced by increasing temperature. How might the magnitude of this effect compare for the polymer in a “poor” solvent or in a “good” solvent? (This is the basis for all weather multi viscosity motor oils.)
3. From the practical standpoint, is it better to use a “good” solvent or a “poor” solvent when measuring polymer molecular weight? Explain.
4. Discuss the value of knowledge of the molecular weight and distribution of a polymer to the polymer scientist and engineer. Which method would you use to obtain this information on a routine basis in the laboratory and in the production respectively? Why? Which method would you use to obtain this information for a new polymer type which is not previously known? Why?
5. What would be the number average, weight average molecular weight and polydispersity of a sample of polypropylene that consists of 5 mol of 1000 unit propylene and 10 mol of 10,000 unit propylene?
6. A 0.5000-g sample of an unsaturated polyester resin was reacted with excess acetic anhydride. Titration of the reaction mixture with 0.0102 *M* KOH required 8.17 mL to reach the end point. What is the number average

Elution time (min.)	Intensity
13.0	0.5
13.5	6.0
14.0	25.7
14.5	44.5
15.0	42.5
15.5	25.6
16.0	8.9
16.5	2.2

molecular weight of the polyester? Would this method be suitable for determining any polyester? Explain.

7. Explain how one might experimentally determine the Mark-Houwink-Sakurada constants K and a for a given polymer. Under what conditions can you use $[\eta]$ to measure $\bar{r}_0^2\bar{M}^{-1}$? How can $\bar{r}_0^2\bar{M}^{-1}$ be used to measure chain branching?
8. The molecular weight of poly(methyl methacrylate) was measured by gel permeation chromatography in tetrahydrofuran at 25°C and obtained the above data:

   The polystyrene standard (PDI ~ 1.0) under the same conditions gave a linear calibration curve with $M = 98{,}000$ eluting at 13.0 min. and $M = 1{,}800$ eluting at 16.5 min.

   a. Calculate $\bar{M}_w$ and $\bar{M}_n$ using the polystyrene calibration curve.
   b. If the PDI of polystyrene is larger than 1.0, what errors you will see in the $\bar{M}_n$ and $\bar{M}_w$ of poly(methyl methacrylate).
   c. Derive the equation that defines the type of molecular weight obtained in the "universal" calibration method in gel permeation chromatography.

9. Please explain why the gel permeation chromatography method can measure both $\bar{M}_n$ and $\bar{M}_w$, but the osmotic pressure method can only measure the $\bar{M}_n$ and the light scattering method can only measure $\bar{M}_w$.
10. Please calculate the end-to-end distance of a polymer with molecular weight of 1 million and intrinsic viscosity of 2.10 dl/g and assume $\Phi = 2.1 \text{ X } 10^{21}$. What is the solution behavior of this polymer? [10]

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Chapter 3
Structure Morphology Flow of Polymer

The chemical composition, configuration and molecular arrangement determine the structure of polymer. The physical structure of polymer is the morphology of polymer. The nonpolar polyethylene chain can be folded into ordered structure to have high crystallinity and exhibit good physical properties of toughness, strength, etc. The polar polymers as shown in Fig. 3.1 exhibit intermolecular interactions that result in high crystallinity and exhibits good physical properties as well. There are some factors which affect polymer flow, such as temperature (kinetic energy), molecular weight (molecular entanglement), and molecular structure. The high crystalline polymer is usually difficult to process due to its high viscosity. The liquid crystalline polymer is an exception. It exhibits both excellent physical properties and low viscosity at liquid state (discuss later). The crosslinked polymer is obtained either by chemically bonding or physically bonding. The polymer is not crosslinked and is in liquid form for the ease of processing but it becomes crosslinked to have good mechanical strength after processing.

3.1 Chemical and Molecular Structure of Polymer

The geometrical arrangement of the atoms in a polymer chain can be divided into two categories. The first category is *configurational arrangements* which are fixed by the chemical bonding in the molecule. The configuration of a polymer chain cannot be altered unless chemical bonds are broken and reformed. The second category is *conformational arrangements* which arise from the rotation of single bonds. Examples involving conformations of polymer chains include trans versus gauche arrangement of consecutive carbon–carbon single bonds and the helical arrangements found in some polymer crystal structures. Polymer configurations include head-to-head, tail-to-tail and head-to-tail arrangements in vinyl polymers, several stereoregular arrangements of 1,2- and 1,4-addition *cis* or *trans* isomers, or *d* and *l* forms, and arrangements around asymmetric carbon atoms.

Stereo-isomerism in polymers arises from different spatial arrangements (configurations) of the atoms or substituents in a molecule. *Tacticity* is the regularity

W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_3,

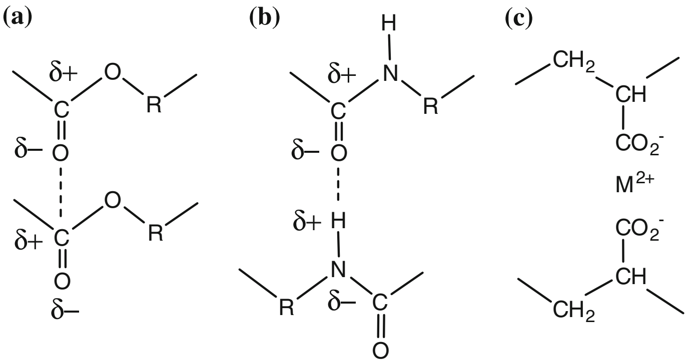


Fig. 3.1 Intermolecular forces in polar polymers: **a** Dipole–dipole interaction in polyester. **b** Hydrogen bonding in polyamide. **c** Ionic bonding in ionomer

in the configurations of successive stereo centers that determines the order of the polymer chain, such as (–CH_2–C*HR–)$_n$ where * is stereo center. Figure 3.2 shows the different examples of tacticity. Atactic is that the *R* group on successive stereo centers are randomly distributed on the two sides of the planar zig–zag polymer chain and thus the polymer chain does not have order. Isotactic is that the stereo center in each repeating unit in the polymer chain has the same configuration. All the *R* groups are located on one side of the plane of the carbon–carbon polymer chain either all above or all below the plane of the chain. Syndiotactic is that the stereo

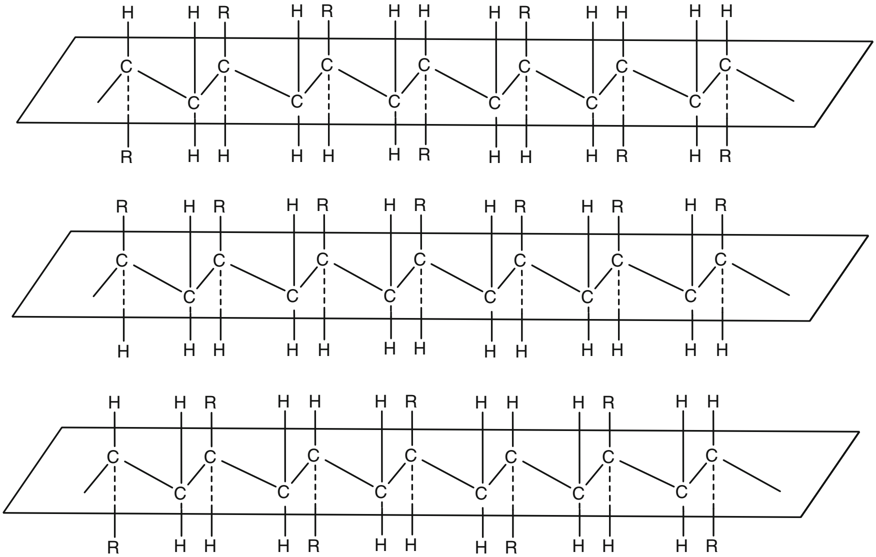


Fig. 3.2 Different polymer structures from a monosubstituted ethylene, –$(CH_2CHR)_n$–, Atactic (*top*), Isotactic (*center*), Syndiotactic (*bottom*) [1]

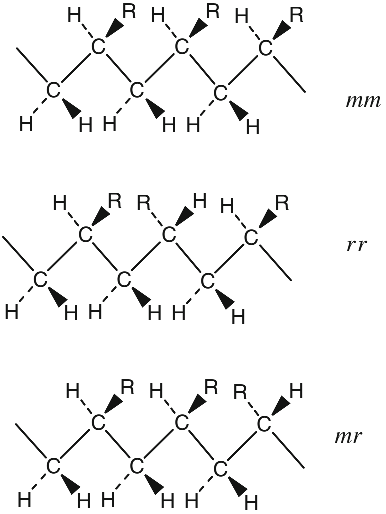


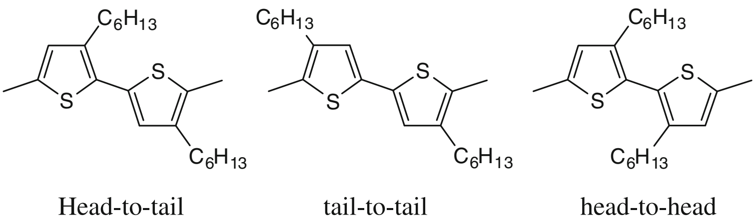
Fig. 3.3 Configurations of *mm*, *mr*, *rr* of poly(methyl methacrylate)

center alternates from one repeating unit to the next with the *R* groups located alternately on the opposite sides of the plane of the polymer chain.

In addition to poly(alpha) olefin, polystyrene, poly(methyl methacrylate) and 1,2 addition of polybutadiene can also exhibit either isotactic or syndiotactic structure. Whether a polymer is isotactic or syndiotactic usually determines its crystal structure, and the assignment of an all-isotactic or all-syndiotactic structure to a polymer can be made from its crystal structure. NMR spectroscopy is a powerful technique to determine the stereospecificity of polymer (the principle of NMR spectroscopy will be discussed in Chap. 5). It allows the determination of the stereoregular configuration of successive monomers in sequences. For example, the NMR spectrum of methylene protons in poly(methyl methacrylate) allows one to distinguish between and determine the relative numbers of sequences of two monomer units (dyads) that have syndiotactic (racemic, *r*) and isotactic (meso, *m*) symmetry. The alpha-methyl proton resonance allows estimation of the numbers of 3-monomer sequences (triads) with configurations *mm*, *mr*, and *rr*. Figure 3.3 shows the configurations of *mm*, *mr*, *rr* of poly(methyl methacrylate).

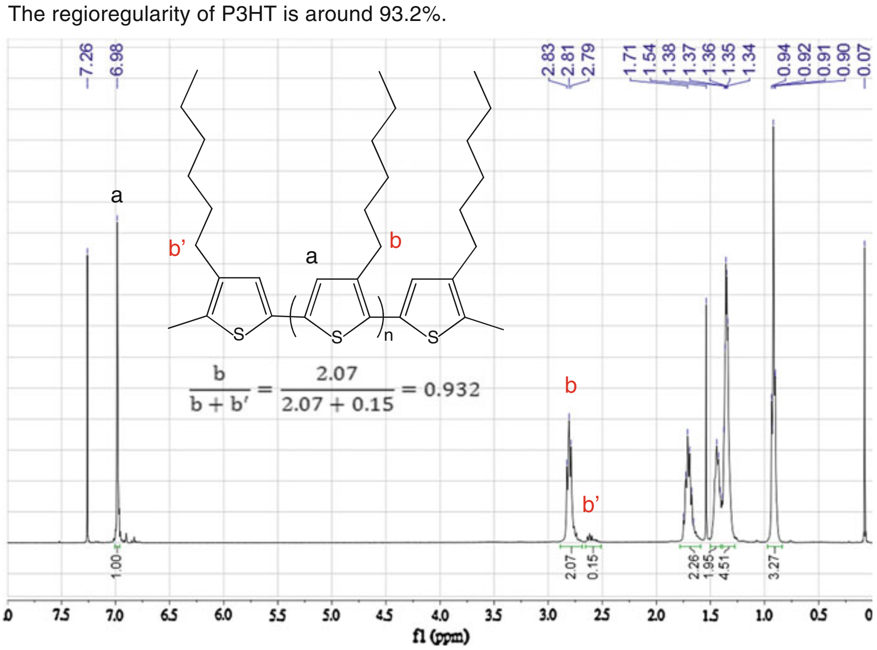
The synthesized poly(3-(*n*-hexyl)thiophene) (P3HT) can have three configurations: head-to-head, tail-to-tail and head-to-tail. Only the head-to-tail configuration shows high crystallinity due to the presence of even spacing among the monomers in the head-to-tail configuration as shown in Fig. 3.4. The stereospecificity of P3HT can also be determined by the NMR as shown in Fig. 3.5. The chemical shift of methylene proton of hexyl side chain of thiophene is different resulted from their position, so it can be easily identified and calculated the stereospecificity of the polymer.

Many polymers are capable of rotating the plane of polarization of light and are optical active such as poly(L-propylene oxide). The optical activity of low molecular weight compound is associated with the presence of asymmetric carbon



Head-to-tail tail-to-tail head-to-head

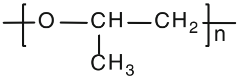
Fig. 3.4 Three configurations of poly(3-(*n*-hexyl) thiophene)



$$\frac{b}{b + b'} = \frac{2.07}{2.07 + 0.15} = 0.932$$

Fig. 3.5 Stereospecificity determination of poly(3-(*n*-hexyl) thiophene) by NMR

atoms. However, it is not universally true in polymers. The every second chain of substituted vinyl polymer is theoretically asymmetric, yet such polymers are not usually optically active, even when isotactic or syndiotactic, because of intramolecular compensation.



$$\left[\mathrm{O} - \underset{\displaystyle \mathrm{CH_3}}{\mathrm{CH}} - \mathrm{CH_2} \right]_n$$

poly(L-propylene oxide)

3.2 Crystal Structure of Homopolymer

The X-ray patterns of most crystalline polymers show both sharp features associated with ordered regions and diffuse features with molecularly disordered regions. Therefore both crystalline structure and amorphous structure coexist in the crystalline polymer. Additional evidence indicates that the density of crystalline polymer is in between the theoretical calculated value of complete crystalline polymer and amorphous polymer as shown in Table 3.1.

The crystallinity of polymers is closely related to the chemically and geometrically regular structure of polymer chain. However, atactic polymer can form crystalline as long as the size of repeating unit can fit into the crystal lattices despite of stereochemical irregularity. Polyethylene can exhibit highly ordered arrangement with all of the carbon atoms in one plane when the C–C bonds form a zig–zag. Figure 3.6a shows these zig–zag sections of chains which easily pack together closely to form orthorhombic crystalline. Single crystal of linear polyethylene has been fabricated from a solution in perchloroethylene as shown in Fig. 3.6b. Irregularities such as branching in the polyethylene or copolymerization with other different structure monomer will reduce crystallinity.

The crystal structure of poly(vinyl alcohol) is similar to that of polyethylene, since the CH(OH) group is small enough to fit into the polyethylene structure in place of a CH_2 group. The unit cell is monoclinic. Pairs of chains are linked together by hydrogen bonds and then linked into sheets, as long as the stereochemical irregularity allows. Fully extended planar zig–zag is 3.3 kJ/mole of molecular dynamic energy less than that of the gauche. Thus, the zig-zag conformation is favored to form crystalline structure unless substituents on the chains cause steric hindrance. Syndiotactic polymers such as poly(vinyl chloride), poly(1,2-butadiene), most polyamides and cellulose exhibit the similar crystalline structure. In most aliphatic polyesters and in poly(ethylene terephthalate), the polymer chains are shortened by rotation about the C–O bonds to allow close packing. As a result, the main chains are no longer planar. However the terephthalate unit in poly(ethylene terephthalate) remains planar as required by resonance. That results in higher packaging and thus higher crystallinity for poly(ethylene terephthalate) as compared with aliphatic polyesters.

Table 3.1 Densities of polymers in bulk, crystalline and amorphous states [2]

Polymer	Density (kg dm^{-3})		
	Typical bulk	Crystalline	Amorphous
Polyethylene (LDPE)	0.91-0.93	1.00	0.86
Polyethylene (LLDPE)	0.93-0.94		
Polyethylene (HDPE)	0.95-0.96		
Polyethylene (VLDPE)	0.90-0.91		
Poly(ethylene terephthalate)	1.41	1.46	1.34
Poly(tetrafluoro ethylene)	2.19	2.30	2.00

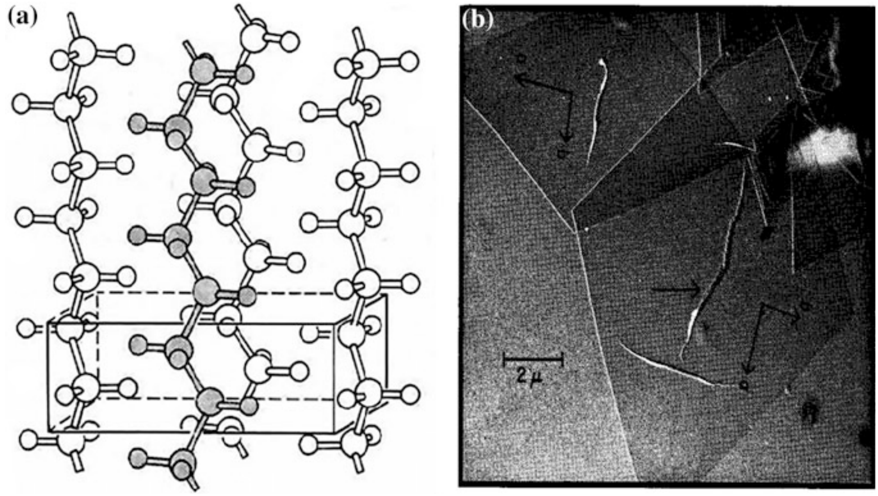
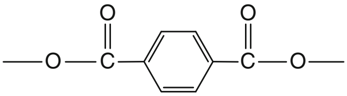


Fig. 3.6 **a** The arrangement of C–H in the crystallites of polyethylene. Reproduced by permission of the Royal Society of Chemistry [3]. **b** Single crystal polyethylene shows platelet like structure. Reproduced by permission of Journal of Applied Physics [4]



terephthalate

The substituted vinyl polymer –(CH_2–CHR)– with large bulky *R* group usually is in amorphous structure through free radical polymerization. For example, poly(methyl methacrylate), polyacrylonitrile, rubber and polystyrene. Amorphous polymers do not scatter light, so they are transparent in visible light. Thus, they can be used as light weight glass such as poly(methyl methacrylate) with a trade name of Flexglas.

The large size substituted polymer can be organized in isotactic structure through coordination polymerization. For example, poly(methyl methacrylate), polystyrene can crystallize with a helical conformation in which alternate chain bonds take *trans* and *gauche* positions. For the gauche position, the rotation is always in the direction that relieves steric hindrance by placing *R* and *H* groups in juxtaposition, generating either a left-hand or a right-hand helix as shown in Fig. 3.7. If the side group is not too bulky, the helix has exactly three units per turn and the arrangement is similar to that in Fig. 3.7a. This form has been found in isotactic polypropylene, poly(1-butene), polystyrene. More bulky side groups require more space, resulting in the formation of looser helices as shown in Fig. 3.7b–d. Isotactic poly(methyl methacrylate) forms a helix with five units in two turns, while polyisobutylene forms a helix with eight units in five turns. The poly(tetrafluoro ethylene) contains larger size of F atom than that of H atom. Two helical conformations are existed. They are twist ribbons in which the fully

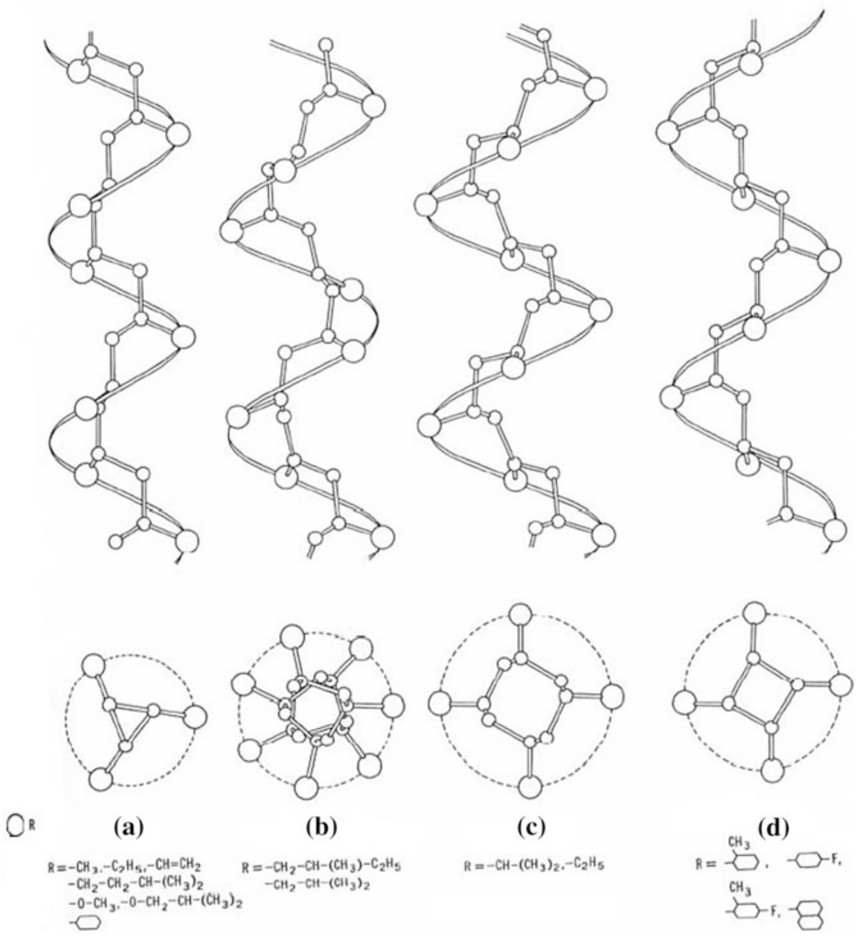


Fig. 3.7 Helical conformation of isotactic vinyl polymers. Reproduced from Wiley-Interscience with permission [5]

extended planar form is distorted to have an 180° twist in 13 CF_2 units in the more stable form at low temperature. Above 19°C, this form is replaced by a slightly untwisted conformation with 15 CF_2 units per half-twist.

3.3 Crystal Structure of Copolymer

Crystallinity is not expected to find in alternating copolymer and random copolymer. The repeating unit of alternating copolymer is too short to form organized structure. If A and B unit in the alternating copolymer are in similar molecular size, the crystallization behavior will be similar to that of homopolymer.

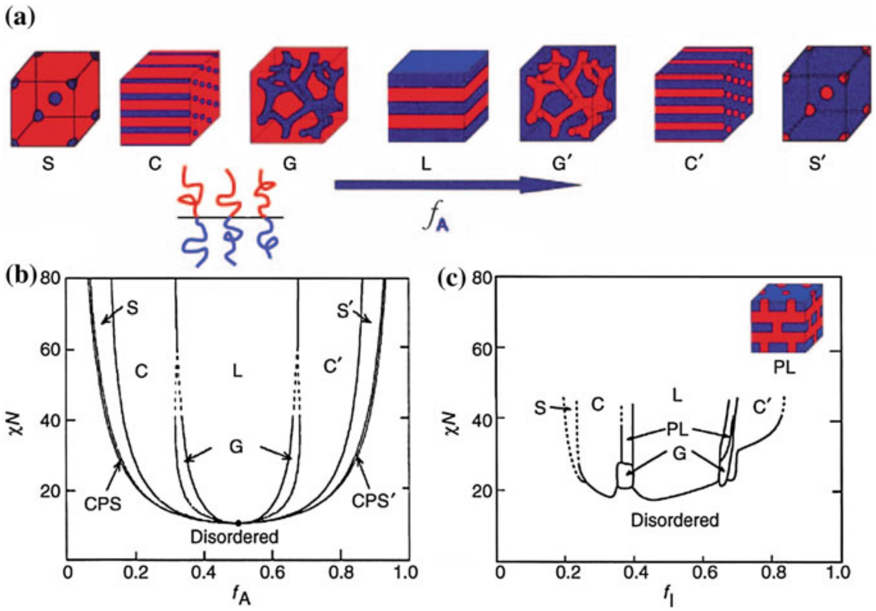


Fig. 3.8 Varieties of nanostructures and phase diagram of block copolymers. Reproduced from Physics Today with permission [6]

The random copolymer does not have regular and ordered sequence, so the crystalline cannot be formed.

For the block copolymer, various crystalline structures can be formed according to their chemical structure, chemical composition and interactions among blocks. The crystalline behaviors of diblock copolymers have been extensively studied. Figure 3.8a shows the varieties of crystalline structure in diblock copolymers with different volume fractions. A phase diagram can be constructed for various diblock copolymer compositions at different temperature as shown in Fig. 3.8b, c. The formation of crystalline structure in diblock copolymer is due to the phase separation between two blocks. It is called self assembly phenomena. The crystalline domain is in the range of 10–20 nm depends on the size of each block. These nanostructured copolymers have generated many interests in the nanodevice applications, because they can be used as low cost nanolithographic resist defining nanopitch circuits without using expensive electron beam exposure unit.

Factors that influence the phase diagram of diblock copolymers are determined by: I (intrinsically immiscible interaction parameter), χ (the degree of thermodynamic incompatibility), N (degree of polymerization). The narrow molecular weight distribution copolymers have to be used, so one can obtain a clear-cut phase boundary. Therefore, the copolymer usually is synthesized using living polymerization (will be discussed in Chaps. 8 and 10). Figure 3.9 shows poly(3-hexyl thiophene)-b-poly(2-vinyl pyridine) can be synthesized by sequential polymerization. The vinyl terminated poly(3-hexyl thiophene) was first

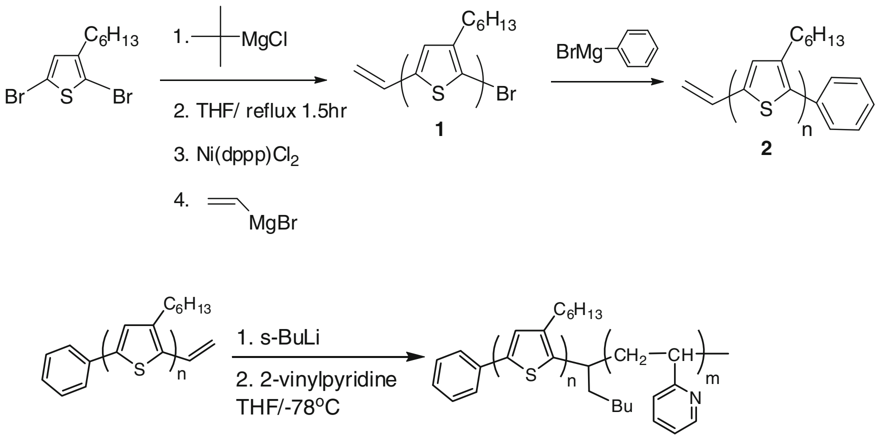


Fig. 3.9 Synthetic scheme of poly(3-hexyl thiophene)-b-poly(vinyl pyridine)

synthesized by Grignard metathesis polymerization with one end capped with phenyl group then subsequently reacted with 2-vinyl pyridine to obtain the block copolymer by anionic polymerization [7].

Various compositions of copolymers can be synthesized using anionic macro-initiator of polythiophene to initiate 2-vinylpyridine monomer to obtain P3HT-b-P2VP copolymers as summarized in Table 3.2. Their TEM microstructures are shown in Fig. 3.10. The copolymer exhibits structures of nanofibrils, lamella, cylinder and sphere by changing the volume fraction of P2VP from 20, 29, 68, 87 % respectively [8]. The P3HT segment is more rigid than P2VP segment, so at lower volume fraction of P2VP, less curvature morphology is observed such as fiber, lamella.

The TEM technique can only examine the morphology of copolymer locally. We have to use small angle X-ray scattering (SAXS) technique to study long range order behaviors of copolymers as shown in Fig. 3.11. The instrument set up is described in Fig. 5.15. The long range order of different copolymers has been observed for all the samples and it is in agreement with TEM observation.

Table 3.2 Molecular parameters of P3HT-b-P2VP block copolymers

Sample	FP2VP(%)*	Mn, P3HT	Mn, P2VP
P3HT	0	6,800	–
HTVP20	20	6,800	1,600
HTVP29	29	6,800	2,600
HTVP46	46	6,800	5,600
HTVP57	57	6,800	8,600
HTVP68	68	6,800	13,800
HTVP76	76	6,800	20,400
HTVP87	87	6,800	41,800

* Volume fraction of P2VP in copolymer

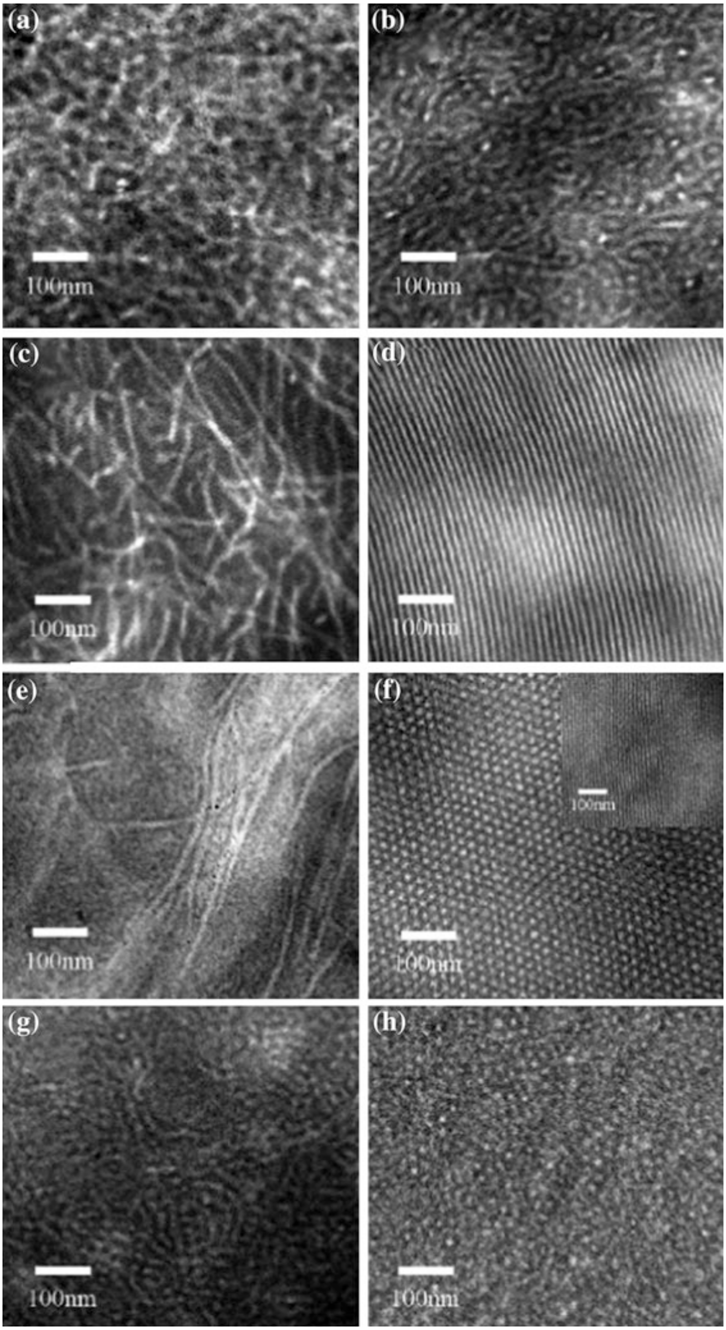


Fig. 3.10 TEM photos of P3HT-b-P2VP microstructure morphology at four copolymer compositions of 20, 29, 68 and 87 % volume of P2VP. **a**, **c**, **e**, **g** are solvent casted samples; **b**, **d**, **f**, **h** are 130°C annealed samples [8]

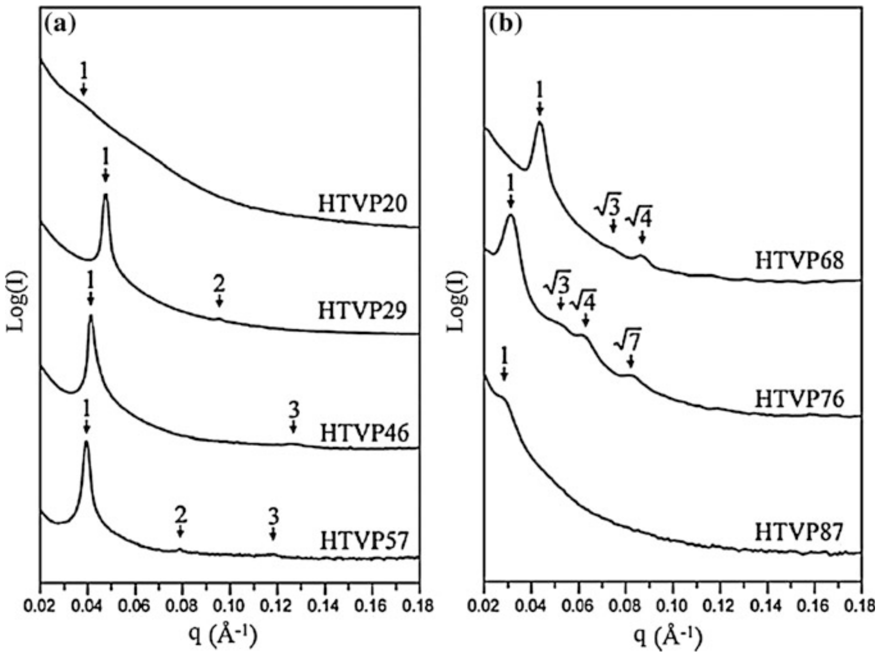


Fig. 3.11 SAXS profiles of P3HT-b-P2VP block copolymers with different compositions. HTVP20 is nanofibril structure; HTVP29, HTVP46, and HTVP57 are lamellar structure; HTVP68 and HTVP76 are hexagonal cylinder structure and HTVP87 is spherical structure [8]

The phase diagram of P3HT-b-P2VP has also been constructed using temperature varied TEM, SAXS and WAXS as shown in Figs. 3.12, 3.13 and 3.14 respectively.

The feature of phase diagram of the self assembly diblock copolymer depends on the chemical structure of each block as shown in Fig. 3.14. Figure 3.15 shows the phase diagrams of different diblock copolymers. The P3HT-b-P2VP is a rod-coil system. The P3HT rod is not flexible enough to obtain gyroid structure easily as observed in coil–coil system. The PPV-b-PI system exhibits simpler phase diagram than the P3HT-b-P2VP system, because the PPV is more rigid (higher aspect ratio of diameter versus length of molecule) as compared with P3HT.

3.4 Liquid Crystalline Polymer

Liquid crystals are neither true liquids nor true solids. Liquid crystallinity (LC) occurs when molecules become aligned in a crystalline array while still in the liquid state that exhibits anisotropic property. The ordered regions in the liquid are

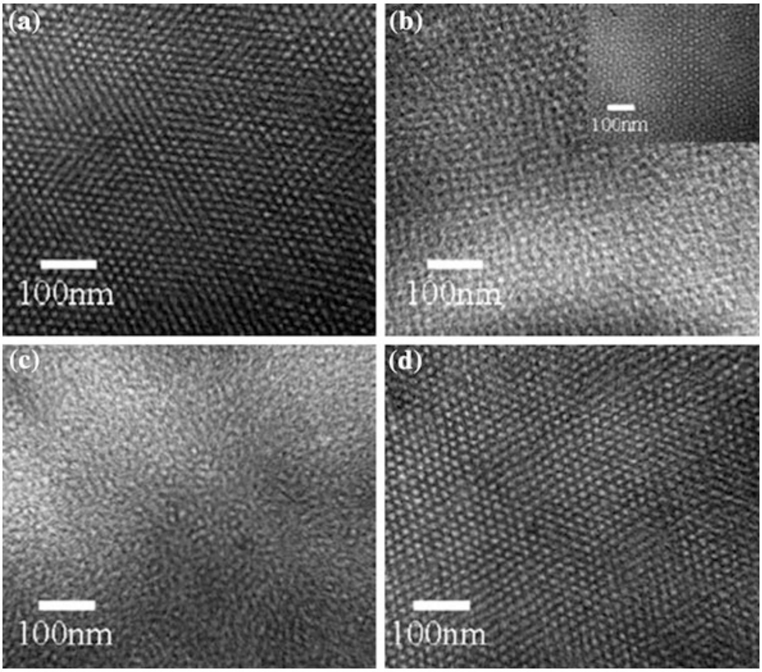
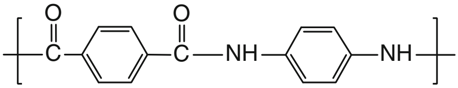


Fig. 3.12 TEM photos of HTVP68 self assembled into **a** hexagonal closed-packed cylinders after annealed at 130°C for 24 h plus liquid nitrogen quenching, **b** a gyroid phase after annealed at 150°C for 24 h plus liquid nitrogen quenching, **c** disordered phase after annealed at 220°C for 24 h plus liquid nitrogen quenching and **d** hexagonal close-packed cylinders after cooling from 220°C and annealing at 130°C for 24 h then liquid nitrogen quenching [8]

called mesophases. Molecules exhibit LC behavior when their structures are relatively rigid, elongated or disc like. The morphology of LC may be influenced by external magnetic or electrical field, shear force, sometimes they change color with temperature. They exhibit fluidity of liquids and the opaqueness of crystalline solids. The LC polymers developed in late 1970. They contain rigid moiety in the polymers. The rigid moiety is called mesogen which is responsible for the mesophases.

There are two major classifications of liquid crystals: lyotropic type and thermotropic type. Lyotropic liquid crystals form under the influence of solvent. A commercially available lyotropic liquid crystalline polymer is the aromatic polyamide (du Pont trade name Kevlar). The structure of Kevlar is shown in below.



Thermotropic liquid crystals form in the melt (upon heating). Copolyesters prepared from terephthalic acid, ethylene glycol, and *p*-hydroxybenzoic acid

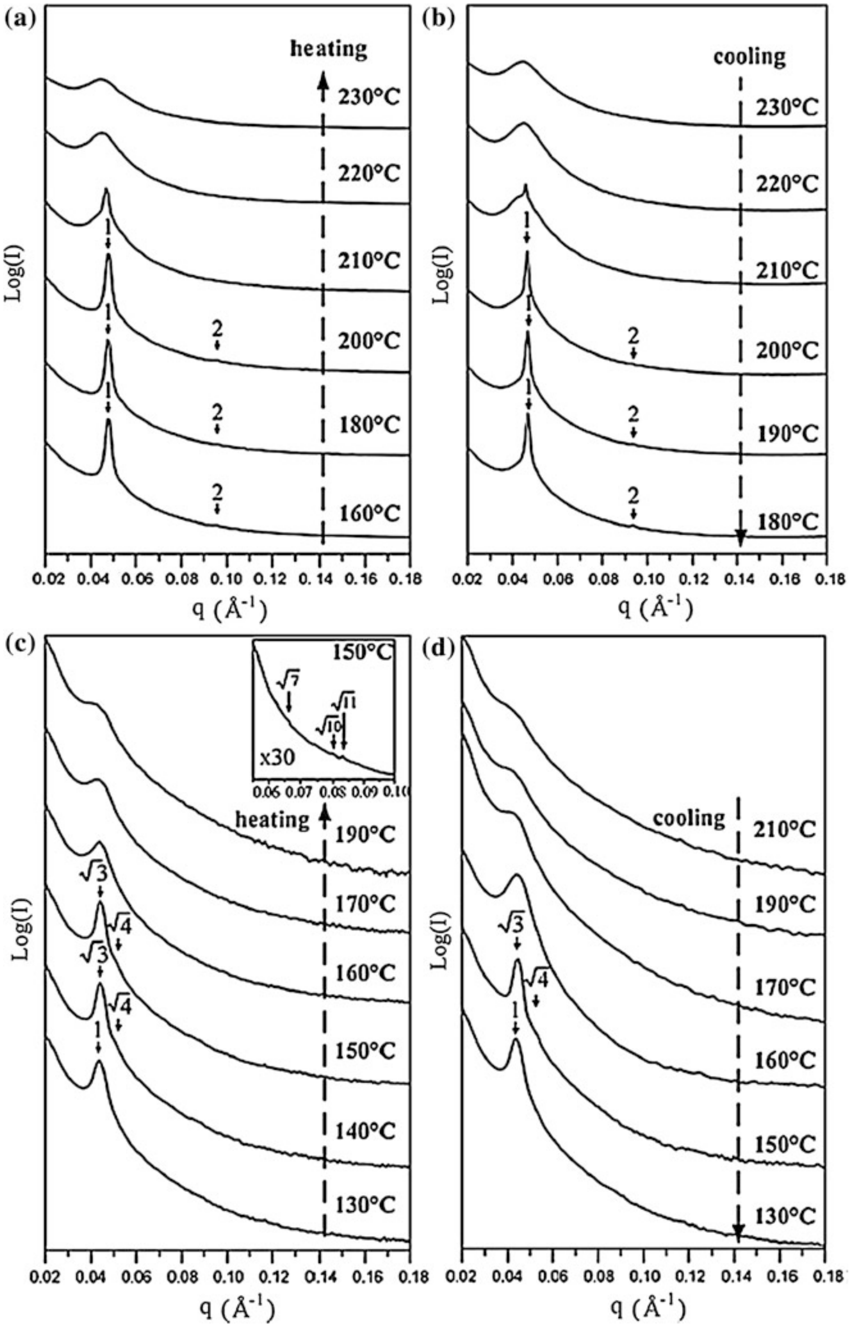


Fig. 3.13 Temperature varied SAXS profiles of P3HT-b-P2VP, **a** and **b** heating and cooling of HTVP29; **c** and **d** heating and cooling of HTVP68 [8]

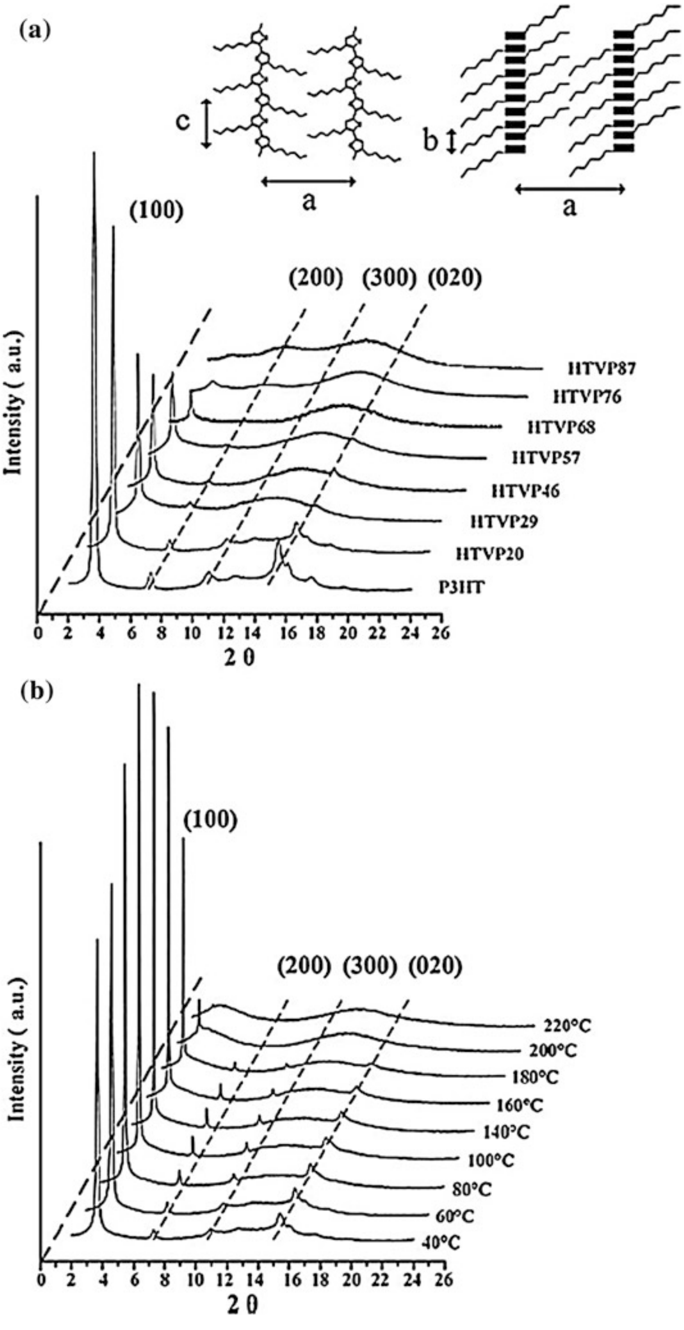


Fig. 3.14 WAXS profiles of P3HT-b-P2VP, **a** room temperature samples after thermal annealing, **b** samples are under varied temperature condition [8]

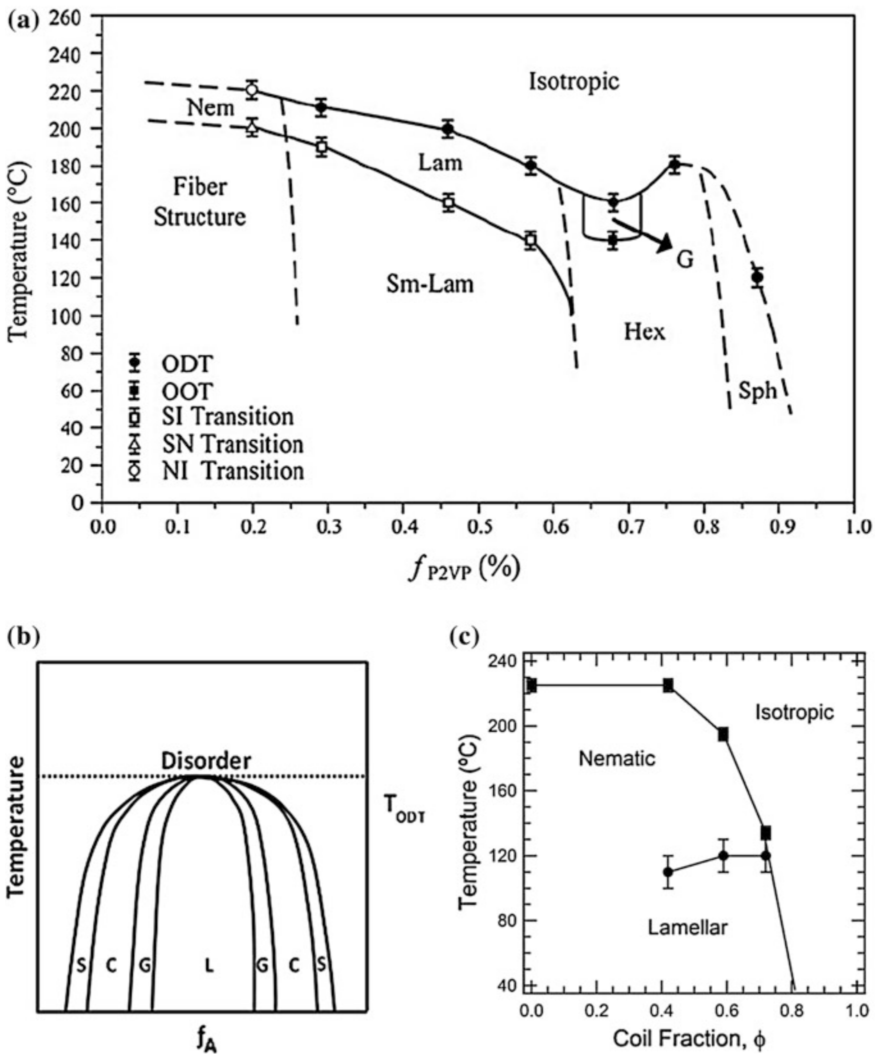
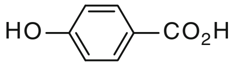


Fig. 3.15 Phase diagrams of **a** P3HT-b-P2VP [8], **b** coil–coil block copolymer [6], and **c** rod-coil DEH-PPV-b-PI [9]

exhibit liquid crystalline behavior. The structures of monomers are shown in below.

$HOCH_2CH_2OH$



The melt viscosity of copolyester was increased initially when the amount of *p*-hydroxy benzoic acid was increased due to the incorporation of “rigid” *p*-hydroxy benzoate unit [10]. At levels of about 30 mol %, however, the melt viscosity

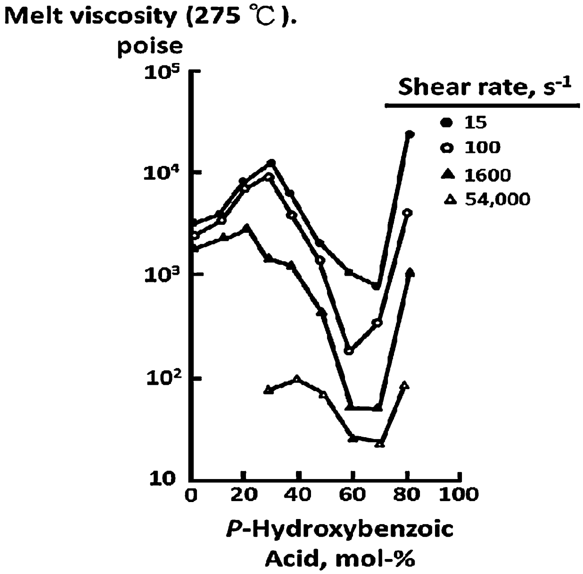


Fig. 3.16 Effect of *p*-hydroxybenzoic acid concentration on melt viscosity of a terephthalic acid/*p*-hydroxybenzoic acid/ethylene glycol copolyester. Reproduced from Journal of Polymer Science with permission [10]

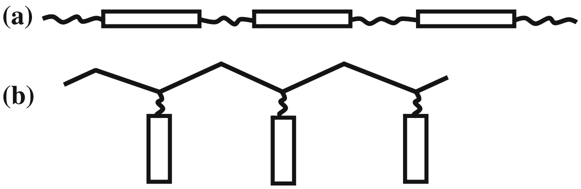
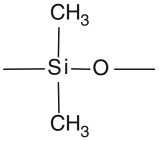


Fig. 3.17 Representations of mesogenic group (*box*) and flexible spacers (〰) in **a** the backbone and **b** the side chain of liquid crystalline polymers [11]

began to decrease, reaching a minimum at about 60–70 mol %. This is shown in Fig. 3.16 at four different shear rates. The decrease in viscosity and increase in opaqueness arises from the onset of LC polymers which is due to the increased backbone rigidity. The increase in rigidity decreases the entanglement of polymer chain which is an effective way to reduce viscosity.

Major drawbacks to liquid crystalline polymers are that they have a very high melting point and are difficult to dissolve in the common organic solvents. One approach to resolve these difficulties is to separate the rigid back bone groups with flexible spacers such as ethylene units, ethylene oxide units, or silane units (their structures are shown below). Another approach is to attach mesogens with flexible spacers to the polymer backbone. Both types of liquid crystalline polymers are illustrated schematically in Fig. 3.17.

$—CH_2CH_2—$ $—CH_2CH_2O—$



$$—\underset{CH_3}{\overset{CH_3}{Si}}—O—$$

3.5 Crosslinked Polymer

The polymers discussed above are thermoplastics which will flow upon heating or dissolving in solvent. Linking polymer chains through covalent or ionic bonds forms a network that decreases molecular freedom, increases thermal resistance and polymer rigidity but decreases the flow property. The crosslinked covalent bonds are usually formed by chemical reaction upon heating. This class polymer is called *thermoset*. The epoxy resin is one of the most common thermosets and used widely in the electrical insulation of electrical equipment where heat will generate during the operation of the equipment. The crosslinked polymers are no longer dissolved but swell in solvent (except ionically crosslinked). The swollen crosslinked polymer is called a gel. The 300–1,000 micron gelled particle of crosslinked polystyrene is called microgels that are used in solid-phase synthesis and catalyst immobilization.

The crosslink density $\mathit{\Gamma}$ is determined by the number average molecular weight between crosslinks $(\bar{M}_n)_c$ dividing the number average molecular weight of un-crosslinked polymer $(\bar{M}_n)_o$ as shown below.

$$\mathit{\Gamma} = \frac{(\bar{M}_n)_c}{(\bar{M}_n)_o} \tag{3.1}$$

Crosslink density is the number of crosslinked monomer units per main chain (theoretical value). For example, as a polymer where one of every 20 molecules is a trifunctional isocyanate, nine of every 20 molecules is a bifunctional isocyanate, and 10 of every 20 molecules is a bifunctional alcohol, we could say the crosslink density of this polymer is 0.05 [1/20]. In practice for actual value, the crosslinking density is measured by swelling ratio and extract ratio test (ASTM D2765-95), and their ratios are equal to:

$$\text{Swell ratio} = \frac{\text{Vol. of crosslinked polymer } + \text{Vol. of absorbed solvent}}{\text{Vol. of crosslinked polymer}} \tag{3.2}$$

$$\text{Extract ratio} = \frac{\text{Weight of extract}}{\text{Weight of crosslinked polymer}} \tag{3.3}$$

By introducing strong secondary bonding attraction between polymer chains, the polymer can exhibit properties of a thermosetting material while remaining thermoplastic behavior. Crystalline polymers fit into this category. Because of the very strong secondary forces arising from close chain packing, many of the mechanical and solution properties of crystalline polymers are similar to those of crosslinked amorphous polymers. For example, thermoplastic elastomer can be crosslinked through hydrogen bonds. A common type of thermoplastic elastomers (TPE) has polyurethane structures. This type of polyurethane can be prepared by reacting excess amount of methylene 4,4′-diphenyl diisocyanate with polyols (hydroxyl terminated long chain aliphatic polyester or polyether) to form

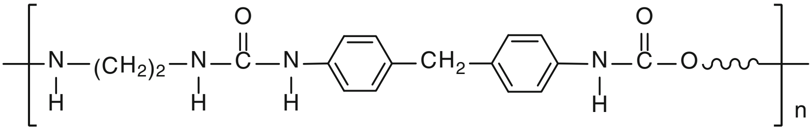


Fig. 3.18 Polyurethane type of thermoplastic elastomer

Fig. 3.19 Representation of aggregation in an ABA block thermoplastic elastomer (〰 represents end blocks, *circle* represents microdomains) [11]

isocyanate terminated oligomer. Then the oligomer is reacted with ethylene diamine to yield polyurethane with the structure shown in Fig. 3.18 [2]. The polymer contains soft segment and hard segment from the polyols domain and urethane urea domain respectively.

Polystyrene-polybutadiene-polystyrene (-ABA-copolymer, rigid-flexible-rigid) is another example. A and B are immiscible, B block aggregates into microdomain within the polymer matrix, as shown in Fig. 3.19 to have physical crosslinking with improved mechanical properties.

3.6 Polymer Blend

Polymer blend is a mixture of two or more polymers without chemical bonding. It is also called polymer alloy. Miscible blend is clear and exhibits one phase transition, for instance, GE Noryl is a polymer blend of polystyrene and poly (oxy-2,6-dimethyl-1,4-phenylene). Immiscible blend is opaque and exhibits more than one phase transition, such as ABS (acrylonitrile–butadiene–styrene) plastics. It is prepared by an amorphous styrene-butadiene copolymer dissolving in styrene and acrylonitrile first and then undergoing further polymerization. Chain transfer reactions may occur to graft one copolymer to the other [11].

The property (P) of miscible binary polymer blend can be quantified by the semi empirical relationship,

$$P = P_1\emptyset_1 + P_2\emptyset_2 + I\emptyset_1\emptyset_2 \tag{3.4}$$

where $\emptyset$ is the volume fraction in the blend and $\boldsymbol{I}$ is the interaction factor that may be negative, zero, or positive. If the property is entirely additive, $\boldsymbol{I} = 0$. If $\boldsymbol{I}$ is

Fig. 3.20 Hypothetical property-concentration relationships for a binary miscible polymer blend [11]

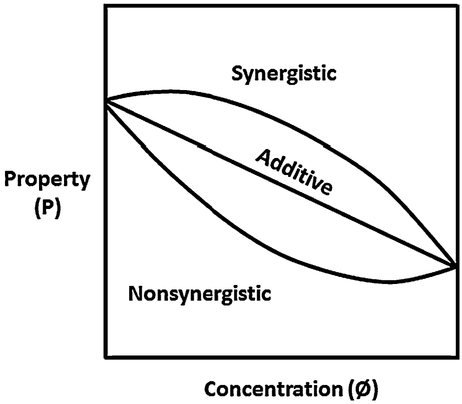
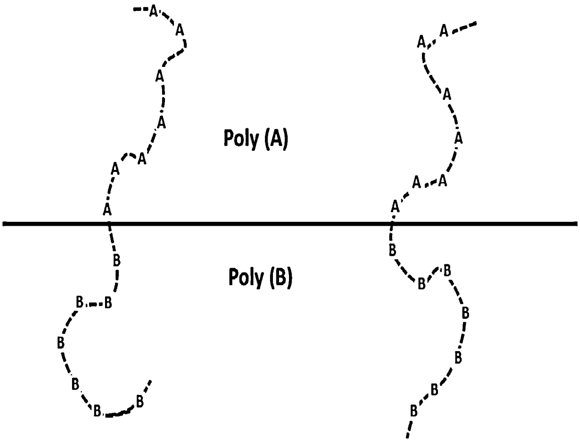


Fig. 3.21 Representation of the use of an AB block copolymer to improve interfacial adhesion in an immiscible polyblend [11]



positive, every component has synergistic effect to each other which results in better property than the weighted average. If I is negative, every component is nonsynergistic, then the property is worse than the weighted average. Figure 3.20 shows these three possible phenomena in the plot of property versus concentration.

When the two polymers are not miscible, by incorporate compatibilizers into the blend, the adhesion between phases can be improved. For example, an incompatible blend of homopolymers of poly(A) and poly(B), by adding the block copolymer made from A and B monomers, the natural affinities of the blocks for their respective homopolymers will localize the copolymer at the phase boundary and help "glue" the two immiscible phases together, as depicted in Fig. 3.21.

3.7 Polymer Flow Under Shear Force

The science of deformation and flow of material is called rheology. To cause a polymer to deform or flow requires the application of a force. If a force is applied, then withdraw quickly, the polymer molecules tend to revert to their previous, undisturbed configuration, this process is called a relaxation–elastic property of polymer. Because of chain entanglement and frictional effects, the flowing liquid will be very viscous. The combination of elasticity and viscous flow is called *viscoelastic properties* of polymer.

A variety of forces are applicable to polymer deformation, and the most important one is *shear* force (or *tangential stress*). Shear is a force applied to one side of a surface in a direction parallel to the surface. If a rectangle is subjected to shear, for example, it becomes a parallelogram as illustrated in Fig. 3.22. Shear stress (τ) is defined as the force (F) in dynes (or newtons) per unit of surface area (A) in square centimeters (or square meters); that is,

$$\tau = F/A \tag{3.5}$$

Shear causes polymer molecule to flow past one another, when a polymer is in the liquid or molten state.

Viscosity is a measure of resistance to flow which has been used in the discussion of polymer solution in Chap. 2. In this chapter, we concentrate on the flow properties of neat polymers. When the polymer is under the shear force $\tau = F/A$, shear strain, γ is the amount of deformation can be expressed by

Fig. 3.22 Illustration of shear force (tangential stress) applied to an object [11]

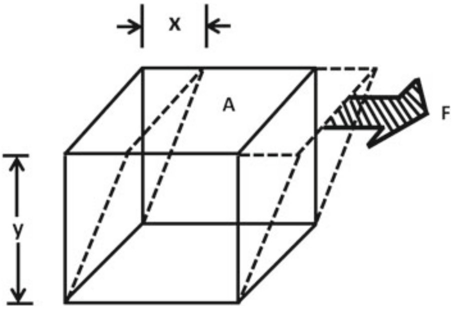


Table 3.3 Viscosity values of different matters

Matter	Viscosity (Pa.s)
Gas	10^{-5}
Water	10^{-3}
Glycerine	1
Polymer	10^{2}–10^{6}

$$\gamma = \frac{X}{Y} \tag{3.6}$$

The resistance to shear is the *shear modulus*, G, which is the ratio of stress to shear strain and expressed by

$$G = \frac{\tau}{\gamma} \tag{3.7}$$

Shear rate, $(\dot{r})$, also called the *velocity gradient*, is the rate at which the planes (see Fig. 3.22) or molecules (in an amorphous liquid) flow relative to one another:

$$\dot{r} = \frac{d\gamma}{dt} \tag{3.8}$$

If the shear stress increases in proportion to the shear rate, the liquid is called *Newtonian* (or ideal) liquid. It follows the Newton's law of viscosity:

$$\tau = \eta\dot{r} \tag{3.9}$$

where the proportionality constant, η, is the viscosity. Units of viscosity are poises (dyne s/cm^2), or in the SI system, Pascal-seconds (Pa s = newton s/m^2). Table 3.3 is the list of viscosity of different matters as compared to glycerine. The polymer exhibits at least two orders higher viscosity than glycerine.

The viscosity of neat polymer can be described by the Williams-Landel-Ferry (WLF) equation for temperature ranged from T_g to $T_g + 100$ K as shown in Eq. 3.10. T_g is the glass transition temperature of polymer which indicates the transition temperature of polymer from rigid solid state to rubber state (the effect of chemical structure on the T_g of polymer will be discussed in Sect. 3.8).

$$\eta = A\exp\left(\frac{B}{T - T_0} + \frac{E_v}{RT}\right) \tag{3.10}$$

where A, B are adjustable constant, R is gas constant, E_v is apparent activation energy for viscous flow which is related to free volume, $T_0 < T_g$ (T_0 is the temperature of free volume being equal to zero). The Arrhenius equation (Arrhenius-Frenkel-Eyring AFE formula) can be used for temperature above $T_g + 100$ K

$$\eta = A\exp\left(\frac{E_v}{RT}\right) \tag{3.11}$$

Table 3.4 Temperature effect on polymer viscosity $\ln \eta = \ln A + \frac{E_v}{RT}$

Polymer	Activation energy	Temperature at	Viscosity
Linear	Small	T_1	Low
Linear	Small	$T_2 (T_2 > T_1)$	Lowered with small extent
Bulky sub.	Large	T_1	High
Bulky sub.	Large	$T_2 (T_2 > T_1)$	Lowered with large extent
Bulky sub.	Large	$T_2 (T_2 < T_1)$	Higher than linear polymer

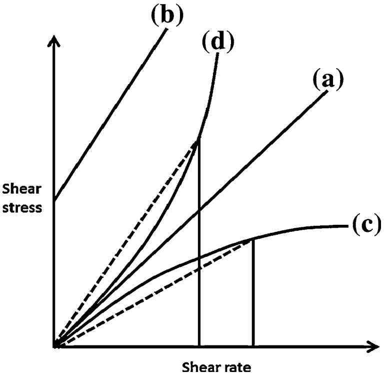


Fig. 3.23 Types of shear flow: **a** Newtonian; **b** Bingham Newtonian; **c** shear thinning; and **d** shear thickening [11]

The shear rate dependence of viscosity can be expressed by Carrean A model as below which is not temperature dependent, so called compensation effects for polymer melts.

$$\eta = \frac{\eta_0}{[1 + (k\dot{r})^2]^s} \tag{3.12}$$

where η is the viscosity at a shear rate of $\dot{r}$; η_0, k, and s are the model parameters. This relation is known to fit most polymer viscosity data obtained from simple shear flow experiment quite well [12]. The viscosity of the polymer depends on the chemical structure of the polymer and temperature. At the same amount of repeating unit of polymer, the bulky structured polymers from bulky branch or substituent have higher E_v than that of linear polymers. At a specific temperature (T_1), the polymer with more bulky chain branch or substituent exhibits higher viscosity because the polymer has less free volume. When the temperature increases from T_1 to T_2, its effect on the viscosity will be less for linear polymer but more for bulky structured polymer. Table 3.4 shows the extent of temperature effect on the polymer viscosity for different chain structures and different activation energy of polymer flow.

Deviations from ordinary Newtonian liquid behavior are common in polymer flow. One type is called a *Bingham Newtonian fluid* which is defined as

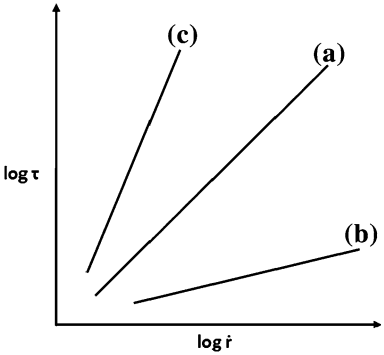


Fig. 3.24 **a** Newtonian (slope = 1); **b** shear thinning (slope < 1); **c** shear thickening (slope > 1) [11]

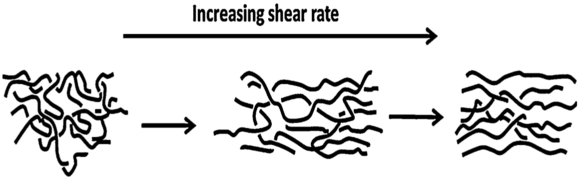


Fig. 3.25 Shear thinning arising from disentanglement [11]

$$\tau = \tau_c + \eta \dot{r} \tag{3.13}$$

where τ_c is the critical shear stress, or threshold stress. It is the stress needed to initiate flow. Other deviations are non-Newtonian. They occur where shear stress does not increase in direct proportion to shear rate. The deviation may be in the direction of *thinning* or *thickening*. These various possibilities are illustrated in Fig. 3.23.

Thixotropic liquid has gel like high viscosity at low stress, but thin out at high shear force such as stirring. The difference between shear thinning and thixotropic is that the former dependent on shear rate, the later is independent of shear rate but dependent on time at a fixed shear rate. Flow behavior may also be expressed by a power law equation:

$$\tau = A\dot{r}^B \tag{3.14}$$

where A is a constant and B an index of flow. For a Newtonian fluid, the relationships of $B = 1$ and $A = \eta\ (\tau = \eta\dot{r})$ are held. A plot of log τ versus log $\dot{r}$ is linear with slope equal to B and intercept equal to log A (Fig. 3.24).

The viscosity of polymer usually decreases at high shear rate due to the decrease in molecular entanglement as shown in Fig. 3.25. In the amorphous state there is considerable entanglement of the chains, and while low shear rates may disrupt this to a degree, the mass retains its entangled character. As shear rate increases, disruption may occur faster than the chains can re-entangle, and the resultant decreasing entanglement allows the molecules to flow with less resistance, hence the decrease in viscosity.

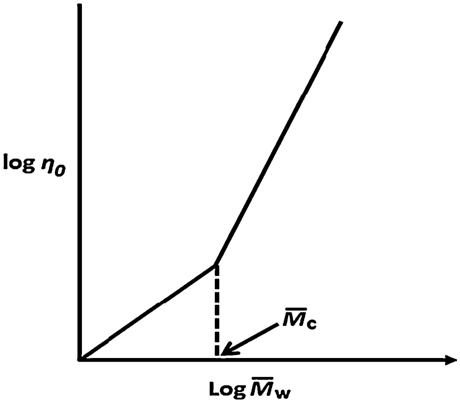


Fig. 3.26 Effect of molecular weight on Newtonian viscosity [11]

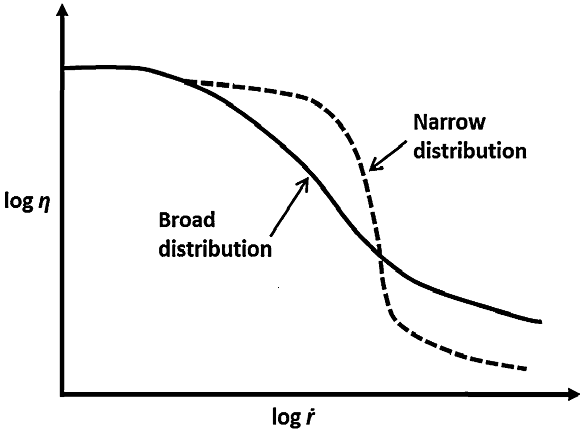


Fig. 3.27 Effect of molecular weight distribution on shear thinning [11]

The molecular entanglement is increased as the molecular weight increases. Therefore, molecular weight is a critical variable in rheology. Studies have shown that there exists a critical molecular weight $(\bar{M}_c)$ for entanglement to begin for flexible chain polymers as illustrated in Fig. 3.26. The slope of log of Newtonian viscosity (η_0) against the log of weight average molecular weight $(\bar{M}_w)$ becomes steep (very large) after the $\bar{M}_c$. For most polymers, the critical molecular weight falls in the range of 4,000–15,000. The critical molecular weight is a function of chain length and equal to average $\overline{DP}$ of 600 (e.g. polyethylene –(CH_2CH_2)–, $600 \times 14 = 8{,}400$). A critical chain length, rather than a critical molecular weight is necessary for entanglement.

Polymer viscosity is increasing logarithmically with molecular weight (Fig. 3.26). The broader the molecular weight distribution, the lower the shear rate at which shear thinning develops (Fig. 3.27). At a given molecular weight, shear rate and temperature, the more highly branched polymer, the lower will be its hydrodynamic volume and the lower its degree of entanglement. Although the branched polymer has low viscosity for ease of processing, it is usually mechanically weaker than the linear polymer due to lack of intermolecular secondary bond. The flow also depends on polymer conformation (shape), more rigid polymers are significantly more viscous according to Mark-Houwink-Sakurada (M–H–S) equation (Eq. 2.22) except liquid crystalline polymers as discussed before. We observed that a varies from 0.5 for random coil to about one for more rodlike extended shape.

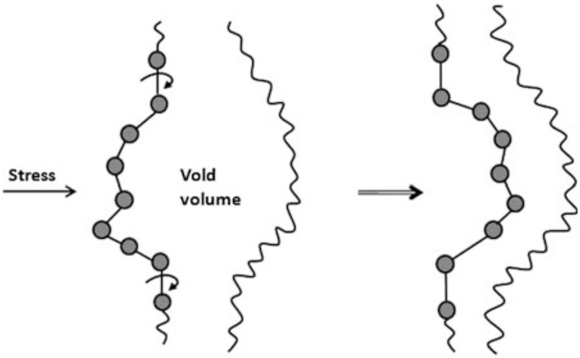


Fig. 3.28 Segmental rotation of a polymer chain into an adjacent void volume under stress, when internal rotation takes place only about two bonds (*hooped arrows*) [2]

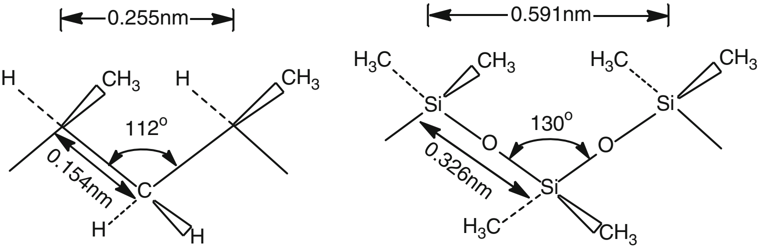
Table 3.5 Typical T_g values of common thermoplastics (atactic forms) [2]

Polymer	CRU structure[a]	T_g (K)
Poly(oxymethylene)	$-CH_2-O-$	198
Polyethylene	$-CH_2-CH_2-$	253
Poly(ethylene oxide)	$-CH_2-CH_2-O-$	206
Polypropylene	$-CH_2-CH(CH_3)-$	267
Poly(propylene oxide)	$-CH_2-CH(CH_3)-O-$	226
Polystyrene	$-CH_2-CH(C_6H_5)-$	381
Poly(α-methylstyrene)	$-CH_2-C(CH_3)(C_6H_5)-$	445
Poly(methylacrylate)	$-CH_2-CH(C(=O)OCH_3)-$	281
Poly(methylmethacrylate)	$-CH_2-C(CH_3)(C(=O)OCH_3)-$	394
Poly(vinyl chloride)	$-CH_2-CH(Cl)-$	354
Polyacrylonitrile	$-CH_2-CH(C\equiv N)-$	378
Poly(ethylene terephthalate)	$-O-CH_2-CH_2-O-C(=O)-C_6H_4-C(=O)-$	340
Nylon 66	$-C(=O)-(CH_2)_4-C(=O)-NH-(CH_2)_6-NH-$	357

[a] CRU = constitutional repeating unit

Table 3.6 Typical values of T_g of common elastomers (rubbers) [2]

Polymer	x	T_g(K)
Poly(*cis*-1,4-butadiene)	H	165
Poly(*cis*-1,4-isoprene)	CH_3	206
Neoprene	Cl	253



Polypropylene Poly (dimethyl siloxane)

Fig. 3.29 Comparison of the geometries of the planar zig–zag conformations of polypropylene and poly(dimethyl siloxane) [2]

3.8 Polymer Flow Under Thermal Stress

The polymer starts to flow at a specific temperature which is called glass transition temperature (T_g). The solid polymer changes from a hard glassy solid to a rubbery (elastomers) or flexible (for themoplastics) state which involves the translational movements of the polymer main chains and the rotational movements of the segments (Fig. 3.28).

The translational movements are related to the molecular weight of the molecule and free volume of the polymers. High crystalline and high density polymers exhibit high T_g due to less free volume. Any structural feature which hinders the rotation of segments of the molecular chain should increase the value of T_g of the polymer. Tables 3.5 and 3.6 list the T_g of some common thermoplastics and elastomers respectively. For the purpose of comparison of thermoplastic with general CRU formula –CH_2–CH(X)–, the T_g of polyethylene is taken as a reference point. Any substituting for the hydrogen atom on the ethylene chain, the T_g will be increased due to increased steric hinderance of large size substituent; the larger the substituent, the higher the T_g becomes. For instance, the T_g of polystyrene (381 K) is higher than that of polypropylene (267 K) and polyethylene (253 K). When the substituent is more polar, the T_g will increase as well, such as poly(vinyl chloride) (354 K) and polyacrylonitrile (378 K). The –Cl and –CN are also larger then –H. This point also can be observed in elastomers with general CRU formula –CH–CH=C(X)–CH–. The –C–O– bond has more free volume than –C–C– bond due to the divalent of –O–, so the T_g of polyoxymethylene is lower than polyethylene (198 K vs. 253 K).

Table 3.7 Values of T_m, $\triangle H_m$, and $\triangle S_m$ of some common polymers [2]

Polymer	T_m (K)	ΔH_m (KJ $mol^{-1)}$	ΔS_m (JK^{-1} mol^{-1})
Polyethylene	414	8.0	19.0
Poly(tetrafluoro ethylene)	672	5.7	8.5
Poly(ethylene oxide)	342	8.7	25.0
Polystyrene (isotactic)	513	9.0	18.0
Polystyrene (syndiotactic)	542	8.6	16.0
Poly(*cis*-1,4-isoprene)	299	4.4	15.0
Poly(*trans*-1,4-isoprene)	347	13.0	37.0

Table 3.8 Comparison between T_m and T_g of diene polymers [11]

Polymer	Isomer	T_g (K)	T_m (K)
1,4-polybutadiene	*cis*	178	279
	trans	190	418
1,4-polyisoprene	*cis*	200	301
	trans	215	347

Polysiloxanes are known commonly as ‘silicones’ and have remarkable properties, including chemical inertness and very low values of T_g. Figure 3.29 compares the geometries of the extended chain structures of isotactic polypropylene ($T_g = 255$ K) and one of the common silicones, poly (dimethyl siloxane) with a T_g of 155 K. It is the relatively large separation of the backbone silicon atoms and their substituents which accounts for the ease of internal rotations and hence the low T_g, which is even over 40 K lower than that of polyoxymethylene (198 K).

The T_m refers to a phase transition in which converts crystalline solid to liquid polymer. The T_m can be expressed by the corresponding changes of enthalpy ΔH_m and entropy ΔS_m. The corresponding Gibbs energy change (ΔG_m) is zero when the process is conducted under equilibrium conditions so that $\Delta H_m = T_m \Delta S_m$ and $T_m = \Delta H_m / \Delta S_m$. Table 3.7 shows representative values of these parameters for various common thermoplastics in which substantial fractions of bulk samples are usually crystalline.

It is interest to observe that a large difference presents in the T_m between polyethylene $(–CH_2–CH_2–)_n$ and poly(tetrafluoro ethylene) (PTFE) $(–CF_2CF_2–)_n$. As shown in Table 3.7, the ΔS_m of PTFE is much lower than that of polyethylene which is mainly responsible for the higher thermal stability of PTFE crystallites. What is obvious is that the fluorine atoms, much larger than hydrogen atoms, form an interlocking sheath along the PTFE chain. This difference is of particular significance for the molten phases, in which PTFE chains will be much stiffer than polyethylene chains, the latter being able to undergo almost free internal rotations to explore a much larger range of conformations. Both T_g and T_m increase as internal rotations in the bond and the backbones of polymer chains become more hindered as shown in Table 3.8. In fact there is a useful approximate rule of thumb

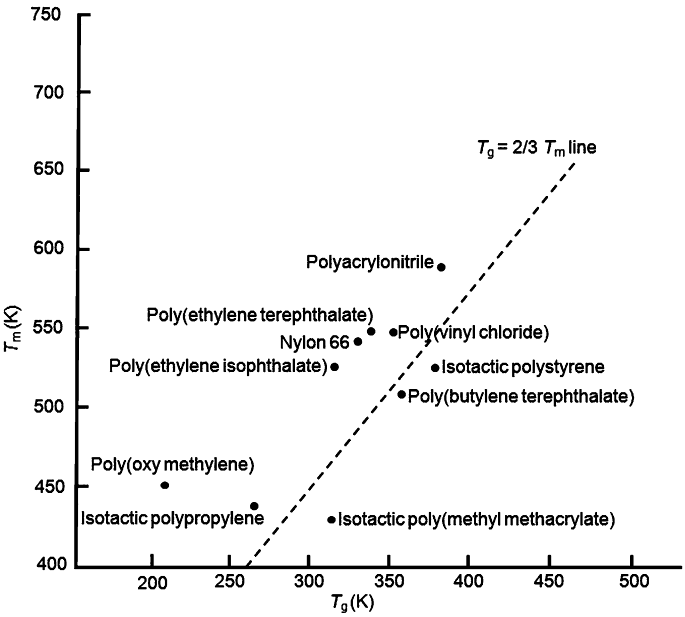


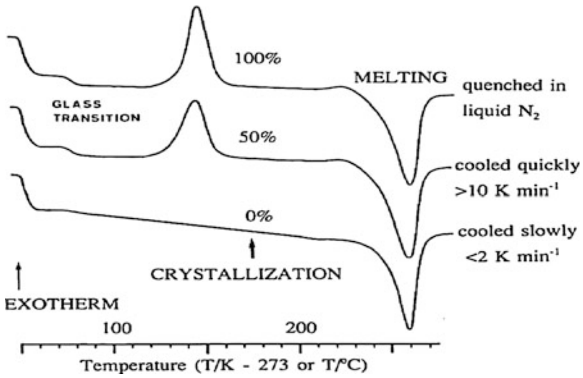
Fig. 3.30 Plot of T_m versus T_g with the points corresponding to several polymers and the line corresponding to T_g (K) = 2/3 T_m (K) shown [2]

which states that T_g(K) is approximately equal to two-thirds (0.67) of T_m(K). The rule is present in the actual case of the common polymers as shown in Fig. 3.30.

For the polymer blends, one T_g is observed for miscible blends such as the blends of polystyrene and poly(oxy-2,6-dimethyl-1,4-phylene) (GE Noryl polymer). Immiscibe blends exhibit more than one T_g such as thermoplastic elastomer of poly(styrene–butadiene–styrene). At room temperature, the polymer behaviors as elastomer with low T_g but the polymer is physical interlocked at the end terminated polymer styrene. At the T_g of polystyrene, the polymer can be soften for ease of processing.

The values of T_m and T_g of copolymers depend on the type of copolymers. For statistical copolymer, the crystallinity of statistical copolymer is lower than that of either of the respective homopolymer because of the decrease in structural regularity. The T_m of any crystalline material formed is usually lower than that of either homopolymer. The T_g will be in between those for the two homopolymers. For block copolymer, each type of block in block copolymer shows its corresponding homopolymer as long as the block lengths are not too short ($\bar{M}_w > 10{,}000$). This offers the ability to combine the properties of two different polymers into one block copolymer. For alternating copolymer has a regular structure, their crystallinity may not be affected significantly unless one of repeating unit containing rigid, bulky or excessively flexible chain segment. The T_g and T_m of alternating copolymer are in between the two corresponding homopolymers.

Fig. 3.31 Curves obtained by differential scanning calorimetry (DSC) on a 5.25 mg sample of poly (ethylene terephthalate) treated in different ways before the measurements [2]



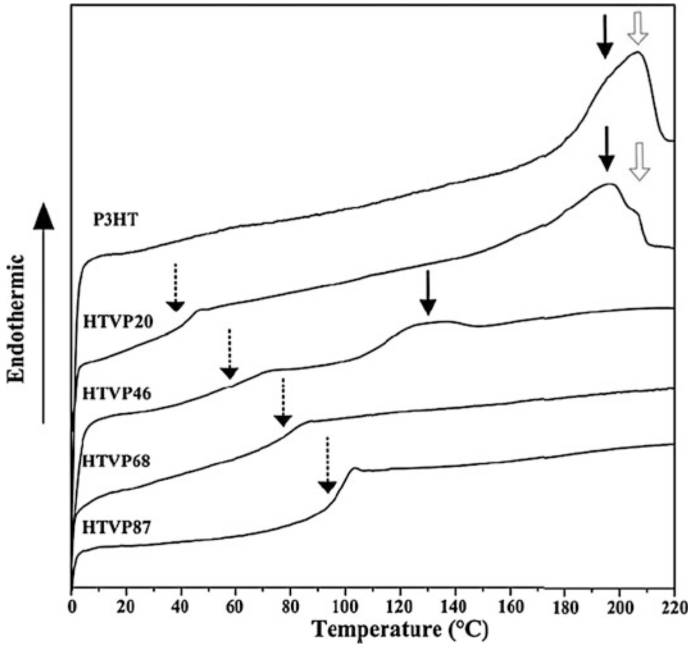


Fig. 3.32 P3HT-b-P2VP thermal properties (cooling slowly then heating) [8]

Accurate T_g and T_m can be determined by the established methods of DSC, DTA, etc. Their principles and instruments will be discussed in Chap. 5. Figure 3.31 shows typical DSC profiles which have been obtained for samples of poly (ethylene terephthalate) (PET) treated in different ways. The top-most profile is for a totally amorphous sample obtained by rapid quenching of melted PET by dropping into liquid nitrogen at 77 K, which allows no time for the development of microcrystallinity. The middle profile is for a PET sample which has been cooled

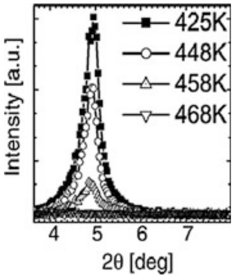


Fig. 3.33 Study of P3HT phase transition by wide angle X-ray diffraction. Reproduced from Ref. [13] with permission

at a moderate rate from the melt and hence has a substantial degree of crystallinity. The bottom-most profile is for a PET sample which has been cooled so slowly that it can be considered to have been annealed. The annealing process is the processing temperature remained near to T_m long enough to develop the maximum possible degree of crystallinity.

The phase transition of the block copolymer, P3HT-b-P2VP has been studied by DSC and shown in Fig. 3.32. The T_g of copolymer is from P2VP homopolymer which is decreased with decreasing the amount of P2VP due to the decreased molecular weight of P2VP. The P3HT homopolymer shows a relative low T_g as compared with the copolymer, but have a T_m at 200°C due to the crystallization of P3HT. However, the crystallization is suppressed by incorporating P2VP segment larger than 20 % by volume, no T_m is observed in copolymer. Figure 3.33 shows the phase transition of pure P3HT at (100) plane using X-ray diffraction measurement. At 425 K, the P3HT is fully crystalline, but the crystallinity decreases with increasing temperature. At 468 K the P3HT is melted which is close to the T_m of P3HT.

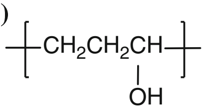
3.9 Problems

1. Write concise definitions of the following terms:

(a) annealing
(b) atactic
(c) crosslink density
(d) glass transition temperature
(e) head-to-tail polymer
(f) isotactic
(g) lyotropic liquid crystal
(h) mesogen
(i) mesophase
(j) nucleation
(k) polyblend
(l) rheology
(m) shear stress
(n) shear thinning
(o) syndiotactic
(p) thermoplastic elastomer
(q) thermotropic liquid crystal
(r) viscoelasticity

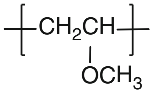
2. Draw the configuration diagram of the following head-to-tail polymers (five to six repeat units):
   (a) syndiotactic poly(vinyl chloride)
   (b) isotactic poly(α-methyl styrene)
   (c) atactic 1,2-polybutadiene
   (d) syndiotactic poly(1,2-difluoroethylene)
   (e) cis-1,4-polychloroprene
3. State the equations relating the melt viscosity of a polymer to (a) molecular weight and (b) temperature.
4. (a) Compare and explain the phase diagram difference between coil–coil block copolymer and coil-rod block copolymer. (b) Compare and explain the phase diagram between P3HT-b-P2VP and PPV-b-PMMA. (Ho [14])
5. Which of the following "isomeric" polymers would you expect to exhibit the greater crystallinity? Explain.

(a)



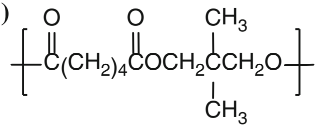
$-\!\left[CH_2CH_2\underset{OH}{\underset{|}{CH}}\right]\!-$

or



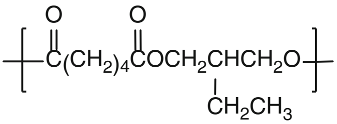
$-\!\left[CH_2\underset{OCH_3}{\underset{|}{CH}}\right]\!-$

(b)



$-\!\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}CH_2O\right]\!-$

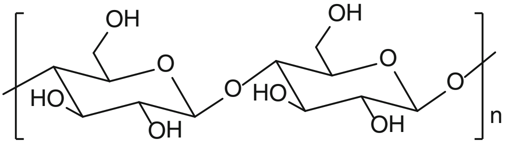
or



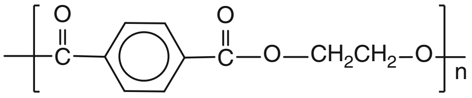
$-\!\left[\overset{O}{\overset{\|}{C}}(CH_2)_4\overset{O}{\overset{\|}{C}}OCH_2\underset{CH_2CH_3}{\underset{|}{CH}}CH_2O\right]\!-$

(c) $-\!\left[CH_2CF_2\right]\!-$ or $-\!\left[CHFCHF\right]\!-$

6. Speculate on why polyester clothing is more wrinkle resistant than cotton. Why is a *hot* iron used to press out the wrinkles? The following figures show their structures respectively.



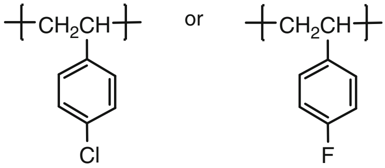
cellulose



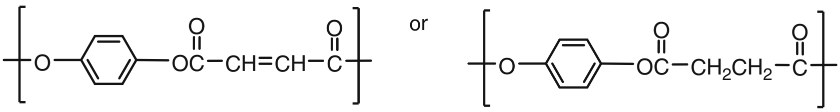
polyester

7. Which polymer in each of the following pairs would you expect to exhibit the higher glass transition temperature? Explain your choice in each case.

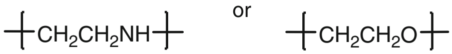
(a)



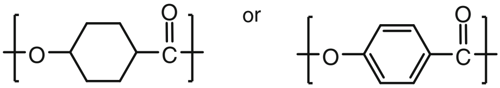
(b)



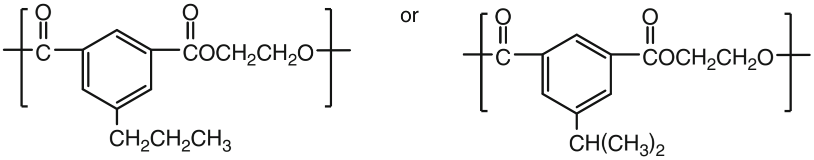
(c)



(d)



(e)



8. Compare the difference in crystallinity and T_g among homopolymer, block-copolymer, alternating copolymer, random copolymer.
9. Compare the differences between conventional polymer and liquid crystalline polymer in terms of their chemical structure, thermal property and flow property.
10. Discuss the differences of self assembly behaviors between diblock copolymer and triblock copolymer. (Bates [15]).

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Chapter 4
Chemical and Physical Properties of Polymers

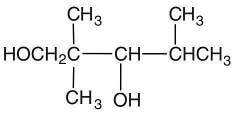
The chemical and physical properties of polymers are dependent on their chemical and physical structures and molecular weight. Their relationship related to the chemical, mechanical, thermal, electrical, and optical properties [1–3] are discussed below.

4.1 Chemical Property of Polymer

The chemical properties of polymer discussed here include chemical resistance, chemical permeation, and weather resistance. The major component of the polymer is hydrocarbon which results in hydrophobic property in general. They are usually resistant to polar solvent but will be attacked by nonpolar solvent. The polarity of the polymer can be increased by incorporating polar group made from atom containing unshared electrons such as oxygen or nitrogen. The polar polymers will interact with polar solvents.

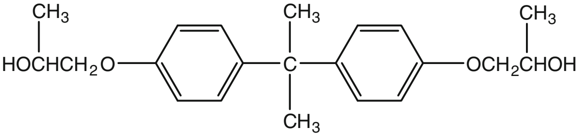
The general rule of "like dissolves like" can be applied in the chemical resistance of polymers while they are in use. The extent of chemical resistance can be classified into four categories: (1) *none* such as water toward polyethylene, (2) *swelling/softening* such as water to Nylon and acetone to poly(vinyl chloride), (3) *dissolving* such as poly(vinyl alcohol) in water, and (4) *reacting* such as nitric acid reacting with cellulose to form nitrocellulose. As compared with metal, most of the polymers are corrosion resistance because it does not react with water. They are usually used as protective coating for metal. Polyester has good film formation characteristic and is a good coating material. Although the ester group of polyester undergoes hydrolysis, its hydrophilic properties can be modified by two approaches: one to increase the steric hindrance about the ester groups, and the other to reduce the number of ester groups per unit chain length. Both increase the hydrophobic nature of the polyesters. For example, 2,2,4-trimethylpentane-1, 3-diol **1** and the bisphenol A-propylene oxide derivative **2** are used for chemical resistant polyester formulations commercially. They have bulky alkyl group substituting for the hydrogen on ethylene glycol (OH–CH_2CH_2–OH).

W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_4,



$\mathrm{HOCH_2C(CH_3)_2{-}CH(OH){-}CH(CH_3)CH_3}$

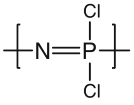
1



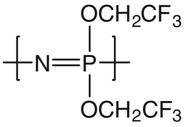
2

The chemical susceptible nature of the end group of polyester, such as –OH or –COOH can be reduced to less susceptible groups of urethane as shown in Fig. 4.1.

Fluorine has proved to be an element that imparts both water and solvent resistance to a variety of polymers due to its low surface energy. The inorganic polyphosphazene **3**, which is very unstable in the presence of moisture, is rendered highly moisture resistant by conversion to **4**. The fluorine, in effect, provides a water-resistant sheath to protect the phosphorus–nitrogen backbone. An ethylene-chlorotrifluoroethylene copolymer is marketed as a chemically resistant coating for underground cables. Because of their chemical inertness, a variety of fluorinated polymers including poly(tetrafluoro ethylene) **5**, poly(vinylidene fluoride) **6**, and copolymers such as poly[hexafluoro propylene-*co*-(vinylidene fluoride)] **7** have been developed commercially with resistance to lubricating fluids for use as gaskets, sealants, valves, and so on.



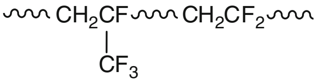
$\mathrm{{-}[N{=}PCl_2]{-}}$



$\mathrm{{-}[N{=}P(OCH_2CF_3)_2]{-}}$

3 **4**

$\mathrm{{-}[CF_2CF_2]{-}}$ $\mathrm{{-}[CH_2CF_2]{-}}$



$\mathrm{\sim CH_2CF(CF_3)\sim CH_2CF_2\sim}$

5 **6** **7**

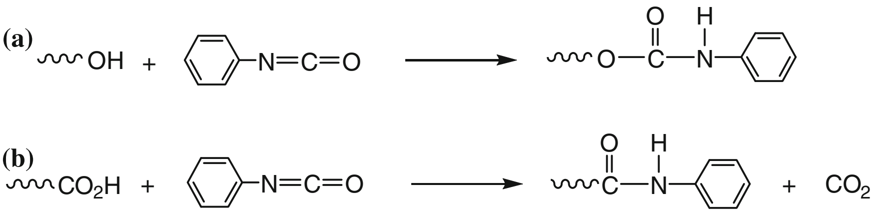


Fig. 4.1 The end functional group (**a**) OH or (**b**) CO_2H of polyester is reacted with isocyanate to form hydrophobic end group

Crystalline polymers are more resistant than amorphous polymers toward solvent resistance, because crystalline polymers are more densely and closely packed that reduce the permeation of solvent. Crosslinked polymers are more resistant toward chemicals than linear polymers due to less free volume available in this type of polymer.

The trend of chemical permeates through polymers should be similar to the extent of chemical resistance of polymer, “like is permeable to like”. Thus, a polymer with many polar groups is sensitive to a polar chemical, that same polymer would be permeable to a polar gas or liquid. Conversely, a nonpolar polymer would be a barrier to polar gases and liquids. For instance, polyethylene has very low water permeation but relatively high oxygen permeation. Poly(vinyl alcohol) has very low oxygen permeation but relatively high water permeation. Amorphous polymer exhibits higher gas and liquid permeation than that of crystalline polymer due to the higher density of crystalline. Table 4.1 shows the barrier properties of some commercially available plastics. The size of the gas or liquid molecule is also extremely important. Small molecules can work their way through the polymer much more easily than large molecules. For instance the permeation of small molecule of helium can be 10^{16} greater than that of a large molecule of pentane. Size effect can, therefore, outweigh all other permeation effects.

Polystyrene and poly(vinyl chloride) can be easily degraded by sunlight because the radical segment can be easily formed from the resonance stabilization of polystyrene or benzylic radical (Fig. 4.2a); stable chlorine radical (Fig. 4.2b) upon photocleavage of the main polymer chain. The free radical scavenger such as benzoquinone is usually added in polystyrene or poly(vinyl chloride) to inhibit the generation of free radical (Fig. 4.2c) for outdoor usage. Widely used polyethylene on the other hand is quite durable in sunlight that causes the environmental

Table 4.1 Barrier properties of common plastics [2]

Polymer	Permeability of oxygen at 25°C, 65 % RH (cc, micron/100 cm^2/24 h)	Permeability of water at 40°C, 90 % RH (cc, micron/100 cm^2/24 h)
Poly(vinyl alcohol)	0.19–0.70	5.4–20.9
Poly(vinylidene chloride)	0.58	0.4
Poly(ethylene terephthalate)	10.1	4.7
Nylon	8.1	39.5
Polyvinyl chloride	19.4–77.5	3.5–19.8
Polyethylene (Low density)	1627.5	3.9–5.8
Polyethylene (High density)	581.3	1.2–1.6
Polypropylene	581.3	2.7
Polystyrene	1356.2	27.1–38.8

Data obtained and changed to metri system from Ref. [2]

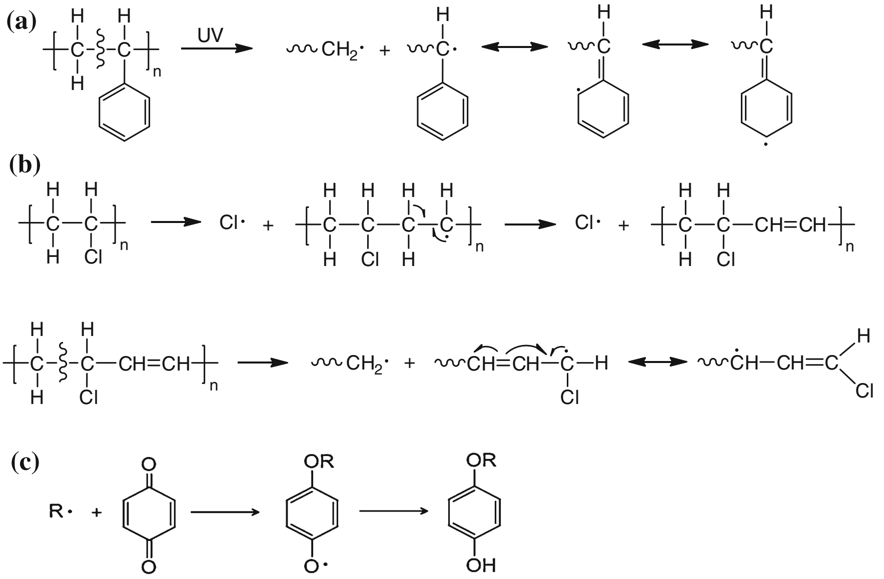


Fig. 4.2 Sunlight degradation reactions toward **a** polystyrene, **b** poly(vinyl chloride), and **c** the inhibition reaction of adding benzoquinone into the polymer

pollution problem. Sunlight degradable polyethylenes have been developed to solve the waste problem. Polymers can be made to degrade photochemically by incorporation of carbonyl groups that absorb ultraviolet (UV) radiation to form excited states energetic enough to undergo bond cleavage. Such processes (referred to as Norrish type II reactions) occur as shown in Fig. 4.3.

Microorganisms degrade polymers by catalyzing hydrolysis and oxidation. By combination of sunlight and microorganisms, the degradation of polymers will be more effective. Controlled release polymers such as starch-graft-polymethacrylate have been used to release chemicals such as medicines, herbicide, etc., by degradation of the starch segment of polymers at controlled rate. Controlled release polymers can also be made from chemical permeable polymeric membrane. The active reagent is encapsulated within the polymeric membrane which can be released gradually with time. Many biodegradable polymers are used for sutures, drug delivery, and tissue engineering. They are synthesized either from α-hydroxy acid or amino acid. The biodegradation occurs through the ester or amide linkage of the polymer chain. Figure 4.4 shows the chemical reactions of their synthesis. The detailed synthesis will be discussed in the subsequent chapters.

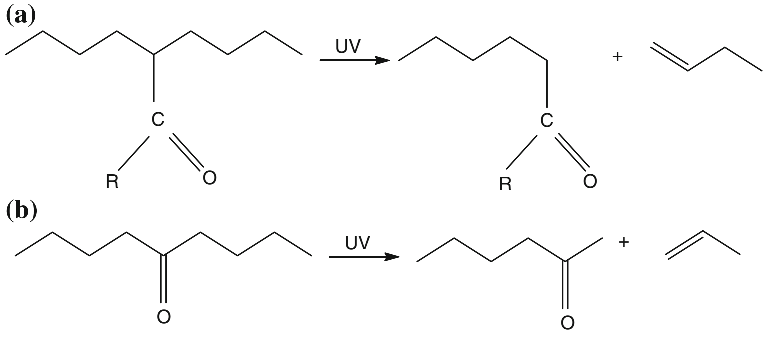


Fig. 4.3 Incorporating UV sensitive carbonyl group into polymer chain for ease of photodegradation of polymer [1]

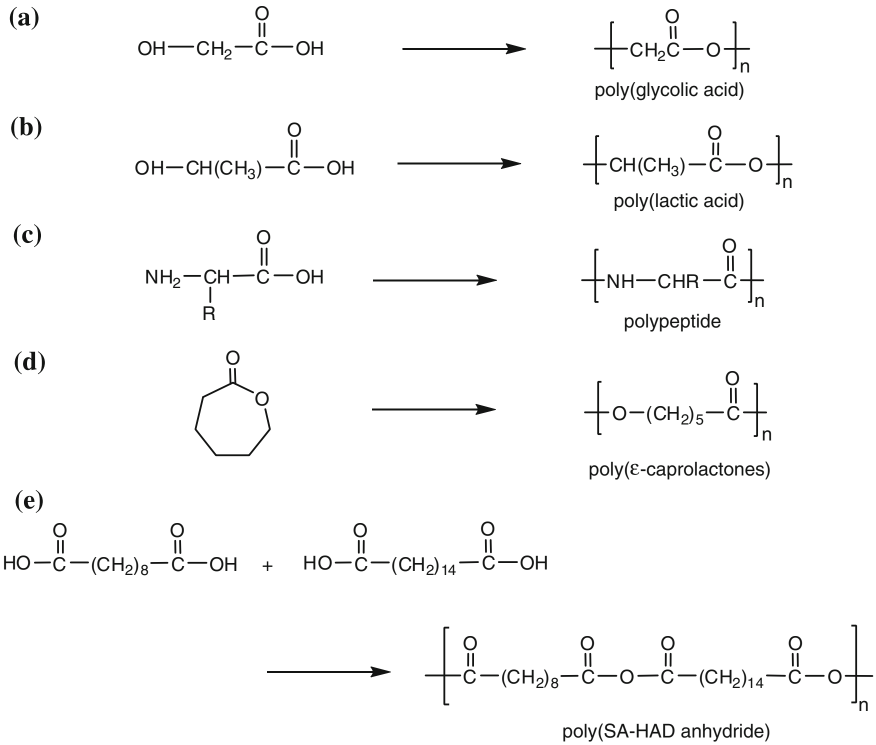


Fig. 4.4 Representative biodegradable polymers prepared from their respective monomers

4.2 Mechanical Property of Polymer

Different chemical structures of polymers can be designed and synthesized to produce polymers with different T_g, T_m, crosslinking, and crystallinity that will result in different mechanical behaviors. The mechanical properties of polymer can be expressed by the stress–strain plot shown in Fig. 4.5. The temperature effect is not considered in this plot. The rigid polymer such as poly(methyl methacrylate) can resist high stress with low strain and is useful for glass-like application due to its high transparency. The fiber such as poly(ethylene terephthalate) can endure higher stress than that of polystyrene with low strain so it is suitable for clothing and rope. The flexible polymer such as polyethylene can be deformed without break under high stress and is used for packaging films. The elastomer such as polybutadiene rubber can be deformed easily under stress. Four important

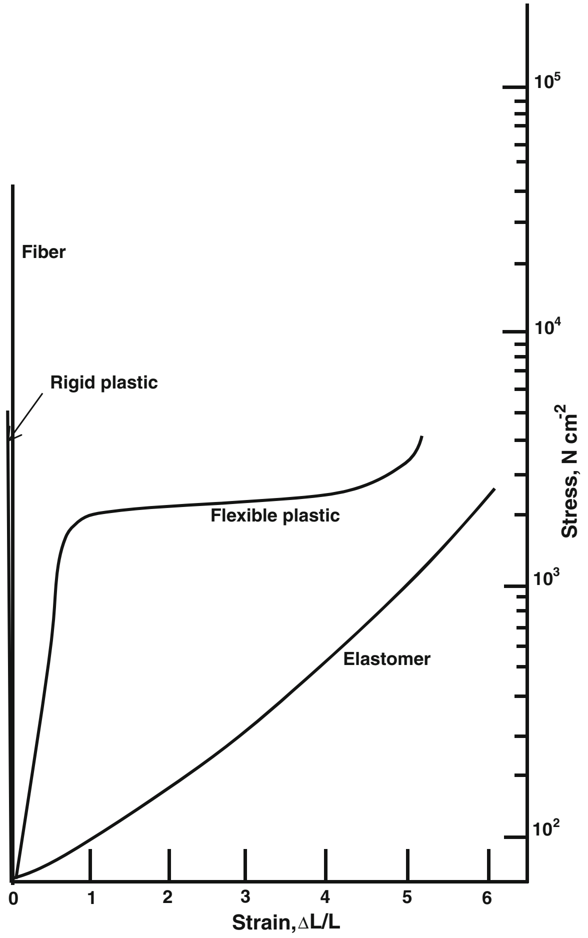


Fig. 4.5 Stress–strain plots for a typical elastomer, flexible plastic, rigid plastic, and fiber [3]

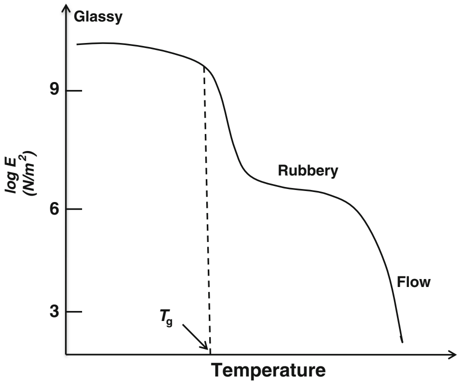
quantities characterize the stress–strain behavior of a polymer: (1) *modulus* (E) that is the resistance to deformation as measured by the initial stress (σ) divided by $\Delta l/l$ (ε) (Eq. 4.1), (2) *ultimate strength* or *tensile strength* that is the stress required to rupture the sample, (3) *ultimate elongation* that is the extent of elongation at the point where the sample ruptures, and (4) *elastic elongation* that is the elasticity as measured by the extent of reversible elongation.

$$\varepsilon = \frac{\Delta l}{l} \tag{4.1a}$$

$$E = \frac{\sigma}{\varepsilon} \tag{4.1b}$$

As the temperature is increased, the modulus will remain high until the glass transition temperature is reached, at which point the modulus drops sharply (Fig. 4.6). The modulus scale is logarithmic. Very high moduli of the order of 3×10^9 N/m^2 are typical in the glassy state, but these decline dramatically once the molecules gain more freedom of movement. The sample remains rubbery until the temperature is sufficiently high to cause flow. A typical plastic would lie somewhere along the glass plateau and an elastomer would lie along the rubbery plateau at room temperature. Figure 4.7 illustrates the modulus-temperature behavior for a variety of polymers. A thermoplastic amorphous polymer shows expected molecular weight dependence in the flow region. The higher the molecular weight is, the higher the temperature is necessary to overcome the increased molecular entanglements. A crosslinked polymer, on the other hand, does not flow. The higher the crosslinking density, the greater will be the modulus (the less the elongation) in the rubbery state. Semicrystalline thermoplastic polymers behave much like crosslinked polymers below the melting temperature, T_m, because of the very strong intermolecular forces arising from close chain packing. How sharp a break occurs at the glass transition temperature depends on the degree of crystallinity. Above T_m, of course, the crystalline polymer will flow.

Fig. 4.6 Effect of temperature on tensile modulus of an amorphous thermoplastic; log E, modulus scale; T_g, glass transitions temperature [1]



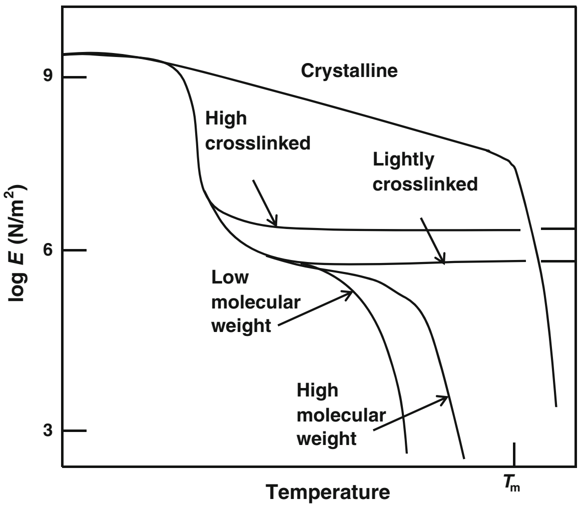


Fig. 4.7 Effect of temperature on tensile modulus (log E scale) of various polymers. T_m is crystalline melting temperature [1]

Table 4.2 gives some representative mechanical properties of common polymers at 25°C. The wide range in properties reflects variations involved in physical testing. In general, the polymer with large side group or containing aromatic structure on the main chain exhibits higher mechanical properties as compared with polyethylene. The crystallinity of the polymer also plays an important role in the mechanical strength of polymer. The high density of polyethylene can have an order increase in modulus as compared with low density of polyethylene (1,070 vs. 172 MPa). The polycarbonate exhibits almost two orders of higher impact strength as compared with other polymers (9.1 vs. 0.23 N/cm) because the main chain contains bulky structure from the bisphenol A segment and –O–C(=O)–O– segment. The bulky main chain provides the polymer with high free volume between polymer chains that can withstand large impact. The airplane window is usually made from polycarbonate to take the impact from the large pressure difference in ascending and descending.

4.3 Thermal Property of Polymer

Most of polymers will flow upon heating at <200°C, so they are easily processed into different goods for the needs of our daily life. When the polymeric good is in use, we do not want its structure and dimension to be changed easily under heat. Therefore, the selection of polymer with adequate thermal stability is extremely important for actual application. When organic substances are heated to high temperatures they have a tendency to form aromatic compounds. Thus, polymers containing aromatic structure exhibit high temperature resistance. Thermally stable polymers should not decompose below 400°C and retain service properties

Table 4.2 Mechanical properties of representative polymers at 25°C [1]

Polymer	Tensile properties at break			Compressive strength (MPa)	Flexural strength (MPa)	Impact strength (N/cm)
	Strength (MPa)	Modulus (MPa)	Elongation (%)			
Polyethylene, low density	8.3–31	172–283	100–650	–	–	No break
Polyethylene, high density	22–31	1,070–1,090	10–1,200	20–25	–	0.23–2.3
Polypropylene	31–41	1,170–1,720	100–600	38–55	41–55	0.23–0.57
Poly(vinyl chloride)	41–52	2,410–4,140	40–80	55–90	69–110	0.23–1.3
Polystyrene	36–52	2,280–3,280	1.2–2.5	83–90	69–101	0.20–0.26
Poly(methyl methacrylate)	48–76	2,240–3,240	2–10	72–124	72–131	0.17–0.34
Poly(tetrafluoro ethylene)	14–34	400–552	200–400	12	–	1.7
Nylon 66	76–83	–	60–300	103	42–117	0.46–1.2
Poly(ethylene terephthalate)	48–72	2,760–4,140	50–300	76–103	96–124	0.14–0.37
Polycarbonate	66	2,380	110	86	93	9.1

near the decomposition temperature. They have high glass transition or crystalline melting temperatures. Some representative thermally stable polymers, along with their initial decomposition temperatures, are given in Table 4.3.

Thermal stability of polymer is primarily determined by the bond energy of chemical bonds in the polymer chain. When the temperature increases to the point where vibration energy causes bond rupture, the polymer degrades. Polymer with cyclic repeating units can exhibit high thermal stability. The breaking of one bond in a ring does not lead to a decrease in molecular weight, and the probability of two bonds breaking within one ring is low. Thus, ladder or semi-ladder polymers are expected to have higher thermal stabilities than open-chain polymers. Table 4.4 shows the different bond strength in diatomic molecules. The bond strength data will provide information to determine how easy the bond will break at high temperature. The polymer contains C–O bond will be more thermal stable than the polymer that contains C–C bond, because the C–O bond has a higher bond strength (1,076 vs. 607 kJ mol^{-1}).

Table 4.3 Representative thermally stable polymers [1]

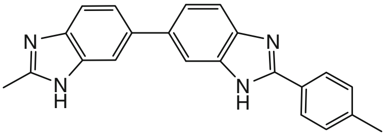
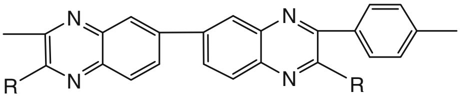
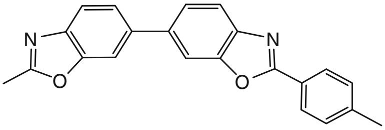
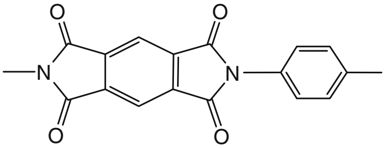
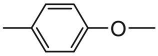
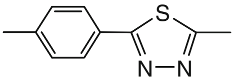
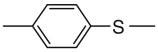
Type	Structure	Decomposition temperature (°C)
Poly(*p*-phenylene)		660
Polybenzimidazole		650
Polyquinoxaline		640
Polyoxazole		620
Polyimide		585
Polyphenylene oxide		570
Polythiadiazole		490
Polyphenylene sulfide		490

Table 4.4 Bond strength in diatomic molecules at 25°C [4]

Molecule	KJ mol^{-1}
C–I	209
C–H	338
C–D	341
C–Cl	397
C–Ti	423
C–Si	452
C–F	552
C–C	607
C–S	714
C–N	754
C–O	1,076

The stability of polymer in air is called thermo-oxidative stability. The presence of oxygen has little effect on the initial decomposition temperature; hence bond rupture is primarily a thermal rather than an oxidative process. Bond breaking is one step process. The oxidation is two steps process including bond breaking and bond formation. The rate of weight loss is usually higher in air than that in nitrogen from the oxidative reaction.

Because synthetic polymers are used increasingly in electronics, construction, and transportation, considerable effort has been expended to develop nonflammable polymers, as well as to understand the mechanism of flame propagation and flame retardation. Other concerns include the suppression of smoke and toxic gases formed during combustion, and the development of nonflammable textile fibers. Figure 4.8 depicts the combustion mechanism of polymer, as a closed cycle in which the combustion of the diffusing gases generates heat that radiates back to sustain the pyrolysis.

An external heat source increases the polymer temperature to a point where it begins to decompose and release of combustible gases. The gases ignite, the temperature increases until the release of combustibles is rapid enough for combustion to be self sustaining so long as sufficient oxygen is available to support the combustion process. From the mechanism of polymer burning and combustion, approaches to promoting flame resistance in polymers focus on three strategies: (1)

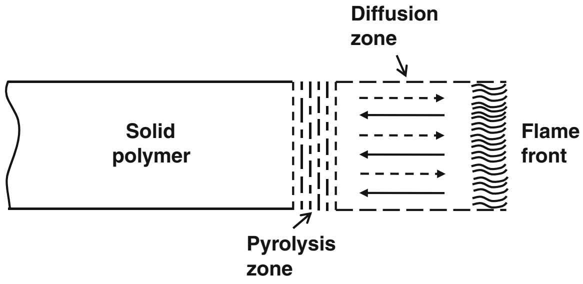


Fig. 4.8 Schematic illustration of the mechanism of polymer burning and combustion; ——→, gas diffusion; ⟶, heat flux [1]

retarding the combustion process in the vapor phase, (2) causing “char” formation in the pyrolysis zone, and (3) adding materials that decompose either to give nonflammable gases or endothermically to cool the pyrolysis zone. Combustion involves free radical reactions from bond breaking process. Halogenated compounds are particularly effective to reduce free radical concentration. The hydrogen halide released from the combustion reacts with free radicals to form less reactive halogen atoms. Thus, poly(vinyl chloride) is nonflammable but the generation of hydrogen halide is a toxic gas. The halogenated compounds are banned in many countries especially in Europe. Antimony oxides are often used in combination with halogen compounds because of a synergistic effect believed to arise from the formation of antimony halides. Inorganic filler functions as barrier and retards the combustion process. Nanocomposites made from the blend of nano clay plate and polymer exhibit excellent nonflammability because the nanoplate retards the air enter into polymer very effectively even at <1 wt.% nanoclay loading.

The char acts as a barrier to inhibit gaseous products from diffusing to the flame and to shield the polymer surface from the heat flux. Aromatic polymers have a natural tendency toward char formation, so they are low flammability. Crosslinking can increase char formation. For example, introduction of chloromethyl groups onto polystyrene can promote crosslinking during pyrolysis. Phosphorus compounds are effective in reducing the flammability of cellulose by promoting dehydration to yield unsaturated compounds that subsequently polymerize to crosslinked char. Hydrated alumina evolves water endothermically to cool the pyrolysis zone. Sodium bicarbonate decomposes to form carbon dioxide that dilutes the combustible gases. Toxic gases will generate from the burning of polymers such as HCN from polyamides and polyurethanes, HCl from poly(vinyl chloride) and CO from all kind of polymers. Smoke arises from the formation of acetylene and benzene which condense to form soot particles. Thus, flame retarded or nonflammable polymers should be used for construction application to reduce the harmful gases formation in case of fire.

4.4 Electrical Property of Polymer

Most of polymers are insulators; because they are formed by covalent bonds without moving freely electrons or ions. However, they will form conductive path under the electrical stress. The tendency to form a conductive path under different conditions for every polymer is different. The electrical properties of polymers can be expressed by many properties including resistivity, dielectric strength, arc resistance, dielectric constant, and dissipation factor [5]. The *resistivity* is the resistance that polymer presents to the flow of electric charge. The *dielectric strength* is the electric breakdown voltage divided by the thickness of the sample. The *arc resistance* is the property that measures the ease of formation of a conductive path along the surface of a sample rather than through the thickness of the sample as in dielectric strength. The *dielectric constant* or *permittivity* is a measure of how well the insulator will act as a dielectric in a capacitor. This constant is defined as the capacitance of the sample in question compared with the capacitance of a vacuum (by ratio). A high dielectric constant polymer indicates that the use of thin dielectric sample in capacitors is permitted. The *dissipation factor* measures the tendency of the polymer to dissipate internally generated thermal energy (heat) resulting from an applied alternating electric field. This heating is caused by the movement of the electrons and atoms within the polymer in response to the changing polarity of an alternating electrical field. Table 4.5 summarizes the electrical properties of common polymers. The electrical properties of nonpolar polymers: polyethylene and poly(tetra fluoroethylene) (top two rows) as compared with the properties of polar polymers indicate the nonpolar polymers exhibit higher resistivity, higher dielectric strength, lower dielectric constant, and lower dissipation factor. The polar group has a higher tendency to move electrons. Therefore, nonpolar polymers will be the material of choice for electrical insulation and capacitor. From molecular design point of view for a new polymer, one will use less polar group to synthesize the polymer to have better insulative properties.

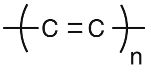
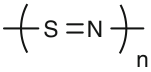
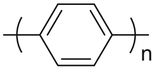
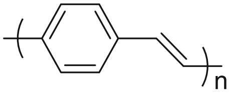
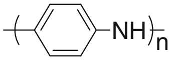
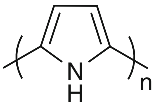
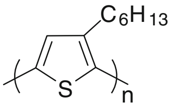
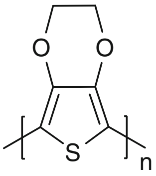
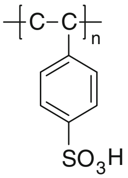
The resistivity of common polymer is in the range of 10^{14} ohm.cm or higher which is 20 orders higher than that of the metal (10^{-6} ohm· cm). However, the polymer contained delocalized π electrons can move electrons as does by the metal. The discoveries of intrinsically conducting poly(sulfur nitride) $–(S{=}N)_n–$ in 1973 and I_2 doped conducting polyacetylene $–(C{=}C)_n–$ in 1977 have stimulated major research effort to elucidate the mechanism of conduction, to search other conducting polymers for applications in battery, transistor, light emitting diode, solar cell, and so on. Table 4.6 shows the comparison of the conductivities between metals and doped conducting polymers. A comparable conductivity to metal can be reached by the doped conducting polymers. Therefore, the conducting polymers are also called synthetic metals.

Most of conjugated polymers are p-type semiconductors. After doping with oxidants like I_2, the electrons release. Although a complete understanding of the

Table 4.5 Electrical properties of common polymers [5]

Polymer	Volume resistivity (Ohm cm)	Dielectric strength (V/micron)	Dielectric constant (60 Hz)	Dissipation factor (60 Hz)
Polyethylene	10^{17}–10^{19}	19	2.3	<0.0005
Poly(tetrafluoro ethylene)	10^{18}	40–80	2.1	0.0002
Polycarbonate	2.1×10^{16}	16	3.2	0.0009
Poly(ethylene terephthalate)	$1–4 \times 10^{16}$	24	3.1–3.3	0.002
Poly(methyl methacrylate)	2.0×10^{16}	20	3.5–4.5	0.03–0.04
Poly(vinyl chloride)	3×10^{14}	1–20	6.0–8.0	0.08–0.11

Table 4.6 Comparison of conductivities between metal and doped conjugated polymers

Material	Structure	Dopants	Conductivity (S/cm)
Copper[a]	Cu	None	5.8×10^5
Gold[a]	Au	None	4.1×10^5
Polyacetylene[a]		I_2	1.0×10^3– 1.5×10^5
Poly(sulfur nitride)[a]		None	10^3–10^4
Poly(p-phenylene)[a]		ASF_5	10^3
Poly(p-phenylenevinylene)[b]		H_2SO_4	10^3
Polyaniline[b]		HCl(1 M)	7.7
Polypyrrole[b]		PF_6	10^2–10^3
Poly(3-hexylthiophene)[b] P3HT		I_2	10^4
Poly(3,4-ethylenedioxythiophene)[c] PEDOT		 PSS	10–10^3

[a] Adapted from Ref. [1]
[b] Adapted from Ref. [6]
[c] Adapted from Ref. [7]

conduction mechanism remains elusive, molecule containing an extended conjugate backbone structure is necessary to have delocalized π electrons upon doping

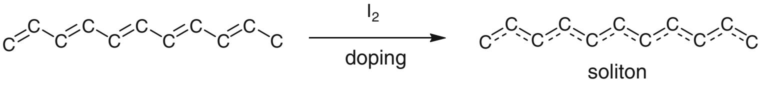


Fig. 4.9 Kivelson mechanism for charge transport involving mobile neutral solutions

for conductivity. Kivelson proposed [8] the following conducting mechanism for charge transport involving mobile neutral solutions (Fig. 4.9).

The dopant can be either electron acceptors (AsF_5 or X) or electron donors (alkali metal, I_2). The configurational structure and conformational structure of polymer (morphology) also have great influence on the conductivity of polymer. For instance, the conductivity of polyacetylene can reach as high as 1.5×10^5 S/cm when the film is properly oriented. Similar to the semiconductor doping, the conductivity of polymer varies with dopant concentration. Another mechanism involving the formation of mobile charge, polaron, was proposed as shown in Fig. 4.10. The removal of one electron from the polythiophene chain (la) produces a mobile charge in the form of a radical cation (1b). The positive charge tends to

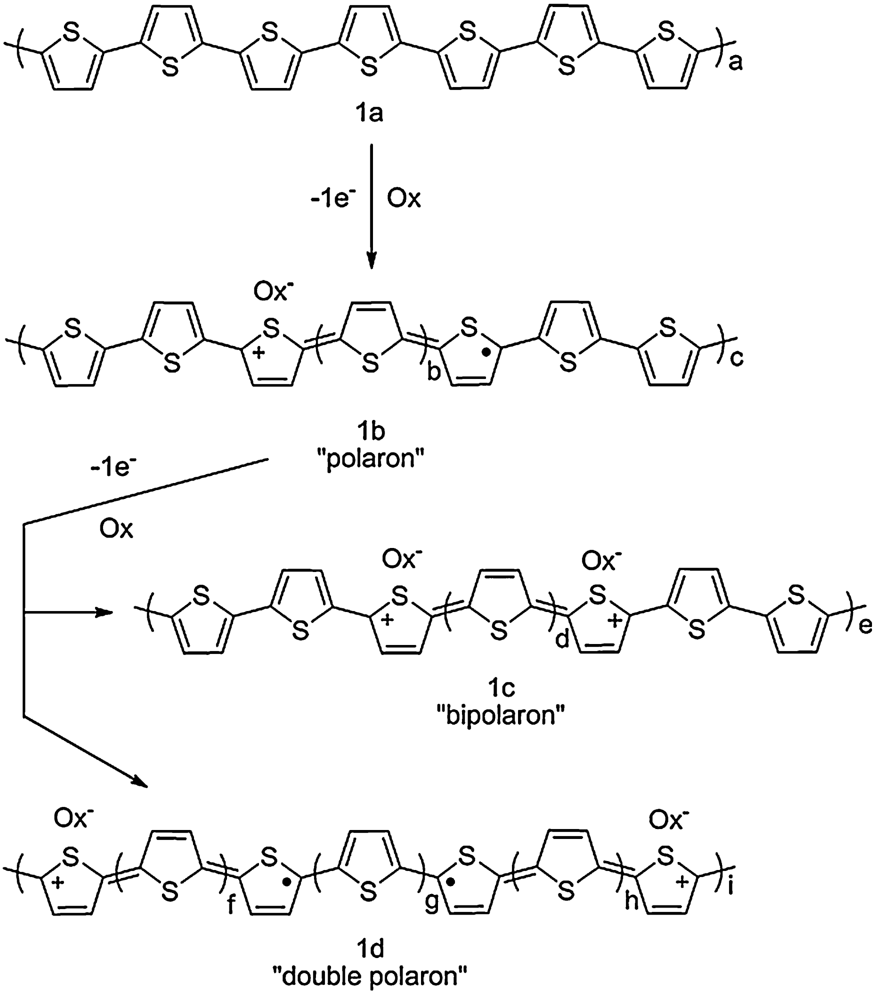
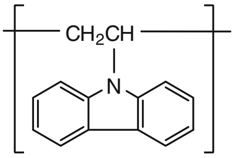


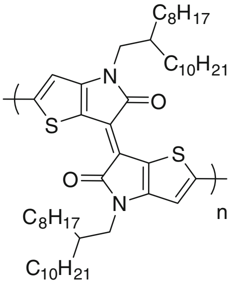
Fig. 4.10 Polaron mechanisms for charge transport in polythiophene [9]

induce local atomic displacements, leading to the polaronic behavior. Further oxidation can either convert the polaron into a spinless bipolaron (1c) or introduce another polaron (1d). In either case, introduction of each positive charge also means introduction of a negatively charged counter ion (Ox^-).

Poly (N-vinyl-carbazole) **8** is a p-type polymer; exhibits photoconducting property which is used widely in photocoping industry. Polyisoindigo **9** is an n-type conducting polymer which will accept electrons. Its conductivity is resulted from the transport of electrons.



8



9

When the common polymers are used as insulator or capacitor, the polymers function as *passive material* and does not transport charge carrier. On the other hand, when the conducting polymers are used for transistor, battery, photovoltaic device, etc., the polymers function as *active material* and are capable of transporting charge carrier.

4.5 Optical Property of Polymer

The optical properties of polymers [10, 11] can also be passive or active depending on their molecular structures. When the polymers used for transmission, reflection, and so on, their optical properties does not change with any external force, they are functioned as passive material. On the contrary, the optical properties of polymers can be changed under external force such as light or electricity. We call them active material. We will discuss passive optical properties of common polymers first, then the active optical properties of special kind polymers.

Insulating polymers are colorless because they do not contain delocalized π electrons. Amorphous polymers such as polyethylene, polystyrene, and poly(methyl methacrylate) are colorless and transparent in visible light, because their refractive indexes are close to air and does not contain easily delocalized π electrons. The refractive index of polymer depends on their chemical structure and conformation. If the polymer can be easily packed to dense structure through intermolecular force, a high refractive index will be resulted. Therefore, the polymer containing aromatic ring has flatter structure than that of aliphatic polymer with ease of packing conformation which can exhibit higher refractive index (Table 4.7). If there is large difference in refractive index between polymer and air, then the light will reflect at the interface. Since crystalline polymers contain crystallite with dimension larger than the wavelength of visible light, the polymer will reflect or scatter the light, and so crystalline polyethylene is not transparent.

Conducting polymers which contain conjugated π electrons can absorb light in visible range. The absorption wavelength depends on the ease of delocalization of π electrons in polymers and the morphology of the polymer. As shown in Fig. 4.11, the $\lambda_{\max}$ of conducting polymer in film is usually longer than that in solution. In addition to the intrinsic delocalization of π-electrons within the molecule, the moving of π-electrons in the solid film also occurs through the hopping between the molecules. As a result, the red shift of wavelength is observed. Whole color spectrum has been discovered from different conducting polymers. Low band gap polymers (LBP) (Eq < 2.0 eV) are desired for solar cell application because the polymer can absorb more solar energy. Table 4.8 summarizes the latest development of low band gap polymers [12–17]. The strategy to obtain low band gap conducting polymer is to have good donor–acceptor pair of alternating copolymer. The copolymer (LBP 6) shows the best power conversion efficiency among the six copolymers due to its strong acceptor moiety.

Polymers which exhibit nonlinear dipole moment response or polarization under an applied electric field are called nonlinear optical polymers. They are active function polymers. The nonlinear optical properties can be expressed either by the change in dipole moment (microscope) as shown in the following equation:

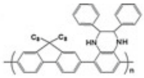
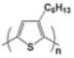
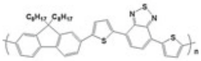
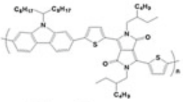
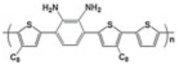
$$\mu = \mu_0 + \alpha E + \beta EE + \gamma EEE + \cdots \tag{4.2}$$

where α is the linear polarizability, β is the second order hyperpolarizability and γ is the third order hyperpolarizability. The second term defines the linear optical response of the dipole and gives rise to conventional reflection, absorption, and transmission. The higher term describes changes in the dipole moment that are nonlinear in the electric field. To sum up the dipole moment of Eq. 4.2 over entire medium, the macroscopic dipole moment per unit volume or polarization is shown as the following:

$$P = P_0 X^{(1)} E + X^{(2)} EE + X^{(3)} EEE \cdots + \tag{4.3}$$

Table 4.7 Refractive index of common polymers [5]

Polymer	Refractive index at 589 nm (n_D)
Poly(phenylene oxide)	1.63
Polystyrene	1.60
Polyethylene(high density, d:0.95 g/cm^3)	1.54
Poly(ethylene terephthalate)	1.53
Polyethylene(low density, d:0.93 g/cm^3)	1.51
Polycarbonate	1.50
Poly(methyl methacrylate)	1.49
Poly(tetrafluoro ethylene)	1.35

Polymer	Chemical Structure	λmax (Film)	λmax (Solution in CB)	Mw	Source*
F8DPQ		468	457	50K	INER
P3HT		560	460	60K	NTU
APFO-3		557	535	10K	NTU
P-CzAl-DTDPP-e		678	661	58K	UCSB
PTC8BA		630	575	25K	INER

*INER: Institute of Nuclear Energy Research, NTU: National Taiwan University, UCSB: University of California at Santa Barbara

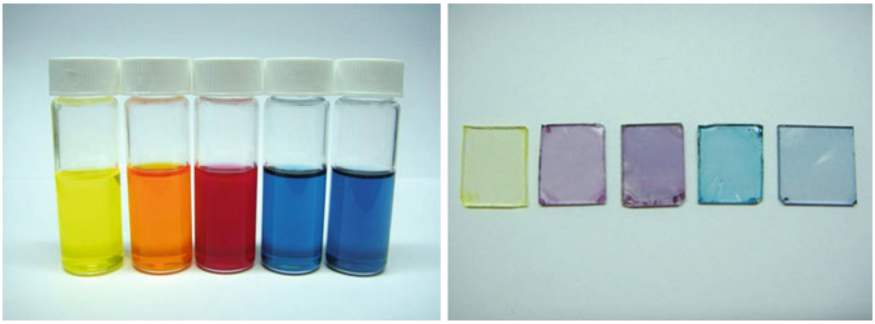


Fig. 4.11 Absorption characteristics of conducting polymers in solution and in film

where $X^{(1)}$ is the linear electric susceptibility, $X^{(2)}$ and $X^{(3)}$ are the second and third order electric susceptibility, respectively. $X^{(1)}$ is directly related to the complex dielectric constant ε, by

$$\varepsilon = 1 + 4\pi X^{(1)} \tag{4.4}$$

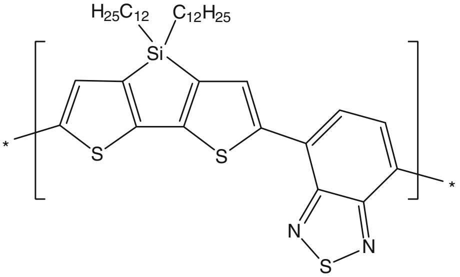
The complex refractive index can be determined approximately by the following:

$$n = (\varepsilon)^{1/2} \tag{4.5}$$

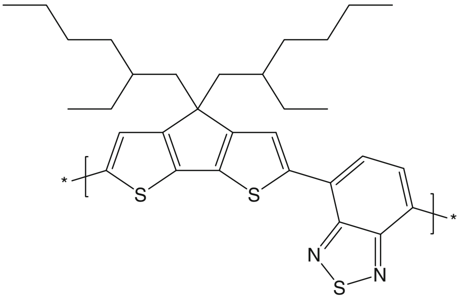
The higher order term of Eq. 4.3 gives rise to optical harmonic generation effect and electro-optic effects. Table 4.9 summarizes the relationships between chemical structure and microscopic nonlinearities. The more delocalized π electrons are between donor groups (–NR_2) and acceptor group (–NO_2), the higher the nonlinear

Table 4.8 Low band gap conducting polymers

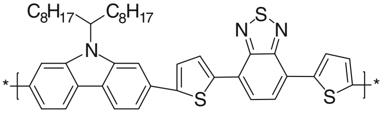
Polymer	Band gap (eV)	HOMO (eV)	LUMO (eV)	$\lambda_{\max}$ (film)	Reference
LBP1	1.4	5.4	N/A	800	[12]
LBP2	1.4	5.3	3.6	775	[13]
LBP3	1.9	5.5	3.6	576	[14]
LBP4	1.4	5.5	3.7	730	[15]
LBP5	1.3	5.2	3.6	722	[16]
LBP6	1.7	5.2	3.5	668	[17]



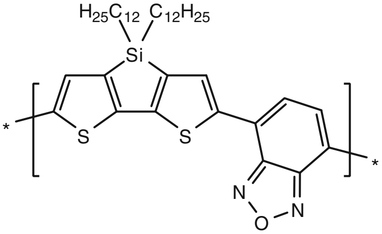
LBP 1



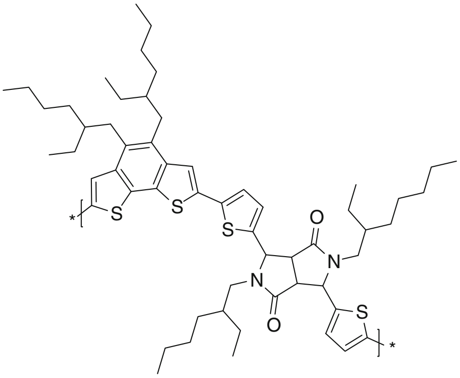
LBP 2



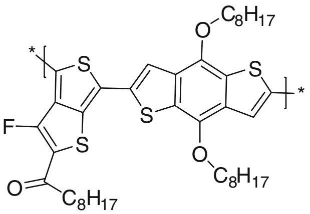
LBP 3



LBP 4



LBP 5



LBP 6

susceptibility is. The relationship between the electric field and oscillation frequency for the polarizability of polymer can be expressed by Eq. 4.6.

$$E = \Sigma_{\omega} E_{o\omega} e^{i\omega t} \tag{4.6}$$

where $E_{o\omega}$ is the amplitude of the electric field, ω is its oscillation frequency. $X^{(1)}$ term will always oscillate at frequency ω of the driving field, giving rise to a polarization and electric field that radiate at ω. The higher order terms can mix the various frequency component of E as shown in Eq. 4.7.

$$E = E_{01}e^{i\omega_1 t} + E_{02}e^{i\omega_2 t} + \text{complexconjugate} \tag{4.7}$$

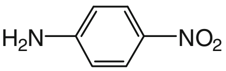
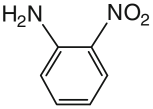
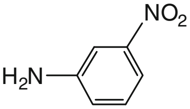
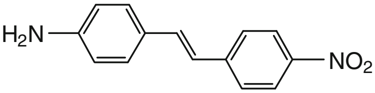
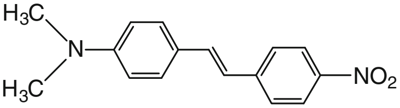
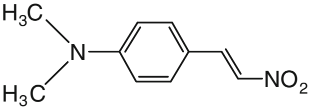
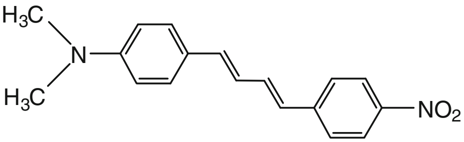
$X^{(2)}$ term will produce a polarization and resulting electric field that oscillate at $2\omega_1$, $2\omega_2$, $\omega_1 - \omega_2$, $\omega_1 + \omega_2$, and ω_0. 2ω terms give rise to optical second harmonic generation (SHG). The electro-optic effect of polymer can be expressed by Eq. 4.8.

$$\Delta\varepsilon = 4\pi X^2 E \ or\ \Delta(1/\varepsilon) = rE \tag{4.8}$$

where r is electro-optic coefficient.

In order to have good electro-optic effect, the material has to be (1) uniform birefringence, (2) minimized scattering losses, (3) transparency, (4) thermal and dimensional stability, and (5) good processability. Figure 4.12 illustrates the schematic of different electro-optic (EO) devices can be fabricated from nonlinear

Table 4.9 Values of β computed from the two-level model compared with experimentally obtained values [10]

Molecule	$\beta_{\text{two level}}$ (10^{-30} esu)	β_{exp} (10^{-30} esu)
	19.6	16.2–34.5
	10.9	10.2
	4	6
	227	225–295
	383	450
	217	180–260
	715	470–790

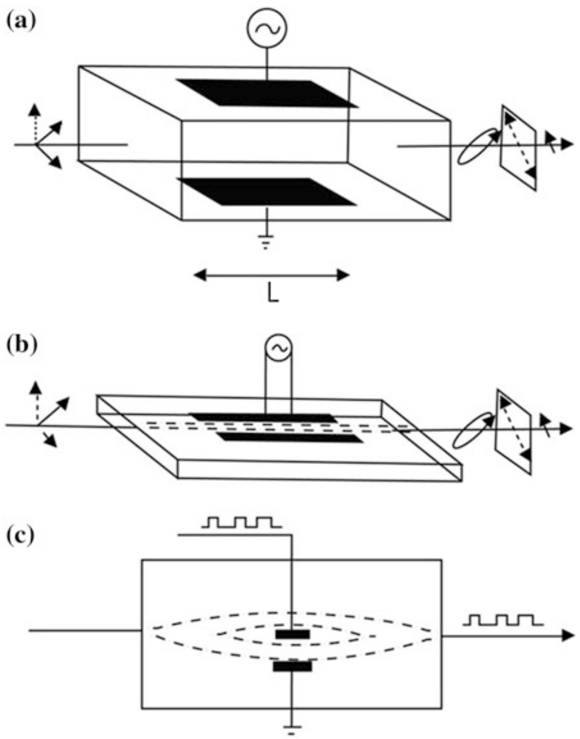


Fig. 4.12 Schematic illustration of different electro-optic (EO) devices (**a**) optical switch, (**b**) waveguide and (**c**) Mac-Zehnder interferometer [11]

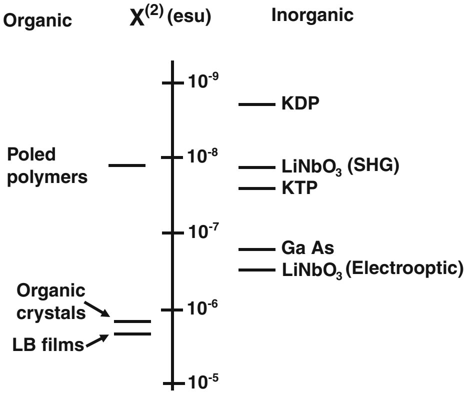


Fig. 4.13 Comparison of $X^{(2)}$ values between organic materials and inorganic materials [10]

optical polymers [11]. In Fig. 4.12a, an optical switch, a voltage is applied to the EO medium phase which shifts one optical field component with respect to the other, allowing the light to pass through the output polarizer, which is at right angles to the input polarization. The same principle is used in the optical waveguide (Fig. 4.12b), where much lower voltages may be used to achieve high fields because of small separation between the electrodes. In the Mach–Zehnder

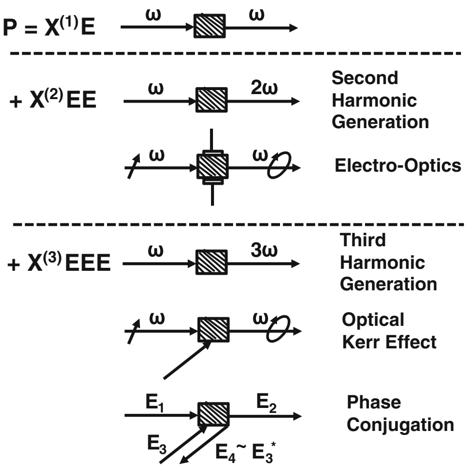
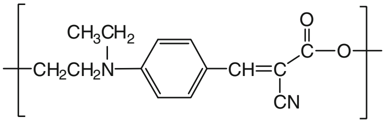


Fig. 4.14 Schematic representation of various nonlinear optical processes [11]

interferometer (Fig. 4.12c), guided light is split into two branches. The EO-induced phase shift in the lower arm modulates the output light intensity as the fields from both branches recombine and interfere. Figure 4.13 shows the comparison of nonlinear susceptibility between organic material and inorganic material [10]. The organic single crystal can exhibit higher nonlinear susceptibility than that of inorganic material. However, the long-term stability of organic crystal is still an issue for practical application. Figure 4.14 shows various nonlinear optical processes that can provide many applications in optical devices [11]. Linear optical or $X^{(1)}$ processes involve reflection, transmission, and absorption of light. $X^{(2)}$ processes include frequency doubling (optical second harmonic generation), and the linear electro-optic (Pockels) effect in which the applied field (E_0) changes the index of refraction of the material, for example, to induce birefringence. $X^{(3)}$ processes include tripling of the incident optical frequency (third harmonic generation); the optical Kerr effect, in which the index of refraction is altered by control light beam; and phase conjugation, which creates a phase conjugate of E_3 that cancels accumulated phase distortions after retracing the path of E_3.

The polarizable chromophores may be incorporated into the polymer as low-molecular weight compounds dissolved in the polymer matrix (host–guest systems) or, more commonly, they are designed into the polymer backbone or into a side chain. Crosslinking may also be employed to stabilize the system. A large number of nonlinear optical (NLO) polymers have been reported; examples having NLO chromophores in the backbone and side chain are the polyester **9** and the polyimide **10**, respectively [1]. They usually have the structures of electron withdrawing and donating groups in the polymers to exhibit polar and non-central symmetrical characteristics.



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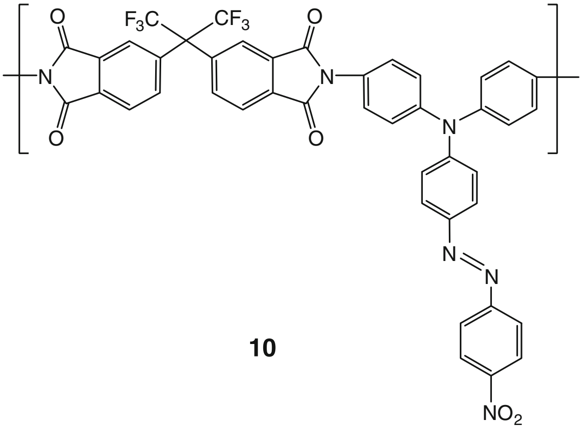

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4.6 Processability of Polymer

As compared with metal or ceramics, polymer can be processed at much lower temperature (>1000 vs. <300°C) because polymers have low T_g. However, fully aromatic polymers exhibit high glass transition temperatures, high melt viscosities, and low solubility from their aromatic rigid backbone structure. They are usually high cost due to the high cost of monomer, difficult to synthesize and process. They are only used mostly in high demanding aerospace industries. Approaches are taken to improve the processability of fully aromatic polymer through chemical structure modification.

One approach is to incorporate flexible groups such as long chain alkyl, ether, or sulfone into the backbone of the polymer but the thermal stability usually suffers from the modification. Another approach is to introduce cyclic aromatic groups that lie perpendicular to the planar aromatic backbone to form so-called cardo polymers [1], usually exhibit improved solubility with no sacrifice of thermal stability. For example, polybenzimidazole **11** has been modified into cardo polymer **12** for ease of processing.

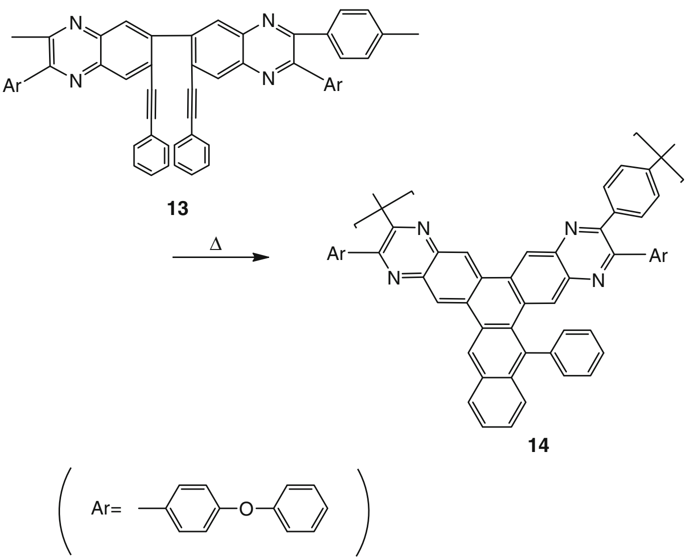

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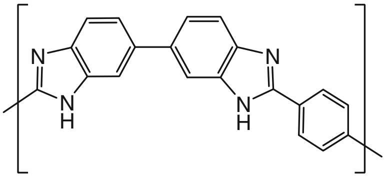
Fig. 4.15 Increasing T_g of a polyquinoxaline by intramolecular cycloaddition [1]



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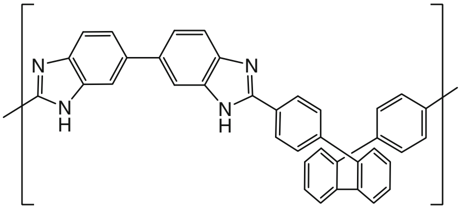

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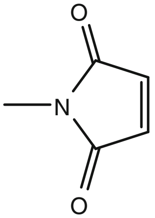
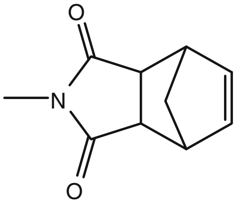
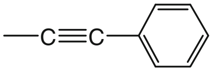
Incorporating reactive groups into the polymer backbone that undergo intramolecular cycloaddition on heating is another way to improve processability. The reactive oligomer or polymer is fluid during the processing, but it becomes rigid through ring formation with increased glass transition temperature. An example, shown in Fig. 4.15, is the conversion of the aromatic polyquinoxaline **13** into **14** via cycloaddition reactions of the phenylethynyl substituents, resulting in a 50°C increase in the glass transition temperature.

The end-capped oligomers melt at relatively low temperatures and are soluble in a variety of solvents. On heating they are converted to thermally stable network

Table 4.10 Some reactive end groups for converting oligomers to network polymers [1]

Type	Structure
Cyanate	$—O—C\equiv N$
Ethynyl	$—C\equiv CH$
Maleimide	
Nadimide	
Phenyl ethynyl	

polymers. End groups that are found in commercially important reactive oligomers especially in aerospace industry are given in Table 4.10. The cyanate terminated compound or oligomer is also useful in high temperature resistant printed wiring board such as cyanate ester. The cyanate esters are generally based on a bisphenol or novolac derivative, in which the hydrogen atom of the phenolic OH group is substituted by a cyanide group. It has been used to react with epoxy resin to form thermally stable heterocyclic structure as shown in Fig. 4.16 [18].

Virtually every polymer in commercial use contains additives, usually a combination of various additives. The purpose of additives is twofold: (1) to alter the properties of the polymer and (2) to enhance processability. Property modifiers are ranged from pigments and odorants for esthetic reasons to plasticizers for modifying mechanical properties. Processing modifiers vary from lubricants to prevent sticking to fabrication machinery, to compounds that alter the chemical structure, such as crosslinking agents and plasticizers. The crosslinking agent will increase the stiffness and thermal stability of the polymer. The plasticizer, on the other hand will increase the flexibility of the polymer and lower the T_g of polymer for increasing the elongation and ease of processing of polymer respectively. Additives may be completely miscible or, as is the case with inorganic reinforcing agents, completely immiscible. Plasticizers are the most widely used additives in the plastic industry, with di-2-ethylhexyl phthalate **15** being the cheapest "general-purpose" plasticizer.

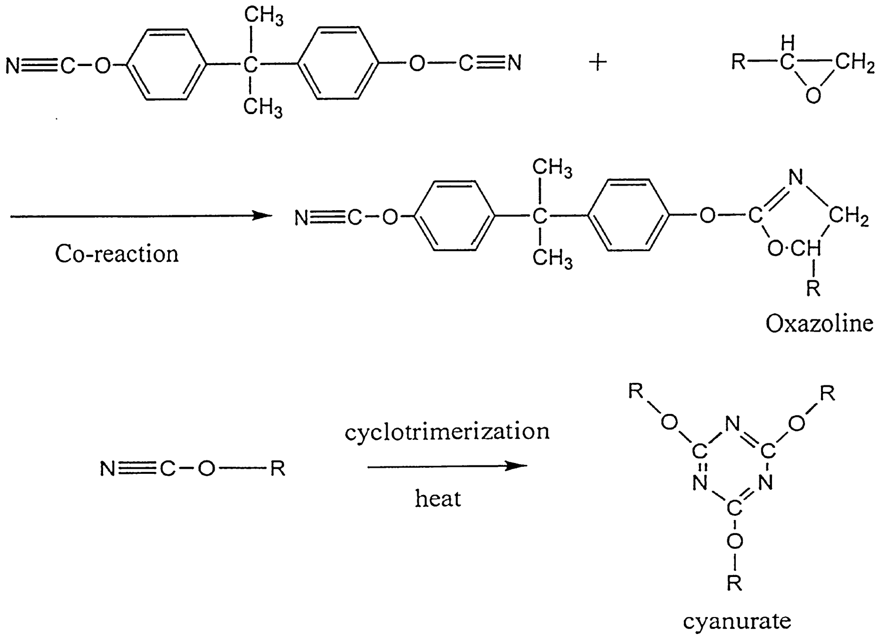
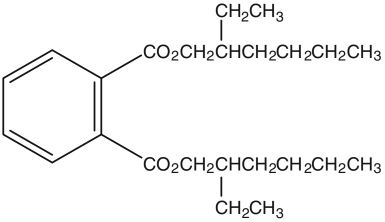


Fig. 4.16 Reactions of cyanate esters with epoxy resin [18]



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4.7 Problems

1. Please define clearly the following terms related to the properties of polymers and provide an example of each for poor property and good property of each term. Provide explanation for your answer. (a) chemical resistance, (b) chemical permeation, (c) weather resistance, (d) modulus, (e) tensile strength, (f) elongation, (g) thermal stability, (h) flammability, (i) resistivity, (j) dielectric strength, (k) dielectric constant, (l) dissipation factor, (m) transmission, (n) reflection, (o) absorption, (p) nonlinear optical property.

2. Please compare the differences between amorphous polymer and crystalline polymer in terms of their chemical resistance, mechanical properties, thermal properties, electrical properties, optical properties, and processability.
3. Explain how the molecular weight of polymer affects its chemical and physical properties. Compare among them from low molecular weight (>10,000), medium molecular weight (>50,000), and high molecular weight (>100,000).
4. Discuss the physical factors in polymer that affect its permeability.
5. Explain how ultraviolet light degrades toward polymer much easier than to ceramic or metal. Show your explanation by reaction mechanism.
6. Polyvinyl alcohol is significantly less flammable than the isomeric polyoxyethylene, why?
7. Explain, in terms of structure and morphology, the rationale behind the three strategies described for improving processability of thermally stable polymers: (a) cardo polymers, (b) intramolecular cyclization, (c) reactive oligomers.
8. Describe the key features of a polymer that would make it become electrically conductive. Explain the molecular weight effect on the conductivity of conducting polymer.
9. The major issues of conducting polymers are environmentally unstable and difficult to process. Please explain why. Compare the environmental stability and ease of process between polythiophene and poly (3-hexyl thiophene). Which polymer is more conducting if we assume they have similar molecular weight?
10. Why does the nonlinear optical polymer need to contain conjugate molecular structure as the conducting polymer has? Are these two properties interchangeable? Please use an example to explain.
11. In elastomer synthesis, 1, 4-hexadiene may be used to impart the unsaturation needed for crosslinking. What advantage might this compound offer over butadiene or isoprene?
12. Explain why plasticizers increase flexibility and elongation in polymers. What is the relationship between plasticizers and the glass transition temperature?

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Chapter 5
Characterization of Polymer

The characterization of polymer is a vital part of polymer technology. Once the polymers are designed and synthesized, we need to characterize them chemically to confirm their chemical structures and to evaluate their properties for physical behaviors and actual usages [1].

5.1 Instruments and Testing Methods for Polymer Characterization

There are numerous instruments available for polymer characterization. For the chemical structure characterization of polymers, infrared spectroscopy (IR), Raman spectroscopy, ultraviolet–visible spectroscopy (UV–Vis), nuclear magnetic resonance spectroscopy (NMR), and electron spin resonance spectroscopy (ESR) are commonly used. To study the structure and morphology of polymers, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM) are used in general. The thermal properties of polymers are characterized by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), thermal mechanical analyzer (TMA), and thermal gravimetric analysis (TGA). The mechanical properties of polymers are studied by Instron. We will discuss the principle of each instrument briefly, and then show examples how the polymers are being characterized by different instrument.

In industry, there are many standard testing methods being developed to characterize polymers by international organization and different countries. The international standard organization (ISO) standard is an international effort to develop standard test. In the USA, there is the American Society for Testing and Materials (ASTM) to set up the standard. The British Standards Institute (BSI) establishes British's standards. In Taiwan, the standards of testing methods (CNS) follow other countries' standards. Please refer to the tests whenever you are in need. They are available by purchasing them through each standard organization. You can also find them in most of libraries and Taiwan Standard Bureau. We will not discuss them here.

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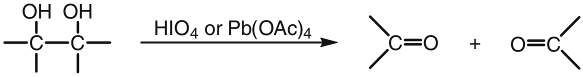
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_5,

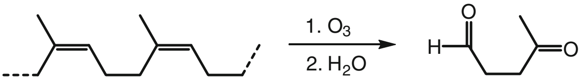
5.2 Characterization of Chemical Structures of Polymers

5.2.1 Chemical Reaction Method

To determine the chemical structure of polymers through chemical reaction method is a low cost analysis but needs large sample size (>1 gram). For example, the location of head to head structure (1, 2-diol) on polyvinyl alcohol can be determined by the following reaction.



The structures of polydienes can be determined via ozonolysis. Ozonolysis of natural rubber, for example, followed by hydrolysis of the intermediate ozonide under reductive conditions, yields 4-ketopentanal, which establishes the structure as the head-to-tail 1, 4-addition polymer of 2-methyl-1, 3-butadiene (isoprene).



The amount of double bonds in the polymer chain can be determined by the bleaching of known amount of iodine solution through the addition of reaction of iodine to the double bonds.

5.2.2 Infrared Spectroscopy

The infrared spectra of polymers are resulted from the different IR absorption of chemical bonds (vibrational transition) of polymers upon irradiation of IR [1]. The amount of vibrational transition can be expressed by

$$v = \frac{1}{2\pi C}\sqrt{\frac{k}{M_x M_y/(M_x + M_y)}} \tag{5.1}$$

where v is stretching frequency in cm^{-1}, M_x, M_y the masses of two atoms involved in stretching, (grams), C is the velocity of light, 2.998×10^{10} cm/s, and k is force constant, dynes/cm; single bond (5×10^5 dynes/cm), double bond (10×10^5 dynes/cm), and triple bond (15×10^5 dynes/cm). Infrared frequency is usually expressed in units of *wavenumber*, defined as the number of waves per centimeter. Ordinary instruments scan the range of about 700–5,000 cm^{-1}. This frequency range corresponds to energies of about 2–12 kcal/mol. This amount of energy is sufficient to affect bond vibrations (motions such as bond stretching or bond bending) but is appreciably less than would be needed to break bonds. These motions are illustrated in Fig. 5.1.

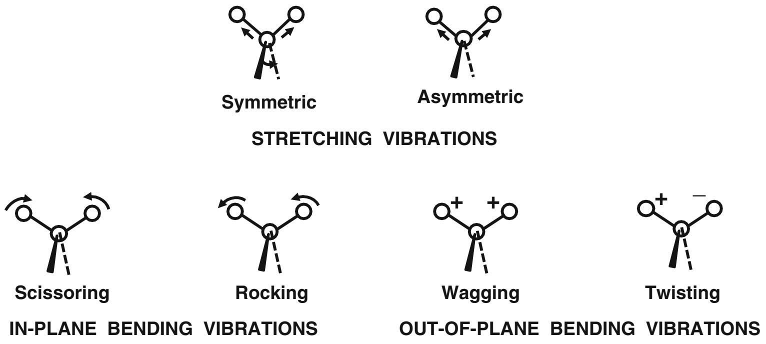


Fig. 5.1 Vibrations of a group of atoms (+ and − signify vibrations perpendicular to the plane of the paper) [2]

Particular types of bonds of organic molecule usually stretch within certain rather narrow frequency ranges which are very useful to determine the chemical structure of molecule. Table 5.1 gives the ranges of stretching frequencies for some bonds commonly found in organic molecules.

The chemical structures of unknown polymers can be recognized mostly through their specific IR absorption frequency. However, their exact chemical structures cannot deduce from IR spectra only, unless they can be compared with known data or from the IR spectra of their monomers. Figure 5.2 shows the difference of IR spectra between polyimide and its chemical repeating unit model compound is at the p-substituting linkage between the aromatic structure of monomers with C–H bending at 650–900 cm^{-1}.

Table 5.1 Infrared stretching frequencies of some typical bonds [2]

Bond type	Class compound	Frequency range (cm^{-1})
Single bonds to hydrogen	alkanes	2,850–3,000
	alkenes and aromatic	3,030–3,140
	alkynes	3,300
	alcohols and phenols	3,500–3,700 (free)
		3,200–3,500 (hydrogen-bonded)
	carboxylic acids	2,500–3,000
	amines	3,200–3,600
	thiols	2,550–2,600
Double bonds	alkenes	1,600–1,680
	imines, oximes	1,500–1,650
	aldehydes, ketones, esters, acids	1,650–1,780
Triple bonds	alkynes	2,100–2,260
	nitriles	2,200–2,400
Subsitute aromatics	ortho	750
	para	830
Halide	C–F	2,962–2,853
	C–Cl	800–600
	C–Br	600–500

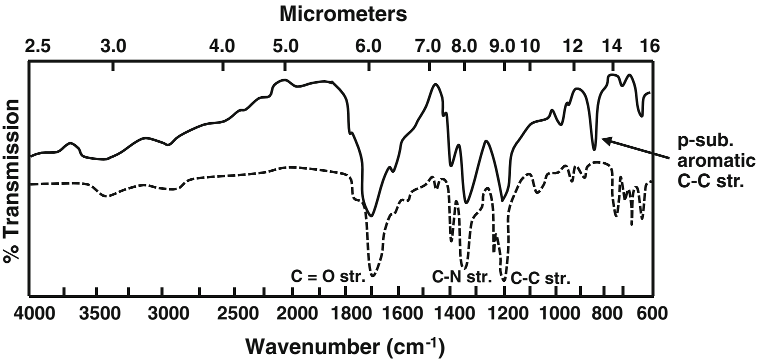


Fig. 5.2 Infrared spectrum (KBr pellets) of polyimide (—) and model compound (- - - -) [3]

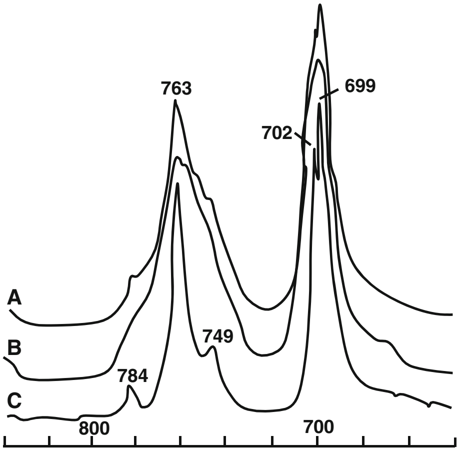


Fig. 5.3 Fourier transform infrared spectra of isotactic polystyrene in the 640–840 cm^{-1} region: (A) semicrystalline; (B) amorphous; and (C) the difference spectrum obtained by subtracting B from A [3]

The IR of isotactic polystyrene can be obtained by subtracting the spectrum of amorphous polystyrene from the spectrum of semicrystalline polystyrene as shown in Fig. 5.3. A well-defined sharp absorption is revealed which indicates the benzene rings are “frozen” into relatively specific conformations in the crystalline state.

5.2.3 Raman Spectroscopy

Like IR spectroscopy, Raman derives from vibrational transitions in molecules. When visible light impinges on molecules, the light is scattered. The frequency of the scattered light varies according to the vibrational modes of the scattering molecules. This referred to as the *Raman effect.* Whereas IR absorption spectra are indicative of unsymmetric bond stretching and bending, the Raman effect responds to the symmetric vibrational modes. Polar groups of a molecule give the most

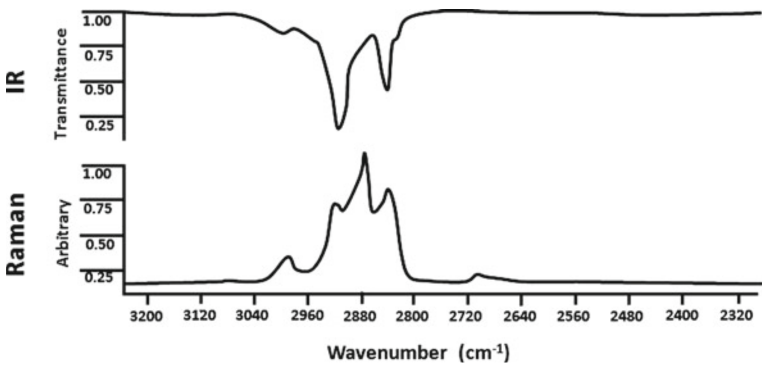


Fig. 5.4 Comparison between IR and Raman of trans-poly pentenamer

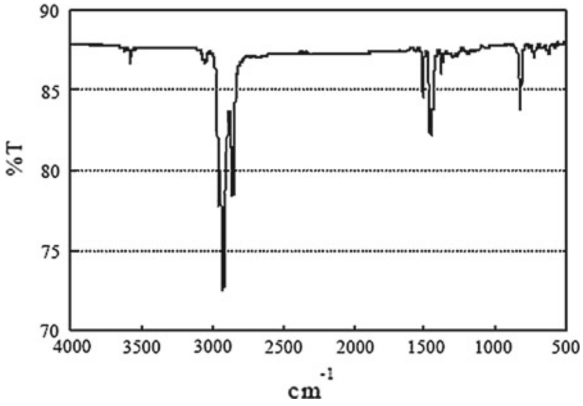
intense IR signals whereas nonpolar ones give rise to most intense Raman signals. Thus IR and Raman spectroscopy are complementary. Paired IR and Raman spectra of the same compound have a synergistic effect in promoting understanding of structural information [4].

Raman is most responsive to symmetrical stretching in C–C bonds. It is useful to study the *conformational structure* of polymer chains by comparing spectra with those of long-chain“model” alkanes. The stereoisomers of polymer is obtained by rotation around single bonds, so the Raman can be used to study the *cis–trans* isomerism in elastomers, sulfur crosslinks in rubber, and polymer deformations. Because Raman scattering by water is negligible compared with water’s intense IR absorption, Raman is particularly useful in conformational studies of biopolymers in aqueous solution. Figure 5.4 shows the comparison between IR and Raman of trans-poly pentenamer. The Raman shows more feature than that of IR due to the symmetrical structure of alkane (–C–C– at 2,900 cm^{-1}) and alkene (–C=C– at 3,000 cm^{-1}). The comparison of IR and Raman spectrum of poly(3-hexyl thiophene) (P3HT) is shown in Fig. 5.5. The symmetrical C–C stretching is dominated in the Raman spectrum while the C–H stretching is dominated in the IR spectrum.

The P3HT is synthesized by Grignard metathesis reaction as shown in Fig. 5.6. The yield can be higher than 70 %. The principle of metathesis synthesis will be discussed in Sect. 9.4.

5.2.4 UV-Visible Spectroscopy

Ultraviolet–visible (UV–Vis) spectroscopy is used to detect the chromophores of matter qualitatively and quantitatively when the matter undergoes $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition upon light irradiation. Because of its sensitivity ($<10^{-5}$ molar), UV–Vis spectroscopy has been particularly useful in identifying the impurities in polymers such as residual monomer, inhibitors, antioxidant, and so on. Styrene monomer in polystyrene, for example, may be determined quantitatively using



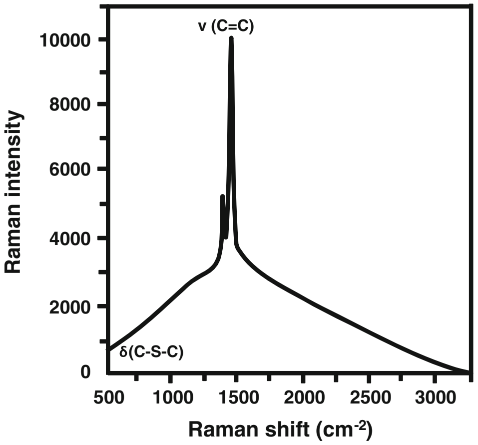


Fig. 5.5 IR spectrum (*top*) and Raman spectrum (*bottom*) of P3HT

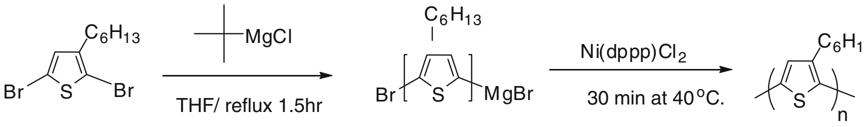


Fig. 5.6 Synthesis of P3HT using Grignard metathesis reaction

styrene's $\lambda_{\max}$ at 292 nm. After the styrene is polymerized, the 292 nm peak of styrene disappears and shows the $\lambda_{\max}$ at 203 and 254 nm of benzene for polymer.

Figure 5.7 shows a typical ultraviolet absorption spectrum of organic compound. Unlike infrared spectra, *UV–Vis spectra* are quite broad and generally show only a small number of peaks. The peaks are reported as the wavelengths where maxima occur. The conjugated, unsaturated ketone whose spectrum is shown in Fig. 5.7 has an intense absorption at $\lambda_{\max} = 232$ nm and a much weaker absorption at $\lambda_{\max} = 330$ nm. The band at shorter wavelength corresponds to a π

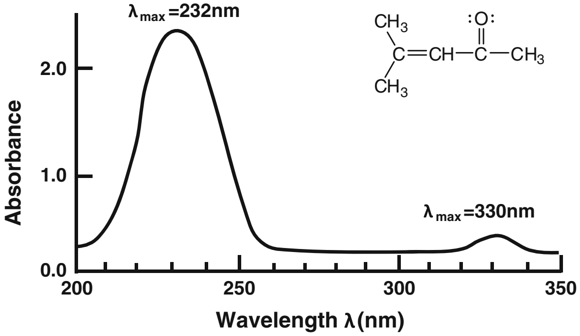


Fig. 5.7 The absorption spectrum of 4-methyl-3-penten-2-one [5]

electron transition, whereas the longer wavelength, weaker intensity band corresponds to a transition of the nonbonding electrons on the carbonyl oxygen atom.

The intensity of an absorption band can be expressed quantitatively. Band intensity depends on the particular molecular structure and also on the number of absorbing molecules in the light path. *Absorbance*, which is the log of the ratio of light intensities entering and leaving the sample, is given by Beer's law as below

$$A = \epsilon c l \tag{5.2}$$

where ϵ is the *molar absorptivity* (sometimes called the *extinction coefficient*), c is the concentration of the solution in moles per liter, and l is the length in centimeters of the sample through which the light passes. The value ϵ for any peak in the spectrum of a compound is a constant characteristic of that particular molecular structure. For example, the values of ϵ for the peaks in the spectrum of the unsaturated ketone shown in Fig. 5.7 are $\lambda_{\max} = 232$ nm ($\epsilon = 12{,}600$) and $\lambda_{\max} = 330$ nm ($\epsilon = 78$).

UV–Vis spectra are most commonly used to detect conjugation. In general, molecules with no double bonds or with only one double bond do not absorb in the region of UV to visible (200–800 nm). Conjugated systems do absorb there, however, and the greater the conjugation, the longer the wavelength of maximum absorption, as seen in Fig. 5.8. Therefore, most of the conjugated polymers exhibit absorption in the visible range (see Fig. 4.11).

5.2.5 Nuclear Magnetic Resonance Spectroscopy (NMR-^{1}H, ^{13}C)

The proton environment in the molecule can be determined by the nuclear magnetic resonance spectroscopy. Each proton in the molecule has its unique chemical shift δ. It is usually expressed in parts per million (ppm) by frequency. It is calculated based on the following equation:

$$\delta = \frac{\Delta \upsilon \times 10^6}{\text{oscillator frequency (cps)}} \tag{5.3}$$

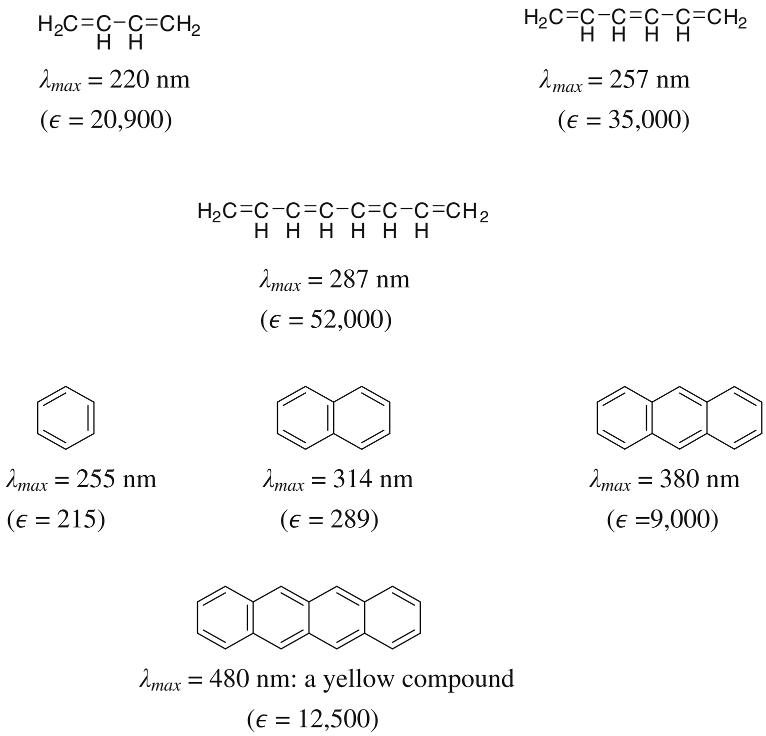


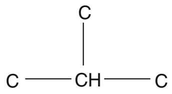
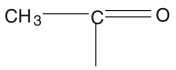
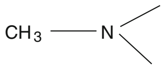
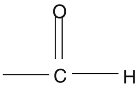
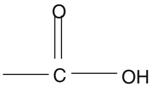
Fig. 5.8 Effect of conjugation length on the $\lambda_{\max}$ and ϵ of organic compounds

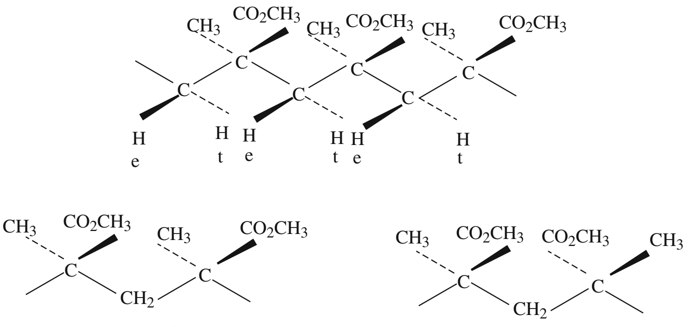
where $\Delta\upsilon$ is the difference in absorption frequencies of the sample and the reference in cps, and oscillator frequency is characteristic of the instrument. Chemical structures can be identified from a combination of chemical shift data and spin–spin splitting; derived from proton–proton interaction. Thus, the NMR is useful to study polymer stereochemistry and monomer sequencing. The chemical shifts of ^{1}H nuclei in various chemical environments have been determined by measuring the ^{1}H NMR spectra of a large number of compounds with known, relatively simple structures. Table 5.2 gives the chemical shifts for several common types of ^{1}H nuclei.

At present, very high resolution NMR instruments are available for polymer scientists to gain insights of polymer stereochemistry and monomer sequencing. For example, pure isotactic poly(methyl methacrylate) can have the possible arrangements for each repeat unit as shown in Fig. 5.9. By using 500-MHz NMR, a sample of poly(methyl methacrylate) has revealed to be predominantly (95 %) isotactic isomer as shown in Fig. 5.10.

The methyl protons of the sample are resolved to the pentad (*mmmm*) level and the methylene protons to the hexad (*mmmmm*) level. The notations of *e* and *t* refer to the *erythro* and *threo* placement, respectively. Of the methylene protons with respect to the ester groups, the *erythro* resonance being further downfield because of the

Table 5.2 Typical ^{1}H chemical shifts (relative to tetramethylsilane) [5]

Type	δ (ppm)		δ (ppm)
$C-CH_3$	0.85-0.95	$-CH_2-F$	4.3-4.4
$C-CH_2-C$	1.20-1.35	$-CH_2-Br$	3.4-3.6
		$-CH_2-I$	3.1-3.3
 $C-\underset{}{\overset{C}{\overset{\vert}{C}H}}-C$	1.40-1.65	$CH_2=C$	4.6-5.0
$CH_3-C=C$	1.6-1.9	$-CH=C$	5.2-5.7
CH_3-Ar	2.2-2.5	$Ar-H$	6.6-8.0
 $CH_3-\underset{\vert}{C}=O$	2.1-2.6	$-C\equiv C-H$	2.4-2.7
 $CH_3-N<$	2.1-3.0	 $-\overset{O}{\overset{\Vert}{C}}-H$	9.5-9.7
CH_3-O-	3.5-3.8	 $-\overset{O}{\overset{\Vert}{C}}-OH$	10-13
$-CH_2-Cl$	3.6-3.8	$R-OH$	0.5-5.5
$-CHCl_2$	5.8-5.9	$Ar-OH$	4-8



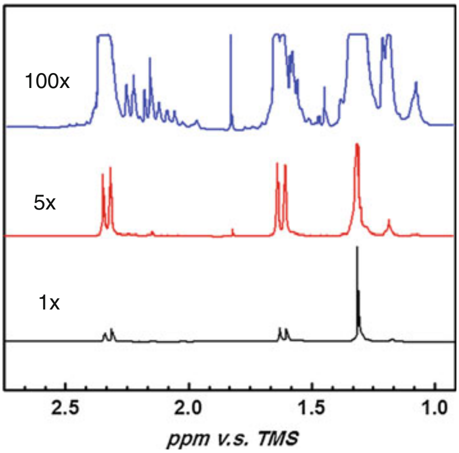
meso (m) dyad

racemtc (r) dyad

Fig. 5.9 Possible repeating unit arrangements of isotactic poly(methyl methacrylate)

deshielding influence of the ester group. At the lowest sensitivity (1X) the spectrum resembles that of almost purely isotactic (all *m*) polymer with the exception of the small *mmrm* pentad at about 1.16 ppm. At higher gain (5 and 100X), deviations from

Fig. 5.10 500-MHz ^{1}H nuclear magnetic resonance spectrum of isotactic poly(methyl methacrylate). For the 1X spectrum, the *left doublet peak* is e-mmmmm, the *middle doublet peak* is t-mmmmm, the *right large singlet peak* is mmmm, the *right small singlet peak* is mmrm [3]



purely isotactic are clearly observed. On the other hand, the syndiotactic placement exhibits predominantly *racemic* (*r*) sequences at about 1.05 ppm for methyl and, because both methylene protons lie in identical magnetic environments, one singlet methylene resonance at 1.83 ppm. The methoxyl protons absorb at 3.42 ppm. Atactic poly(methyl methacrylate) would display a broad range of sequences in its NMR spectrum, in this sample, the largest peaks of impurity correspond to those of syndiotactic placement.

Figure 5.11 shows high-resolution proton-decoupled ^{13}C spectra of polypropylene of varying tacticity. Fine structure in the spectra may again be correlated with pentad sequences.

The combination of cross-polarization and magic angle spinning (CP-MAS) along with proton decoupling yields spectra of solids approaching the resolution of those obtained with solutions. As an example, Fig. 5.12 shows the solid-state ^{13}C NMR spectrum of polycarbonate with and without cross-polarization magic angle spinning, in the spectral region encompassing the carbonyl and ring carbon resonances.

5.2.6 Electron Spin Resonance

Electron paramagnetic resonance (ESR) works on the same principle as NMR except that microwave rather than radiowave frequencies are employed, and spin transitions of unpaired electrons rather than nuclei recorded. The NMR spectra record the absorption directly, but ESR spectrometers plot the first derivative of the absorption curve. The ESR in polymer chemistry is primarily for studying free radical process such as polymerization, degradation, and oxidation. For example, when poly (vinyl chloride) is irradiated with ultraviolet light, the formation of radical can be detected by ESR. The chemical reaction is shown below and its corresponding ESR spectrum is shown in Fig. 5.13.

Fig. 5.11 24-MHz ^{13}C nuclear magnetic resonance spectra of polypropylene (3.5 % weight/volume in 1, 2, 4-trichlorobenzene at 135 °C) [3]

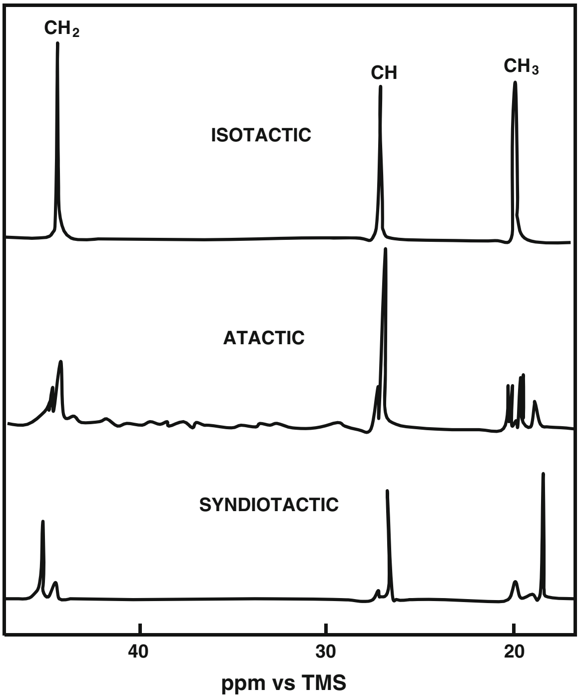
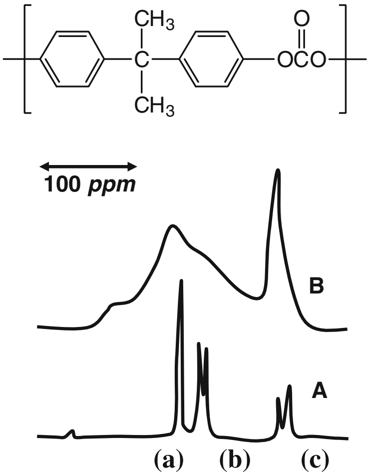
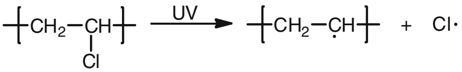


Fig. 5.12 Solid-state proton decoupled ^{13}C nuclear magnetic resonance spectra of polycarbonate (A) with and (B) without cross-polarization magic angle spinning. Peak assignment: (**a**) carbonyl carbon, (**b**) substituted ring carbons, and (**c**) unsubstituted ring carbons [3]





$$-\!\left[CH_2-\underset{Cl}{CH}\right]\!- \xrightarrow{UV} -\!\left[CH_2-\dot{C}H\right]\!- + Cl\cdot$$

The six-line signals arise from the interaction of unpaired electron with five surrounding protons (4β and 1α). This phenomenon is called *hyperfine splitting*.

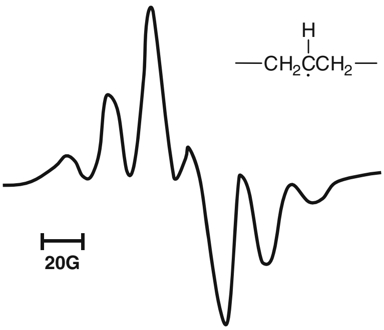


Fig. 5.13 Electron spin resonance spectrum inline of UV-irradiated poly(vinyl chloride) at −196 °C [3]

Information on the radical structure can be obtained by the line shape, intensity, position, and hyperfine splitting of the ESR spectrum.

5.3 Characterization of Morphology and Physical Structure of Polymer

Polymer morphology and structure may be elucidated from usual examination and mathematical interpretation of the pattern and intensity of diffracted and scattered X-ray, electron and neutron radiations on polymer sample. The results can provide the information of degree of crystallinity, dimension of crystalline domains, bond distance and angles, and type of conformation in the crystalline regions. Precautions need to be taken for these experiments especially involving electrons, because electrons may cause free radical reactions (chain scission, cross-linking) in the samples. Transmission electron microscopy (TEM) resolution can have up to several angstroms. Neutron scattering can study chain folding in crystalline lamellae. The AFM analyzes the surface profile of polymer thin film at nanoscale without using high vacuum and electron source.

5.3.1 Transmission Electron Microscopy

TEM is a very powerful tool to study the morphology of polymer. Here, we use the TEM study of rod-coil block copolymer of poly(diethylhexyloxy-p-phenylene vinylene)-b-poly (methyl methacrylate) (DEHPPV-b-PMMA) as an example. Figure 5.14 shows TEM images of the copolymer at various compositions. The last number in the copolymer denotations is the % volume fraction of coil PMMA [6]. The DEHPPV is a rigid rod segment and PMMA is a flexible coil segment. Due to the difference in miscibility of each segment, the copolymer is self assembled into highly ordered structure. The polymers stained with RuO_4 demonstrate light PMMA-rich nanodomains and dark DEH-PPV-rich nanodomains. Lamellae are continuous and very long. The orientation of lamellae is correlated across several

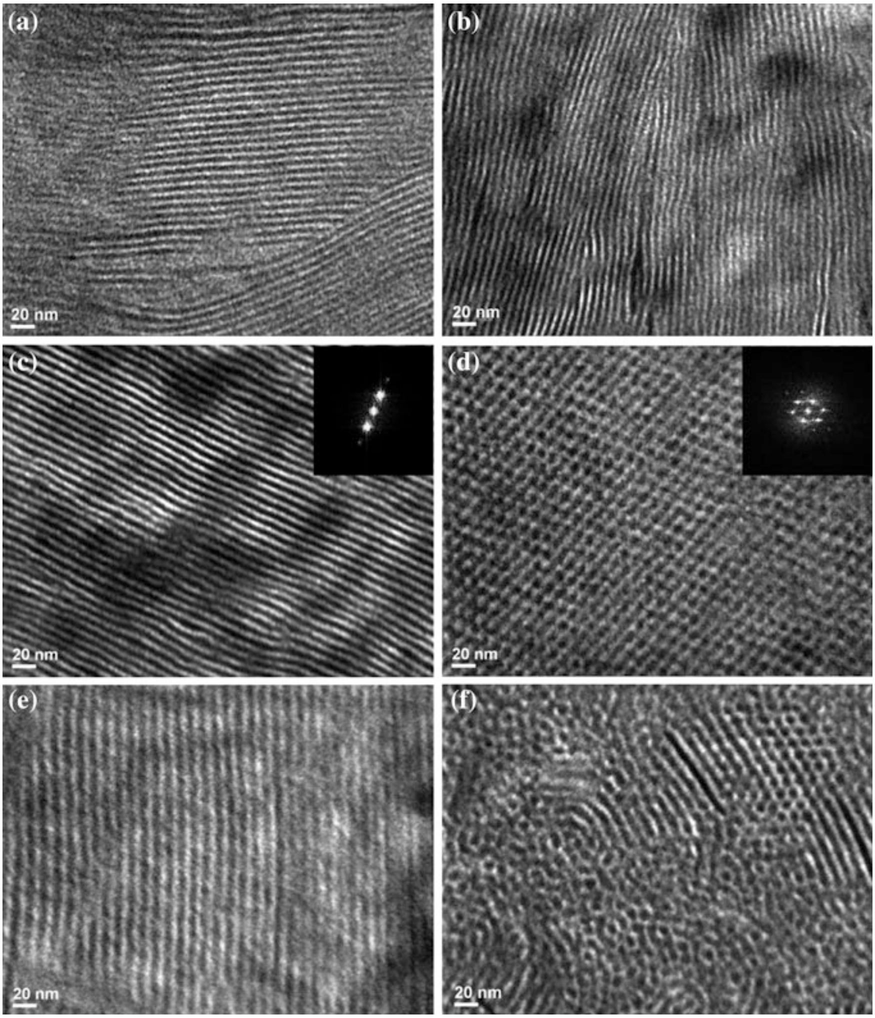


Fig. 5.14 TEM images of PPV-b-PMMA block copolymers; **a** PPV_{10}-$PMMA_{13}$-30, **b** PPV_{10}-$PMMA_{36}$-43, **c** PPV_{10}-$PMMA_{49}$-53, **d** PPV_{10}-$PMMA_{84}$-66, **e** the lateral view of PPV_{10}-$PMMA_{84}$-66, and **f** PPV_{10}-$PMMA_{126}$-74 [6]

hundreds of nanometer, or even up to a micrometer. Moreover, the lamellae have remarkable persistence length (at least several hundred nm) indicating a very high bending modulus of the DEH-PPV rod lamellar domain. Inset in Fig. 5.14c is a 2D Fourier transformation of DEH-PPV_{10}-$PMMA_{49}$-53 demonstrating the 2-fold symmetry indicative of lamellar structure and a high degree of orientation. The defects observed in the lamellae of the DEH-PPV-b-PMMA system involve curvature and T junction, with only instances of abruptly ending lamellae due to dislocations and dilations of DEH-PPV rich regions. We interpret the results as the free energy penalty associated with additional inter-block contacts at the core of a dislocation was much higher than the bending penalty imparted by the rod rigidity. As a result, this system's higher segregation strength results in greater lamellar continuity and a greater presence of curvature defects instead of lamellar breaks.

TEM images of the more asymmetric block copolymers (i.e., volume fraction of copolymer is apart from 50 %), as shown in Fig. 5.14d, show that the DEH-PPV rods are packed into short strip-like aggregates assembled onto a hexagonal lattice. Moreover, the 2D Fourier transformation inset in Fig. 5.14d has 6-fold symmetry indicative of the hexagonal structure with high degree of orientation. The lateral view of the polymer is also investigated by tilting the sample. TEM image, as shown in Fig. 5.14e, shows that alternating stripes with light and dark are observed. However, the stripes in the hexagonal structure are shorter than the stripes in the lamellar polymers. The short strip-like aggregates with the hexagonal packing appear again, while the lamellae across the boundary. In summary, in asymmetric copolymers, the DEH-PPV rods pack into hexagonally arranged strips. These strip aggregates are much longer in the third dimension than the two small dimensions.

TEM image gives complementary information for the block copolymer with coil volume fraction at 74 %, as shown in Fig. 5.14f. Short strip-like aggregates and longer strip-like aggregates with intermediate orientational order still can be observed. As compared to the structure of DEH-PPV$_{10}$-PMMA$_{64}$-66, the structure of DEH-PPV$_{10}$-PMMA$_{126}$-74 is similar to the hexagonal structure.

5.3.2 *X-Ray Scattering*

X-ray technique is the most important method to determine the spatial arrangements of all the atoms in polymers [3]. X-rays are generated in cathode ray tubes when high energy electrons impinge on metal target such as copper. When X-rays are focused on a polymer sample, two types of scattering occur. If a sample is crystalline, the X-rays are scattered coherently; that is, there is no change in wavelength or phase between the incident and scattered rays. Coherent scattering is commonly referred to as X-ray diffraction. If the sample has a nonhomogeneous (semicrystalline) morphology, the scattering is incoherent; there is change in both wavelength and phase. Incoherent scattering is referred to as diffuse diffraction or simply as scattering.

Coherent scattering is determined by wide-angle measurements and incoherent scattering by small angle measurements as shown in Fig. 5.15. The former is called wide-angle X-ray scattering (WAXS) and the latter is named small-angle X-ray scattering (SAXS). The wide angle diffraction pattern consists of a series of concentric cones arising from scattering by the crystal planes. It is recorded as concentric rings on the X-ray plate superimposed on a diffuse background of incoherent scatter as shown in Fig. 5.15. On the contrary, small-angle scatter patterns are very diffuse (Fig. 5.15). Another way to present the two dimensional scattering spectrum of the polymer is making a plot of intensity versus angle of scattering. The patterns and intensity of X-ray scattering can provide considerable

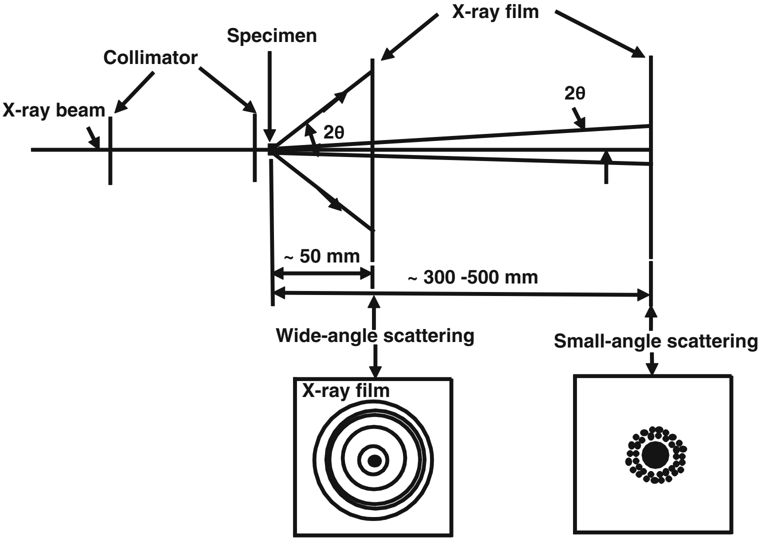


Fig. 5.15 Wide-angle and small-angle X-ray scattering techniques [3]

information regarding the polymer morphology and structure through visual examination and mathematical modeling interpretation. Examples of scattering patterns of P3HT-b-P2VP copolymer and P3HT were discussed earlier in Sects. 3.3 and 3.8, respectively.

5.3.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is used to monitor the surface roughness and hardness of polymer; phase separation of polymer blends. The essential features of AFM are shown in Fig. 5.16. The atomic scale probe is scanned through the

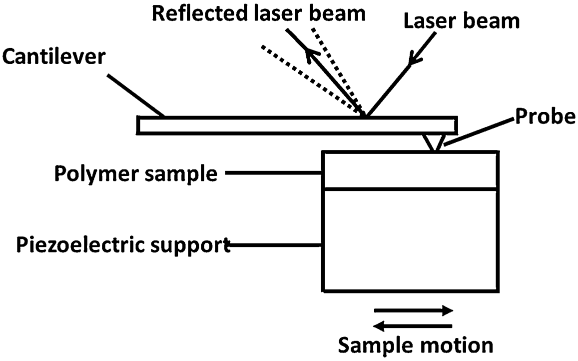


Fig. 5.16 Schematic diagram of an atomic force microscope [3]

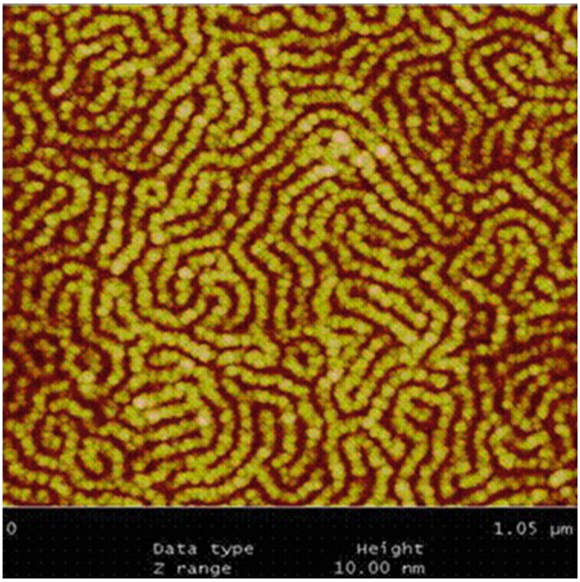


Fig. 5.17 AFM image of PS-b-PMMA

surface of sample, the change in depth is monitored by laser beam irradiated on the cantilever, fed back by piezoelectric force that response to surface variations sensed by the probe. The sample is mounted on the piezoelectric support. Figure 5.17 shows the phase separation of polystyrene and poly(methyl methacrylate) diblock copolymers (PS-b-PMMA) on glass substrate. The light color image is PS and the dark color image is PMMA. The PS has a higher depth profile and is toward air because of its hydrophobic characteristics.

5.4 Characterization of Thermal Properties of Polymers

Thermal analysis is used to study the thermal stability, melting point, glass transition temperature (Tg), and flammability, etc. The methods include DTA, DSC, DMA, TMA, and TGA. The full name and principle of each method is described in the following sections.

5.4.1 Differential Thermal Analysis and Differential Scanning Calorimetry

Before the invention of DSC, the differential thermal analysis (DTA) is commonly used to determine the thermal stability of polymer. The DTA, both sample and reference are heated by the same heat source and the difference in temperature ΔT between the two is recorded. When a transition occurs in a sample, a temperature

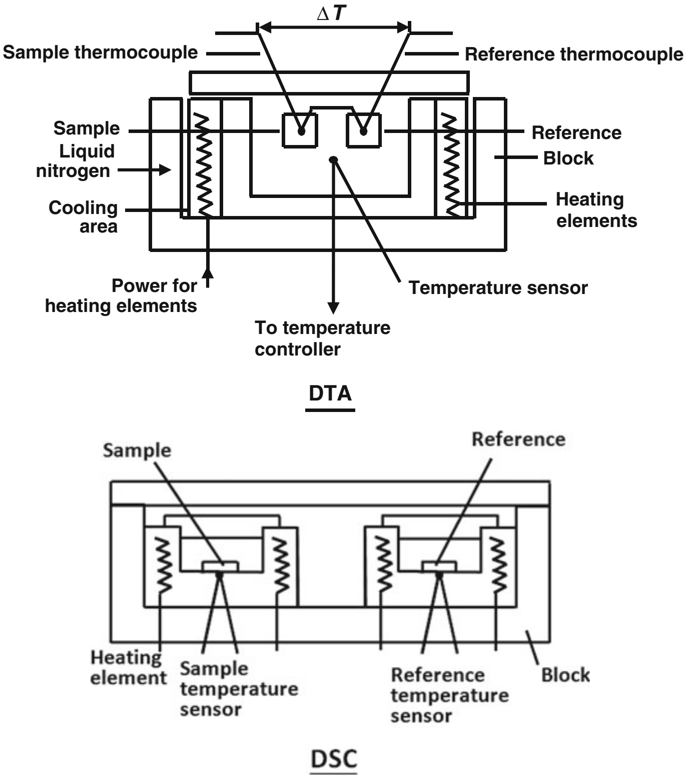


Fig. 5.18 Schematic illustrations of DTA and DSC measuring cells [3]

lag will show as endothermic or exothermic depends on the transition. For DSC, sample and reference are provided with individual heaters, and energy is supplied to keep the sample and reference temperatures constant. The electrical power difference between sample and reference is recorded as dΔQ/dt. Schematic representations of DTA and DSC cells are given in Fig. 5.18. The DTA data only report the softening (phase transition) temperature of polymer while the DSC also provide the amount of heat involved in the softening process. The DSC is more preferred in the polymer characterization because the precise control and measurement of heat varied in the heating process.

Data are plotted as Δ*T* (for DTA) or dΔQ/dt (for DSC) on the ordinate against temperature on the abscissa. Such plots are called *thermograms*. Although Δ*T* and dΔQ/dt are not linearly proportional, they are both related to heat capacity. Thus, DSC and DTA thermograms have the same form. An idealized DSC or DTA thermogram for a hypothetical crystallizable polymer is depicted in Fig. 5.19. The figure shows the types of transitions that are interested to polymer scientists.

In reporting transition temperatures, it is important to indicate whether one is referring to the onset of the transition or to the inflection point peak maximum, as shown in Fig. 5.20. Both conventions are used.

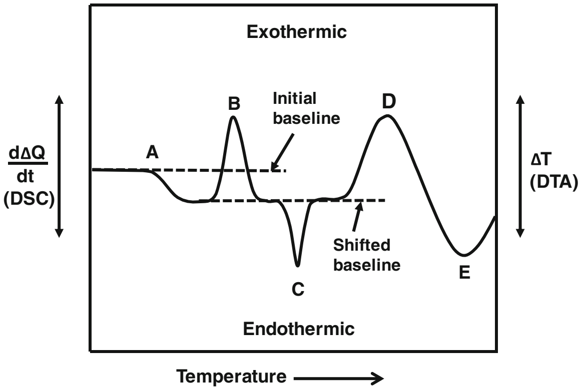
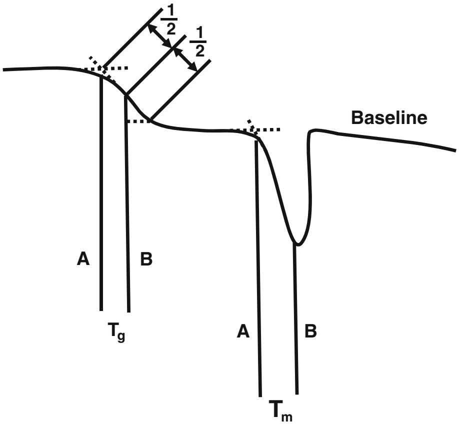


Fig. 5.19 Idealized differential scanning calorimetry (DSC) or differential thermal analysis (DTA) thermogram: (A) temperature of glass transition, T_g; (B) crystallization; (C) crystalline melting point, T_m; (D) crosslinking; and (E) vaporization. dΔQ/dt is the electrical power difference between sample and reference; ΔT is the difference in temperature between sample and Ref. [3]

Fig. 5.20 Methods of reporting transition temperatures: (A) at the onset, and (B) at the inflection point or maximum. T_g = glass transition temperature. T_m = crystalline melting point [3]



5.4.2 Thermomechanical Analysis (TMA)

TMA employs a sensitive probe in contact with the surface of a polymer sample under a defined load. As the sample is heated, the probe senses thermal transition such as T_g or T_m by detecting either a change in volume or a change in modulus. TMA is generally more sensitive than DSC or DTA for detecting thermal transitions, especially for thermoset because the TMA probe is in direct contact with the sample. Figure 5.21 shows bisphenol epoxy resin (BP) was cured with phenolic resin (PF5110) and the thermoset transition occurred at 150 °C [7].

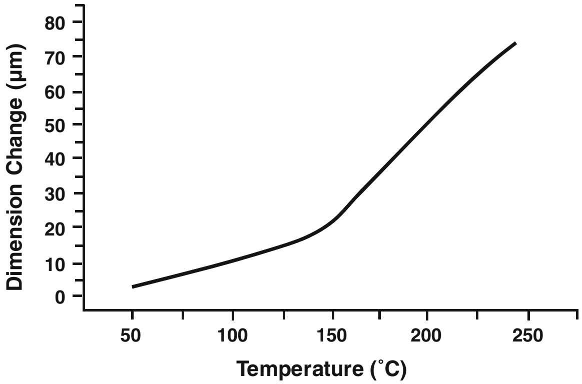


Fig. 5.21 Thermomechanical analysis of phenolic resin (PF5110) cured epoxy resin (BP) [7]

5.4.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used primarily for determining thermal stability of polymers. The most widely used TGA method is based on continuous measurement of weight on a sensitive balance (called a *thermobalance*) as sample temperature is increased in air or in an inert atmosphere. Data are recorded as a weight loss versus temperature. A typical thermogram illustrating the difference in thermal stability between a wholly aromatic polymer and a partially aliphatic polymer of analogs structure is shown in Fig. 5.22.

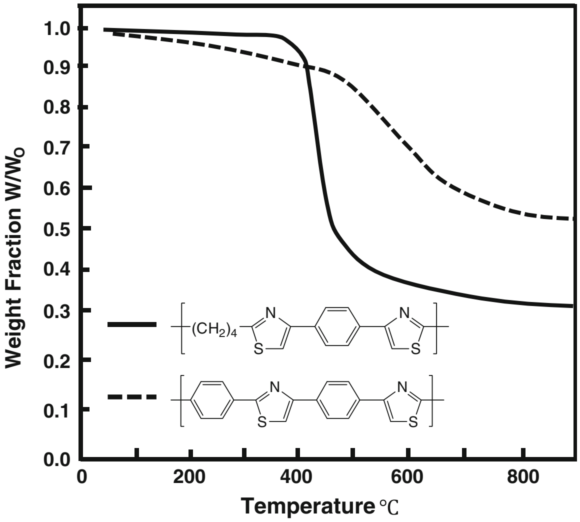


Fig. 5.22 Thermogram of thermogravimetric analysis of polythiazoles [3]

5.4.4 Flammability Test

Flammability is difficult to measure because the result does not correlate directly the burning behavior in true fire conditions of polymer. Currently, the *limiting oxygen index* (LOI) of polymer is employed as an indication of flammability of polymer. The LOI is the minimum percentage of oxygen in an oxygen–nitrogen mixture that will initiate and support for three minutes the candle like burning of a polymer sample; that can be expressed by Eq. 5.4. The test can be easily carried out in the laboratory using a small-scale fire.

$$\mathrm{LOI} = \frac{\mathrm{vol.}\,O_2}{\mathrm{vol.}\,O_2 + \mathrm{vol.}\,N_2} \times 100 \tag{5.4}$$

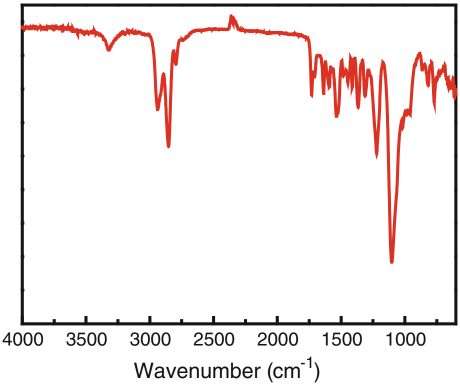
Representative LOI values for some common polymers are given in Table 5.3. Note the large difference in LOI between poly(ethylene oxide) and poly(vinyl alcohol), although they have similar structure. The dehydration of polyvinyl alcohol will cool the polymer during burning. The polymers contained ether linkage exhibit low LOI due to the presence of oxygen atom. Although the polycarbonate contains oxygen, it releases fire extinguishing CO_2 during burning which increases the LOI value. The polymers having aromatic structure especially in the backbone show high LOI, because the aromatic chain is more difficult to break and burn than that of alkyl chain such as poly(phenylene oxide). The inclusion of Si in the polymer increases the LOI because Si is nonflammable as compared to C. The chloride bond of polyvinyl chloride is easy to break under heat and function as an extinguisher to reduce the burning which results in high LOI. The poly(tetrafluoro ethylene) exhibits the highest LOI among the polymers because of the strong C–F bonding and dense structure of the polymer.

Table 5.3 Limiting oxygen indexes (LOI) of some common polymers [3]

Polymer	LOI
Poly(oxy methylene)	15
Poly(ethylene oxide)	15
Poly(methyl methacrylate)	17
Polypropylene	17
Polyethylene	17
Polystyrene	18
Poly(1,3-butadiene)	18
Poly(vinyl alcohol)	22
Polycarbonate	27
Poly(phenylene oxide)	28
Polysiloxane	30
Poly(vinyl chloride)	45
Poly(vinylidene chloride)	60
Poly(tetrafluoro ethylene)	95

5.5 Problems

1. A copolymer of propylene and vinyl chloride contains 35wt. % chlorine. What is the molar ratio of vinyl chloride to propylene in the copolymer?
2. What kind of polymer can you deduce from the following IR spectrum?



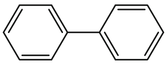
3. One stereoregular form of polystyrene (A) has a ^{1}H NMR spectrum containing a triplet centered at about 1.4 ppm and a quintet at about 1.9 ppm. Another stereoregular form (B) has an octet at about 1.6 ppm. Interpret the spectra and determine which corresponds to isotactic and which to syndiotactic.
4. How would you distinguish between the following two polymers by IR and NMR?

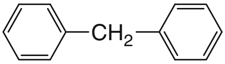
$$[p-C_6H_4-CH_2]_n-, \ -[o-C_6H_4-CH_2]_n-$$

5. What changes would be observed in the XRD patterns of rubber that has been stretched?
6. Please use a spectroscopic method to determine the following and explain your answer. (a) The amount of styrene in a styrene-butadiene copolymer. (b) The amount of 1,2- polymer in poly(1,3-butadiene). (c) The stereochemistry of double bonds in 1,4-poly(1,3-butadiene). (d) Unreacted polyacrylonitrile (PAN) is present in a sample of carbon fiber prepared by pyrolysis of PAN. (e) Poly(vinyl acetate) has undergone hydrolysis on exposure to moisture. (f) A polyester surgical implant has been coated with polyterafluoroethylene completely to improve its chemical resistance.
7. Which technique would you use to solve the following problems, (a) locate a crystalline melting temperature, (b) determine the degree of orientation, (c) determine the arrangement of molecular chains in a polymer crystal, (d) locate the glass transition temperature, (e) characterize the double bond in the diene polymer, (f) measure the enthalpy of fusion, (g) investigate the mechanism of oxidation of a polymer, (h) study the molecular motion of polymer chains, (i)

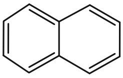
estimate the degree of crystallinity, (j) measure the amide content of an ester-amide copolymer.

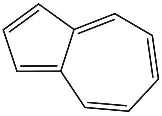
8. Show how NMR can be used to (a) distinguish between head-to-head and head-to-tail polymerization in polymer, (b) distinguish between a random copolymer and a mixture of homopolymers.
9. Draw typical DSC and DTA thermograms for a crystalline polymer, showing the glass transition, crystallization, crystalline melting and thermal degradation.
10. Please answer the following questions:
    (a) Which of the following aromatic compounds do you expect to absorb at the longer wavelength?





    (b) Naphthalene is colorless, but its isomer azulene is blue. Which compound has the lower-energy pi electronic transition?


naphthalene


azulene

    (c) Does the molecular weight affect the absorption wavelength (λ_{max}) of polymer? Please compare the difference of UV–Vis spectrum of polythiophene between molecular weight of 3000 and 30,000. Explain your answer.

References

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6. C.C. Ho, Y.H. Lee, C.A. Dai, R. Segalman, W.F. Su, Macromolecules **42**(12), 4208–4219 (2009)
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Chapter 6
Step Polymerization

The step polymerization builds up the molecular weight of polymer by stepwise function. Sometimes, the polymerization involves the release of small molecule by-product, so it is also called condensation polymerization. It is the earliest polymerization technique in the synthetic polymers. In 1907, Leo Baekeland of Germany created the first completely synthetic polymer, Bakelite, by reacting phenol and formaldehyde. It is also called phenolic resin. The molecular weight of the phenolic resin builds up stepwise by removing water. The product was commercialized in 1909 by forming a company bearing his name as Bakelite until present day.

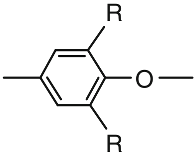
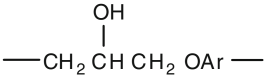
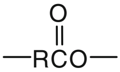
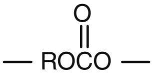
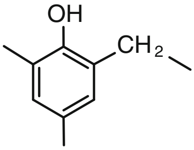
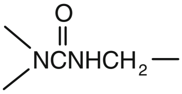
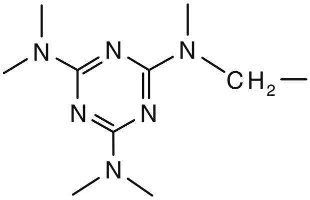
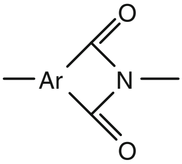
Table 6.1 lists some of the commercially important polymers prepared by step-reaction polymerization. The reaction mechanisms, kinetics of polyesters and polyamides have been thoroughly studied. Thus, we are discussing the degree of polymerization $\overline{DP}$ and the polymerization rate of step polymerization using these two polymers as examples.

6.1 Chemical Reactions and Reaction Mechanisms of Step Polymerization

The type of products formed in step polymerization is determined by the functionality of the monomers, i.e., by the average number of reactive functional groups per monomer molecule. Monofunctional monomers give only low molecular weight products. Bifunctional monomers give linear polymers. Polyfunctional monomers, with more than two functional groups per molecule, give branched or crosslinked polymers. The properties of the linear and the crosslinked polymers differ widely. The mechanism of step polymerization is discussed below according to the type of chemical reaction [2].

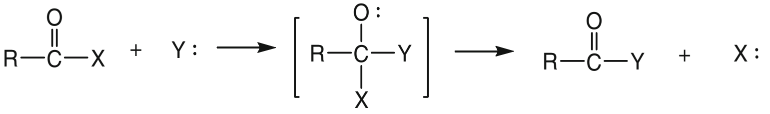
W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_6,

Table 6.1 Commercially important polymers prepared by step polymerization [1]

Polymer type	Repeating functional unit
Polyether [poly(phenylene oxide)]	
Polyether (epoxy resin)	 $-\mathrm{CH_2}\overset{\mathrm{OH}}{\overset{\vert}{\mathrm{C}}}\mathrm{H\,CH_2\,OAr}-$
Polysulfide	$-\mathrm{ArS}-$
Poly(alkylene polysulfide)	$-\mathrm{RS}_x-$
Polysulfone	$-\mathrm{ArSO}_2-$
Polyester	 $-\mathrm{R}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$
Polycarbonate	 $-\mathrm{RO}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{O}-$
Polyamide	 $-\mathrm{R}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{NH}-$
Polyurea	 $-\mathrm{RNH}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{NH}-$
Polyurethane	 $-\mathrm{RO}\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}\mathrm{NH}-$
Phenol–formaldehyde (complex network structure)	
Urea–formaldehyde (complex network structure)	
Melamine–formaldehyde (complex network structure)	
Polyimide	

6.1.1 Carbonyl Addition: Elimination Reaction Mechanism

The reaction mechanism involves the addition and elimination at the carbonyl double bond of carboxylic acids and their derivatives to form polymer as shown below:



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}X \;+\; Y\!: \longrightarrow \left[R{-}\overset{\overset{\displaystyle O:}{|}}{\underset{\underset{\displaystyle X}{|}}{C}}{-}Y \right] \longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}Y \;+\; X\!: \qquad (6.1)$$

Where R may be alkyl or aryl groups, X may be OH, OR′, O–C(=O)R′, or Cl; and Y may be $R'O^-$, $R'OH$, $R'NH_2$, or $R'COO^-$. The species in the bracket is a metastable intermediate, which can either return to the original state by eliminating Y or proceed to the final state by eliminating X. The following section provides some typical examples of polymers made by this reaction mechanism.

6.1.1.1 Direct Reaction

Polyester has been prepared by direct reaction of a dibasic acid and a glycol. A strong acid or acidic salt often serves as a catalyst. The reaction may be carried out by heating the reactants together and removing water, usually applying vacuum in the later stages.

Polyamide can be synthesized by direct reaction of dibasic acid and a diamine. The use of their salt such as hexamethylene diamine salt of adipic acid to synthesize Nylon 66 can meet stringent requirement of stoichiometric equivalent to obtain high molecular weight polymer by heating salt to above its melting point in an inert atmosphere.

6.1.1.2 Interchange

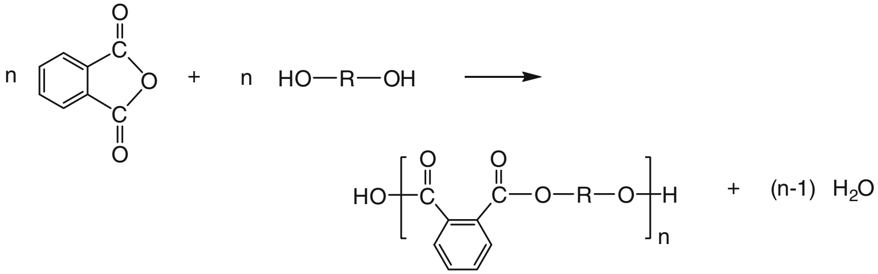
The ester exchange has been used to synthesize polyester using a glycol and ester as the following:

$$\begin{aligned} & n\,HO{-}R{-}OH \;+\; n\,R''OOC{-}R'{-}COOR'' \longrightarrow \\ & \qquad R''O{\left[CO{-}R'{-}COO{-}R{-}O \right]}_n H \;+\; (2n\text{-}1)\,R''{-}OH \end{aligned} \qquad (6.2)$$

The alcohol by-product is easier to remove than the water, so a higher molecular weight can be achieved faster. The ester monomer also has an advantage over acid monomer on the solubility in solvent. This reaction has been used routinely in the synthesis of polyester using ethylene glycol and dimethyl terephthalate in the industry. The other interchange reactions such as amine-amide, amine-ester, and acetal-alcohol are well-known for polymerization.

6.1.1.3 Acid Chloride or Anhydride

Either acid chloride or anhydride can be reacted with a glycol or an amine to give a polymer. The anhydride reaction is widely used to form an alkyd resin from phthalic anhydride and a glycol:



(6.3)

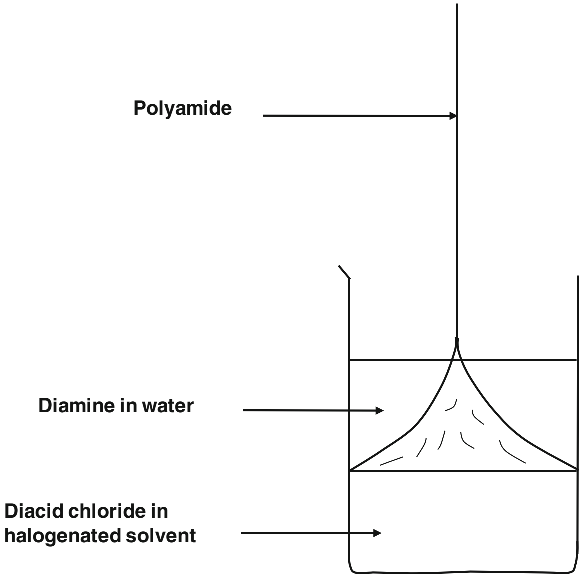
The reaction between acid chloride and a glycol is not useful because of side reactions leading to low molecular weight products. However, the reaction of an acid chloride with a diamine is a good way to prepare polyamides. The amine is a much stronger nucleophile toward acid chloride than the alcohol, so the polymerization can be achieved quantitatively.

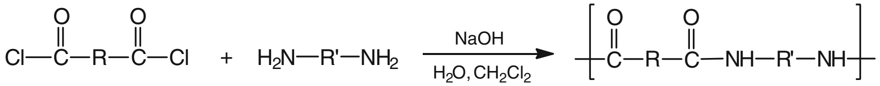
6.1.1.4 Interfacial Condensation

The reaction of an acid halide with a glycol or a diamine proceeds rapidly to high molecular weight polymer if carried out at the interface between two liquid phases, each containing one of the reactants. Typically, an aqueous phase containing the diamine or glycol and an acid is layered at room temperature over an organic phase containing the acid chloride. The polymer formed at the interface can be pulled off as a continuous film or filament (Fig. 6.1). The method has been applied to the formation of polyamides, polyurethanes, polyureas, polysulfonamides, and polyphenyl esters. It is particularly useful for synthesizing polymers that are unstable at higher temperature.

A typical example is the Schotten-Baumann synthesis of polyamide from a diacid chloride dissolved in an organic solvent, and a diamine dissolved in aqueous base. The base is needed to neutralize the by-product HCl, which would otherwise react with the diamine to form amine hydrochloride. Rapid stirring to maximize the interfacial area increases the yield of polymer.

Fig. 6.1 Interfacial synthesis of polyamide

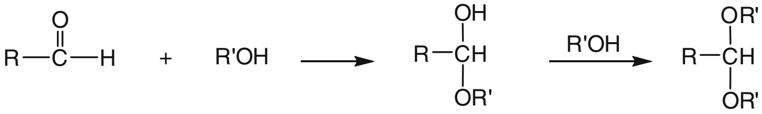




$$\mathrm{Cl-\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-Cl} + \mathrm{H_2N-R'-NH_2} \xrightarrow[\mathrm{H_2O,\,CH_2Cl_2}]{\mathrm{NaOH}} \left[\mathrm{\overset{\overset{O}{\|}}{C}-R-\overset{\overset{O}{\|}}{C}-NH-R'-NH}\right] \tag{6.4}$$

6.1.2 Carbonyl Addition: Substitution Reaction Mechanism

This reaction mechanism has been used in the synthesis of polyacetal from aldehyde and alcohol. The reaction mechanism involves first addition and then substitution at the carbonyl groups of aldehyde from alcohol to form polyacetal.

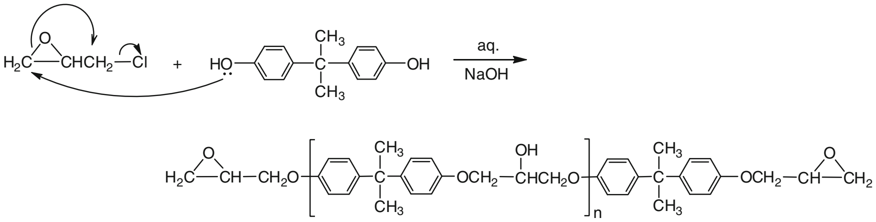


$$\mathrm{R-\overset{\overset{O}{\|}}{C}-H} + \mathrm{R'OH} \longrightarrow \mathrm{R-\underset{\underset{OR'}{|}}{\overset{\overset{OH}{|}}{CH}}} \xrightarrow{\mathrm{R'OH}} \mathrm{R-\underset{\underset{OR'}{|}}{\overset{\overset{OR'}{|}}{CH}}} \tag{6.5}$$

The phenolic resin made from formaldehyde and phenol is underwent similar reaction mechanism.

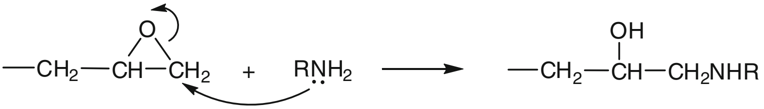
6.1.3 Nucleophilic Substitution Reaction Mechanism

This reaction mechanism is used in the synthesis of epoxy resin as shown in the following:



(6.6)

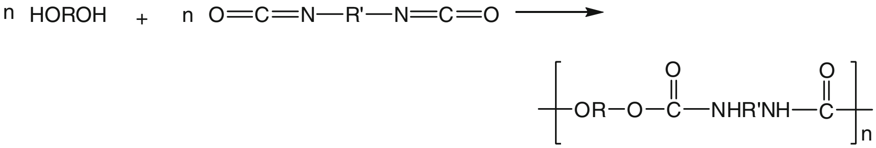
Here, the nucleophile is bisphenol A to react with epichlorohydrin to substitute chlorine by ring closure reaction to form epoxy resin. The size of epoxy resin can be controlled by the amount of epichlorohydrin. Usually, the excess amount of epichlorohydrin is used to obtain low molecular weight liquid epoxy resin with n is equal to 0 or 1. This low molecular weight epoxy resin can be further reacted with multifunctional amine or anhydride to obtain cured thermoset epoxy resin by the following reaction:



(6.7)

6.1.4 Double-Bond Addition Reaction Mechanism

This reaction mechanism is typically used to synthesize polyurethane. Polyurethane is prepared by adding the hydroxyl group of polyol into the double bond of isocyanate as shown in the following. The polyol can be either polyester polyol or polyether polyol. The polyol is usually synthesized by ring opening polymerization which will be discussed in Chap. 11.

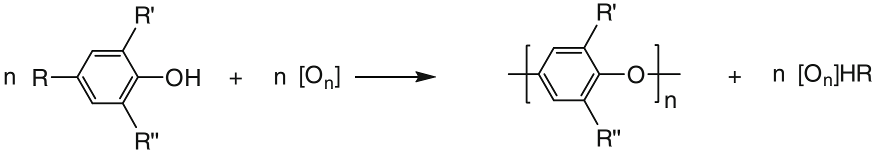


$$n\ HOROH + n\ O{=}C{=}N{-}R'{-}N{=}C{=}O \longrightarrow \left[OR{-}O{-}\overset{O}{\overset{\|}{C}}{-}NHR'NH{-}\overset{O}{\overset{\|}{C}} \right]_n$$

(6.8)

6.1.5 *Free-Radical Coupling*

This reaction mechanism is used to synthesize arylene ether polymers, polymer containing acetylene units, and arylene alkylidene polymers as shown below:

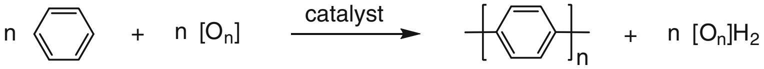


(6.9)

where $[O_n]$ is an oxidizing agent.

6.1.6 *Aromatic Electrophilic-Substitution Reaction Mechanism*

The poly(*p*-phenylene) synthesis can be obtained by this reaction mechanism as shown in the following:



(6.10)

6.2 Reaction Kinetics of Step Polymerization

Linear polymers are synthesized either from difunctional monomers of the AB type or from a combination of AA and BB difunctional monomers. Network polymers are formed from monomers having functionality greater than two. Polymers retain their functionality as end groups at the completion of polymerization. A single reaction is responsible for the formation of polymer. Molecular weight increases slowly even at high levels of conversion. In 1920, Wallace Carothers proposed a Carothers equation relating $\overline{DP}$ to monomer conversion (p) as Eq. 6.11. High-yield reactions and an exact stoichiometric balance are necessary to obtain a high molecular weight linear polymer.

$$\overline{DP} = \frac{1}{1-p} \tag{6.11}$$

If the polymerization reaction is first order with respect to each functional group reactant, A and B, then the rate of reaction can be expressed by:

$$-\frac{d[A]}{dt} = k[A][B] \tag{6.12}$$

For high molecular weight polymer, we need $[A] = [B]$, then the rate of reaction becomes

$$-\frac{d[A]}{dt} = k[A]^2 \tag{6.13}$$

or, by integration,

$$\frac{1}{[A]} - \frac{1}{[A_o]} = kt \tag{6.14}$$

At any particular time, t, in the polymerization process, $\overline{DP}$ is equal to the ratio of monomer molecules present initially to the total number at that time; that is,

$$\overline{DP} = \frac{[A_o]}{[A]} \tag{6.15}$$

Combining Eq. 6.15 with the Carothers equation and solving for $[A]$, one has

$$[A] = [A_o](1 - p) \tag{6.16}$$

By substitution in Eq. 6.14, one obtains

$$\frac{1}{[A_o](1-p)} - \frac{1}{[A_o]} = kt \tag{6.17}$$

Since $\overline{DP} = 1/(1-p)$, Eq. 6.17 can be rearranged into

$$\frac{\overline{DP}}{[A_o]} - \frac{1}{[A_o]} = kt \tag{6.18}$$

or

$$\overline{DP} = [A_o]kt + 1 \tag{6.19}$$

From initial monomer concentration $[A_o]$ and time t, we can calculate molecular weight. For the synthesis of polyester, in the absence of acid catalyst, the monomer of carboxylic acid A, assumes the role of catalyst, and the rate of reaction then becomes second order in acid, or third order overall:

$$-\frac{d[A]}{dt} = k[A]^2[B] \tag{6.20}$$

Assuming $[A]$ and $[B]$ are equal,

$$-\frac{d[A]}{dt} = k[A]^3 \tag{6.21}$$

Integration then gives

$$\frac{1}{[A]^2} - \frac{1}{[A_o]^2} = 2kt \tag{6.22}$$

Substituting for $[A]$ from Eq. 6.16 and rearranging

$$\frac{1}{[A_o]^2(1-p)^2} - \frac{1}{[A_o]^2} = 2kt \tag{6.23}$$

or

$$\frac{1}{(1-p)^2} = 2kt[A_o]^2 + 1 \tag{6.24}$$

and

$$\overline{DP}^2 = 2kt[A_o]^2 + 1 \tag{6.25}$$

For uncatalyzed polyesterification (6.25), the molecular weight increases slower than that of acid catalyzed polyesterification (6.19). The above equation deviates at both low and high levels of extent of conversion of monomers. As shown in Fig. 6.2, in the early stage, highly polar alcohol and acid are converted to much lower polarity ester. The more polar the medium, the more association through hydrogen bonding inhibits reactivity. At high conversion, water by-product is difficult to remove in high-viscosity environment (high molecular weight) that reduces the rate of conversion.

6.3 Molecular Weight Control in Step Polymerization

Three approaches have been used extensively to limit the molecular weight of polymer in step-reaction polymerization. One can quench the polymerization reaction by lowering the reaction temperature or by adding monofunctional monomer. For example, fatty acid has been added into unsaturated polyester synthesis, acetic acid added into Nylon 66 synthesis. One can also obtain low molecular weight epoxy resin by using one reactant in excess as described earlier.

When a nonstoichiometric amount of functional groups is used, the relationship between $\overline{\mathrm{DP}}$ and reaction conversion can be quantified by a modification of the Carothers equation. We use a factor, r, representing the *stoichiometric imbalance*. For a polymerization reaction of AA and BB, when the molar equivalent of AA

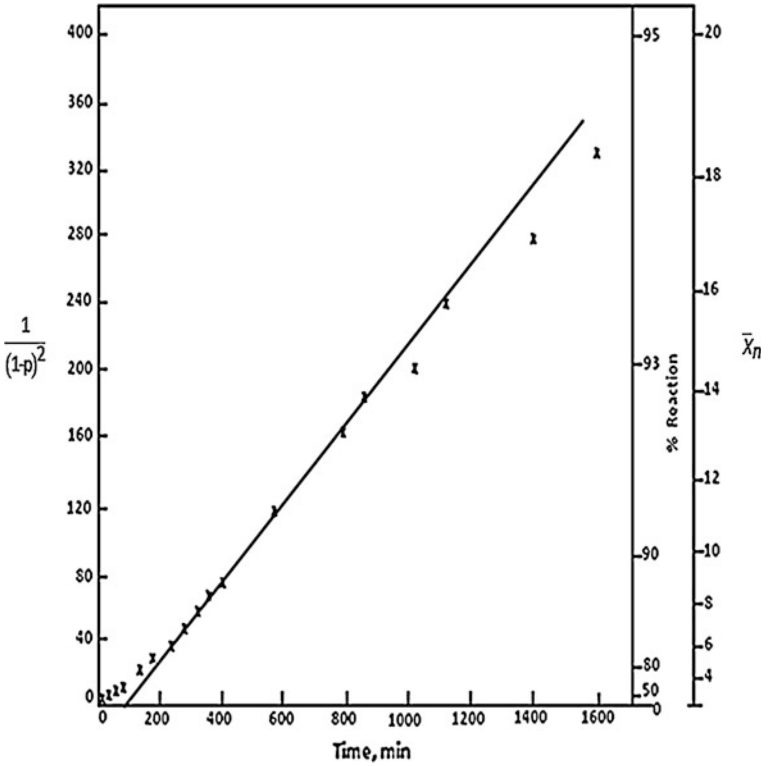


Fig. 6.2 Third-order plot of the self-catalyzed polyesterification of adipic acid with diethylene glycol at 166 °C [3]

monomer (N_A^o) is different from the molar equivalent of BB monomer (N_B^o), the stoichiometric imbalance factor, r, can be expressed by:

$$r = \frac{N_A^o}{N_B^o} \tag{6.26}$$

By convention, r is always less than unity (except, when $N_A^o = N_B^o$). As before, p is the reaction conversion, which in this case represents the fraction of A groups that have reacted. Because the reaction of each A group consumes one B group, the fraction of B reacted at conversion p is equal to N_A^o, or prN_B^o. The number of unreacted groups, N_A and N_B, is then given by:

$$\begin{gathered} N_A = (1-p)N_A^o \quad \text{and} \\ N_B = (1-pr)N_B^o = (1-pr)\frac{N_A^o}{r} \end{gathered} \tag{6.27}$$

At this time, the number of A and B end groups is equal to $N_A + N_B$, and, because there are two end groups per molecule, the number of molecular chains, N, is given by:

$$N = \frac{1}{2}(N_A + N_B) \tag{6.28}$$

that is,

$$N = \frac{1}{2}\left[(1-p)N_A^o + (1-pr)\frac{N_A^o}{r}\right] \tag{6.29}$$

and reduces to

$$N = \frac{N_A^o}{2}\left(1 + \frac{1}{r} - 2p\right) \tag{6.30}$$

One repeating unit is formed after each reaction of A and B functional group, thus, the total number of repeating units, N_r, is given by:

$$N_r = \frac{1}{2}\left(N_A^o + N_B^o\right) \tag{6.31}$$

Since $r = N_A^o/N_B^o$,

$$N_r = \frac{1}{2}\left(N_A^o + \frac{N_A^o}{r}\right) = \frac{N_A^o}{2}\left(\frac{r+1}{r}\right) \tag{6.32}$$

The average degree of polymerization is equal to the number of monomeric units divided by the number of chains; that is,

$$\overline{DP} = \frac{N_r}{N} = \frac{\left(N_A^o/2\right)[(r+1)/r]}{\left(N_A^o/2\right)[1 + (1/r) - 2p]} \tag{6.33}$$

and reduces to

$$\overline{DP} = \frac{1+r}{r+1-2rp} \tag{6.34}$$

From Eq. 6.34, at given the stoichiometric imbalance factor, r, one can calculate the extent of reaction necessary to achieve a given degree of polymerization. If $r = 1$, the relationship reduces to

$$\overline{DP} = \frac{1}{1-p} \tag{6.35}$$

which becomes, the Carothers equation. When monomer A is completely used up in the polymerization (i.e,, when $p = 1$), the equation becomes

$$\overline{DP} = \frac{1 + r}{1 - r} \tag{6.36}$$

If monofunctional reagent is added to control the molecular weight of polyester, the imbalance factor r (Eq. 6.26) needs to be redefined as r' as the following:

$$r' = \frac{N_A^o}{N_B^o + 2N_B^o} \tag{6.37}$$

where N_B^o, is the number of monofunctional B groups. The factor 2 takes into account the fact that each monofunctional B′ molecule is equally as effective as one excess BB monomer in limiting the molecular weight.

6.4 Molecular Weight Distribution

Using statistical methods derived by Paul Flory, the molecular weight distribution in step polymerization can be related to the reaction conversion. One needs to determine the probability of finding a chain containing x monomer units and a single unreacted A or B group at time t for a polymerization reaction of AA and BB. The probability that $x-1$ of A or B has reacted is p^{x-1}, where p is the reaction conversion, defined previously as

$$p = \frac{N_o - N}{N_o} \tag{6.38}$$

The probability of finding an unreacted group is $1 - p$. The probability of finding a molecule containing x units and an unreacted A or B group is then $p^{x-1}(1 - p)$. If the total number of molecules present at time t is N, then the fraction that contains x units, N_x is given by:

$$N_x = Np^{x-1}(1 - p) \tag{6.39}$$

Knowing that $N/N_o = 1 - p$ (Carothers equation), one can rewrite the expression for N_x as the following:

$$N_x = N_o(1 - p)^2 p^{x-1} \tag{6.40}$$

where N_o is the number of monomer units present initially. The above relationship can be plotted and shown in Fig. 6.3.

The figure shows, even at 99 % conversion, monomer still represents the most abundant species present. This is misleading. One can have a more reasonable picture expressing the molecular weight distribution in terms of the weight

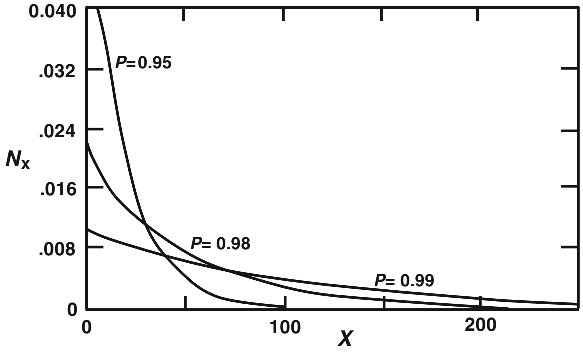


Fig. 6.3 Mole fraction distribution in linear step polymerization [1]

fraction. The molecular weight can be expressed by the weight fraction as shown in the following equations:

$$w_x = \frac{xN_x\mathrm{M_o}}{N_o\mathrm{M_o}} = \frac{xN_x}{N_o} \tag{6.41}$$

where $\mathrm{M_o}$ is the mass of the repeating unit, substituting the expression of N_x, one obtains

$$w_x = x(1-p)^2p^{x-1} \tag{6.42}$$

Figure 6.4 shows the plot of w_x versus x at four levels of conversion. Both figures confirm that high degrees of polymerization can be achieved by very high conversion.

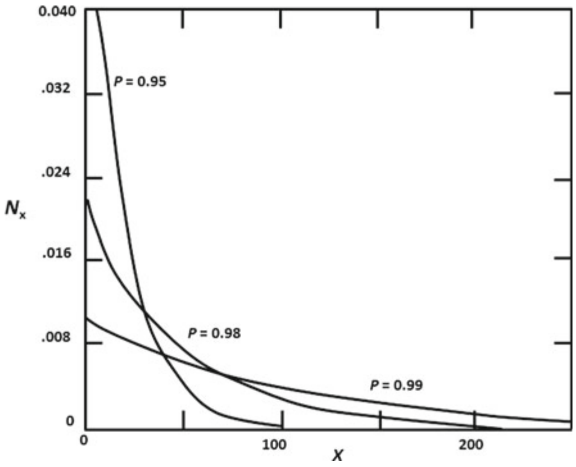


Fig. 6.4 Weight fraction distribution in linear step polymerization [1]

To determine the polydispersity index ($\bar{M}_w/\bar{M}_n$) at a given conversion, one needs to define $\bar{M}_w$ and $\bar{M}_n$ in terms of p. Given that $\bar{M}_n$ is the product of $\overline{DP}$ and M_o, and $\overline{DP} = 1/(1-p)$, one can write

$$\bar{M}_n = \frac{M_o}{1-p} \tag{6.43}$$

For $\bar{M}_w$, one can have the following expression:

$$\bar{M}_w = \Sigma\, w_x M_x \tag{6.44}$$

and rewrite it for x units as

$$\bar{M}_w = \Sigma\, w_x x M_o \tag{6.45}$$

Substituting the expression for w_x above, one obtains

$$\bar{M}_w = M_o(1-p)^2 \Sigma\, x^2 p^{x-1} \tag{6.46}$$

The series $\Sigma\, x^2 p^{x-1}$ reduces to $(1+p)/(1-p)^3$; therefore,

$$\bar{M}_w = \frac{M_o(1+p)}{1-p} \tag{6.47}$$

Then, one can have the polydispersity index as the following:

$$\frac{\bar{M}_w}{\bar{M}_n} = 1+p \tag{6.48}$$

6.5 Network Formation from Step Polymerization

If monomers contain functionality greater than two are used in the step polymerization, then chain branching and crosslinking are resulted. The crosslinked polymer exhibits superior physical and chemical properties as compared with linear polymer. If the reaction is carried to a high enough conversion, gelation occurs. *Gel point* is a sudden increase in viscosity during the polymerization, polymer liquid changes into solid gel. When the gelation occurs in the reactor, it is very difficult to take the gel out of the reactor. Special attention needs to pay during the polymerization using multifunctional monomers. It is desirable to be able to predict the gel point from manufacturing point of view. When the monomers with different functionality are used in the correct amount, the gelation of the polymerization can be controlled as shown in the following equations.

Given that

$$p = \frac{N_o - N}{N_o} \tag{6.49}$$

where N_o and N are the number of monomer molecules initially and at conversion p, respectively, then the number of functional groups that have reacted is $2(N_o - N)$. The number of functional groups initially is $N_o f_{av}$. Thus,

$$p = \frac{2(N_o - N)}{N_o f_{av}} \tag{6.50}$$

Since $\overline{DP} = N_o/N$, the above expression may be rewritten as:

$$p = \frac{2}{f_{av}} - \frac{2}{\overline{DP} f_{av}} \tag{6.51}$$

By rearranging Eq. 6.51, one can obtain the number average degree of polymerization as

$$\bar{X}_n = \frac{1}{1 - f_{av}p/2} \tag{6.52}$$

and the weight-average (degree of polymerization) by

$$\bar{X}_w = xW_x = \frac{1 + p}{1 - (f_{av} - 1)p} \tag{6.53}$$

At the gel point, the weight-average degree of polymerization becomes infinite. As may be seen in Fig. 6.5, where both averages are plotted against p. The very large values of $\bar{X}_w/\bar{X}_n$ near the gel point illustrate the extreme breadth of the distributions.

It is assumed that gelation occurs when $\overline{\mathrm{DP}}$ becomes infinite, at which point the second term of Eq. (6.51) becomes zero. Then

$$p_c = \frac{2}{f_{av}} \tag{6.54}$$

where p_c denotes the *critical reaction conversion* at which gelation occurs.

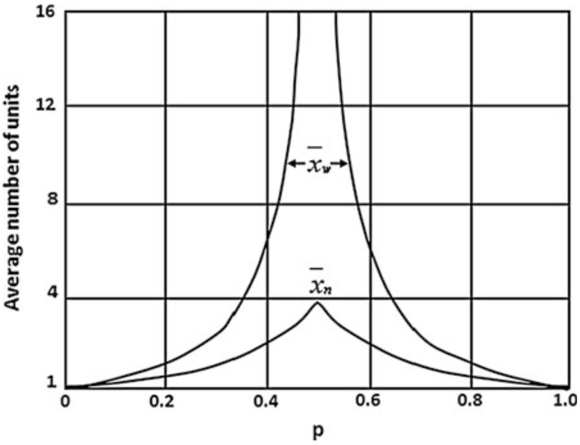
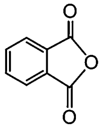
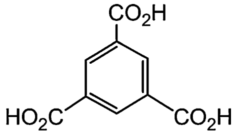


Fig. 6.5 Weight- and number-average degree of polymerization as a function of p for a trifunctional step polymerization [2]

The following are two examples of gel point calculation for equivalent amounts of acid and alcohol functional groups. Their chemical structures are shown in the following:



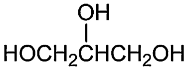
1



2

$HOCH_2CH_2OH$

3



$HOCH_2\overset{OH}{C}HCH_2OH$

4

1. For an equimolar mixture of phthalic anhydride (**1**, f = 2), trimellitic acid (**2**, f = 3), ethylene glycol (**3**, f = 2), and glycerol (**4**, f = 3), one can calculate f_{av} and p_c as

$$f_{av} = (2 + 3 + 2 + 3)/4 = 2.5$$

$$p_c = 2/2.5 = 80\,\%$$

If only difunctional monomers are in the mixture, then

$$\overline{DP} = 1/(1 - p_c) = 1/(1 - 0.8) = 50$$

2. For a mixture of 3 mol of **1** and 2 mol of **4**, the f_{av} and p_c as

$$f_{av} = [(3 \times 2) + (2 \times 3)]/5 = 2.4$$

$$p_c = 2/f_{av} = 2/2.4 = 83\,\%$$

In real case, such mixture gels at about 77 % conversion. The discrepancy arises primarily from the greater contribution of high molecular weight fraction.

In terms of critical gel point for nonequivalent amount of acid and alcohol, we can derive the following relationship. A mixture consisting of three monomers A, B, C; A and C have the same functional groups but different functionality, B contains a different functional group and in excess. Then the average functionality is given by:

$$f_{av} = \frac{2rf_Af_Bf_C}{f_Af_C + r\rho f_Af_B + r(1-\rho)f_Bf_C} \tag{6.55}$$

where the constants r and ρ are given by:

$$r = \frac{N_Af_A + N_Cf_C}{N_Bf_B} \tag{6.56}$$

and

$$\rho = \frac{N_C f_C}{N_A f_A + N_C f_C} \tag{6.57}$$

The critical conversion, p_c, then refers to the extent of reaction of the A groups only.

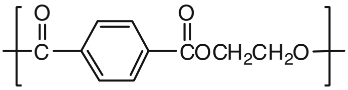
Statistical methods have also been developed that predict gelation at a lower level of conversion than that predicted by the Carothers equation. For the case of f_A and f_B each equivalent to 2, and $f_C > 2$, the method will derive p_c as the following:

$$p_c = \frac{1}{[r + r\rho(f-2)]^{1/2}} \tag{6.58}$$

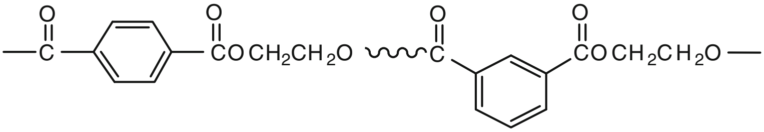
where f is the functionality of C. Experimental value of p_c fall between the values calculated by the statistical and nonstatistical method.

6.6 Step Copolymerization

A copolymer is defined in step polymerization as one having more than one kind of repeating unit. Thus, a polyester **5** prepared from terephthalic acid and ethylene glycol is a homopolymer, but a polyester **6** made with a 1:1:2 mixture of terephthalic acid, isophthalic acid, and ethylene glycol is a copolymer. In synthesizing copolymers such as **6**, the distribution of monomer units is random because the two dicarboxylic acids have virtually equal reactivity.



5



6

Alternating step copolymers can also be synthesized. Consider the hypothetical case of two different monomers, AA and BB, both of which react with monomer CC. A 1:1:2 mixture of AA, BB, and CC yields a random copolymer. If, however, AA is first reacted with CC, then the product is reacted with BB, an alternating copolymer is formed. This is shown schematically in Eq. 6.59. Figure 6.6 illustrates an example of synthesis of polyurethane elastomers using this approach.

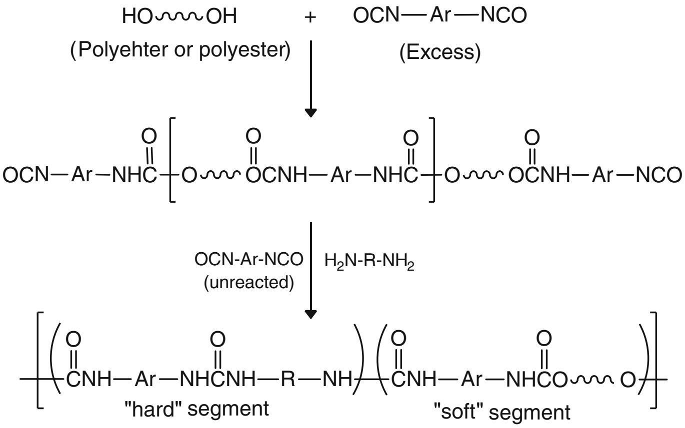
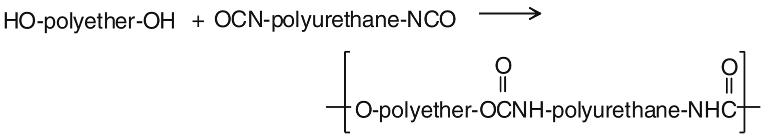


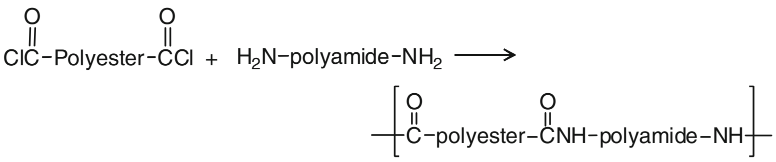
Fig. 6.6 Synthesis of elastomeric polyurethane

$$\mathrm{AA} + 2\mathrm{CC} \longrightarrow \mathrm{CC\text{-}AA\text{-}CC} \xrightarrow{\mathrm{BB}} \left[\mathrm{CC\text{-}AA\text{-}CC\text{-}BB}\right] \qquad (6.59)$$

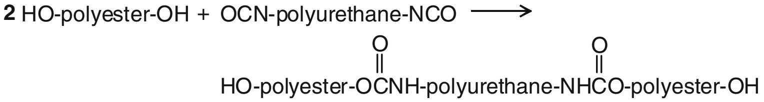
Step polymers are true telechelic polymers, so one can easily prepare block copolymers by linking homopolymers together through co-reactive functional groups. As shown in Eq. 6.60, the AB block copolymer of polyether and polyurethane can be synthesized by reacting hydroxyl-terminated polyether with isocyanate-terminated polyurethane. The AB block copolymer of polyester and polyamide can be obtained by reacting an acid chloride-terminated polyester with an amine-terminated polyamide as shown in Eq. 6.61. Alternatively, one could react an isocyanate-terminated polyurethane with two equivalents of hydroxyl-terminated polyester to form an ABA block copolymer as shown in Eq. 6.62.



$$\mathrm{HO\text{-}polyether\text{-}OH} + \mathrm{OCN\text{-}polyurethane\text{-}NCO} \longrightarrow \left[\mathrm{O\text{-}polyether\text{-}O}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{NH\text{-}polyurethane\text{-}NH}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\right] \qquad (6.60)$$



$$\mathrm{Cl}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{\text{-}Polyester\text{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{Cl} + \mathrm{H_2N\text{-}polyamide\text{-}NH_2} \longrightarrow \left[\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{\text{-}polyester\text{-}}\overset{\overset{\displaystyle O}{\|}}{\mathrm{C}}\mathrm{NH\text{-}polyamide\text{-}NH}\right] \qquad (6.61)$$



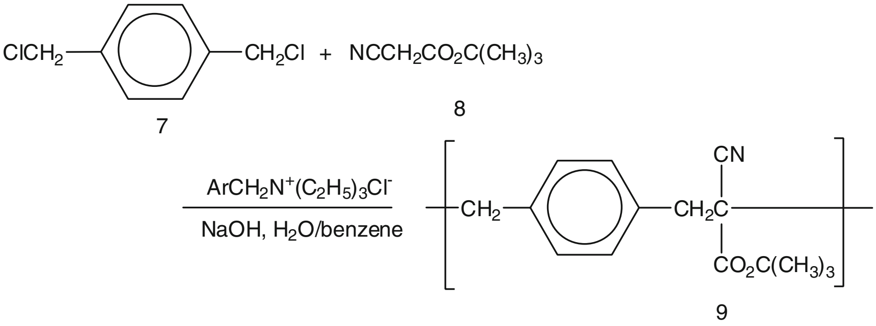
$$\mathbf{2}\ \text{HO-polyester-OH} + \text{OCN-polyurethane-NCO} \longrightarrow \text{HO-polyester-O}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{NH-polyurethane-NH}\overset{\overset{\displaystyle \text{O}}{\|}}{\text{C}}\text{O-polyester-OH} \tag{6.62}$$

6.7 Techniques of Step Polymerization

Four step polymerization techniques have been developed for synthetic polymers: (a) homogeneous bulk polymerization, (b) homogeneous solution polymerization, (c) heterogeneous interfacial polymerization, and (d) heterogeneous phase-transfer catalyzed polymerization. For homogeneous bulk polymerization, it has the advantage of providing a product free of contaminants other than by products or side reactions. The major disadvantage is that high viscosities necessitate the use of elevated temperature and inert atmosphere (avoid oxidative decomposition). For homogeneous solution polymerization, it minimizes the high-viscosity problem and can assist in removal of by-product by azeotropic distillation. The major disadvantage of the process is the necessary of the removal of the solvent.

For heterogeneous interfacial polymerization, the reaction involves solutions of the two monomers in separate, immiscible solvents. When the two solutions are brought into contact, polymer is formed at the interface. Some examples have been discussed in Sect. 6.1.1.4. Interfacial polymerization differs significantly from bulk or solution polymerization. The reaction goes rapidly at low temperature. The diffusion of monomer to the interface is a rate determining step. Monomer reacts with the growing chains at the interface more rapidly than it diffuses through the polymer film to initiate new chain (similar to chain polymerization) hence molecular weights tend to be significantly higher. Thus, an exact stoichiometric balance is not necessary. High cost of acid chlorides and the usage of large volumes of solvent make the interfacial method prohibitively expensive for many polymers relative to bulk or solution processes.

For heterogeneous phase-transfer catalyzed polymerization [1], the method involves an aqueous phase and an organic phase, each containing one of monomers. It is also an interfacial technique. Quaternary ammonium salt transports a nucleophilic monomer from the aqueous phase to the organic phase. Its nucleophilicity is greatly enhanced because of reduced solvation effects. *Phase-transfer catalysis* (PTC), although commonly employed in organic synthesis, has limited application in polymerization reactions. The polymer **9** can be synthesized by the reaction of α,α'-dichloro-*p*-xylene **7** and *t*-butyl cyanoacetate **8** using benzyltriethylammonium chloride (Eq. 6.63). In this case, an anion derived from **8** by reaction with NaOH is transported to the benzene solution as the soluble benzyltriethylammonium salt, where it reacts rapidly with **7** by nucleophilic displacement. Polymer is formed because **8** contains two active hydrogens.



(6.63)

6.8 Synthesis of Dendritic Polymers (Dendrimers)

Dendrimers [1] are defined by their three component parts: A central core, an interior dendritic structure, and an exterior surface. Their macromolecular dimensions are easily controlled by the number of the repeating level of the synthesis steps. Dendrimers are more soluble than linear polymers because of their high surface functionality. The surface functionality has potential application in target drug delivery and molecular sensors. Their viscosity is usually lower than that of linear polymer because no chain entanglement. They are useful for rheology modifiers. Supramolecular assemblies may be constructed by incorporating guest molecules among the interior branches of the dendrimer. Thus, they are useful for drug delivery systems, controlled release of agricultural chemicals. Figure 6.7 shows the size prospective of dendrimers as compared with other matters. The size of dendrimer can be precisely controlled by stepwise polymerization as discussed by two following synthetic methods.

6.8.1 Divergent Method

For the synthesis of polyamidoamine (PAMAM), NH_3 is used as core. In first generation: NH_3 is added to methylacrylate via Michael addition, the resultant triester **10** is then reacted with excess 1,2-ethanediamine to form amide-amine **11**. Each new generation results from a repetition of the two-step reaction sequence as shown below:

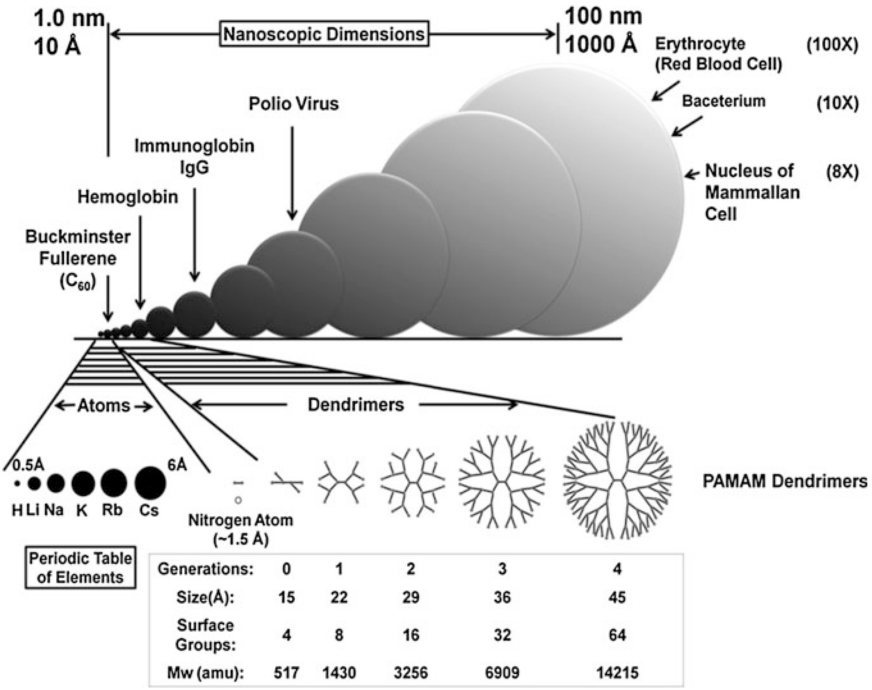


Fig. 6.7 Size comparisons of different matters

$$NH_3 + \mathbf{3}\ H_2C{=}CHCO_2CH_3 \longrightarrow \underset{\mathbf{10}}{N(CH_2CH_2CO_2CH_3)_3}$$

$$\mathbf{10} + H_2NCH_2CH_2NH_2 \longrightarrow \underset{\mathbf{11}}{N(CH_2CH_2CONHCH_2CH_2NH_2)_3}$$

For generations 2 and 3, they are schematically shown in Fig. 6.8. With each new generation, the number of surface functional group doubles, reaching 3072 by the 10th generation. It is called starburst polymer.

6.8.2 Convergent System

Figures 6.9 and 6.10 show the convergent synthesis of a polyether dendrimer. The branching unit, 3,5-dihydroxybenzyl alcohol **13**, is first reacted with the benzylic bromide **12** to yield **14** in the presence of base. The alcohol group of **14** is then converted to bromide, and reacted again with **12** (Fig. 6.9). The steps are repeated until the desired segment size is reached. The polyether dendrimer is then assembled by condensing a benzylic bromide-terminated segment with a polyfunctional phenol (Fig. 6.10).

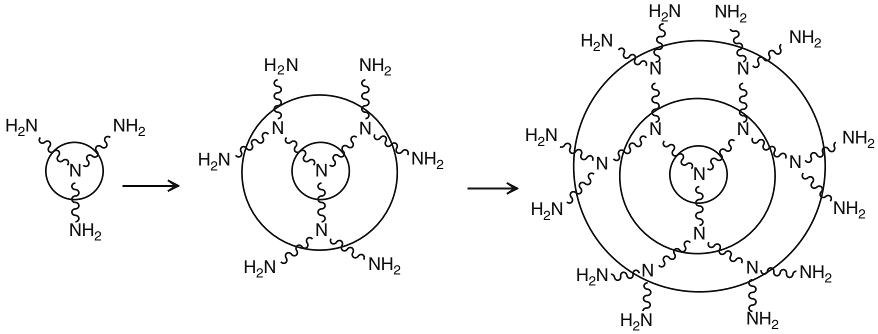


Fig. 6.8 Formation of second and third generation of PAMAM dendrimer. Reaction sequence: (1) excess $CH_2{=}CHCO_2CH_3$ and (2) excess $H_2NCH_2CH_2NH_2$ [1]

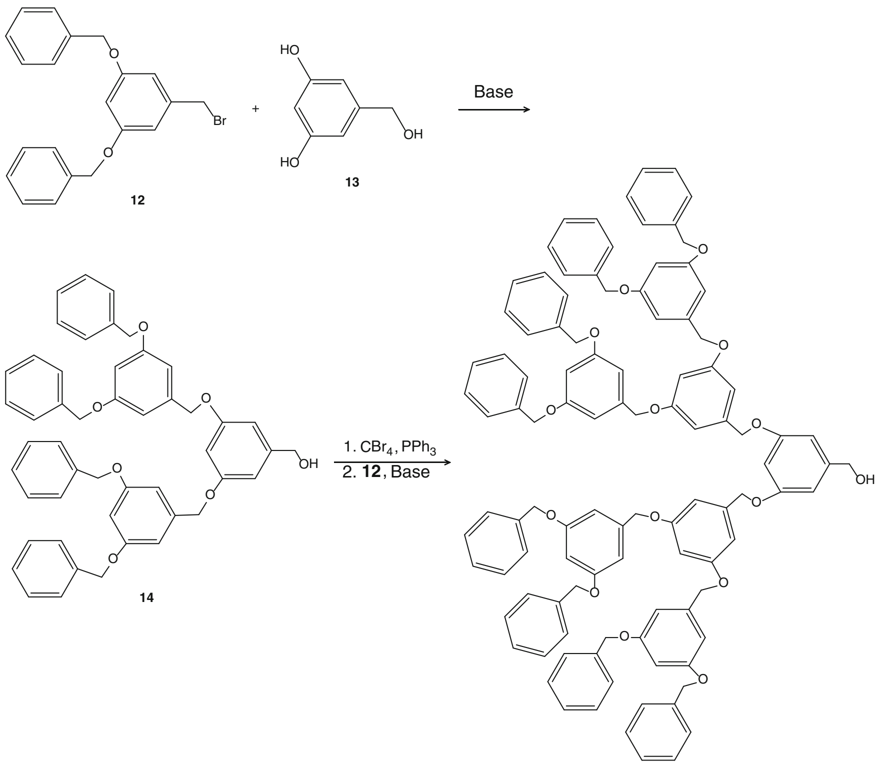


Fig. 6.9 Formation of polyether dendritic segment [1]

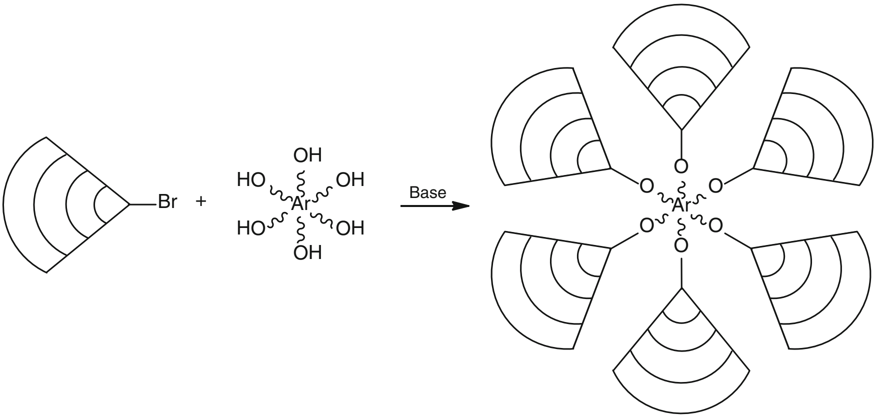


Fig. 6.10 Convergent synthesis of a dendrimer from dendritic segments [1]

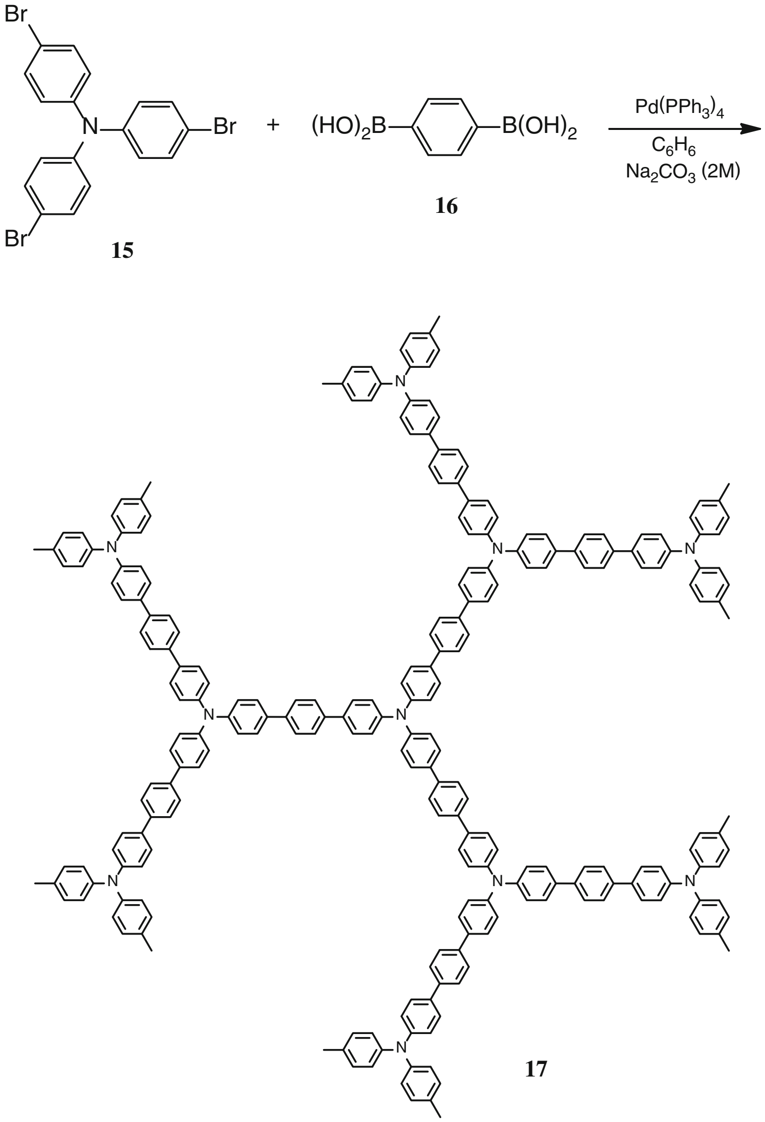
6.8.3 *Molecular Weight of Dendrimer*

The size of dendrimer is self limited because of steric congestion. Dendrimers with molecular weights in the hundreds of thousands have been achieved. Their molecular dimensions lie in the nanometer range, so they are called nanomaterials.

6.9 Hyperbranched Copolymer

The hyperbranched aromatic copolymer can be synthesized by Suzuki coupling reaction. The reaction was first reported in 1979 by Akira Suzuki, the reaction couples aromatic boronic acids to aromatic halides [4]. The reaction relies on a palladium catalyst such as tetrakis(triphenylphosphine)palladium(0) to take in part of the transformation. This reaction has been extensively used in the synthesis of donor–acceptor of alternating conjugated copolymer for polymer solar cell application [5]. The 2010 Nobel Prize in Chemistry was awarded in part to Suzuki for his discovery and development of this very versatile mild reaction to link aromatic molecule together.

For example, a conjugated alternate copolymers constituted of triphenylamine and phenylene units can be obtained by palladium catalyzed coupling of tris(*p*-bromophenyl)amine **15** and benzene-1,4-diboronic acid **16** (Fig. 6.11) [6]. Amine **15** and acid **16** are trifunctional (B_3) and difunctional (A_2) monomers, respectively. Hyperbranched polymers can be prepared through intermediate AB_2 monomers formed from B_3 and A_2 monomers. The copolymer (**17**) was soluble in organic solvents such as chloroform and tetrahydrofuran. GPC indicated that it had an average molecular weight of 5,400.



15

16

17

Fig. 6.11 Example of synthetic route of hyperbranched copolymer

6.10 Problems

1. Considering the reaction conditions for bulk polycondensations, suggest reasons other than those given in the chapter for deviations in the plots of $\overline{\mathrm{DP}}$ versus *t* for polyesters.

2. To what percent conversion should a batch of 11-amino undecanoic acid be processed to yield polyamide having a number average molecular weight of 2.5×10^4?
3. Rate constants for polyesterification of adipic acid and 1,10-decanediol at 161°C are 0.0012 $(\text{eq/kg})^2$/min (uncatalyzed) and 0.079 (eq/kg)/min (catalyzed). How long would it take to prepare a polyester of number average molecular weight 15,000 (bulk processing) under each set of condition? (Assume equimolar amounts of each reactant and 2 equivalents per mole, and that bulk mass remains constant.) What would the polydispersity index be for the polymer?
4. If 5 mol % excess diol was used in the previous problem, what number average molecular weight would be obtained if the reaction was carried to the same conversion?
5. Using the Carothers relationship, please calculate the percent conversion at the gel point for (a) 3:1:3 and (b) 1:1:2 molar ratio of phthalic anhydride, trimellitic acid, and glycerol.
6. Calculate $\bar{X}_n$ and $\bar{X}_w$ for an equal molar mixture of a diacid and a glycol at the following extent of reactions: 0.500, 0.750, 0.950, 0.980, 0.990, and 0.995.
7. A polyester, made with an equivalent amount of terephthalic acid and ethylene glycol, the molecular weight of the polyester was controlled at $\bar{X}_n = 100$ by adding methanol. (a) How much methanol is required? (b) Calculate $\bar{X}_w$ and the weight and number fractions of monomer in the resulting polymer, (c) If the glycerol was added instead of methanol. Will the mixture gel if the reaction is carried to completion?
8. Explain why aliphatic polyamides but not aliphatic polyesters can be prepared by interfacial polymerization.
9. Write equations illustrating the synthesis of (a) an alternating copolyamide from isophthaloyl chloride, terephthaloyl chloride, and m-diaminobenzene, and (b) an ABA block copolymer of poly(11-undecanoamide) (A) with the polyamide (B) formed in (a).
10. Please propose the reaction mechanism of Suzuki coupling reaction for the formation of diphenyl (hint: review Ref. [7]).

References

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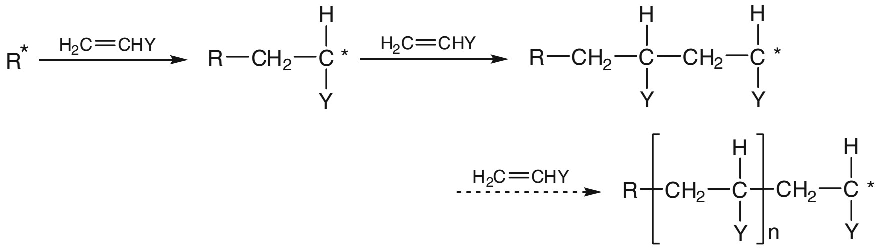
Chapter 7
Radical Chain Polymerization

The polymerization of unsaturated monomers typically involves a chain reaction. In a chain polymerization, one act of initiation may lead to the polymerization of thousands of monomer molecules. Table 7.1 lists the characteristics of chain polymerization as compared with step polymerization. The chain polymerization starts with an active center responsible for the growth of the chain which is associated with a single polymer molecule through the addition of many monomer units. Thus polymeric molecules are formed from the beginning, and almost no intermediate species between monomer and high molecular weight polymer are found.

Chain polymerization is initiated by a reactive species *R** produced from an *initiator I*:

$$I \rightarrow R^* \tag{7.1}$$

The reactive species, which may be a free radical, cation, or anion, adds to a monomer molecule by opening the π-bond to form a new radical, cation, or anion center. The process is repeated as many more monomer molecules are successively added to continuously propagate the reactive center as the following:



$$R^* \xrightarrow{H_2C{=}CHY} R-CH_2-\overset{H}{\underset{Y}{C}}\,{}^* \xrightarrow{H_2C{=}CHY} R-CH_2-\overset{H}{\underset{Y}{C}}-CH_2-\overset{H}{\underset{Y}{C}}\,{}^*$$

$$\overset{H_2C{=}CHY}{\dashrightarrow} R\left[CH_2-\overset{H}{\underset{Y}{C}}\right]_n CH_2-\overset{H}{\underset{Y}{C}}\,{}^* \tag{7.2}$$

*R**: Radical, cationic, anionic.

Polymer growth is terminated at some point by destruction of the reactive center by an appropriate reaction depending on the type of reactive center and the particular reaction conditions.

W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_7,

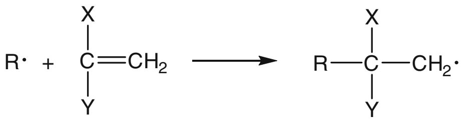
Table 7.1 Comparison of chain polymerization and step polymerization

Situation	Chain polymerization	Step polymerization
Molecular weight	High molecular weight formed immediately, doesn't change with time	High molecular weight molecule formed at the end of reaction, change with time
Monomer concentration	Change throughout the course of the reaction	Only available in the beginning of the reaction, then form dimer, trimer, etc
Any time of the reaction	Contain monomer, high polymer, and growing chain	Beginning—monomer Middle—growing chain End—high polymer
Polymerization step	Only monomer and propagation species can react	Any two molecules can react
Reaction time	Short	Long
Reaction temperature	Low	High

In this chapter, we only discuss free radical chain polymerization. The ionic chain polymerization will be discussed in Chap. 8. Table 7.2 lists some common free radical chain-growth polymers and their uses. The chain-growth polymers count more than 80 % total usage of polymers in our daily life.

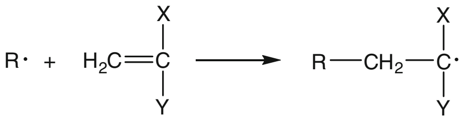
7.1 Effect of Chemical Structure of Monomer on the Structural Arrangement of Polymer

There are two possible points of attachment on monosubstituted ($X = H$) or 1,1-disubstituted monomers for a propagating radical, either on carbon 1 to form I or on carbon 2 to form II as the following:



$$R\cdot + \underset{Y}{\overset{X}{C}}{=}CH_2 \longrightarrow R{-}\underset{Y}{\overset{X}{C}}{-}CH_2\cdot \tag{7.3}$$

I

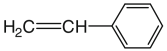
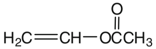
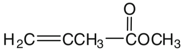


$$R\cdot + H_2C{=}\underset{Y}{\overset{X}{C}} \longrightarrow R{-}CH_2{-}\underset{Y}{\overset{X}{C}}\cdot \tag{7.4}$$

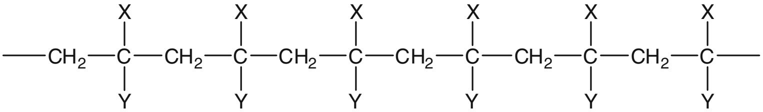
II

If each successive addition of monomer molecules to the propagating radical occurs in the same manner as Eqs. 7.3 or 7.4, the final polymer product will have

Table 7.2 Some commercial chain-growth (vinyl) polymers prepared by free radical polymerization [1, 2]

Monomer name	Formula	Polymer	Uses
Ethylene (ethene)	$H_2C{=}CH_2$	Polyethylene	Sheets, films, bottles, toys and house wares, wire and cable, coverings, shipping containers, insulation
Propylene (propene)	$H_2C{=}CHCH_3$	Polypropylene	Carpeting, car and truck parts, packaging, toys, house wares, pipes, insulation
Styrene		Polystyrene	Packaging and containers (Styrofoam), toys, appliance parts, disposable food containers and utensils, insulation
Acrylonitrile (propenenitrile)	$H_2C{=}CHCN$	Polyacrylonitrile (Orion, Acrilan)	Sweaters, clothing, fiber
Vinyl acetate (ethenyl ethanoate)	 $H_2C{=}CH{-}O\overset{O}{\overset{\Vert}{C}}CH_3$	Poly(vinyl acetate)	Adhesives, latex paints
Methyl methacrylate (methyl 2-methylpropenoate)	 $H_2C{=}CCH_3{-}\overset{O}{\overset{\Vert}{C}}OCH_3$	Poly(methyl methacrylate) (Plexiglas, Lucite)	Lens, windows, coatings
Vinyl chloride (chloroethene)	$H_2C{=}CHCl$	Poly(vinyl chloride)(PVC)	Plastic pipe and pipe fittings, films and sheets, floor tile, records, coatings, building materials, insulation
Tetrafluoroethylene (tetrafluoroethene)	$F_2C{=}CF_2$	Poly(tetrafluoro ethylene) (Teflon)	Coatings for utensils, electric insulators, battery, solar cell

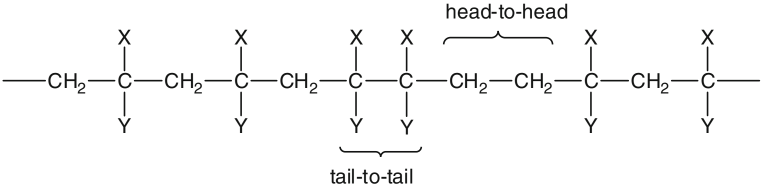
an arrangement of monomer units in which the substituents are on alternate carbon atoms as shown in Eq. 7.5:



$$-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}- \tag{7.5}$$

III

This type of arrangement III is usually referred to as a *head-to-tail* (H–T) or 1,3-*placement* of monomer units. An inversion of this mode of addition, by the polymer chain propagating alternately via Eqs. 7.3 and 7.4, would lead to a polymer structure with a 1,2-placement of substituents at one or more places in the final polymer chain. The 1,2-placement is usually referred to as *head-to-head* (H–H) placement as shown in Eq. 7.6.



$$-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}-CH_2-\underbrace{\underset{Y}{\overset{X}{C}}-\underset{Y}{\overset{X}{C}}}_{\text{tail-to-tail}}-\overbrace{CH_2-CH_2}^{\text{head-to-head}}-\underset{Y}{\overset{X}{C}}-CH_2-\underset{Y}{\overset{X}{C}}- \tag{7.6}$$

The head-to-tail placement is predominant, since successive propagations by Eq. 7.4 are favored on both steric and resonance grounds. The propagating radical (radical II) formed by attachment of a radical at carbon 2 is the more stable one. The radical II can be stabilized by the resonance effects of the X and Y substituents. The substituents cannot stabilize radical I, since they are not attached to the carbon bearing the unpaired electron. Furthermore, the attachment of a propagating radical at the unsubstituted carbon 2 of a monomer molecule is much less sterically hindered compared with the attachment at the substituted carbon 1. A propagation proceeding with predominantly H–T placement is a *regioselective* process, that is, one orientation (H–T) is favored over another (H–H). The term *isoregic* has been used to indicate a polymer structure with exclusive head-to-tail placements. The terms *syndioregic* and *aregic* are used for polymer structures with alternating and random arrangements, respectively, of H–T and H–H placements.

These theoretical predictions have been experimentally verified for a number of polymers. The presence of no more than 1–2 % head-to-head placement in various polymers of vinyl esters such as poly (vinyl acetate) has been determined by hydrolysis of the polymer to poly(vinyl alcohol) and the periodate oxidation of the 1,2-glycol units (see Sect. 5.2.1). Other polymers with head-to-head arrangement have been determined by ^{19}F, ^{13}C, and ^{1}HNMR analysis.

The H–T propagation is indeed the predominant (>98–99 %) mode of propagation in chain polymerization. For instance, the synthesis of styrene, there is no

Table 7.3 The extent of H–H replacement in fluoro polymers [3]

Reaction	% Head–Head
$C{=}CF \rightarrow (-C-CF-)_n$	10
$C{=}CF_2 \rightarrow (-C-CF_2-)_n$	5
$CF{=}CF_2 \rightarrow (-CF-CF_2-)_n$	12
$CFCl{=}CF_2 \rightarrow (-CFCl-CF_2-)_n$	2

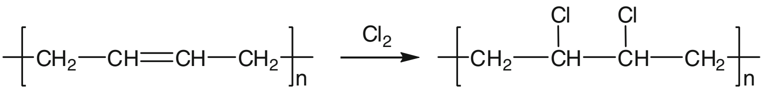
Table 7.4 Reaction temperature effect on the extent of H–H replacement of polymer [3]

Polymer	Temperature (°C)	% Head–Head
Poly(vinyl acetate)	40	1
	100	2
Poly(trifluoro ethylene)	−80	10
	80	14

detectable H–H placement of polystyrene. The only exceptions occur when the substituents on the double bond are small (and do not offer appreciable steric hindrance to the approaching radical) and do not have a significant resonance stabilizing effect, specifically when fluorine is the substituent. Table 7.3 shows the extent of H–H placements of fluoro polymers.

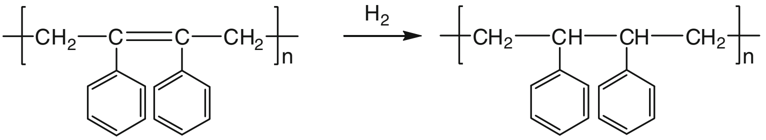
By increasing the polymerization temperature, the extent of H–H placement is increased, but the effect is small. Table 7.4 shows the compositions of polymers with the effects from reaction temperature.

Some polymers consisting entirely of head-to-head (H–H) placements have been deliberately synthesized to determine if significant property differences exist compared to the head-to-tail polymers. The synthetic approach involves an appropriate choice of monomer for the particular H–H polymer. For example, H–H poly (vinyl chloride) was obtained by chlorination of 1,4-poly-1,3-butadiene (Eq. 7.7).



$$\left[-CH_2-CH{=}CH-CH_2-\right]_n \xrightarrow{Cl_2} \left[-CH_2-\underset{}{\overset{Cl}{CH}}-\overset{Cl}{CH}-CH_2-\right]_n \quad (7.7)$$

H–H polystyrene was obtained by hydrogenation of 1,4-poly-2,3-diphenylbutadiene (Eq. 7.8).



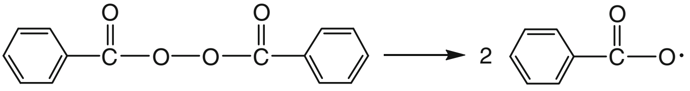
(7.8)

7.2 Initiators of Radical Chain Polymerization

Ideally, the initiators should be relatively stable at room temperature but should decompose rapidly enough at polymer processing condition to ensure a practical reaction rate. A large number of free radical initiators are available [2–4]; they may be classified into three major types: (1) *thermal initiators* including peroxides and azo compounds, (2) *redox initiators*, and (3) *photoinitiators*, certain compounds that form radicals under influence of light. Electrons can be used as initiating agent to generate radical ions for chain polymerization.

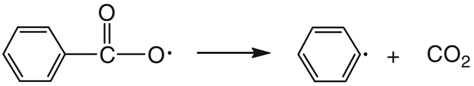
7.2.1 Thermal Initiators

The most commonly used peroxide is benzoyl peroxide **1**, which undergoes thermal homolysis to form benzoyloxy radicals (Eq. 7.9). The benzoyloxy radicals may undergo a variety of reactions besides adding to monomer, including recombination (reverse of Eq. 7.9), decomposition to phenyl radicals and carbon dioxide (Eq. 7.10), and radical combination (Eqs. 7.11 and 7.12). These secondary reactions occur because of the confining effect of solvent molecules (cage effect), and as a result, the concentration of initiator radicals is depleted. Another "wastage" of initiator reaction is induced decomposition (Eq. 7.13).

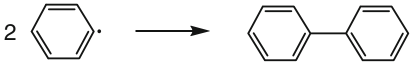


(7.9)

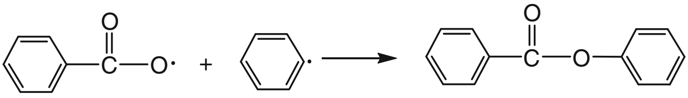
1



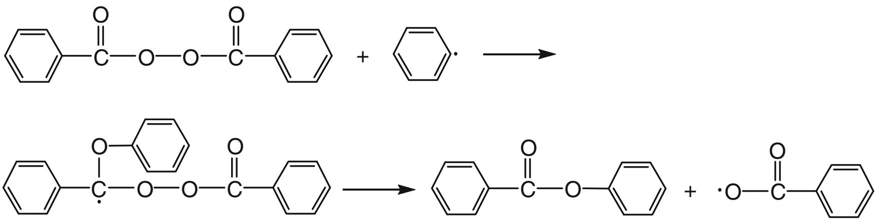
(7.10)



(7.11)

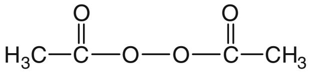


(7.12)

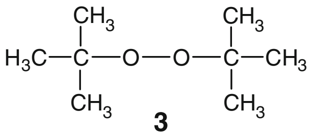


(7.13)

Two other common peroxide initiators are diacetyl peroxide **2** and di-t-butyl peroxide **3**.

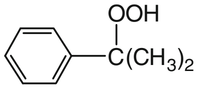


2



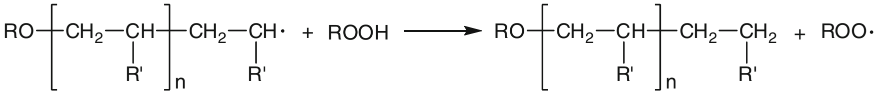
3

Hydroperoxides such as cumyl hydroperoxide **4** decompose to form alkoxy and hydroxyl radicals (Eq. 7.14). Because hydroperoxides contain an active hydrogen atom, induced decomposition occurs readily, for example, by a chain-end radical (Eq. 7.15). Peroxy radicals may also combine with subsequent formation of oxygen (Eq. 7.16).



4

$$\mathrm{ROOH} \longrightarrow \mathrm{RO\cdot} + \mathrm{\cdot OH} \tag{7.14}$$

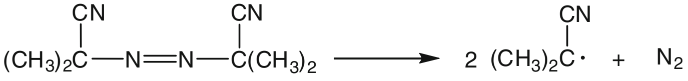


$$\mathrm{RO}\!\left[\mathrm{CH_2{-}\underset{R'}{CH}}\right]_n\!\mathrm{CH_2{-}\underset{R'}{CH}\cdot} + \mathrm{ROOH} \longrightarrow \mathrm{RO}\!\left[\mathrm{CH_2{-}\underset{R'}{CH}}\right]_n\!\mathrm{CH_2{-}\underset{R'}{CH_2}} + \mathrm{ROO\cdot} \tag{7.15}$$

$$2\ \mathrm{ROO\cdot} \longrightarrow \left[\mathrm{ROO{-}OOR}\right] \longrightarrow 2\ \mathrm{RO\cdot} + \mathrm{O_2} \tag{7.16}$$

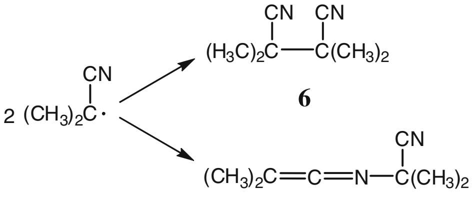
The extent of side reactions depends on the structure of peroxide, the stability of the initially formed radicals, and the reactivity of the monomers.

α, α'-Azobis(isobutyronitrile) **5**, is the most widely used azo compound which decomposes at relatively low temperatures. The driving force for decomposition is the formation of nitrogen and the resonance-stabilized cyanopropyl radical (Eq. 7.17). The initially formed radicals can also combine in the solvent cage to deplete initiator concentration as with the peroxide decomposition. The combination of the radicals leads to both tetramethylsuccinonitrile **6** (Eq. 7.18) and the ketenimine **7** (Eq. 7.19).



$$(CH_3)_2\overset{CN}{\overset{|}{C}}-N=N-\overset{CN}{\overset{|}{C}}(CH_3)_2 \longrightarrow 2\ (CH_3)_2\overset{CN}{\overset{|}{C}}\cdot\ +\ N_2 \qquad (7.17)$$

5



(7.18)

6

(7.19)

7

The stability of thermal initiator is expressed by their half-life at different temperature as discussed below.

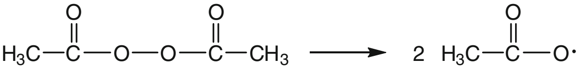
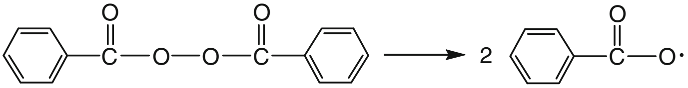
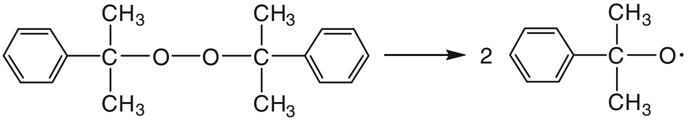
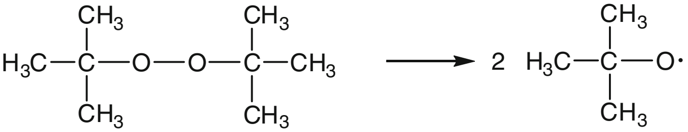
7.2.2 Decomposition Temperature and Half-Life of Thermal Initiators

The *thermal, homolytic dissociation* of initiators is the most widely used mode of generating radicals to initiate polymerization for both commercial polymerization and theoretical studies. Polymerizations initiated in this manner are often referred to as *thermal initiated* or *thermal catalyzed* polymerizations. Thermal initiators are usually having dissociation energies in the range 100–170 kJ mol^{-1}. Compounds with higher or lower dissociation energies will dissociate too slowly or too rapidly. Only a few classes of compounds—including those with O–O, S–S, or N=N bonds—possess the desired range of dissociation energies. The peroxides are most extensively used as radical sources. Several common peroxy compounds are tabulated in Table 7.5.

The differences in the decomposition rates of various initiators are conveniently expressed in terms of the *initiator half-life* ($t_{1/2}$) defined as the time for the concentration of I to decrease to one half its original value. The rate of initiator disappearance is

$$\frac{-d[I]}{dt} = k_d[I] \qquad (7.20)$$

Table 7.5 Peroxides and their decomposition temperature [3]

Peroxide	Decomposition temperature (°C)
 Acyl peroxide	70–90
 Benzoyl peroxide	80–95
 Cumyl peroxide	120–140
 Di-t-butyl peroxide	120–140

with integration yields

$$[I] = [I]_0 e^{-k_d t} \tag{7.21a}$$

or

$$\ln \frac{[I]_0}{[I]} = k_d t \tag{7.21b}$$

where $[I]_0$ is the initiator concentration at the start of polymerization. $t_{1/2}$ is obtained by setting $[I] = [I]_0/2$, then

$$t_{1/2} = \frac{0.693}{k_d} \tag{7.22}$$

Table 7.6 lists the initiator half-life for several common initiators at various temperatures. The peroxides are rather unstable. They should store in the refrigerator to prolong their shelf life. Azobis (isobutyronitrile), benzoyl peroxide, and acetyl peroxide are decomposed at relatively low temperature, so they usually add into monomer right before the polymerization to avoid any premature decomposition and polymerization. *t*-Butyl peroxide and t-butyl hydroperoxide are

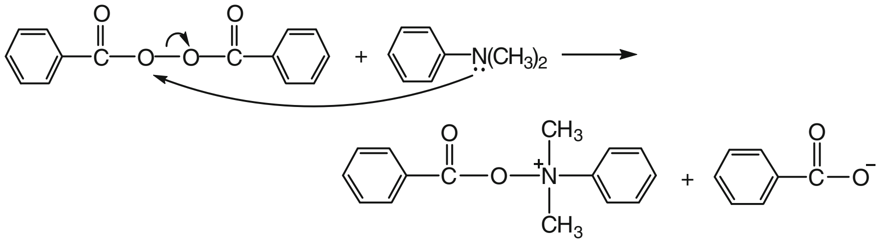
Table 7.6 Half-life of initiators [3]

Initiator	Half-Life at									
	50°C	60°C	70°C	85°C	100°C	115°C	130°C	145°C	155°C	175°C
Azobis (isobutyronitrile)	74 h		4.8 h		7.2 min					
Benzoyl peroxide			7.3 h	1.4 h	19.8 min					
Acetyl peroxide	158 h		8.1 h	1.1 h						
Lauryl peroxide	47.7 h	12.8 h	3.5 h	31 min						
t-Butyl peracetate				88 h	12.5 h	1.9 h	18 min			
Cumyl peroxide						13 h	1.7 h	16.8 min		
t-Butyl peroxide					218 h	34 h	6.4 h	1.38 h		
t-Butyl hydroperoxide					338 h				44.9 h	4.81 h

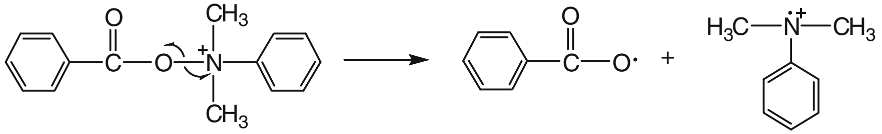
decomposed at high temperature. They can be mixed with monomer and stored in room temperature without premature reaction for more than 3 months.

7.2.3 Initiation Promoters

Decomposition of peroxides can be induced at lower temperatures by the addition of *promoters*. For example, addition of *N*, *N*-dimethylaniline to benzoyl peroxide causes the latter to decompose rapidly at room temperature. Kinetics studies indicate that the decomposition involves formation of an unstable ionic intermediate (Eq. 7.23) that reacts further to give benzoyloxy radical and a radical cation (Eq. 7.24).



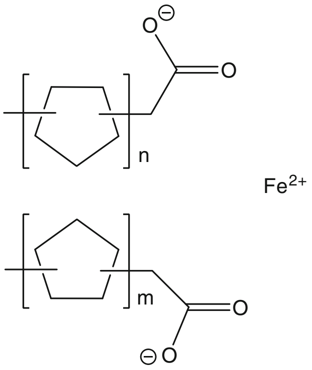
(7.23)



(7.24)

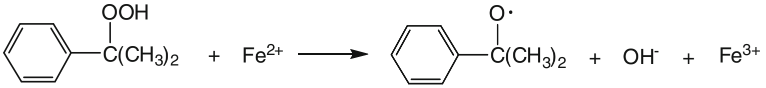
7.2.4 Redox Initiators

The redox initiators are useful in initiation of low temperature polymerization and emulsion polymerization. Reaction rates are easy to control by varying the concentration of metal ion or peroxide. For nonaqueous polymerization, metal ions: Co^{2+}, Mn^{2+}, Cu^{2+}, and Fe^{2+} are generally introduced as the naphthenates shown in below. Cobalt naphthenate is commonly used as unsaturated polyester (Alkyd resin) drying agents for the autoxidative crosslinking of the double bond.



Iron Naphthenate

Some typical examples of redox initiators are given in Eqs. 7.25–7.27. They have been used in the emulsion copolymerization of styrene and butadiene to form styrene—butadiene rubber in low temperature. Hydrogen peroxide or persulfate systems, Eqs. 7.26 and 7.27, are used in the emulsion polymerization. They can produce radicals in an aqueous phase.



(7.25)

$$\mathrm{HOOH} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{HO}\cdot + \mathrm{OH}^- + \mathrm{Fe}^{3+} \tag{7.26}$$

$$^-\mathrm{O_3SOOSO_3}^- + \mathrm{S_2O_3}^{2-} \longrightarrow \mathrm{SO_4}^-\cdot + \mathrm{SO_4}^{2-} + \cdot\mathrm{S_2O_3}^- \tag{7.27}$$

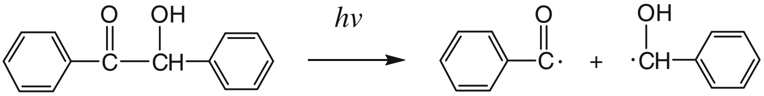
7.2.5 Photoinitiators

Peroxides and azo compounds dissociate photolytically as well as thermally. The major advantage of photoinitiation is that the reaction is essentially independent of temperature. Furthermore, better control of the polymerization reaction is generally possible because narrow wavelength bands may be used to initiate decomposition (less side reactions), and the reaction can be stopped simply by removing the light source. The reaction is fast (s vs. min) as compared to the thermal initiation. A wide variety of photolabile compounds are available, including disulfides (Eq. 7.28), benzoin **8** (Eq. 7.29), and benzyl **9** (Eq. 7.30). Table 7.7 lists some commercial available photoinitiators and their decomposition wavelength. It is interesting to note that most of the initiators contain benzoyl group which can form stable benzoyl radical through the resonance stabilization of phenyl ring.

Table 7.7 Commercial photoinitiators and their initiated wavelength [5]

Chemicals	$\lambda_{\max}(nm)$
1-hydroxy-cyclohexyl-phenyl-ketone	245
2-methyl-1-[4-(methylthio)phenyl)-2-(4-morpholinyl)-1-propanone	307
2-benzyl-2-(dimethylamino)-1-[4-(4-morpholinyl)phenyl]-1-butanone	324

$$\mathrm{RSSR} \xrightarrow{h\nu} 2\ \mathrm{RS}\cdot \tag{7.28}$$



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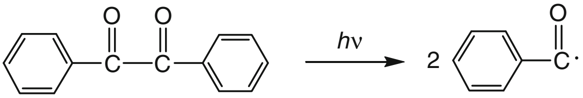
(7.29)



9

(7.30)

7.2.6 Electrochemical Initiation

Electrolysis of a solution containing both monomer and electrolyte can be used to initiate polymerization. At the cathode an electron may be transferred to a monomer molecule to form a radical anion (Eq. 7.31), and at the anode a monomer molecule may give up an electron to form a radical cation (Eq. 7.32). The radical ions in turn initiate free radical or ionic polymerization or both, depending on electrolysis conditions.

$$\mathrm{RHC{=}CH_2} + e^- \longrightarrow \mathrm{RH}\overset{\overline{\cdot\cdot}}{\mathrm{C}}\text{—}\dot{\mathrm{C}}\mathrm{H_2} \tag{7.31}$$

$$\mathrm{RHC{=}CH_2} \longrightarrow \mathrm{RH}\overset{+}{\mathrm{C}}\text{—}\dot{\mathrm{C}}\mathrm{H_2} + e^- \tag{7.32}$$

7.3 Techniques of Free Radical Chain Polymerization

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion. Ionic and other nonradical polymerizations are usually confined to solution techniques. Each of the methods has advantages and disadvantages, as outlined in Table 7.8.

7.3.1 Bulk Polymerization

The bulk polymerization is the simplest polymerization reaction without contamination of solvent and other impurities or using especial equipment. However, it is usually difficult to control due to the exothermic polymerization reaction. When polymer is insoluble in monomer, polymer precipitates and the viscosity of the medium does not change appreciably. The polymer droplet may contain free radicals that can lead to *autoacceleration*—a rapid increase in the polymerization rate. The bulk polymerization is usually used in the casting large sheet of PMMA plastics or in the low molecular weight polymers synthesis for applications in adhesives, plasticizers, tackifiers, etc.

7.3.2 Suspension Polymerization

The suspension polymerization involves mechanically dispersing monomer in a noncompatible liquid, usually water. Then, the resultant monomer droplets are polymerized by use of a monomer soluble initiator. Monomer is kept in suspension

Table 7.8 Free radical polymerization techniques

Method	Advantages	Disadvantages
Bulk	Simple; no contaminants added	Reaction exotherm difficult to control; high viscosity
Suspension	Heat readily dispersed; low viscosity; polymer obtained in granular form and may be used directly	Washing and/or drying required; agglomeration may occur; contamination by stabilizer
Solution	Heat readily dispersed; low viscosity; may be used directly as solution	Added cost of solvent; solvent difficult to remove; possible chain transfer with solvent; possible environmental pollution
Emulsion	Heat readily dispersed; low viscosity; high molecular weight obtainable; may be used directly as emulsion; works on tacky polymers	Contamination by emulsifier and other ingredients; chain transfer agents often needed to control degree of polymerization; washing and drying necessary for bulk polymer

by continuous agitation and the use of *stabilizers* such as polyvinyl alcohol or methyl cellulose (ether). Granular beads are obtained which are easy to handle and can be isolated by filtration, etc. Polystyrene, poly(vinyl chloride), and poly(methyl methacrylate) have been prepared by this method.

7.3.3 Solution Polymerization

Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully to avoid chain transfer reactions that may limit the growth of molecular weight of polymer. Apart from the environmental concerns associated with organic solvents, a major problem in solution polymerization is that it is often difficult to remove solvent. As a result, supercritical carbon dioxide has been used to do the polymerization as a solvent. However, it is only suitable for polar monomers such as acrylates; there is need for more development work for other monomers.

7.3.4 Emulsion Polymerization

Emulsion polymerization and suspension polymerization are two water-based heterogeneous polymerizations that are used extensively to control the thermal, viscosity, and environmental problems of polymer industry. However, they are quite different in the components and behaviors in the polymerization. The comparison between the two polymerization processes is summarized in Table 7.9. The major difference between the two polymerizations is the reaction site, micelle for emulsion polymerization, and monomer for suspension polymerization.

When the concentration of a surfactant exceeds its *critical micelle concentration* (CMC), the excess surfactant molecules aggregate together to form small colloidal

Table 7.9 Comparison between suspension polymerization and emulsion polymerization [3]

Component/Characteristic	Emulsion	Suspension
Particle size	1–10 μm monomer 2–10 nm micelle	5–500 μm monomer droplets
Monomer/water ratio	30/70 to 60/40	25/75 to 50/50
Surfactant	0.2–3 % in micelle form	0.1 %
Initiator	Water soluble	Oil soluble
Water-soluble stabilizer	None	>1 %
Product particle size	0.05–0.2 μm	0.5–10 μm
Phase	One	Two
Polymerization site	Micelle	Monomer

clusters called *micelles*. Typical micelles have dimensions of 2–10 nm, with each micelle containing 50–150 surfactant molecules. The largest portion of the monomer (>95 %) is dispersed as *monomer droplets* whose size depends on the stirring rate. Monomer droplets have diameters in the range 1–100 μm. Thus, in a typical emulsion polymerization system, the monomer droplets are much larger than the monomer-containing micelles. Consequently, while the concentration of micelles is 10^{19}–10^{21} L^{-1}, the concentration of monomer droplets is at most 10^{12}–10^{14} L^{-1}. A further difference between micelles and monomer droplets is that the total surface area of the micelles is larger than that of the droplets by more than two orders of magnitude.

Polymerization takes place exclusively in micelle. Monomer droplets do not compete effectively with micelles in capturing radicals produced in solution because of the much smaller total surface area of the droplets. The micelles act as a meeting place for the organic (oil soluble) monomer and the water-soluble initiator. The micelles are favored as the reaction site because of their high monomer concentration compared to the monomer in solution. As polymerization proceeds, the micelles grow by the addition of monomer from the aqueous solution whose concentration is replenished by dissolution of monomer from the monomer droplets. A simplified schematic representation of an emulsion polymerization system is shown in Fig. 7.1. The system consists of three types of particles: monomer droplets, inactive micelles in which polymerization is not occurring, and active micelles in which polymerization are occurring. The latter are no longer considered as micelles but are referred to as *polymer particles*. An emulsifier molecule is shown as ○— to indicate one end (○) is polar or ionic and the other end (—) is nonpolar.

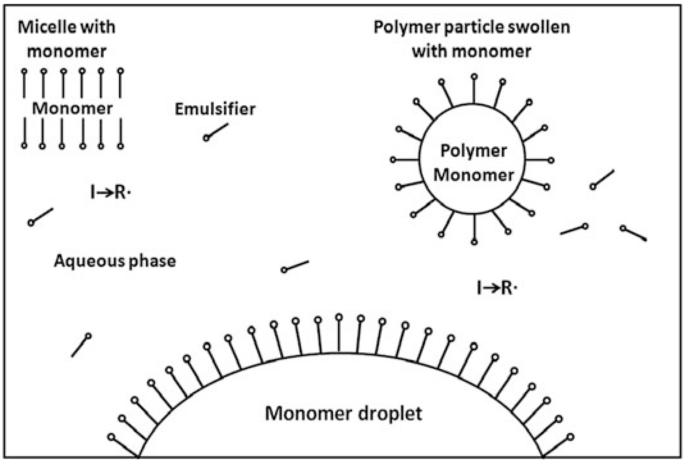
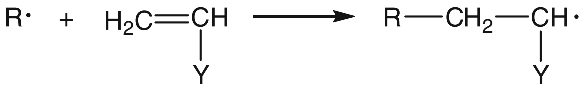


Fig. 7.1 Simplified representation of an emulsion polymerization system [3]

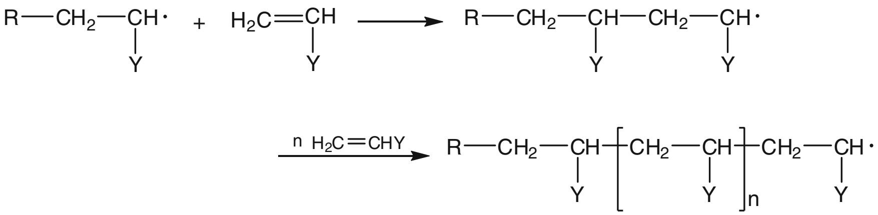
7.4 Reaction Mechanism of Free Radical Chain Polymerization

Two reactions are involved in the initiation of free radical chain polymerization: formation of the initiator radical (Eq. 7.33), and addition of the initiator radical to monomer (Eq. 7.34). The end group analysis of propagating chain shows the initiator radicals are incorporated into the polymer. The propagation reactions comprise addition of monomer radical to another monomer molecule, followed by successive additions of oligomer and polymer radicals to available monomer (Eq. 7.35).

$$\text{Initiator} \longrightarrow \mathrm{R}\cdot \tag{7.33}$$



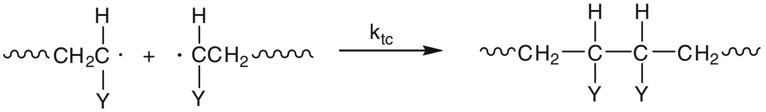
$$\mathrm{R}\cdot + \mathrm{H_2C}{=}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{R{-}CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\cdot \tag{7.34}$$



$$\mathrm{R{-}CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\cdot + \mathrm{H_2C}{=}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}} \longrightarrow \mathrm{R{-}CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\cdot$$

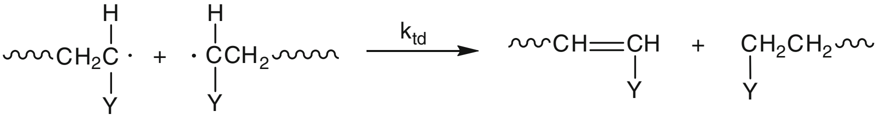
$$\xrightarrow{n\ \mathrm{H_2C{=}CHY}} \mathrm{R{-}CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\mathrm{{-}}\left[\mathrm{CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\right]_n\mathrm{{-}CH_2{-}}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}}\cdot \tag{7.35}$$

Propagation continues until some reaction occurs to terminate it. Two radicals are easily be terminated by a *combination (coupling)* reaction as shown in Eq. 7.36.



$$\sim\!\sim\mathrm{CH_2}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{Y}}{\mathrm{C}}}\cdot + \cdot\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{Y}}{\mathrm{C}}}\mathrm{CH_2}\sim\!\sim \xrightarrow{k_{tc}} \sim\!\sim\mathrm{CH_2{-}}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{Y}}{\mathrm{C}}}\mathrm{{-}}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{Y}}{\mathrm{C}}}\mathrm{{-}CH_2}\sim\!\sim \tag{7.36}$$

On the other hand, more rarely, they can be terminated by a *disproportionation* reaction, in which a hydrogen radical that is *beta* to one radical center is transferred to another radical center. This results in the formation of two polymer molecules—one saturated and one unsaturated as shown in Eq. 7.37:



$$\sim\!\sim\mathrm{CH_2}\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{Y}}{\mathrm{C}}}\cdot + \cdot\overset{\displaystyle \mathrm{H}}{\underset{\displaystyle \mathrm{Y}}{\mathrm{C}}}\mathrm{CH_2}\sim\!\sim \xrightarrow{k_{td}} \sim\!\sim\mathrm{CH}{=}\underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{CH}}} + \underset{\displaystyle \mathrm{Y}}{\underset{|}{\mathrm{C}}}\mathrm{H_2CH_2}\sim\!\sim \tag{7.37}$$

The two different modes of termination can be represented in general term by

$$M_n \cdot + M_m \cdot \xrightarrow{k_{tc}} M_{n+m} \tag{7.38}$$

$$M_n \cdot + M_m \cdot \xrightarrow{k_{td}} M_n + M_m \tag{7.39}$$

where k_{tc} and k_{td} are the rate constants for termination by coupling and disproportionation, respectively. One can also express the termination step by

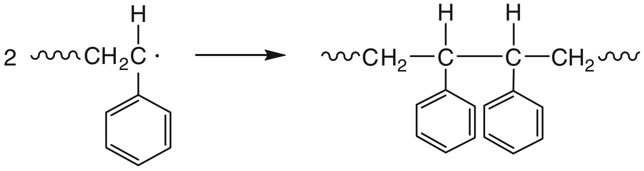
$$M_n \cdot + M_m \cdot \rightarrow \text{dead polymer} \tag{7.40}$$

where the particular mode of termination is not specified and

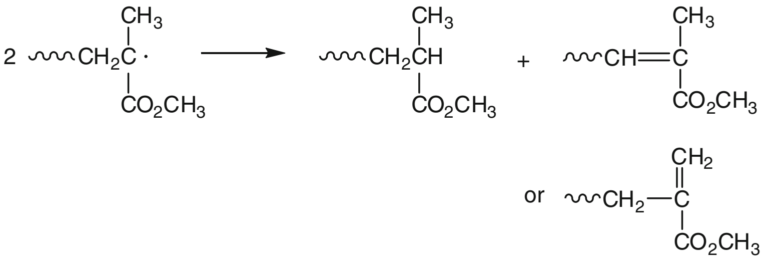
$$k_t = \alpha k_{tc} + (1 - \alpha) k_{td} \tag{7.41}$$

where α and $(1 - \alpha)$ are the fractions of termination by coupling and disproportionation, respectively.

Typical termination rate constants are in the range of 10^6–10^8 dL mol^{-1} s^{-1} or orders of magnitude greater than the propagation rate constants. The much greater value of k_t (whether k_{tc} or k_{td}) compared to k_p does not prevent propagation because the radical species are present in very low concentrations and the polymerization rate is only dependent on the one half power of k_t. Thus, whether termination occurs by coupling or by disproportionation depends on monomer structure or, more exactly, on the structure of the chain-end radical, e.g., steric repulsion, electrostatic repulsion (raise the activation energy for coupling), and availability of alpha hydrogen. Polystyryl radicals undergo coupling (Eq. 7.42) almost exclusively at low temperatures, whereas poly(methyl methacrylate) radicals undergo mainly disproportionation (Eq. 7.43). The polystyryl radical is more reactive than methacrylate radical due to the resonance stabilization, so it will undergo coupling instead of disproportionation.



(7.42)



$$2\ \sim\!CH_2C(CH_3)(CO_2CH_3)\cdot \longrightarrow \sim\!CH_2CH(CH_3)(CO_2CH_3) + \sim\!CH{=}C(CH_3)(CO_2CH_3)\ \text{or}\ \sim\!CH_2{-}C({=}CH_2)(CO_2CH_3) \tag{7.43}$$

Another possible termination reaction involves combination of initiator radicals with chain end radicals (Eq. 7.44) called *primary radical termination.* This process occurs at high initiator concentration or high viscosity that limits the diffusion of polymer radicals.

$$\sim\!CH_2CH(Y)\cdot + \cdot R \longrightarrow \sim\!CH_2CHR(Y) \tag{7.44}$$

7.5 Kinetics of Free Radical Chain Polymerization

Radical chain polymerization is a chain reaction consisting of a sequence of three steps—*initiation*, *propagation*, and, *termination*. The initiation step involves two reactions (Eqs. 7.45 and 7.46). The first is the production of free radicals by homolytic dissociation of an initiator species I to yield a pair of radicals $R\cdot$

$$I \xrightarrow{k_d} 2R\cdot \tag{7.45}$$

where k_d is the rate constant for the catalyst dissociation. The second part of the initiation involves the addition of this radical to the first monomer molecule to produce radical $M_1\cdot$

$$R\cdot + M \xrightarrow{k_i} M_1\cdot \tag{7.46}$$

Propagation consists of the growth of $M_n\cdot$ by the successive additions of large numbers (hundreds and perhaps thousands) of monomer molecules. Each addition creates a new radical that has the same identity as the one previously, except that it is larger by one monomer unit. The successive additions may be represented by

$$M_n\cdot + M \xrightarrow{k_p} M_{n+1}\cdot \tag{7.47}$$

Monomer disappears by the initiation reaction (Eq. 7.45) as well as by the propagation (Eq. 7.46). The *rate of monomer disappearance*, also called the *rate of polymerization*, is given by

$$-\frac{d[M]}{dt} = R_i + R_p \tag{7.48}$$

where R_i and R_p are the rates of initiation and propagation, respectively. However, the number of monomer molecules reacting in the initiation step is far less than the number in the propagation step for a process producing high polymer. Thus, the rate of initiation can be neglected and the polymerization rate is given simply by the rate of propagation. The rate of propagation, and therefore the rate of polymerization, is the sum of many individual propagation steps. Since the rate constants for all the propagation steps are the same, one can express the polymerization rate by

$$-\frac{d[M]}{dt} = R_p = k_p[M\cdot][M] \tag{7.49}$$

where $[M]$ is the monomer concentration and $[M\cdot]$ is the total concentration of all chain radicals, that is, all radicals of size $M_1\cdot$ and larger.

The polymerization rate (Eq. 7.49) is not directly usable because it contains a term of radical concentration. Radical concentrations are difficult to measure quantitatively, since they are very low ($\sim 10^{-8}M$), and it is therefore desirable to eliminate $[M\cdot]$ from Eq. 7.49. In order to do this, one can use *steady-state* assumption: the concentration of radicals increases initially, but almost instantaneously reaches a constant, steady-state value. That means the rate of change of the concentration of radicals is zero during the course of the polymerization. Therefore, the rates of initiation R_i and termination R_t of radicals are equal

$$R_t = R_i = 2k_t[M\cdot]^2 \tag{7.50}$$

Rearrange Eq. 7.50 to obtain

$$[M\cdot] = \left(\frac{R_i}{2k_t}\right)^{1/2} \tag{7.51}$$

and substitute Eq. 7.51 into Eq. 7.49 that yields the rate of polymerization equation.

$$R_p = k_p[M](R_i/2k_t)^{1/2} \tag{7.52}$$

7.5.1 Rate of Polymerization

The rate of polymerization equation can be modified to include the initiator efficiency (*f*) as shown in Eq. 7.53. The equation indicates the polymerization rate is proportional to the square root of initiator concentration and to the first power of monomer concentration. Thus, doubling the initiator concentration causes the rate

Table 7.10 Representative propagation and termination rate constants, k_p and k_t [2]

Monomer	Temperature (°C)	k_p (L/mol-s)	$k_t \times 10^{-6}$ (L/mol-s)
Acrylonitrile	60	1,960	782
Ethylene	83	240	540
Methyl acrylate	60	2,090	9.5
Methyl methacrylate	60	515	25.5
Styrene	60	176	72
Vinyl acetate	50	2,640	116.8
Vinyl chloride	50	11,000	2,100
Tetrafluoroethylene	40	7,400	7.4×10^{-5}

to increase by a factor of about 1.4. This relationship has been confirmed experimentally for a variety of free radical polymerizations. Propagation and termination rate constants, for several commercially important monomers are given in Table 7.10. The tetrafluoroethylene has an extremely low k_t which results in higher molecular weight polymer as compared with the polymerization of ethylene.

$$R_p = k_p[M]\sqrt{\frac{fk_d[I]}{k_t}} \tag{7.53}$$

7.5.2 Average Kinetic Chain Length $\overline{\nu}$

Another important parameter related to polymerization rate is the *average kinetic chain length*, $\overline{\nu}$, which is defined as the average number of monomer units polymerized per chain initiated, which is equal to the rate of polymerization per rate of initiation. Since $R_i = R_t$ under steady-state conditions,

$$\overline{\nu} = \frac{R_p}{R_i} = \frac{R_p}{R_t} \tag{7.54}$$

Substituting for R_p and R_t into Eq. 7.54:

$$\overline{\nu} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{2k_t[M\cdot]} \tag{7.55}$$

Substituting the expression for $[M\cdot]$ from Eq. 7.51,

$$\overline{\nu} = \frac{k_p[M]}{2(fk_tk_d[I])^{1/2}} \tag{7.56}$$

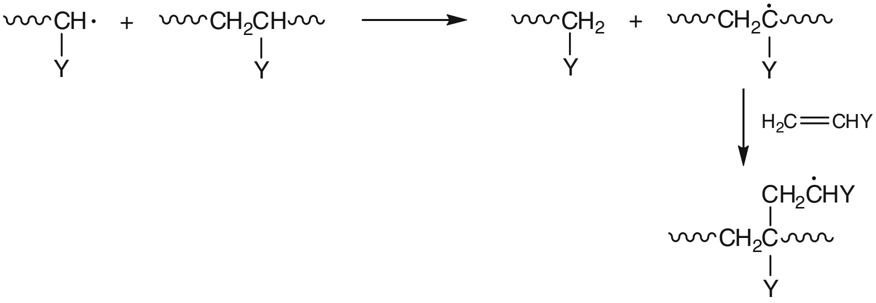
Kinetic chain length is related to a variety of rate and concentration parameters. It will decrease as both of initiator concentration and initiator efficiency increase.

This is reasonable because increasing the number of growing chains increases the probability of termination. Thus, varying initiator concentration can control molecular weight. In the absence of any side reactions, kinetic chain length is related directly to degree of polymerization depending on the mode of termination. If termination occurs exclusively by disproportionation, $\overline{DP} = \overline{v}$; if it occurs by coupling, $\overline{DP} = 2\overline{v}$.

Autoacceleration, a marked increase in polymerization rate, can occur at very viscous medium even though the chain mobility is reduced and the termination is reduced. The small monomer molecules can still diffuse to the active chain ends to be polymerized. Autoacceleration may cause processing difficulties, particularly in bulk polymerizations, because the increase in rate is usually accompanied by an increase in reaction exotherm and gelation of polymer.

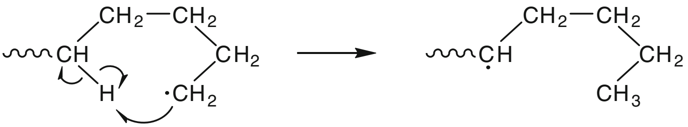
7.5.3 Chain Transfer Reactions

Chain transfer reactions are the process transferring the growing polymer chain to another species which terminates the chain, but at the same time generates a new radical. The chain transfer reactions result in low molecular weight polymer and broad molecular weight distributions. Chain transfer can occur among polymer, monomer, initiator, solvent in the reaction mixture. Equations 7.57 and 7.58 show the polymer inter- and intrachain transfer reactions, respectively. A chain-end radical may abstract a hydrogen atom from a chain, leading to a reactive site for chain branching (Eq. 7.57).



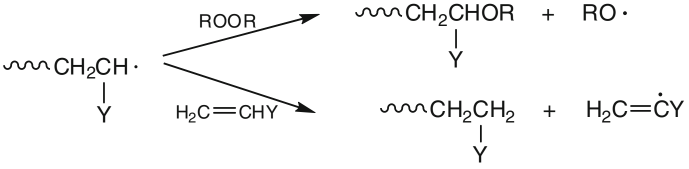
(7.57)

Hydrogen abstraction may also occur intramolecularly, a process referred to as *backbiting*. Polyethylene, produced by high-pressure free radical polymerization of ethylene, is highly branched through backbiting involving five- or six-membered cyclic transition states (Eq. 7.58). The properties of branched polymers are expected to differ remarkably from those of the corresponding linear polymers as we discussed in Chaps. 3 and 4.



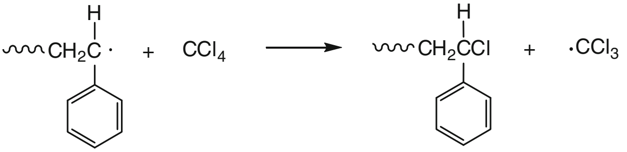
(7.58)

Chain transfer may also occur with initiator (Eq. 7.59) or monomer (Eq. 7.60), or it may take place with solvent. Polystyrene prepared in carbon tetrachloride, for example, contains chlorine at the chain end of polymer due to chlorine transfer (Eq. 7.61) and initiation by the resultant $\cdot CCl_3$ radicals (Eq. 7.62). Transfer to monomer is particularly important with monomers containing allylic hydrogen, such as propylene, because the formation of resonance-stabilized allylic radicals (Eq. 7.63) is highly favorable. Thus, high-molecular-weight polypropylene cannot be prepared using conventional free radical polymerization described here. The coordination polymerization is used to obtain high molecular weight polypropylene (detailed in Chap. 9).

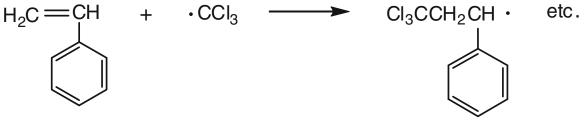


$$\sim CH_2\underset{\underset{Y}{|}}{C}H\cdot \xrightarrow{ROOR} \sim CH_2\underset{\underset{Y}{|}}{C}HOR + RO\cdot \qquad (7.59)$$

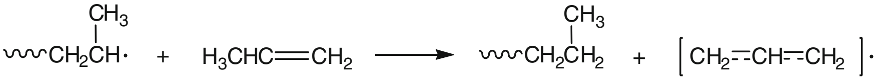
$$\sim CH_2\underset{\underset{Y}{|}}{C}H\cdot \xrightarrow{H_2C=CHY} \sim CH_2\underset{\underset{Y}{|}}{C}H_2 + H_2C=\dot{C}Y \qquad (7.60)$$



(7.61)



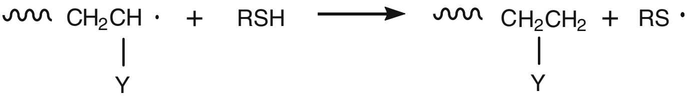
(7.62)



$$\sim CH_2\overset{\overset{CH_3}{|}}{C}H\cdot + H_3CHC{=}CH_2 \longrightarrow \sim CH_2\overset{\overset{CH_3}{|}}{C}H_2 + \left[CH_2{=}CH{=}CH_2\right]\cdot$$

(7.63)

From the molecular weight control point of view, the chain transfer agent plays the most effective way. For instance, a thiol compound has been used widely as chain transfer agent due to its high affinity for hydrogen transfer as



$$\sim\!\!\sim CH_2\underset{\displaystyle Y}{\underset{|}{C}}H\cdot + RSH \longrightarrow \sim\!\!\sim CH_2\underset{\displaystyle Y}{\underset{|}{C}}H_2 + RS\cdot \tag{7.64}$$

When a chain transfer agent is used in polymerization, it is necessary to redefine the kinetic chain length as being the ratio of propagation rate to the combined rates of termination and transfer, as

$$\bar{\nu}_{tr} = \frac{R_p}{R_i + R_{tr}} \tag{7.65}$$

Since transfer reactions are second order, with

$$R_{tr} = k_{tr}[M\cdot][T] \tag{7.66}$$

where T is the transfer agent, one can rewrite the expression for $\bar{\nu}_{tr}$, taking into account all possible transfer reactions, as

$$\bar{\nu}_{tr} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2 + \sum k_{tr}[M\cdot][T]} = \frac{k_p[M]}{2k_t[M\cdot] + \sum k_{tr}[T]} \tag{7.67}$$

It is known that

$$\bar{\nu} = \frac{k_p[M]}{2k_t[M\cdot]}$$

One can write the reciprocal of Eq. 7.67 for $\bar{\nu}_{tr}$ as

$$\frac{1}{\bar{\nu}_{tr}} = \frac{1}{\bar{\nu}} + \frac{\sum k_{tr}[T]}{k_p[M]} \tag{7.68}$$

The ratio of the transfer rate constant to that of propagation is commonly defined as the chain transfer constant, C_T, for a particular monomer:

$$\frac{k_{tr}}{k_p} = C_T \tag{7.69}$$

Substituting Eq. 7.69 into Eq. 7.68, one obtains

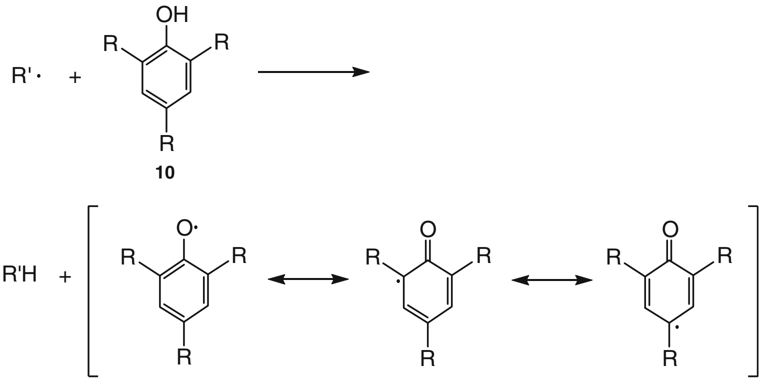
$$\frac{1}{\bar{\nu}_{tr}} = \frac{1}{\bar{\nu}} + \frac{\sum C_T[T]}{[M]} \tag{7.70}$$

As the rate of transfer and concentration of the transfer agent increase, the kinetic chain length becomes progressively smaller. Chain transfer constants for a number of compounds and monomers are available in the polymer literature, several of which are given in Table 7.11.

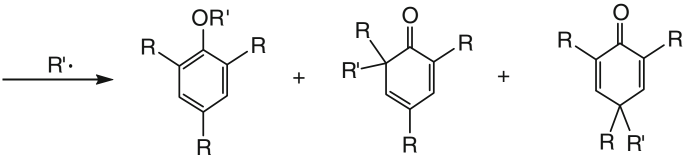
Table 7.11 Representative chain transfer constants C_T, propagation rate constants k_p, and termination rate constants k_t, for styrene and methyl methacrylate (reaction temperature 60°C) [3]

Transfer Agent	$C_T \times 10^4$	
	Styrene	Methyl Methacrylate
Benzene	0.023	0.04
Toluene	0.125	0.20
Chloroform	0.5	1.77
Carbon tetrachloride	90	2.40
Carbon tetrabromide	22,000	2,700
1-Butanethiol	210,000	6,600
k_p (L/mol-s)	176	515
$k_t \times 10^{-6}$ (L/mol-s)	73	25.5

When the concentration of transfer agent is high and k_{tr} is much greater than k_p, very low molecular weight polymers called telomers are obtained. The process is called *telomerization*. Chain transfer reactions can also be used to prevent free radical polymerizations. One type of compound, added as a stabilizer to vinyl monomers, is an alkylated phenol **10**, which can transfer its phenolic hydrogen to form a new radical (Eq. 7.71) that undergoes coupling reaction (Eq. 7.72) rather than initiating polymerization. Such compounds, called *inhibitors*, are commonly added to monomers to prevent premature polymerization during shipment or storage.



(7.71)



(7.72)

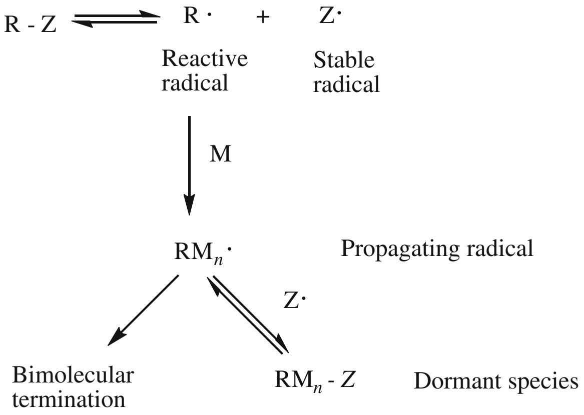
7.6 Living Polymerization

When the termination reaction is not present in the polymerization of monomers, we call the polymerization is living polymerization. An important consequence of living polymerization is that the average degree of polymerization is simply equal to the ratio of the initial monomer concentration to the initiator concentration as shown in Eq. 7.73. There are different approaches to achieve living radical polymerizations which are discussed below.

$$\overline{DP} = \frac{[M]_0}{[I]_0} \tag{7.73}$$

7.6.1 Living Radical Polymerization

The living radical polymerization is also called controlled radical polymerization. The formal IUPAC name of this type of polymerization is called reversible deactivation radical polymerization (RDRP) [6]. The lifetime in the conventional radical polymerization is very short (in second) because of the presence of bimolecular termination. The living radical polymerization can be achieved by minimizing normal bimolecular termination and prolonging the lifetime of living polymers. Special mode of reaction for the propagating radicals by either reversible termination or reversible transfer has been developed [3]. Living radical polymerization (LRP) with reversible termination generally proceeds as follows:



(7.74)

(7.75)

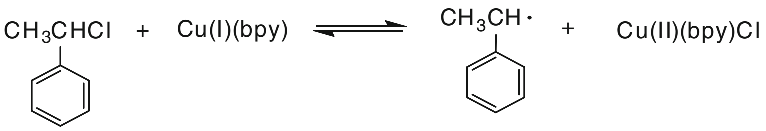
(7.76)

The initiator RZ undergoes homolytic bond breakage to produce one reactive and one stable free radical (Eq. 7.74). The reactive radicals quickly initiate polymerization (Eq. 7.75), but the stable radicals are too stable to initiate polymerization. However, the stable radicals preserve the propagation chain being living without any termination (Eq. 7.76). For living polymerization, it is important to have all the initiator decomposes at once so that all propagating radicals grow almost at the same time. Fast initiation is important, but it is the fast equilibrium between the propagating radical and dormant species with an appropriate equilibrium constant that determines the living characteristics of polymerization. The equilibrium constant must be low but not too low; that is, the concentration of propagating radical must be sufficient to achieve a reasonable propagation rate but not so high that normal bimolecular termination becomes important.

At the beginning of the reaction, the concentrations of propagating and stable radicals are equal, but they change rapidly with the progress of reactions. The concentrations of stable radicals are increasing while the concentrations of propagating radicals are decreasing because the reactions are shifted toward more stable species as shown in Eqs. 7.74 and 7.76. Overall, the concentration of stable radicals is about four orders higher than that of propagating radicals. The concentration of propagating radicals is about the same or lower than the conventional radical polymerization. The stable radicals function as controlling agent to form reversible dormant species with propagating radicals. The equilibrium favors the dormant species by several orders of magnitude as compared with the propagating radicals. Thus, the concentration of dormant species is about six orders higher than that of propagating radical. In short summary, the introduction of the dormant species in the radical polymerization suppresses the bimolecular termination reaction to have a living polymer. The average life time of the living polymer has been increased by at least four orders of magnitude. Thus, the living free radical polymerization becomes possible due to the formation of stable radicals and reversible dormant species. By sequential living polymerization of one kind of monomer to another kind of monomer, well-defined block copolymers can be obtained through living polymerization. The second type of monomers usually has to add quickly after the first kind monomers are consumed to avoid any bimolecular reactions among propagating radicals. Currently, reversible termination reactions and reversible chain transfer reactions are employed in the living free radical polymerizations. They are discussed below.

7.6.2 Atom Transfer Radical Polymerization

The reactions of atom transfer radical polymerization (ATRP), involves an atom transfer, usually a halogen atom, to form propagating radicals and dormant species from the complex of atom transfer agent and copper (I) catalyst [6]. For instance, the polymerization of styrene using 1-chloro-1-phenylethane (**11**, or the bromo analog) as initiator in the presence of a copper (I) bipyridyl (bpy) complex. Initiation occurs when a halogen atom is transferred from **11** to the complex (Eq. 7.77). The resultant 1-phenylethyl radical in turn adds to a styrene molecule (Eq. 7.78). The halogen atom is then reversibly transferred to the styryl radical (Eq. 7.79), thus preventing radical termination reactions from occurring while allowing the propagation reaction to proceed.



(7.77)

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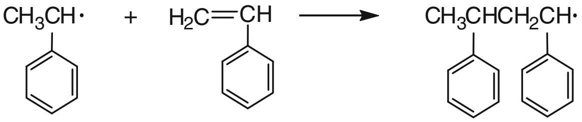

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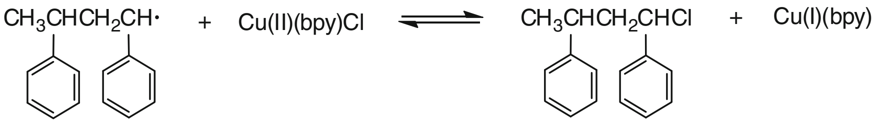
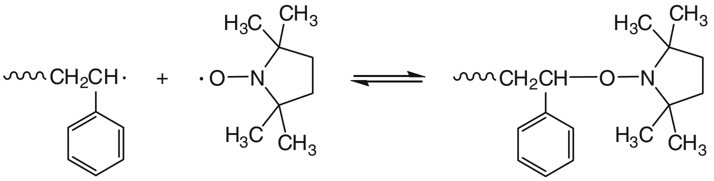


(7.79)

7.6.3 Nitroxide-Mediated Polymerization (NMP)

Stable nitroxide radical such as TEMPO **12** can mediate polymerization as shown in Eq. 7.80. The TEMPO is too stable to initiate polymerization, but it does promote decomposition of benzoyl peroxide to benzoyloxy radicals which initiate chain growth. Then TEMPO combines reversibly with the growing polymer chain ends which protect the chain end radicals from termination. Dissociation in turn frees the chain end radical to add to other styrene molecules.

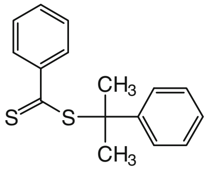


(7.80)

12

7.6.4 Radical Addition-Fragmentation Transfer (RAFT)

ATRP and NMP control chain growth by reversible termination. RAFT living polymerizations control chain growth through reversible chain transfer. A chain-transfer agent R'CSSR, such as cumyl dithiobenzoate **13** reversibly transfer a labile end group (a dithioester end group) to a propagating chain (Eq. 7.81). The polymerization is carried out with a conventional initiator such as a peroxide or AIBN in the presence of the chain-transfer agent. The key that makes RAFT a living polymerization is the choice of the RAFT transfer agent. Living polymerization occurs with dithioesters because the transferred end group in the polymeric dithioester is as labile as the dithioester group in R'CSSR. This results in an equilibrium between dormant polymer chains and propagating radicals (Eq. 7.82 with $K = 1$), which controls the living polymerization.



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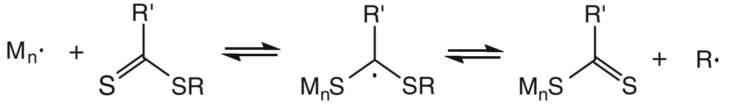
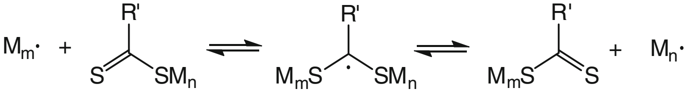


(7.81)



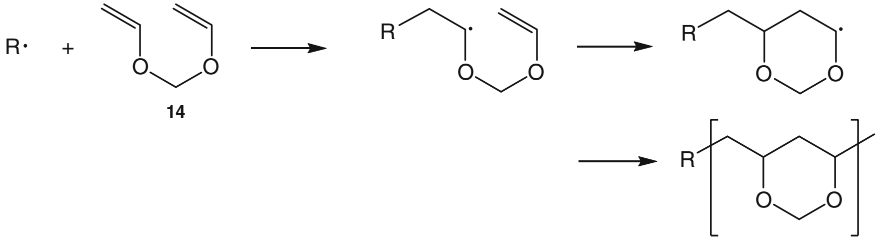
(7.82)

RAFT works with a wider range of monomers than TEMPO and ATRP. RAFT does not produce polymers with metal catalysts but produce polymers with dithioester group with odors and colors. The design and synthesis of RAFT agent has been thoroughly reviewed and outlined. The methods are extended to functional RAFT agent and macro-RAFT agent [7].

The limitations of living radical polymerization are that irreversible bimolecular termination of propagating radicals will occur at high monomer conversion, polyfunctional initiators, high initiator concentration, and high target molecular weight (>100,000).

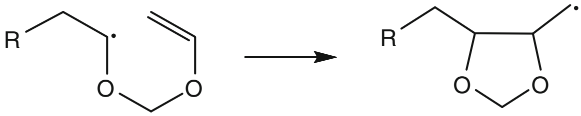
7.7 Polymerization of Dienes

Polymerization of isolated dienes leads to crosslinked polymers when the double bonds react independently of each other. In certain cases, the addition reactions can occur within the double bonds of molecule and lead to cyclic polymers. Polymerization of divinylformal **14** illustrates this process as shown in Eq. 7.83.



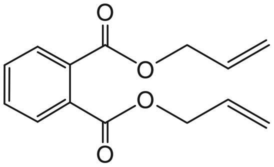
(7.83)

The normal (head-to-tail) mode of addition yields the six-membered ring, whereas abnormal (head-to-head) addition (Eq. 7.84) gives the five-membered ring. The former is preferred, but both are formed in significant amounts.



(7.84)

Several diallyl monomers such as **15** and **16** are used commercially to prepare highly cross-linked thermosetting *allyl resins* or for crosslinking other polymers. Diallyl phthalate **15** is used widely in the manufacturing of printed wiring boards, electrical insulations, fiber reinforced composites, etc. Diethylene glycol bis (allyl carbonate) **16** is used to make optical clear polymers for the applications in eyewares, lenses, camera filters, panel covers, and the like.



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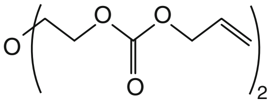

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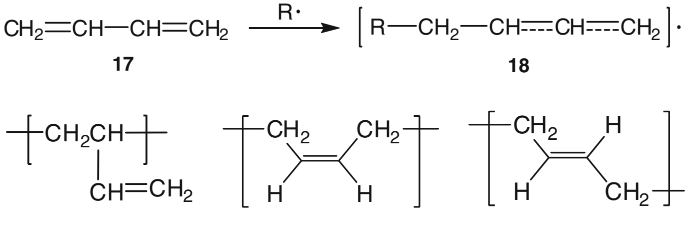
Conjugated dienes such as 1,3-butadiene **17** undergo both 1,2- and 1,4-addition to obtain polymers through the delocalized radical intermediate **18** (Eq. 7.85). Thus 1,2-addition gives polymer **19** with pendant vinyl groups, while 1,4-addition leads to polymer with unsaturation in the chain. In the latter case, both *cis* **20** and *trans* **21** configurations are possible.

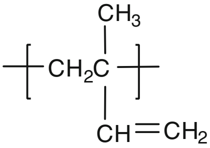


17 **18**

19 **20** **21**

(7.85)

With substituted dienes like isoprene (2-methyl-1,3-butadiene) the situation is more complicated; 1,2 and 3,4 structures (**22** and **23**, respectively) as well as *cis*- and *trans*-1,4 (**24** and **25**), are possible. All are formed in free radical polymerization but as expected the head-to-tail*trans*-1,4 **25** predominates. Natural *Hevea* rubber contains the head-to-tail of 1,4-polyisoprene units with *cis* structure **24**.



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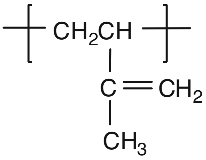

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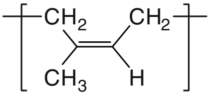

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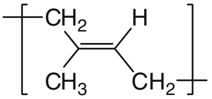


25

Table 7.12 lists the percentages of each structural unit at different polymerization temperatures for the three most important diene monomers—butadiene, isoprene, and chloroprene (2-chloro-1,3-butadiene). It is interesting to note that, for isoprene, the amount of *cis*-1,4 structure increases with increasing temperature up to about 100 °C, then it decreases. The total amount of 1,2 and 3,4 polymer (approximately 10 %) does not change appreciably with temperature; however, the 3,4 structure is favored at higher temperatures. With chloroprene, the *trans*-1,4 structure also decreases with increasing temperature, but the amount of *trans*-1,4 is slightly higher than that of isoprene over the temperature range measured. The results may be from the larger size of Cl group than that of CH_3 group, a steric hinderance dominated factor.

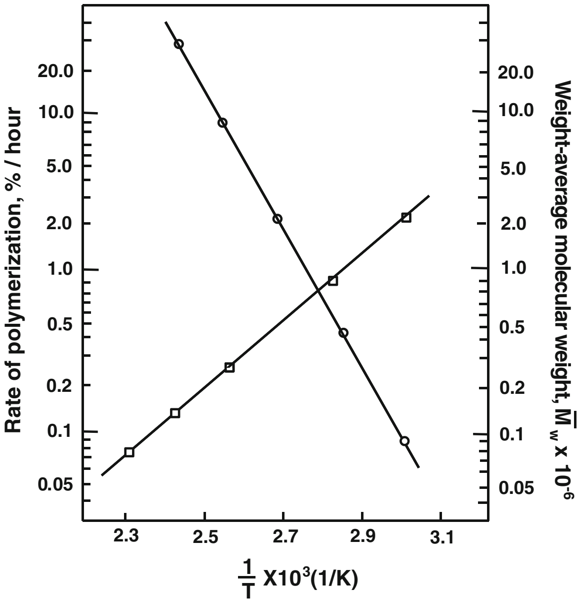
Table 7.12 Compositions of free radical-initiated diene polymers [2]

Monomer	Polymerization temperature(°C)	Percent			
		cis-1,4	trans-1,4	1,2	3,4
Butadiene	−20	6	77	17	–
	20	22	58	20	–
	100	28	51	21	–
	233	43	39	18	–
Isoprene	−20	1	90	5	4
	−5	7	82	5	5
	50	18	72	5	5
	100	23	66	5	6
	257	12	77	2	9
Chloroprene	−46	5	94	1	0.3
	46	10	81–86	2	1
	100	13	71	2.4	2.4

7.8 Temperature Effect of the Free Radical Polymerization

By varying the polymerization temperature, there is big effect on the rate and degree of polymerization [3]. When the temperature increases, the rate of polymerization increases, but the degree of polymerization decreases as shown in Fig. 7.2. The quantitative effect of temperature is complicated and is discussed in the following sections.

Fig. 7.2 Dependence of the polymerization rate (○) and polymer molecular weight (□) on the temperature for the thermal self-initiated polymerization of styrene [3]



7.8.1 Activation Energy and Frequency Factor

The quantitative effect of temperature on rate of polymerization (R_p) and degree of polymerization ($\overline{X}_n$) is very complex since they depend on a combination of three rate constants of initiation (k_d), propagation (k_p) and termination (k_t). Each of the rate constants can be expressed by an Arrhenius equation

$$k = Ae^{-E/RT} \tag{7.86}$$

or

$$\ln k = \ln A - \frac{E}{RT} \tag{7.87}$$

where A is the collision frequency factor, E the Arrhenius activation energy, and T the kelvin temperature. A plot of ln k versus $1/T$ allows the determination of both E and A from the slope and intercept, respectively. Table 7.13 shows the values of the frequency factor and activation energy of propagation (E_p) and termination (E_t) of several monomers.

The variations in the values of the frequency factor of propagation (A_p) are greater than those in E_p which indicates that steric effects are probably the more important factor to determine the absolute value of k_p. Thus, the more hindered monomers such as methyl methacrylate have lower k_p and A_p values than the less hindered ones such as methyl acrylate. The A_p values in general are lower than the usual value (10^{11}–10^{13}) of the frequency factor of a bimolecular reaction. The result is probably due to a large decrease in entropy on polymerization. The variations in the values of the frequency factor of termination (A_t), generally follow the trend of A_p values, but with larger values.

Table 7.13 Kinetic parameters in radical chain polymerization[a] [3]

Monomer	E_p	$A_p \times 10^{-7}$	E_t	$A_t \times 10^{-9}$
1,3-Butadiene	24.3	12	–	–
2-Vinylpyridine	33	–	21	–
Acrylonitrile	16.2	–	15.5	–
Ethylene	18.4	–	1.3	–
Methyl acrylate	29.7	10	22.2	15
Methyl methacrylate	26.4	0.087	11.9	0.11
Styrene	26	0.45	8.0	0.058
Vinyl acetate	18	3.2	21.9	3.7
Vinyl chloride (50°C)	16	0.33	17.6	600
Tetrafluoroethylene(83°C)	17.4	–	–	–

[a] E_p values are in kJ/mole of polymerizing monomer; E_t values are in kJ/mole of propagating radicals; A_p and A_t values are in liters/mole-second. The data are obtained at 60°C unless otherwise noted

7.8.2 Rate of Polymerization

For a polymerization initiated by the thermal decomposition of an initiator, the polymerization rate depends on the ratio of three rate constants $k_p(k_d/k_t)^{1/2}$ according to Eq. 7.53. The temperature dependence of this ratio can be obtained by combining three separate Arrhenius equations as below

$$\ln\left[k_p\left(\frac{k_d}{k_t}\right)^{1/2}\right] = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] - \frac{\left[E_p + \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)\right]}{RT} \tag{7.88}$$

The overall activation energy of rate of polymerization E_R is equal to $E_p + (E_d/2) - (E_t/2)$. From Eq. 7.53, one can rewrite the above equation as

$$\ln R_p = \ln\left[A_p\left(\frac{A_d}{A_t}\right)^{1/2}\right] + \ln\left[(f[I])^{\frac{1}{2}}[M]\right] - \frac{E_R}{RT} \tag{7.89}$$

By plotting $\ln R_p$ versus $1/T$, one can obtain E_R and $A_p(A_d/A_t)^{1/2}$ from the slope and intercept, respectively.

Table 7.14 shows the thermal properties of commonly used initiators. The activation energy of initiator decomposition is in the range of 120–150 kJ mole^{-1} in general. The E_p and E_t value of most monomers are in the ranges of 20–40 kJ mole^{-1} and 8–20 kJ mole^{-1} respectively (Table 7.13). Thus the E_R of most polymerization initiated by thermal initiator decomposition is about 80–90 kJ mole^{-1}. This corresponds to a two to three time rate increase for every 10°C temperature increase. The situation is different for other mode of initiation. The redox initiation (e.g., Fe^{2+} with thiosulfate or cumene hydroperoxide) usually takes place at lower temperature as compared to the thermal polymerizations because the former has lower activation energy. The E_d value of redox initiation is only about 40–60 kJ mole^{-1} or about 80 kJ mole^{-1} less than that of thermal initiation. This leads to an E_R redox polymerization about 40 kJ mole^{-1} or about half of the nonredox initiators.

The initiation step of photo polymerization is temperature independent ($E_d = 0$), because the decomposition of initiator is induced by light rather than by

Table 7.14 Properties of common thermal initiators[a,b] [3]

Initiator	$k_d \times 10^5$	T (°C)	E_d
2,2′-Azobisisobutyronitrile	0.845	60	123.4
Acetyl peroxide	2.39	70	136.0
Benzoyl peroxide	5.50	85	124.3
Cumyl peroxide	1.56	115	170.3
t-Butyl peroxide	3.00	130	146.9
t-Butyl hydroperoxide	0.429	155	170.7

[a] All data are for decompositions in benzene solution

[b] The units of k_d are s^{-1} ; the units of E_d are kJ/mole

heat. The overall activation energy of photo polymerization is then only about 20 kJ mole^{-1} which indicates this polymerization is relatively insensitive to temperature. However, most photo initiators can also be decomposed thermally; the initiators may undergo appreciable thermal decomposition in addition to photo decomposition at higher temperatures. In such cases, one must take into account both the thermal and photo initiations. The initiation and overall activation energies for a purely thermal self-initiated polymerization are approximately the same as for initiation by the thermal decomposition of an initiator. For the thermal, self-initiated polymerization of styrene, its E_d is 121 kJ mole^{-1} and E_R is 86 kJ mole^{-1}. However, pure thermal polymerization proceeds at very slow rates because of very low frequency factor (10^4–10^6) resulting in very low probability of initiation process.

7.8.3 Degree of Polymerization

The effect of temperature on the molecular weight of the polymer produced by thermally initiated polymerization will be determined by the ratio of $k_p/(k_d/k_t)^{1/2}$ according to Eq. 7.56 of the degree of polymerization, if transfer reactions are negligible. The variation of the ratio with temperature can be expressed by

$$\ln\left[\frac{k_p}{(k_d k_t)^{1/2}}\right] = \ln\left[\frac{A_p}{(A_d A_t)^{1/2}}\right] - \frac{\left[E_p - \left(\frac{E_d}{2}\right) - \left(\frac{E_t}{2}\right)\right]}{RT} \tag{7.90}$$

The overall activation energy of degree of polymerization ($E_{\overline{X}_n}$) is equal to $\left[E_p - (E_d/2) - (E_t/2)\right]$. Then the temperature effect on the degree of polymerization can be expressed by

$$\ln\overline{X}_n = \ln\left[\frac{A_p}{(A_d A_t)^{1/2}}\right] + \ln\left[\frac{[M]}{(f[I])^{1/2}}\right] - \frac{E_{\overline{X}_n}}{RT} \tag{7.91}$$

$E_{\overline{X}_n}$ has a value of about −60 kJ mole^{-1} and $\overline{X}_n$ decreases rapidly with increasing temperature. $E_{\overline{X}_n}$ is about the same for a purely thermal, self-initiated polymerization (Fig. 7.2). For a pure photo polymerization, $E_{\overline{X}_n}$ is positive by approximately 20 kJ mole^{-1}, since E_d is zero, and $\overline{X}_n$ increases moderately with temperature. For all other cases, $\overline{X}_n$ decreases with temperature.

When chain transfer occurs in the polymerization, the temperature effect on the $\overline{X}_n$ depends on the relative importance of the chain transfer reaction. For the case where chain transfer to chain transfer agent T, one can obtain the following equation according to Eq. 7.70.

Table 7.15 Activation parameters for chain transfer in styrene polymerization (60°C) [3]

Transfer agent	$-(E_p - E_{tr,S})$	$\log(A_{tr,S}/A_p)$
Benzene	62.0	3.9
Carbon tetrachloride	20.9	1
Cyclohexane	56.1	3.1
Ethyl benzene	23.0	−0.55
Isopropyl benzene	23.0	−0.47
n-Butyl bromide	46.1	2
n-Butyl chloride	58.6	4
n-Butyl iodide	29.3	1
t-Butyl benzene	57.4	3.8
Toluene	42.3	1.7

$$-\ln\left[\frac{[M]}{[T]}\left(\frac{1}{\overline{X}_n}-\frac{1}{\left(\overline{X}_n\right)_0}\right)\right]=\ln\frac{k_p}{k_{tr}}=\ln\frac{A_p}{A_{tr}}-\frac{(E_p-E_{tr})}{RT} \tag{7.92}$$

Now, $E_{\overline{X}_n}$ is equal to $(E_p - E_{tr})$ and can be obtained by plotting the left side of equation versus $1/T$. The $(E_p - E_{tr})$ is usually in the range of -20 to -65 kJ more^{-1} and the molecular weight decreases with increasing temperature. Table 7.15 shows the activation parameters for chain transfer in styrene polymerization using different chain transfer agents. The frequency factors for transfer reactions are usually greater than those of propagations.

7.9 Thermodynamics of Free Radical Polymerization

The thermodynamics of free radical polymerization [3] can be expressed by $\Delta G_p = \Delta H_p - T\Delta S_p$. The ΔG_p, ΔH_p, and ΔS_p for a polymerization are the difference in *free energy*, *enthalpy,* and *entropy*, respectively, between 1 mol of monomer and 1 mol of repeating units in the polymer product. The thermodynamic properties of a polymerization relate only to the propagation step, since polymerization consists of single acts of initiation and termination and a large number of propagation steps.

Chain polymerizations of alkene are exothermic (ΔH_p is “negative”) and exoentropic (ΔS_p is “negative”). The exothermic nature of polymerization arises because the process involves the exothermic conversion of π-bonds (less stable) in monomer molecules into σ-bond (more stable) in the polymer. The negative ΔS_p for polymerization arises from the decreased degrees of freedom for the polymer relative to the monomer. Thus, polymerization is favorable from the enthalpy viewpoint, but unfavorable from the entropy viewpoint. Table 7.16 shows the wide range of ΔH_p values for various monomers and also shows the general thermodynamic feasibility for any carbon–carbon double bond (ΔG_p is negative). However, thermodynamic feasibility does not indicate the experimental conditions of

Table 7.16 Enthalpy and entropy of polymerization at 25 °C[3]

Monomer	$-\triangle H$	$-\triangle S$
Ethylene	93	155
Propene	84	116
1-Butene	83.5	113
Isobutylene	48	121
1,3-Butadiene	73	89
Isoprene	75	101
Styrene	73	104
α-Methylstyrene	35	110
Vinyl chloride	72	–
Vinylidene chloride	73	89
Tetrafluoro ethylene	163	112
Acrylic acid	67	–
Acrylonitrile	76.5	109
Maleic anhydride	59	–
Vinyl acetate	88	110
Methyl acrylate	78	–
Methyl methacrylate	56	117

$\triangle H$ refer to the conversion of liquid monomer to amorphous or (slightly) crystalline polymer. $\triangle S$ refers to the conversion of monomer (at a concentration of 1 M) to amorphous or slightly crystalline polymer. The subscripts lc are often used with $\triangle H$ and $\triangle S$ to show the initial and final states (that is, $\triangle H_{lc}$ and $\triangle S_{lc}$). The units of $\triangle H$ are kJ/mole of polymerized monomer; the units of $\triangle S$ are J/K-mole

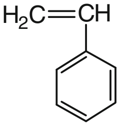
polymerization. The ΔS_p values fall in a narrower range of values. ΔS_p is in a small range $\sim$100 to $\sim$150 J/K-mol and ΔG_p is "negative" due to $-T\Delta S_p$ over weight ΔH_p. Thus, polymerization is a favored reaction from thermodynamic point of view.

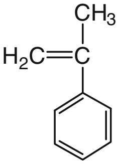
7.9.1 Monomer Reactivity

Although the polymerization reaction is thermodynamically favored, the kinetic feasibility of polymerization varies considerably from one monomer to another depending on the stability of monomer radical and polymer radical [3].

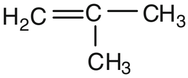
As shown in Table 7.16, the ΔH values for ethylene, propene, and 1-butene are very close to the difference (82–90 kJ/mole) between the bond energies of the π-bond in an alkene and the σ-bond in an alkane. The ΔH values for the other monomers vary considerably. The variations in ΔH for differently substituted ethylenes arise from any of the following effects: (1) differences in the resonance stabilization of monomer and polymer due to differences in conjugation or hyperconjugation, (2) steric strain differences in the monomer and polymer arising from bond angle deformation, bond stretching, or interactions between nonbonded atoms, and (3) differences in hydrogen bonding or dipole interactions in the monomer and polymer. The following monomers (I) can be stabilized through resonance that decreases Δ*H* of polymerization. However, the monomer (II) is poorly conjugated and its Δ*H* is similar to that of ethylene.

Type I Monomer

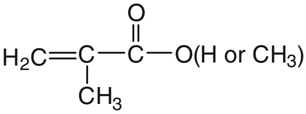




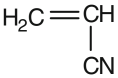
$CH_2{=}CH{-}CH{=}CH_2$



$$\mathrm{H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH_3}$$

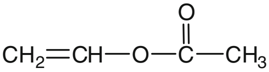


$$\mathrm{H_2C{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O(H\ or\ CH_3)}$$



$$\mathrm{H_2C{=}\underset{\displaystyle CN}{\underset{|}{CH}}}$$

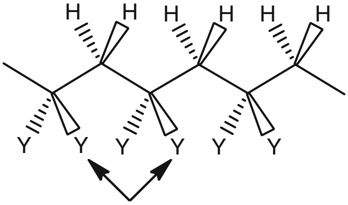
Type II Monomer



$$\mathrm{CH_2{=}CH{-}O{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}CH_3}$$

Many substituents stabilize the monomer but have no appreciable effect on polymer stability, since resonance is only possible with the former. The net effect is to decrease the exothermicity of the polymerization. Thus, hyperconjugation of alkyl groups with the C=C lowers Δ*H* for propylene and 1-butene polymerizations. Conjugation of the C=C with substituents such as the benzene ring (styrene and α-methylstyrene), and alkene double bond (butadiene and isoprene), the carbonyl linkage (acrylic acid, methyl acrylate, methyl methacrylate), and the nitrile group (acrylonitrile) similarly leads to stabilization of the monomer and decreases enthalpies of polymerization. When the substituent is poorly conjugating as in vinyl acetate, the Δ*H* is close to the value for ethylene.

The effect of 1,1-disubstitution manifests itself by decreased Δ*H* values [3]. This is a consequence of steric strain in the polymer due to interactions between substituents on alternating carbon atoms of the polymer chain. In **25**, the polymer chain is drawn in the plane of the text with the H and Y substituents placed above and below the plane of the text. The dotted and triangular lines indicate substituents below and above this plane, respectively. Such interactions are referred to as 1,3-interactions and are responsible for the decreased ΔH values in monomers such as isobutylene, α-methyl styrene, methyl methacrylate, and vinyl chloride. The effect in α-methyl styrene is especially significant. The ΔH value of -35 kJ/mole is the smallest heat of polymerization of any monomer. To summarize, the stability of the polymer radical is more important than the stability of the monomer toward addition of a free radical in the propagation reactions.



1,3-Interaction in polymer

25

7.9.2 Ceiling Temperature

The reversibility of vinyl polymerization reactions has been observed which depends on the monomer reactivity and the stability of polymer radical as shown in the following:

$$M_x \cdot + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{(x+1)} \cdot \tag{7.93}$$

where k_{dp} is the depropagation rate constant. Just as radical stability retards propagation, it enhances depropagation. As the polymerization temperature is raised, the depropagation rate increases until a point is reached where the forward and back reactions are equal. The temperature at which this occurs is called the *ceiling temperature* (T_c), and at that temperature ΔG of polymerization is zero, or

Table 7.17 Representative ceiling temperatures, T_c, of pure liquid monomers [3]

Monomer	T_c (°C)
1,3-Butadiene	585
Ethylene	610
Isobutylene	175
Isoprene	466
Methyl methacrylate	198
α-Methyl styrene	66
Styrene	395
Tetrafluoro ethylene	1,100

$$T_c = \frac{\Delta H}{\Delta S} \tag{7.94}$$

It follows that whatever affects ΔH or ΔS for a given monomer (e.g., monomer concentration, pressure) will also affect T_c. Table 7.17 lists ceiling temperatures for several pure liquid monomers.

7.9.3 *Characteristics of ΔS Values of Free Radical Polymerization*

While the ΔH values vary over a wide range for different monomers, the ΔS values are less sensitive to monomer structure, being relatively constant within the range of ~100–120 J/K-mole. The $T\Delta S$ contribution to the ΔG of polymerization will be small and will vary only within a narrow range. Thus, the variation in the $T\Delta S$ term at 50°C for all monomers is in the narrow range of 30–40 kJ/mole. The ΔS of polymerization arises primarily from the loss of the translation entropy of the monomer. Losses in the rotational and vibration entropies of the monomers are essentially balanced by gains in the rotation and vibration entropies of the polymer. Thus, ΔS for polymerization is essentially the translational entropy of the monomer, which is relatively insensitive to the structure of the monomer.

7.10 Molecular Weight Distribution at Low Conversion

The molecular weight of radical chain polymerization is complicated because several possible terminations–disproportions, coupling, and various transfer reactions are involved. Molecular weight changes with % conversion, due to the changes in the concentrations of monomer and catalyst, and the rate constant of propagation and termination.

At low conversion where all of the kinetic parameters $([M], [I], k_d, k_p, k_t)$ are approximately constant. Under these conditions, the polymer molecular weight does not change with conversion. The molecular weight distributions can be derived as did in the step polymerization and are shown in Eqs. 7.95, 7.96, 7.97, 7.98, 7.99, and 7.100 as the number-fraction, number-, and weight-fraction distributions, the number- and weight-average degrees of polymerization, and the breadth of the distribution, respectively.

$$\underline{N}_x = p^{x-1}(1-p) \tag{7.95}$$

$$N_x = N_0(1-p)^2 p^{x-1} \tag{7.96}$$

$$W_x = x(1-p)^2 p^{x-1} \tag{7.97}$$

$$\overline{X}_n = \frac{1}{(1-p)} \tag{7.98}$$

$$\overline{X}_w = \frac{(1+p)}{(1-p)} \tag{7.99}$$

$$\frac{\overline{X}_w}{\overline{X}_n} = 1+p \tag{7.100}$$

Disproportional or chain transfer or a combination of two: one polymer molecule is produced from each kinetic chain. When p is used as the probability to continue propagation, the molecular weight distribution can be shown in the following.

$$p = R_p/(R_p + R_t + R_{\mathrm{tr}}) \tag{7.101}$$

where R_p, R_t, and R_{tr} are the rates of propagation, termination by disproportionation, and chain transfer, respectively. The breadth of the size distribution $\overline{X}_w/\overline{X}_n$ is equal to 2 as p approaches unity. For termination by coupling ($R_{\mathrm{tr}} = 0$ and R_t is the rate of coupling), a polymer arises from the combination of two kinetic chains, the size distribution is narrow.

Consider the probability $\underline{N}_{Y+Z}$ of formation of an x-sized polymer by the coupling of y- and z-sized propagating radicals. $\underline{N}_{Y+Z}$is the product of the probabilities, $\underline{N}_Y$ and $\underline{N}_Z$, of forming the y- and z-sized propagating radicals.

According to Eq. 7.95, $\underline{N}_Y$ and $\underline{N}_Z$ are given in the following:

$$\underline{N}_Y = (1-p)p^{y-1} \tag{7.102}$$

$$\underline{N}_Z = (1-p)p^{z-1} \tag{7.103}$$

$$\because y + z = x$$

$$\therefore \underline{N}_Z = (1-p)p^{x-y-1} \tag{7.104}$$

$$\text{Then} \qquad \underline{N}_{y+Z} = (1-p)^2 p^{x-2} \tag{7.105}$$

Equation 7.105 gives the probability of forming an x-sized polymer molecule by only one of many equally probable pathways. There are (x−1) possible pathways of producing an x-sized polymer molecule when x is an even number. Each of the pathways has the same probability. Therefore, the total probability $\underline{N}_x$ of forming an x-sized polymer molecule is given by

$$\underline{N}_x = (x-1)(1-p)^2 p^{x-2} \tag{7.106}$$

where $\underline{N}_x$is mole or number-fraction distribution.

When x is an odd number there are x pathways

$$\underline{N}_x = x(1-p)^2 p^{x-2} \tag{7.107}$$

For polymerization yielding in high polymer, the difference between x and $(x + 1)$ is negligible and can be ignored. Then, we can have the following relationship:

$$W_x = \frac{1}{2} x(1-p)^3 (x-1) p^{x-2} \tag{7.108}$$

$$\overline{X}_n = 2/(1-p) \tag{7.109}$$

$$\overline{X}_w = (2+p)/(1-p) \tag{7.110}$$

$$\frac{\overline{X}_w}{\overline{X}_n} = (2+p)/2 \tag{7.111}$$

At high conversion, the size distributions become much broader than those described above for low concentration case. Kinetic chain length $\overline{v}$ is defined below:

$$\overline{v} = k_p[M]/2(fk_d k_t[I])^{1/2} \tag{7.56}$$

then,

$$\overline{v} \propto [M]/[I]^{\frac{1}{2}} \tag{7.112}$$

The molecular weight is increased according to Eq. 7.56. Because $[I]$ is decreased faster than $[M]$, then the molecular weight of polymer is increased with % conversion. For polymer having practical usage, we want its PDI as narrow as possible. Sometimes, it is necessary to have multiple addition of initiator, monomer during the polymerization to minimize the molecular weight broadening. For auto-acceleration, the PDI is even larger with a value of 5–10. For chain transfer branch polymer, is also large with a PDI of 20–50, because chain transfer to polymer increases as the polymer size increases.

7.11 Synthesis of Commercial Polymers

The synthesis of some common polymers in the industrial scale is discussed below.

7.11.1 Polyethylene

Radical chain polymerization of ethylene to polyethylene is carried out at high pressures of 120–300 MPa and at temperature above the T_m of polyethylene. Batch processes are not useful since the long residence time gives relatively poor control of product properties. Long-chain branching due to intermolecular chain transfer becomes excessive with deleterious effects on the physical properties. Continuous processes allow better control of the polymerization.

The polyethylene produced by radical polymerization is referred to as *low-density polyethylene* (LDPE) or *high-pressure polyethylene* to distinguish it from the polyethylene synthesized using coordination catalysts. The latter polyethylene is referred to as *high-density polyethylene* (HDPE) or *low-pressure polyethylene*. Low-density polyethylene is more highly branched (both short and long branches) than high-density polyethylene and is therefore lower in crystallinity (40–60 % vs. 70–90 %) and density (0.91–0.93 g cm^{-3} vs. 0.94–0.96 g cm^{-3}).

Low-density polyethylene (LDPE) has a wide range and combination of desirable properties. Its very low T_g of about -120°C and moderately crystallinity and T_m of 105–110°C, give it flexibility and utility over a wide temperature range. Commercial low-density polyethylenes have number-average molecular weights in the range of 20,000–100,000, with $\overline{X}_w/\overline{X}_n$ in the range of 3–20.

Film application accounts for over 60 % of polyethylene consumption. Injection molding of toys, housewares, paint-can lids, and containers accounts for another 10–15 %. About 5 % of the LDPE produced is used as electrical wire and cable insulation. Extrusion coating of paper to produce milk, juice, and other food cartons and multiwall bags accounts for another 10 %. Trade names for polyethylene include *marlex*, *nipolon,* etc.

7.11.2 Polystyrene

Continuous solution polymerization is the most important method for the commercial production of polystyrene although suspension polymerization is also used. Emulsion polymerization is important for the synthesis of copolymer of acrylonitrile butadiene styrene(ABS). Commercial polystyrene (PS) has number-average molecular weights in the range of 50,000–150,000 with $\overline{X}_w/\overline{X}_n$ values of 2–4. Although completely amorphous ($T_g = 85$ °C), its bulky rigid chains (due to phenyl–phenyl interactions) impart good strength with high-dimensional stability (only 1–3 % elongation); PS is a typical rigid plastic. Expandable polystyrene, either crystal polystyrene or styrene copolymers impregnated with a blowing agent, e.g., pentane, is used to produce various foam products such as disposable drinking cap, egg cartons, etc.

7.11.3 Polyvinyl Chloride

Most poly(vinyl chloride) (PVC) is commercially produced by suspension polymerization. A typical polymerization includes 180 parts water, and 100 parts vinyl chloride monomer, chain transfer agent (trichloro ethylene). The reactants are then heated in the closed system to about 50°C, and the pressure rises to about 0.5 MPa. Typical number-average molecular weights for commercial PVC are in the range of 30,000–80,000. Tough and rigid PVC became flexible by using plasticizers (e.g., di-i-octylphthalate, tritolyl phosphate, epoxidized oils). Rigid pipe is used for home and construction, vinyl siding, window frames, rain-gutter, packaging, and gloves.

7.11.4 Polyvinyl Acetate

Polyvinyl acetate (PVAC) $[–CH_2–C(H)(O–CO–CH_3)–]_n$ is synthesized from vinyl acetate monomer via emulsion or solution polymerization. The T_g of PVAC is about 28°C which is not very useful, but widely used in water based paints, adhesives for papers, textiles, and wood. PVAC is also used for producing polyvinylalcohol (PVA) by hydrolysis that is used as thickening agents, coatings, and adhesives.

7.11.5 Polyvinylidene Chloride

Polyvinylidene chloride $(–CH_2–CCl_2–)_n$ and its copolymer with vinyl chloride, acrylonitrile, and acrylates, usually prepared by suspension or emulsion polymerization. They are useful as oil, fat, oxygen and moisture-resistant packaging films (Saran wrap), container, coatings, tank liners, and monofilaments in drapery fabrics and industrial filter cloths.

7.11.6 Acryl Polymer

Poly(methyl methacrylate) (PMMA) can be polymerized by bulk, solution, suspension, and emulsion processes. PMMA is completely amorphous but has high strength and excellent dimensional stability due to the rigid polymer chains ($T_g = 105°C$). Polyacrylates differ considerably from the polymethacrylates. They are softer since the polymer chains are not nearly as rigid [e.g., poly(ethyl acrylate) (PEA), $T_g = -24°C$], due to the absence of the methyl groups on alternating carbons of the polymer chains.

Various rigid PMMA products, such as sheet, rod, and tube, are produced by bulk polymerization in a *casting* process. Polymerization is carried out in stages to allow easier dissipation of heat and control of product dimensions since there is a very large (21 %) volume contraction on polymerization. Partially polymerized monomer like syrup (about 20 % conversion) is produced by heating for about 10 min at 90°C with a peroxide. The syrup is cooled to ambient temperature and poured into a mold, and then the assembly is heated in a water or air bath to progressively higher temperatures. The maximum temperature used is 90 °C, since higher temperatures can lead to bubble formation in the product as the boiling point of methyl methacrylate is 100.5°C. Trade name for acrylate and methacrylate polymer products includes *Acrylite*, *Plexiglas*, *Lucite*, etc.

In commercial production, polyacrylonitrile ($[\text{–C–C(CN)–}]_n$) (PAN) is synthesized by either solution or suspension polymerization. Polyacrylonitrile contains polar group to have high secondary force, so it exhibits good fiber property. PAN is a source of carbon fiber which is produced by cyclization of polymer at 2,000 °C or above.

From the viewpoint of sales volume, all other members of the acrylic family constitute a small fraction of the total. However, many of them are useful specialty products. Polyacrylamide, poly(acrylic acid), and poly(methacrylic acid) and some of their copolymers are used in various applications that take advantage of their solubility in water. Poly(acrylic acid) and poly(methacrylic acid) are used as thickening agents, adhesives, dispersants for inorganic pigments in paints, flocculants, and crosslinked ion-exchange resins.

7.11.7 Fluoropolymers

The fluoropolymers are obtained mainly by suspension polymerization; emulsion polymerization is also practiced. The most important members of this family are poly(tetrafluoro ethylene) (PTFE), poly(chloro trifluoro ethylene) (PCTFE), poly (vinyl fluoride) (PVF), and poly(vinylidene fluoride) (PVDF). High molecular weight PTFE is usually obtained due to lack of chain-transfer reactions and precipitation of growing radicals (leading to greatly decreased termination). Fluoropolymers can withstand a wide variety of chemical environments and are useful at temperatures as low as −200°C and as high as 260°C. The various copolymers of tetrafluoro ethylene and the other fluoropolymers, possessing lower T_m and crystallinity, were developed to overcome the lack of melt processability of PTFE. A true melt processable PTFE has been developed by blending two different molecular weight polymers [8]. They are DuPont Zonyl MP 1000 and Zonyl MP 1,500 J at a specific mixing window of weight ratio of 40/60 and 20/80, respectively. The PVDF exhibits novel piezoelectric properties which are useful for the applications of actuators, artificial arms/legs, and so on.

7.11.8 Cost of Common Polymers

The cost of common polymers depends on the ease of synthesis and raw material cost. Fluoropolymer is usually a high cost polymer compared to other polymers. The cost comparison is in the increasing order of PE ~ PS < phenolic alkyds < PMMA < Nylon < PTFE. The raw materials used for polymer synthesis are derived from petroleum, with the increase in petroleum price and possible depletion someday. Raw materials obtained from renewable source such as plants or biomolecules are currently under intensive development. For instance, polylactic acid can be obtained from bacterial fermentation of corn starch. It is biodegradable and has been used in disposable cups and plates.

7.12 Problems

1. Polymers can be synthesized via free radical polymerization among monomers of ethylene, monosubstituted ethylene, 1,1-disubstituted ethylene. However, polymers are difficult to obtain from 1,2-disubstitute ethylene by free radical polymerization. Please explain.
2. Please show how degree of polymerization depends on temperature in (a) polymerization initiated by thermal decomposition of an initiator, (b) photopolymerization (i.e., without initiator), and (c) without transfer reactions to control molecular weight.
3. Please derive kinetic equations for radical chain polymerization in the presence of an inhibitor such that, essentially, all the chains are terminated by reaction with the inhibitor. Show how the rate of polymerization depends on the concentrations of monomer, initiator, and inhibitor at the steady state.
4. Please write the possible reaction products of two thermal initiators: diacetyl peroxide, di-t-butyl peroxide, respectively.
5. In normal free radical processes with added initiator, the polymerization rate and $\overline{DP}$ are proportional to the first power of monomer concentration. What would be the effect of monomer concentration on $\overline{DP}$ in the thermal polymerization of styrene? Derive a kinetics expression to support your conclusion. (*Reminder*: Initiation involves two monomer molecules.)
6. If equal concentrations of acrylonitrile ($k_p = 1{,}960$ L/mol-s, $k_t = 782 \times 10^{-6}$ L/mol-s) and methyl methacrylate ($k_p = 515$ L/mol-s, $k_t = 25.5 \times 10^{-6}$ L/mol-s) were each polymerized at 60°C with equal concentrations of the same initiators, which polymer would have the higher $\overline{DP}$ and by how much? Assume polyacrylonitrile undergoes termination only by radical combination and PMMA by disproportionation. Which polymer would have the higher $\bar{M}_n$, and by how much?
7. A certain monomer is polymerized by benzoyl peroxide labeled in the benzene ring with carbon-14. (a) Analysis by carbon counting shows that the polymer

contains an average of 1.27 labeled phenyl groups per molecule. Assuming no chain transfer occurred, what does this indicate about the mechanism of termination? (b) Vigorous basic hydrolysis removed 60 % of the carbon-14. What does this indicate about the mechanism of initiation?

8. Predict the order of polymer molecular weight obtainable (highest to lowest) by the free radical solution polymerization of styrene in benzene, toluene, ethyl benzene, t-butyl benzene, and isopropyl benzene.
9. Poly(vinyl acetate) of number-average molecular weight 100,000 is hydrolyzed to poly(vinyl alcohol). Oxidation of the latter with periodic acid to cleave 1,2-diol linkages yield a poly(vinyl alcohol) with degree of polymerization of 200. Calculate the percentages of head-to-tail and head-to-head linkages in the poly(vinyl acetate).
10. The living character of living radical polymerization is limited under certain conditions, such as high monomer conversion, high initiator concentration, and high targeted molecular weight(>100,000). Please explain why these conditions result in broadening of PDI and some difficulties in producing block copolymers with well-defined block lengths of the different monomers.

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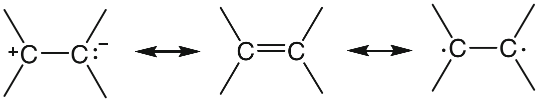
Chapter 8
Ionic Chain Polymerization

The carbon–carbon double bond can be polymerized either by free radical or ionic methods. The difference arises because the π-bond of a vinyl monomer can respond appropriately to the initiator species by either homolytic or heterolytic bond breakage as shown in Eq. 8.1.



(8.1)

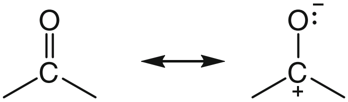
Although radical, cationic, and anionic initiators are used in chain polymerizations, they cannot be used indiscriminately, since all three types of initiation do not work for all monomers. Monomers show varying degrees of selectivity with regard to the type of reactive center that will cause their polymerization. Most monomers will undergo polymerization with a radical initiator, although at varying rates. However, monomers show high selectivity toward ionic initiators [1]. Some monomers may not polymerize with cationic initiators, while others may not polymerize with anionic initiators. The coordination polymerization requires coordination catalyst to synthesize polymers. It has been used extensively to polymerize high performance polyolefin but seldom used in the polymerization of polar monomer [2]. The detailed mechanisms of coordination polymerization will be discussed in Chap. 9. The various behaviors of monomers toward polymerization can be seen in Table 8.1. The types of initiation that bring about the polymerization of various monomers to high-molecular-weight polymer are indicated. Thus, although the polymerization of all monomers in Table 8.1 is thermodynamically feasible, kinetic feasibility is achieved in many cases only with a specific type of initiation.

The carbon–carbon double bond in vinyl monomers and the carbon–oxygen double bond in aldehydes and ketones are the two main types of linkages that undergo chain polymerization. The polymerization of the carbon–carbon double bond is by far the more important of the two types of monomers. The carbonyl group is not prone to polymerization by radical initiators because of its polarized nature:

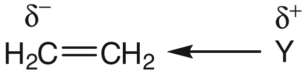
W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_8,

Table 8.1 Types of chain polymerization suitable for unsaturated monomers [3]

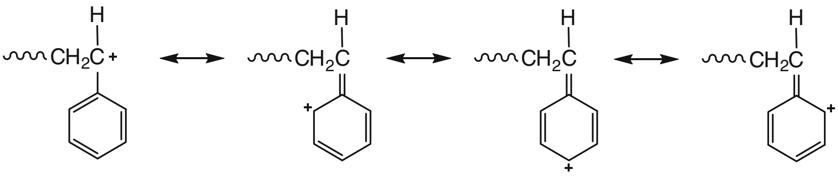
Monomer type	Radical	Cationic	Anionic	Coordination
Ethylene	+	–	–	+
1-Alkyl olefins (α-olefins)	–	–	–	+
1,1-Dialkyl olefins	–	+	–	+
1,3-Dienes	+	+	+	+
Styrene, α-methyl styrene	+	+	+	+
Halogenated olefins	+	–	–	–
Vinyl ethers	–	+	–	–
Vinyl esters	+	–	–	–
Acrylic and methacrylic esters	+	–	+	–
Acrylonitrile and methacrylonitrile	+	–	+	–
N-Vinyl carbazole	+	+	–	–
N-Vinyl pyrrolidone	+	+	–	–
Aldehydes, ketones	–	+	+	–


(8.2)

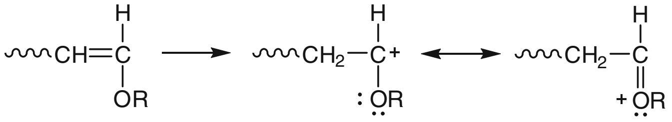
The type of substitute (Y) on the C=C double bond of monomer determines the ease of what kind of chain polymerization. If Y is an electron donating group, the electron density on the C=C double bond is shown as below:


$$\overset{\delta^-}{H_2C}{=}CH_2 \longleftarrow \overset{\delta^+}{Y}$$

The alkoxy substituent allows a delocalization of the positive charge. If the substituent was not present, the positive charge would be localized on the single α-carbon atom. The presence of the alkoxy group leads to stabilization of the carbocation by delocalization of the positive charge over two atoms—the carbon and the oxygen. Similar delocalization effects occur with phenyl, vinyl, and alkyl substituents, for example, for styrene polymerization:


(8.3)

Certain vinyl compounds are best polymerized via cationic rather than free-radical intermediates. For instance,



$$\sim\!\sim\mathrm{CH}{=}\underset{\mathrm{OR}}{\overset{\mathrm{H}}{\mathrm{C}}} \longrightarrow \sim\!\sim\mathrm{CH_2}{-}\underset{:\underset{\cdot\cdot}{\mathrm{O}}\mathrm{R}}{\overset{\mathrm{H}}{\mathrm{C}^{+}}} \longleftrightarrow \sim\!\sim\mathrm{CH_2}{-}\underset{+\underset{\cdot\cdot}{\mathrm{O}}\mathrm{R}}{\overset{\mathrm{H}}{\mathrm{C}}} \qquad (8.4)$$

The most common commercial cationic polymerization is the polymerization of isobutylene ($CH_3{-}C(CH_3){=}CH_2$) which can be polymerized with Friedel–Crafts catalysts in a reaction that involves tertiary carbocation intermediates. The reaction is sensitive to temperature, solvent, nucleophile impurities that are discussed later.

8.1 Characteristics of Ionic Chain Polymerization

Ionic polymerizations are highly selective. The cationic polymerization will undergo cationic intermediate as shown below:

$$\mathrm{C{=}CX} \xrightarrow{\text{cationic}} \mathrm{C{-}CX}^{\oplus} \xrightarrow{\mathrm{C=CX}} \mathrm{C{-}CX{-}C{-}CX}^{\oplus} \longrightarrow \left(\!-\mathrm{C{-}CX}-\!\right)_n$$

The X has to be an electron donating group such as alkoxy, phenyl, vinyl, 1,1-dialkyl, and so on to stabilize the cationic intermediate. The anionic polymerization will undergo anionic intermediate as shown below:

$$\mathrm{C{=}CY} \xrightarrow{\text{anionic}} \mathrm{C{-}CY}^{\ominus} \xrightarrow{\mathrm{C=CY}} \mathrm{C{-}CY{-}C{-}CY}^{\ominus} \longrightarrow \left(\!-\mathrm{C{-}CY}-\!\right)_n$$

The Y has to be an electron withdrawing group such as –CN, CO, phenyl, vinyl, and so on to stabilize the anionic intermediate.

Thus the selectivity of ionic polymerization is due to the very strict requirements for stabilization of anionic and cationic propagating species. The commercial utilization of cationic and anionic polymerizations is rather limited because of this high selectivity of ionic polymerizations compared to radical polymerizations.

Ionic polymerizations, especially cationic polymerizations, are not as well understood as radical polymerization because of experimental difficulties involved in their study. The nature of the reaction media in ionic polymerizations is often not clear since heterogeneous inorganic initiators are often involved. Further, it is extremely difficult in most instances to obtain reproducible kinetic data because ionic polymerizations proceed at very rapid rates and are extremely sensitive to the presence of small concentrations of impurities and other ionic reactive species. The rates of ionic polymerizations are usually faster than those of radical polymerizations. These comments generally apply more to cationic than anionic polymerizations. Anionic systems are more reproducible because the reaction components are better defined and more easily purified.

Table 8.2 Commercially important polymers prepared by ionic polymerization [4]

Polymer or copolymer	Major uses
Cationic[a]	
Polyisobutylene and polybutenes[b] (low and high molecular weight)	Adhesives, sealants, insulating oils, lubricating oil and grease additives, moisture barriers
Isobutylene-isoprene copolymer[c] ("butyl rubber")	Inner tubes, engine mounts and springs, chemical tank linings, protective clothing, hoses, gaskets, electrical insulation
Isobutylene-cyclopentadiene copolymer	Ozone-resistant rubber
Hydrocarbon[d] and polyterpene resins	Inks, varnishes, paints, adhesives, sealants
Coumarone-indene resins[e] and poly (vinyl ether)s	Flooring, coatings, adhesives, polymer modifiers, tackifiers, adhesives
Anionic[f]	
cis-1,4-Polybutadiene	Tires
cis-1,4-Polyisoprene	Tires, footwear, adhesives, coated fabrics
Styrene-butadiene rubber(SBR)[g]	Tire treads, belting, hoses, shoe soles, flooring, coated fabrics
Styrene-butadiene block and star copolymers	Flooring, shoe soles, artificial leather, wire, and cable insulation
ABA block copolymers (A = styrene, B = butadiene or isoprene)	Thermoplastic elastomers
Polycyanoacrylate[h]	Adhesives

[a] $AlCl_3$ and BF_3 most frequently used coinitators

[b] "Polybutenes" are copolymers based on C_4 alkenes and lesser amounts of propylene and C_5 and higher alkenes from refinery streams

[c] Terpolymers of isobutylene, isoprene, and divinylbenzene are also used in sealant and adhesive formulations

[d] Aliphatic and aromatic refinery products

[e] Coumarone (benzofuran) and indene (benzocyclopentadiene) are products of coal tar

[f] n-Butyllithium most common initator

[g] Contains higher cis content than SBR prepared by free radical polymerization

[h] Monomer polymerized by trace amount of water

Cationic and anionic polymerizations have many similar characteristics. The formation of ions with sufficiently long lifetimes for propagation to yield high-molecular-weight products generally requires stabilization of the propagating centers by solvation. Relatively low or moderate temperatures are also needed to suppress termination, transfer, and other chain-breaking reactions which destroy propagating centers.

Although solvents of high polarity are desirable to solvate the ions, they cannot be employed for several reasons. The highly polar hydroxylic solvents (water, alcohols) react with and destroy most ionic initiators. Other polar solvents such as ketones prevent initiation of polymerization by forming highly stable complexes with the initiators. Ionic polymerizations are, therefore, usually carried out in solvents of low or moderate polarity. Table 8.2 summarizes some commercially important polymers prepared by ionic polymerization and their major usages. It is interesting to note that most products are rubber-based polymers which were established during the World War II period in search of man-made rubber.

8.2 Cationic Polymerization

In cationic chain polymerization, the propagating species is a carbocation. Initiation is brought about by addition of an electrophile to a monomer molecule as shown in Eq. 8.5.

$$E^+ + H_2C = CR_2 \rightarrow E - CH_2 - CR_2^+ \tag{8.5}$$

8.2.1 Initiators of Cationic Polymerization

Compounds used most frequently to initiate cationic polymerization are mineral acids, particularly H_2SO_4 and H_3PO_4, and Lewis acids such as: $AlCl_3$, BF_3, $TiCl_4$, and $SnCl_4$. Lewis acids need the presence of trace amounts of water (proton or cation source) which form the electrophilic species to initiate polymerization. Examples are the reactions of BF_3 with water (Eq. 8.6) and aluminum chloride with an alky chloride (Eq. 8.7). Water is called *initiator*, and the Lewis acid is called *coinitiator*. They form an *initiating system*. With certain very active Lewis acids, *autoionization* (Eq. 8.8) may occur.

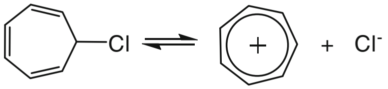
$$BF_3 + H_2O \rightleftharpoons HOBF_3^- H^+ \tag{8.6}$$

$$AlCl_3 + RCl \rightleftharpoons AlCl_4^- R^+ \tag{8.7}$$

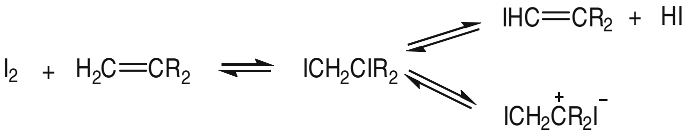
$$2AlBr_3 \rightleftharpoons AlBr_4^- AlBr_2^+ \tag{8.8}$$

Other cationic initiators can be obtained from compounds that can easily form cations as shown in the following:

$$(C_6H_5)_3CCl \rightleftharpoons (C_6H_5)_3C^+ + Cl^- \tag{8.9}$$



(8.10)



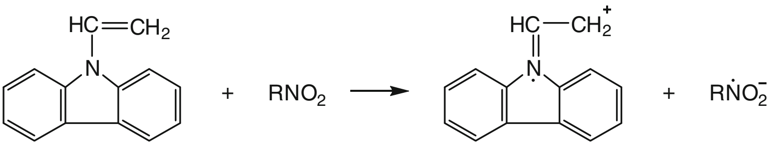
(8.11)

(8.12)

$$I_2 + H_2C{=}CR_2 \rightleftharpoons ICH_2CIR_2 \rightleftharpoons IHC{=}CR_2 + HI \tag{8.11}$$

$$ICH_2CIR_2 \rightleftharpoons ICH_2\overset{+}{C}R_2I^- \tag{8.12}$$

$$\mathrm{M} + \mathrm{A} \longrightarrow \mathrm{M}^{+\bullet} + \mathrm{A}^{-\bullet} \tag{8.13}$$



(8.14)

Cations can also be formed by photo initiation. Aryldiazonium salt ($ArN_2{}^+Z^-$), diaryliodonium salt ($Ar_2{}^+IZ^-$), and triarylsulfonium salt ($Ar_2S^+Z^-$) are effective photoinitiators of cationic polymerization, where Z^- is a nonnucleophilic and photostable anion such as tetrafluoroborate ($BF_4{}^-$), hexafluoroantimonate ($SbF_6{}^-$), and tetraperfluorophenylborate [$(C_6F_5)_4B^-$], and hexafluorophosphate ($PF_6{}^-$). Diaryliodonium and triarylsulfonium salts act as photoinitiators of cationic polymerization. Photolytic cleavage of an Ar–I or Ar–S bond yields a radical—cation (Eq. 8.15) that reacts with HY to yield an initiator–coinitiator complex that acts as a proton donor to initiate cationic polymerization. HY may be solvent or some other deliberately added substance such as an alcohol with labile hydrogen. Overall, the process is a photolytically induced redox reaction between the cation–radical and HY. These initiators have been used in deep UV photo-resist applications.

$$\mathrm{Ar_2l^+(PF_6)^-} \xrightarrow{\mathrm{h}\upsilon} \mathrm{Arl^+\cdot\ (PF_6)^-} + \cdot\,\mathrm{Ar} \xrightarrow{\mathrm{HY}} \mathrm{Arl} + \mathrm{Y^-} + \mathrm{H^+(PF_6)^-} \tag{8.15}$$

$$\mathrm{Ar_3S^+(SbF_6)^-} \xrightarrow{\mathrm{h}\upsilon} \mathrm{Ar_3S^+\cdot (SbF_6)^-} + \cdot\,\mathrm{Ar} \xrightarrow{\mathrm{HY}} \mathrm{Ar_3S^+Y^-} + \mathrm{H^+(SbF_6)^-} \tag{8.16}$$

Not all initiating systems are equally effective. Relatively stable carbocations of the triphenylmethyl or tropylium type are only useful with very reactive monomers such as vinyl ethers. Mineral acid initiators seldom lead to very high molecular weight polymers.

8.2.2 Reaction Mechanisms of Cationic Polymerization

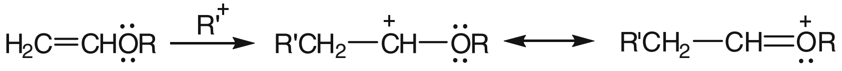
The cationic polymerization is a chain polymerization that involves three steps: (1) initiation, (2) propagation, and (3) termination. The feasibility of polymerization depends on the ease of cation formation from monomer. The reaction can occur with the addition of the electrophile (carbocation) to monomer and form more stable intermediate. The rate of addition to aliphatic monomers is of the order of

$$(CH_3)_2C = CH_2 > CH_3CH = CH_2 > CH_2 = CH_2$$

Only isobutylene provides the requisite carbocation stability for cationic polymerization. For a series of para-substituted styrene, the reactivity for substituent groups in cationic initiation is of the order of ring activation as

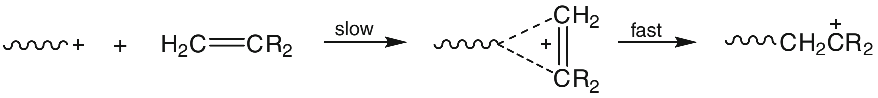
$$OCH_3 > CH_3 > H > Cl$$

Ortho substituents retard the addition regardless of whether they are activating or deactivating. Vinyl ethers are particularly reactive toward cationic initiators because the unshared electron of oxygen can participate in the resonance stabilized intermediate structure as in the following:



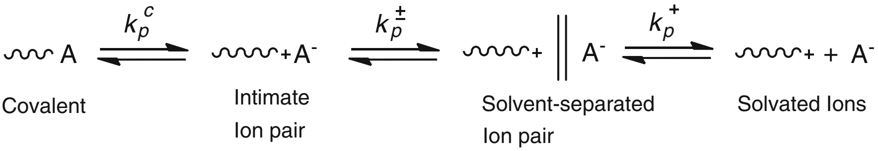
$$H_2C{=}CH\underset{..}{\ddot{O}}R \xrightarrow{R'^{+}} R'CH_2{-}\overset{+}{C}H{-}\underset{..}{\ddot{O}}R \longleftrightarrow R'CH_2{-}CH{=}\underset{..}{\overset{+}{O}}R \tag{8.17}$$

The cationic polymerization is favored by increasing carbocation stability. The reaction mechanisms may involve two steps—a rate-limiting formation of a pi complex between the chain end and an approaching monomer molecule, followed by covalent bond formation (Eq. 8.18). In free radical polymerization, the covalent bond formation is a rate limiting step.



(8.18)

The solvent effects on the rate of cationic polymerization are more complicated than the free radical polymerization. Due to the formation of ionic species in the initiation step, one can expect that the polar solvent favors the initiation step. The opposite is expected in propagation because the charge is dispersed in the transition state. Another complicating factor is the degree of association between the cationic chain end and the anion (A^-). Between the extremes of pure covalent bonds and solvated ions are intimate ion pairs and solvent-separated ion pairs as the following:



(8.19)

By increasing the solvent polarity of poor solvent, the propagating rate for poor solvents are increased by shifting the equilibrium away from intimate ion pairs to have more free ions. As the solvating power of the solvent increases, the shift will be in the opposite direction and propagation is retarded and cation is no longer labile. The cation is fully solvated by polar solvent.

Table 8.3 Effect of solvent on cationic polymerization of *p*-methoxystyrene by iodine at 30 °C [5]

Solvent	k_p (L/mol-s)
CH_2Cl_2	17
CH_2Cl_2/CCl_4, 3/1	1.8
CH_2Cl_2/CCl_4, 1/1	0.31
CCl_4	0.12

Polymerization rates and polymer molecular weights increase with increasing solvent polarity because there is a shift in concentrations from the unreactive (dormant) covalent species toward the ion pairs and free ions. For the perchloric acid polymerization of styrene, there is an increase in overall reaction rate by about three orders of magnitude when polymerization is carried out in 1,2-dichloroethane ($\varepsilon = 9.72$) as compared with carbon tetrachloride ($\varepsilon = 2.24$). Table 8.3 shows data for the polymerization of *p*-methoxystyrene by iodine in different solvents. The apparent propagation rate constant increases by more than two orders of magnitude by changing the solvent from nonpolar carbon tetrachloride ($\varepsilon = 2.24$) to polar methylene chloride ($\varepsilon = 9.08$).

The initiator ion pair (consisting of the carbocation and its negative counterion) produced in the initiation step proceeds to propagate by successive additions of monomer molecules as shown in Eq. 8.20.

$$\mathrm{HMn^+(IZ)^-} + \mathrm{M} \xrightarrow{k_p} \mathrm{HMnM^+(IZ)^-} \tag{8.20}$$

where propagation rate constant: $k_p = k_p^+ + k_p^c + k_p^\pm$ decreases with increasing solvent polarity, and solvent stabilizes the reactant more than the transition state. The $k_p^\pm$ increases with increasing solvent polarity when the transition state has a higher dipole moment than ion pair. However, the $k_p^\pm$ decreases with increasing solvent polarity when the transition has a lower dipole moment than ion pair. The k_p^c is the rate constant for propagation by covalent species. The k_p^c has the opposite effect as $k_p^\pm$ since the transition state involves the development of charged center from neutral reactants such as styrene polymerized by CH_3SO_3H, CF_3SO_3H, CH_3COOH. Table 8.4 summarizes the solvent effect on cationic polymerization by using the polar solvent in the first row and nonpolar solvent in the second row as the starting discussion point. The polarity of solvent is varied from solvent type by either increasing the polarity of the polar solvent or nonpolar solvent. The effect is quite different between polar solvent and nonpolar solvent.

Table 8.5 summarizes the solvent effect on the radiation cationic polymerization of isopropyl vinyl ether at 30 °C. When a nonpolar solvent benzene is used in the polymerization, the k_p^+ is decreased as compared with bulk polymerization of isopropyl vinyl ether. It is interesting to note that the k_p^+ is further decreased using polar solvent. The results clearly indicate that the transition state has a higher dipole moment than the reactants.

Table 8.4 Summary of solvent effect on cationic polymerization

Solvent	k_p^+	k_p^c	$k_p^\pm$
Polar	Decrease	Decrease for high dipole moment transition state	Increase for high dipole moment transition state
Nonpolar	Increase	Increase	Decrease

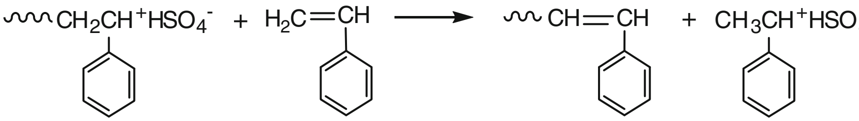
Table 8.5 Effect of solvent on k_p^+ in radiation polymerization of isopropyl vinyl ether at 30 °C [5]

Solvent	ε	k_p^+(L/mol-s)
Benzene	2.7	57
None	3.0	130
$(C_2H_5)_2O$	3.7	34
CH_2Cl_2	6.0	1.5
CH_3NO_2	19.5	0.02

The need for solvation of ionic propagating species in cationic polymerization has been demonstrated in the reactions carried out in low dielectric constant media. In addition to lowering the polymerization rates in poor solvating media, one frequently encounters increased kinetic order in one of the reactants (monomer, initiator or coinitiator). The polymerization rate may show an increased order of dependence on the monomer, initiator, or coinitiator. For example, the polymerization of styrene by tin (IV) chloride initiator, its rate of polymerization depends on $[M]^2$ in benzene solution and $[M]^3$ in carbon tetrachloride solution. Carbon tetrachloride is a poor solvating agent compared to benzene, and the higher order in styrene concentration is due to styrene taking part in solvation of propagating species. At high concentrations of styrene or in neat styrene, the order in styrene decreases to two as the reaction medium becomes equivalent to the benzene system. The polymerization of styrene by trichloroacetic acid illustrates the situation where the initiator solvates ionic propagating species. The kinetic order in the concentration of trichloroacetic acid increases from one in the highly polar nitroethane to two in the less polar 1,2-dichloroethane, to three in neat styrene.

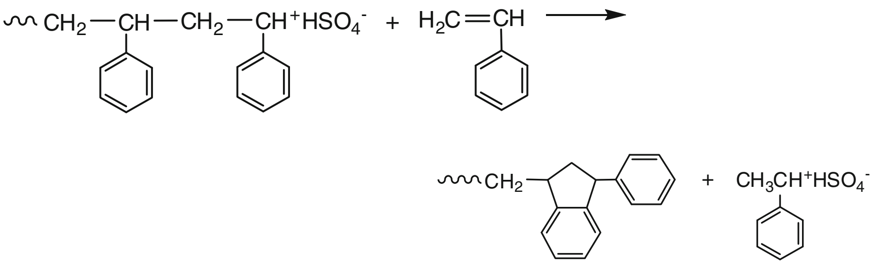
Chain transfer reactions are common in cationic polymerization. For example, in the polymerization of styrene with sulfuric acid, possible chain transfer reactions include:

1. With monomer:



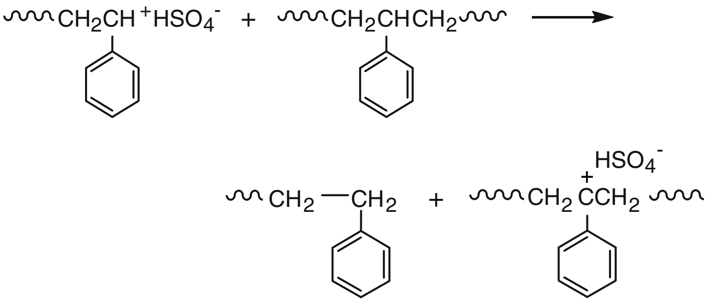
(8.21)

2. By ring alkylation:



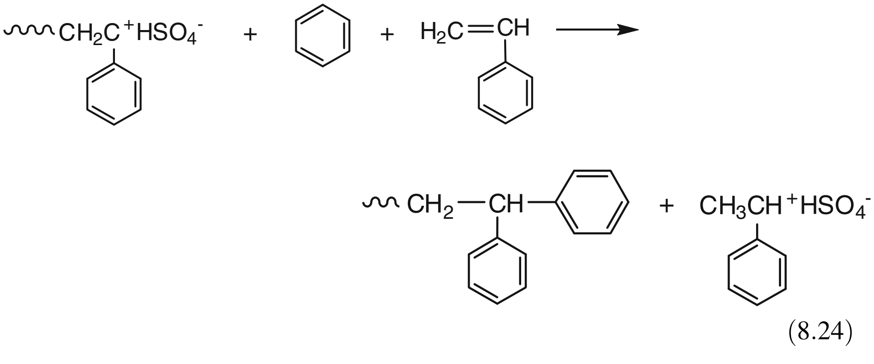
(8.22)

3. By hydride abstraction from the chain to form a more stable ion:



(8.23)

4. With solvent, for example, with benzene by electrophilic substitution:

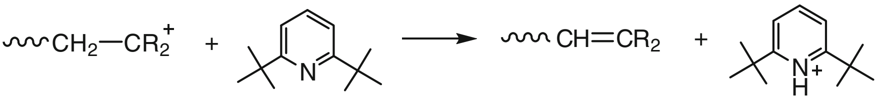


(8.24)

Chain branching occurs via reaction (Eq. 8.23) or by intermolecular ring alkylation (Eq. 8.24).

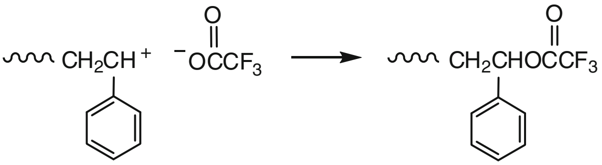
Chain transfer to monomer is so common in cationic polymerizationthat it is necessary to reduce the reaction by adding *proton trap*, such as 2,6-di-*t*-

butylpyridine, which intercepts the proton before it transfers to monomer (Eq. 8.25). The result is a lower overall yield but higher molecular weight and lower polydispersity index. The bulky *t*-butyl groups prevent reaction with electrophiles larger than the proton.

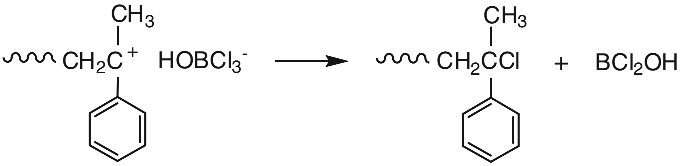


(8.25)

Termination reactions resulting from the combination of chain end with counterion (i.e., a change from ionic to covalent bonding) are observed in the polymerization of styrene, as in the trifluoroacetic acid initiated polymerization (Eq. 8.26), and chain end chlorination in the BCl_3/H_2O initiated polymerization (Eq. 8.27)

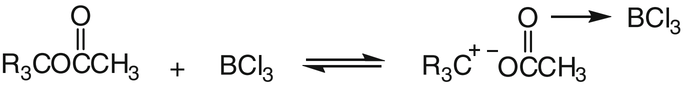


(8.26)

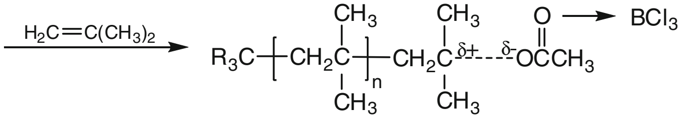


(8.27)

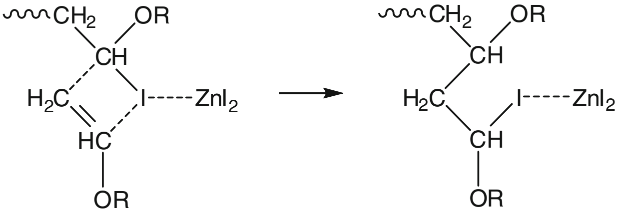
Living cationic polymerization is possible. Polymerization of isobutylene with a tertiary ester and BCl_3, for example, involves formation of a tertiary carbocation initiating species (Eq. 8.28) and polymerization (Eq. 8.29) to yield polyisobutylene terminated with a very tightly bound but still active ion pair. A similar situation occurs when I_2/HI or I_2/ZnI_2 is used as the initiating system. In this case, the mechanism of propagation apparently involves insertion of vinyl ether into an activated carbon iodine bond (Eq. 8.30).



$$R_3CO\overset{\overset{O}{\|}}{C}CH_3 + BCl_3 \rightleftharpoons R_3C^{+}\ {}^{-}O\overset{\overset{O \longrightarrow BCl_3}{\|}}{C}CH_3 \tag{8.28}$$



$$\xrightarrow{H_2C{=}C(CH_3)_2} R_3C\left[CH_2\overset{CH_3}{\underset{CH_3}{C}}\right]_n CH_2\overset{CH_3}{\underset{CH_3}{C}}{}^{\delta+}\text{---}{}^{\delta-}O\overset{\overset{O \longrightarrow BCl_3}{\|}}{C}CH_3 \tag{8.29}$$



(8.30)

8.2.3 Kinetics of Cationic Polymerization

The initiation process of cationic polymerization can be generalized as

$$\mathrm{I} + \mathrm{ZY} \overset{K}{\rightleftharpoons} \mathrm{Y}^+(\mathrm{IZ})^- \tag{8.31}$$

$$\mathrm{Y}^+(\mathrm{IZ})^- + \mathrm{M} \xrightarrow{k_i} \mathrm{YM}^+(\mathrm{IZ})^- \tag{8.32}$$

The propagation reaction is expressed in the following:

$$\mathrm{YM}^+(\mathrm{IZ})^- + \mathrm{M} \xrightarrow{k_p} \mathrm{YMM}^+(\mathrm{IZ})^- \tag{8.33}$$

Termination occurs due to a combination of the propagating center with the counterion.

$$\mathrm{YM}^+(\mathrm{IZ})^- \xrightarrow{k_t} \mathrm{YMIZ} \tag{8.34}$$

The overall kinetics depends on the mode of termination in a particular system. If the termination is exclusively due to the combination of propagating center with counterion, one can follow the rate expression used in the radical polymerization basis on the steady-state conditions. The rates of initiation, propagation, and termination are given by

$$R_i = Kk_i[\mathrm{I}][\mathrm{ZY}][\mathrm{M}] \tag{8.35}$$

$$R_p = k_p[\mathrm{YM}^+(\mathrm{IZ})^-][\mathrm{M}] \tag{8.36}$$

$$R_t = k_t[\mathrm{YM}^+(\mathrm{IZ})^-] \tag{8.37}$$

At steady state $R_i = R_t$, then

$$[\mathrm{YM}^+(\mathrm{IZ})^-] = \frac{Kk_i[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]}{k_t} \tag{8.38}$$

Combining Eq. 8.36 and Eq. 8.38 yields the rate of polymerization as

$$R_p = \frac{R_i k_p[\mathrm{M}]}{k_t} = \frac{Kk_i k_p[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]^2}{k_t} \tag{8.39}$$

The number-average degree of polymerization is obtained as the propagation rate divided by the termination rate:

$$\bar{X}_n = \frac{R_p}{R_t} = \frac{k_p[M]}{k_t} \tag{8.40}$$

Similar to radical polymerization, chain transfer reactions are also involved in cationic polymerization such as chain transfer to monomer, spontaneous termination, and chain transfer to chain transfer agent S. In addition to combination with the counterion, if there are chain transfer reactions present, the concentration of the propagating species remains unchanged, and the polymerization rate is again given by Eq. 8.39. However, the degree of polymerization is decreased by these chain transfer reactions and is given by the polymerization rate divided by the sum of all chain transfer reactions:

$$\bar{X}_n = \frac{R_p}{R_t + R_{ts} + R_{tr,\mathrm{M}} + R_{tr,\mathrm{S}}} \tag{8.41}$$

The rate of spontaneous termination (R_{ts}) and the two transfer reactions ($R_{tr,\mathrm{M}}$ and $R_{tr,\mathrm{S}}$) are given by

$$R_{ts} = k_{ts}[\mathrm{YM}^+(\mathrm{IZ})^-] \tag{8.42}$$

$$R_{tr,\mathrm{M}} = k_{tr,\mathrm{M}}[\mathrm{YM}^+(\mathrm{IZ})^-][\mathrm{M}] \tag{8.43}$$

$$R_{tr,\mathrm{S}} = k_{tr,\mathrm{S}}[\mathrm{YM}^+(\mathrm{IZ})^-][\mathrm{S}] \tag{8.44}$$

Combining Eq. 8.41 with Eqs. 8.36, 8.37, 8.42 to 8.44 yields

$$\bar{X}_n = \frac{k_p[\mathrm{M}]}{k_t + k_{ts} + k_{tr,\mathrm{M}}[\mathrm{M}] + k_{tr,\mathrm{S}}[\mathrm{S}]} \tag{8.45}$$

or

$$\frac{1}{\bar{X}_n} = \frac{k_t}{k_p[\mathrm{M}]} + \frac{k_{ts}}{k_p[\mathrm{M}]} + \mathrm{C_M} + \mathrm{C_S}\frac{[\mathrm{S}]}{[\mathrm{M}]} \tag{8.46}$$

where C_M and C_S are the chain-transfer constants for monomer and chain-transfer agent S, which are defined by $k_{tr,\mathrm{M}}/k_p$ and $k_{tr,\mathrm{S}}/k_p$ respectively. Equation 8.46 is the same as the Mayo Equation for radical polymerization.

When chain transfer to S terminates the kinetic chain, the polymerization rate is decreased and is given by

$$R_p = \frac{Kk_i k_p[\mathrm{I}][\mathrm{ZY}][\mathrm{M}]^2}{k_t + k_{tr,\mathrm{S}}[\mathrm{S}]} \tag{8.47}$$

The above rate expressions are derived on the basis of R_i is a rate determination step as shown in Eq. 8.32. If Eq. 8.31 is the rate determination step, then R_i is independent of monomer concentration and is expressed by

$$R_i = k_1[\mathrm{I}][\mathrm{ZY}] \tag{8.48}$$

The polymerization rate expressions (Eq. 8.39) will then be modified by replacing Kk_i *with* k_1, and there will be one order lower dependence of R_p on [M]. The degree of polymerization is unchanged and still described by Eq. 8.45.

The expressions for R_p in cationic polymerization (Eq. 8.39) point out a very significant difference between cationic polymerization and radical polymerization. Radical polymerization shows a half-order dependence of R_p on R_i, while cationic polymerizations show a first-order dependence of R_p on R_i. The difference is a consequence of their different modes of termination. Termination is second order in the propagating species in radical polymerization but only first order in cationic polymerization.

In the absence of any chain transfer, the kinetic chain length $\bar{v}$, is equal to $\overline{DP}$ and is expressed as

$$\bar{v} = \overline{DP} = \frac{R_p}{R_t} = \frac{k_p[\mathrm{M}][\mathrm{M}^+]}{k_t[\mathrm{M}^+]} = \frac{k_p[\mathrm{M}]}{k_t}$$

If the chain transfer is the predominant mechanism for controlling chain growth, then

$$\bar{v} = \overline{DP} = \frac{R_p}{R_{tr}} = \frac{k_p[\mathrm{M}][\mathrm{M}^+]}{k_{tr}[\mathrm{M}][\mathrm{M}^+]} = \frac{k_p}{k_{tr}}$$

The molecular weight of cationic polymerization is independent of initiator concentration, unlike free radical polymerization, where $\overline{DP}$ is inversely proportional to $[\mathrm{I}]^{1/2}$ in the absence of chain transfer. The difference arises from radical disproportionation and combination reactions characteristic of free radical termination. By increasing initiator concentration, the probability of radical termination is increased, which is not the case in ionic polymerization.

Table 8.6 summarizes kinetic parameters of different monomers that undergo cationic polymerization. A comparison of the k_p^+ and $k_p^\pm$ values for the styrene, *p*-methoxystyrene, and *N*-vinyl carbazole polymerizations shows the free ion propagation rate to be an order of magnitude higher than the ion pair propagation rate constant. The results indicate that the presence of counterion in the ion pair reduces the effective frequency factor in the cationic polymerization. Although there are relatively few reliable data of k_p^+ and $k_p^\pm$ in other systems, it is generally agreed that the reactivity of free ions is no more than a factor of 5–20 greater than the reactivity of ion pairs. The counterion is typically quite large for cationic polymerization (e.g., $\mathrm{SbCl_6^-}$, $\mathrm{CF_3SO_3^-}$). The ion pair is a very loose ion pair, so the availability of the positive charge center for reaction has not much difference as compared to the free ion.

Table 8.6 Comparison of polymerization kinetic parameters of some monomers [5]

Parameter	Styrene	*i*-Butyl vinyl ether	*p*-Methoxy styrene	*N*-Vinyl carbazole
[Styrene], M	0.27–0.40	–	–	
[CF_3SO_3H], M	3.8–7.1 × 10^{-3}	–	–	
[$\phi_3C^+SbCl_6$], M	–	6.0 × 10^{-5}	–	
k_i, L/mol-s	10–23	5.4		
k_d, mol/L	4.2 × 10^{-7}	–		
k_p^+, L/mol-s	1.2 × 10^6	7.0 × 10^3	3.6 × 10^5	6.0 × 10^5
$k_p^{\pm}$, L/mol-s	1.0 × 10^5	–	4.1 × 10^4	5.0 × 10^4
$k_{ts} + k_t$, s^{-1}	170–280	0.2	–	–
$k_{tr,\,M}$, L/mol-s	1–4 × 10^3	1.9 × 10^2	–	–

A comparison of Table 8.6 with corresponding data for radical chain polymerization as shown in Table 8.7 allows us to understand why cationic polymerizations are generally faster than radical polymerizations. The propagation rate constants in cationic polymerization are similar to or greater than those for radical polymerization. However, the termination rate constants are considerably lower in cationic polymerization. The polymerization rate is determined by the ratio of rate constants k_p/k_t in cationic polymerization and $\left(k_p/k_t\right)^{1/2}$ in radical polymerization. The former ratio is larger than the latter by up to four orders of magnitude depending on the monomers being compared. Cationic polymerization is further favored, since the concentration of propagating species is usually much higher than in a radical polymerization. The concentration of propagating species of radical polymerization is typically 10^{-7}–10^{-9} M, much lower than that in cationic polymerization.

Consider the situation where one polymer molecule is produced from each kinetic chain. This is the case for termination by disproportionation or chain transfer or a combination of the two, but without combination. The molecular weight distribution is similar to the linear step polymerization as shown in Eq. 8.49. One difference in the use of the equation for radical chain polymerizations compared to step polymerization is the redefinition of p as the probability that a propagating radical will continue to propagate instead of terminating. The value of p is given as the rate of propagation divided by the sum of the rates of all reactions that a propagating radical may undergo (Eq. 8.50).

$$\bar{X}_w/\bar{X}_n = (1 + p) \tag{8.49}$$

$$p = R_p/\left(R_p + R_i + R_{tr}\right) \tag{8.50}$$

For the cationic polymerization, the PDI can be determined by Eq. 8.49. It has a limit of 2 (at low conversion). For rapid initiation, PDI will be narrow. For very slow termination and transfer reaction, PDI will be close to 1. The existence of chain transfer reactions, PDI will be between 1 and 2, mostly larger than 2

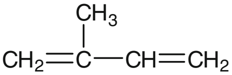
Table 8.7 Comparison of rate constants of cationic polymerization and free radical polymerization

Rate constant	Cationic	Free radical
k_t	Low	High
k_p	High	Low
R_p	k_p/k_t high	$(k_p/k_t)^{1/2}$ low

depending on the chain transfer reactions and their rates relative to propagation. At high conversion, the concentration of propagating centers, monomer, and transfer agent as well as rate constants change, and the PDI increases.

8.2.4 Commercial Cationic Polymerization

Cationic polymerizations are used extensively in the industry for the synthesis of rubbers [5]. Low molecular weight polyisobutylenes (up to $\bar{M}_v$ 5–10 × 10^4) ranged from viscous liquids to tacky semi-solids are synthesized by reacting isobutylene with $AlCl_3$ at −40 to 10 °C. High molecular weight polyisobutylenes ($\bar{M}_v > 10^5$) are rubbery solids and are obtained at considerably lower reaction temperatures (−100 to −90 °C) by using a process similar to that for butyl rubber. Butyl rubber (BR) is a copolymer of isobutylene and a small amount of isoprene **1** (0.5–2.5 %) produced by $AlCl_3$ in CH_2Cl_2. The initiation system is produced by passing methyl chloride through beds of aluminum chloride at 30–45 °C followed by dilution with methyl chloride and the addition of the initiator. The reaction is carried out at −100 to −90 °C.



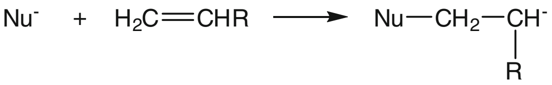
$$CH_2{=}\overset{\displaystyle CH_3 \atop |}{C}{-}CH{=}CH_2$$

1

The isoprene incorporates double bonds into the polymer chains, which is used for cross-linking (called curing in the rubber industry). Molecular weights of at least 200,000 are needed to obtain products that are non-tacky. The molecular weight is controlled by regulating the amount of transfer agent and terminating agent at low reaction temperature. The butyl rubber exhibits better chemical and physical properties than those of natural rubber due to the former having lower degree of unsaturation.

8.3 Anionic Polymerization

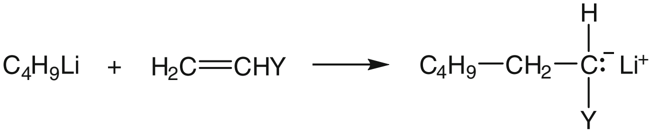
In anionic vinyl polymerization, the propagating chain is a carbanion which is formed by initiator undergoing nucleophilic addition to monomer (Eq. 8.51). Monomers having substituent groups capable of stabilizing a carbanion through resonance or induction are most susceptible to anionic polymerization. Examples of such groups are nitro, cyano, carboxyl, vinyl, and phenyl.



$$Nu^- + H_2C{=}CHR \longrightarrow Nu{-}CH_2{-}\underset{\displaystyle R}{\underset{|}{CH^-}} \tag{8.51}$$

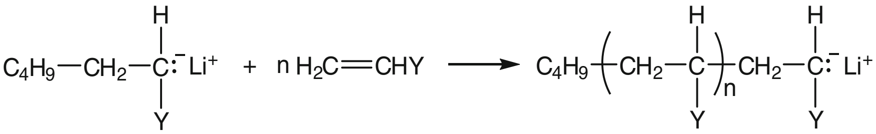
8.3.1 Reaction Mechanisms of Anionic Polymerization

The anionic polymerization is the same as other chain polymerizations which involve three reaction steps: (1) initiation, (2) propagation, and (3) termination, using the base or nucleophile as an initiator, e.g., $NaNH_2$, $LiN(C_2H_5)_2$, alkoxides, hydroxides, cyanides, phosphines, amines, and organometallics compounds such as n-C_4H_9Li and C_6H_5–MgBr. Alkyl lithium is the most useful initiator and used to initiate 1,3-butadiene and isoprene commercially. It is soluble in hydrocarbon solvents. Initiation proceeds by addition of the metal alkyl to monomer as



$$C_4H_9Li + H_2C{=}CHY \longrightarrow C_4H_9{-}CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Y}{\underset{|}{C\!:^-}}}}\,Li^+ \tag{8.52}$$

followed by propagation:



$$C_4H_9{-}CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Y}{\underset{|}{C\!:^-}}}}\,Li^+ + n\,H_2C{=}CHY \longrightarrow C_4H_9\left(CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Y}{\underset{|}{C}}}}\right)_n CH_2{-}\overset{\displaystyle H}{\overset{|}{\underset{\displaystyle Y}{\underset{|}{C\!:^-}}}}\,Li^+ \tag{8.53}$$

Monomer reactivity increases with increasing ability to stabilize the carbanion charge. Very strong nucleophiles such as amide ion or alkyl carbanion are needed to polymerize monomers, such as styrene, 1,3-butadiene with relatively weak electron withdrawing substituents. Weaker nucleophiles, such as alkoxide and hydroxide ions, can polymerize monomers with strongly electron withdrawing substituents, such as acrylonitrile, methyl methacrylate, and methyl vinyl ketone. Methyl-α-cyanoacrylate C=C(CN)–CO–OMe, containing two electron-withdrawing groups, can be polymerized by a very weak nucleophile such as Br^-, CN^-, amines, and phosphines. This monomer is used to make “superglue” or magic glue, and can be polymerized by water, which was used as wound repair agent during the Vietnam War.

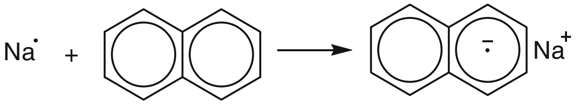
Electron-transfer initiation from other radical-anions, such as those formed by reactions of sodium with nonenolizable ketones, azomethines, nitriles, azo, and azoxy compounds, has also been studied. In addition to radical-anions, initiation by electron transfer has been observed when one uses certain alkali metals in liquid ammonia. Polymerization initiated by alkali metals in liquid ammonia proceeds by two different mechanisms. The mechanism of polymerization is considered to involve the formation of a *solvated electron*:

$$Li + NH_3 \longrightarrow Li^+(NH_3) + e^-(NH_3) \tag{8.54}$$

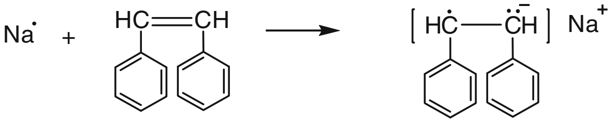
Such ammonia solutions are noted by their characteristic deep blue color. The solvated electron is then transferred to the monomer to form a radical-anion,

$$e^-(NH_3) + H_2C{=}CHY \longrightarrow \left[H_2\dot{C}{-}\ddot{C}HY \longleftrightarrow H_3\ddot{C}{-}\dot{C}HY\right]^-(NH_3) \tag{8.55}$$

Stable addition complexes of alkali metals that initiate polymerization by electron transfer are formed by reaction of metal and compound in an inert solvent. Examples are the reactions of sodium with naphthalene (Eq. 8.56) or stilbene (Eq. 8.57). A general equation for the reaction of this type of donor D^- with monomer M may be written as Eq. 8.58.



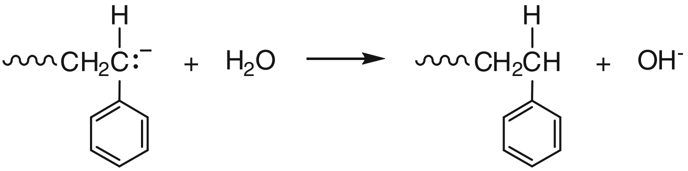
(8.56)



(8.57)

$$D^{\overset{-}{\cdot}} + M \longrightarrow D + M^{\overset{-}{\cdot}} \tag{8.58}$$

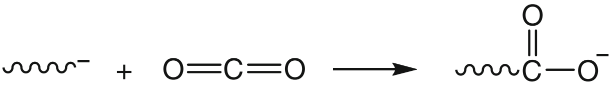
Many anionic polymerizations, such as styrene, 1,3-butadiene, nonpolar monomer have no termination reaction (reacts with counterion). By adding proton donor such as water or alcohol to the living polymers, the living chain can be terminated as shown in Eq. 8.59. The hydroxide ion is usually not sufficiently nucleophilic to reinitiate polymerization.



(8.59)

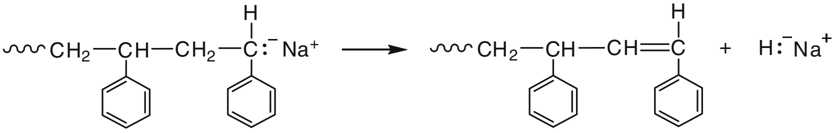
Most anionic polymerization is carried out in an inert atmosphere with rigorously purified reagents and cleaned glassware. Oxygen and carbon dioxide add to propagating carbanion to form peroxy (Eq. 8.60) and carboxyl anions (Eq. 8.61). They are not reactive enough to continue propagation.

$$\sim\!\sim\!\sim^{-} + O{=}O \longrightarrow \sim\!\sim\!\sim O{-}O^{-} \qquad (8.60)$$

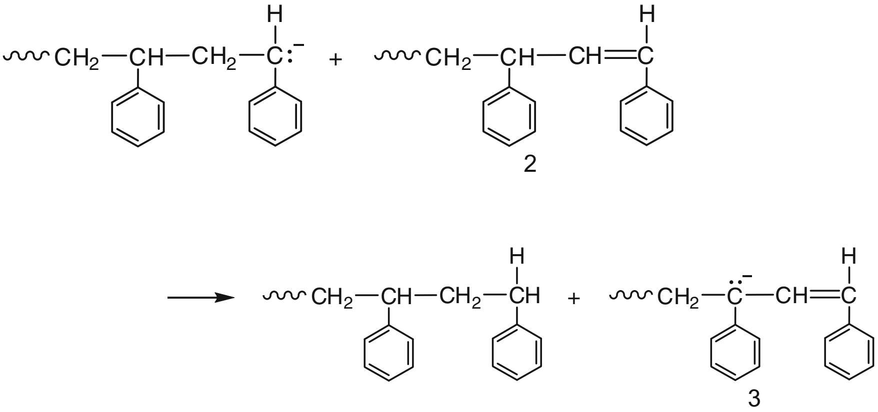


$$\sim\!\sim\!\sim^{-} + O{=}C{=}O \longrightarrow \sim\!\sim\!\sim \overset{\overset{\displaystyle O}{\|}}{C}{-}O^{-} \qquad (8.61)$$

Living polymers do not live forever. In the absence of terminating agents, the concentration of carbanion centers decays with time. Polystyrol carbanions are the most stable of living anionic systems; they are stable for weeks in hydrocarbon solvents. Stability is enhanced by storage below 0 °C. The mechanism for the decay of polystyryl carbanions, referred to as *spontaneous termination*, is based on spectroscopy of the reaction system and final polymer after treatment with water. The reaction consists of *hydride elimination* (Eq. 8.62) followed by abstraction of an allylic hydrogen from **2** and by a carbanion center to yield the unreactive 1,3-diphenyl allyl anion **3**.

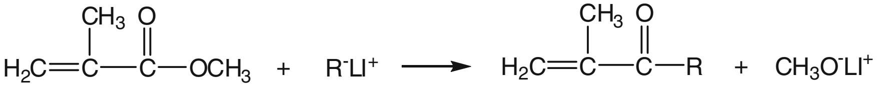


(8.62)



(8.63)

Several different nucleophilic substitution reactions have been observed in the polymerization of methyl methacrylate (MMA). Attack of initiator on monomer converts the active alkyllithium to the less active alkoxide initiator. Furthermore, MMA can be converted to isopropenyl alkyl ketone as shown in Eq. 8.64.



$$H_2C{=}C(CH_3){-}C({=}O){-}OCH_3 + R^-Li^+ \longrightarrow H_2C{=}C(CH_3){-}C({=}O){-}R + CH_3O^-Li^+ \quad (8.64)$$

The resulting polymerization is a copolymerization between these two monomers, not a homopolymerization of MMA. More importantly, this results in a slower reaction since the carbanion derived from the ketone is not as reactive as the carbanion from MMA. To avoid this side reaction, one can use bulky anionic initiator such as diphenyl ethylene s-Bu lithium and carry out the reaction at −78°C in tetrahydrofuran [6].

8.3.2 Kinetics of Anionic Polymerization with Termination

The kinetic and mechanistic aspects of anionic polymerization are better understood than those of cationic polymerization. In the case of the potassium amide-initiated polymerization in liquid ammonia, initiation involves dissociation (Eq. 8.65) followed by addition of amide ion to monomer (Eq. 8.66).

$$KNH_2 \overset{K}{\rightleftharpoons} K^+ + NH_2^- \quad (8.65)$$

$$NH_2^- + M \xrightarrow{k_i} H_2N - M^- \quad (8.66)$$

Because the second step is slow relative to the first step,

$$R_i = k_i[\mathrm{H_2N :^-}][\mathrm{M}] \tag{8.67a}$$

or

$$R_i = k_iK[\mathrm{M}][\mathrm{KNH_2}]/[\mathrm{K^+}] \tag{8.67b}$$

Propagation proceeds according to

$$\mathrm{H_2N - M_n^-} + \mathrm{M} \xrightarrow{k_p} \mathrm{H_2N - M_nM^-} \tag{8.68}$$

Rate expressions for propagation may be written in the conventional way:

$$R_p = k_p[\mathrm{M}][\mathrm{M^-}] \tag{8.69}$$

The chain transfers to solvent (NH_3) results that an anion produces without termination.

$$\mathrm{H_2N - M_n^-} + \mathrm{NH_3} \xrightarrow{k_{tr,\mathrm{NH_3}}} \mathrm{H_2N - M_n - H} + \mathrm{NH_2^-} \tag{8.70}$$

However, the chain transfers to impurities, such as H_2O, results in a termination.

$$\mathrm{H_2N - M_n^-} + \mathrm{H_2O} \xrightarrow{k_{tr,\mathrm{H_2O}}} \mathrm{H_2N - M_n - H} + \mathrm{OH^-} \tag{8.71}$$

The transfer rates for solvent and impurities can be expressed as Eqs. 8.72 and 8.73

$$R_{tr,\mathrm{NH_3}} = k_{tr,\mathrm{NH_3}}[\mathrm{M^-}][\mathrm{NH_3}] \tag{8.72}$$

$$R_{tr,\mathrm{H_2O}} = k_{tr,\mathrm{H_2O}}[\mathrm{M^-}][\mathrm{H_2O}] \tag{8.73}$$

Assuming a steady state whereby $R_i = R_t$, and combining Eqs. 8.67b, 8.69, and 8.73, one obtains

$$R_P = Kk_ik_p[\mathrm{M}]^2[\mathrm{KNH_2}]/k_{tr,\,\mathrm{H_2O}}[\mathrm{K^+}][\mathrm{H_2O}] \tag{8.74}$$

Therefore, the inverse average kinetic chain length is expressed as

$$1/\bar{X}_n = \mathrm{C_{NH_3}}[\mathrm{NH_3}]/[\mathrm{M}] + \mathrm{C_{H_2O}}[\mathrm{H_2O}]/[\mathrm{M}] \tag{8.75}$$

where the C_{NH_3} and C_{H_2O} are defined as follows:

$$\mathrm{C_{NH_3}} = k_{tr,\,\mathrm{NH_3}}/k_p; \mathrm{C_{H_2O}} = k_{tr,\,\mathrm{H_2O}}/k_p \tag{8.76}$$

The propagation rate constant and the polymerization rate of anionic polymerization are affected by solvent and counterion. Table 8.8 shows the effect of solvent on the polymerization of styrene by sodium naphthalene. Polar solvents (tetrahydrofuran and 1,2-dimethoxy ethane) have higher k_p^{app} than nonpolar solvent

Table 8.8 Effect of solvent on anionic polymerization of styrene [5]

Solvent	Dielectric constant	k_p^{app} L/mol-s
Benzene	2.2	2
Dioxane	2.2	5
Tetrahydrofuran	7.6	550
1,2-Dimethoxy ethane	5.5	3,800

(benzene and dioxane). The reaction has a higher k_p in 1,2-dimethoxy ethane than in tetrahydrofuran (THF), due to the solvation effect of dimethoxy ethane. The increase in k_p^{app} with increased solvating power of the reaction medium is due mainly to the increased fraction of free ions present relative to ion pairs.

The rate of polymerization is the sum of the rates for the free propagating anion P^- and the ion pair $P^-(C^+)$.

$$R_p = k_p^-[P^-][M] + k_p^{\mp}[P^-(C^+)][M] \tag{8.77}$$

Where k_p^- and $k_p^{\mp}$ are the propagation rate constants for the free ion and ion pair, respectively, $[P^-]$ and $[P^-(C^+)]$ are the concentrations of the free ion and ion pair, and [M] is the monomer concentration. C^+ is the positive counterion.

$$R_p = k_p^{app}[M^-][M] \tag{8.78}$$

Comparison of Eqs. 8.77 and 8.78 yields the apparent k_p as

$$k_p^{app} = \frac{k_p^-[P^-] + k_p^{\mp}[P^-(C^+)]}{[M^-]} \tag{8.79}$$

The two propagating species are in equilibrium according to

$$P^-(C^+) \overset{K}{\rightleftharpoons} P^- + C^+ \tag{8.80}$$

governed by the dissociation constant K that is given by

$$K = \frac{[P^-][C^+]}{[P^-(C^+)]} \tag{8.81}$$

When $[P^-] = [C^+]$, the concentration of free ions is

$$[P^-] = (K[P^-(C^+)])^{1/2} \tag{8.82}$$

The extent of dissociation is small under most conditions, the concentration of ion pairs is close to the total concentration of free ions and Eq. 8.81 can be rewritten as

$$[P^-] = (K[M^-])^{1/2} \tag{8.83}$$

The concentration of ion pairs is given by

$$[\mathrm{P}^-(\mathrm{C}^+)] = [\mathrm{M}^-] - (K[\mathrm{M}^-])^{1/2} \tag{8.84}$$

Combination of Eqs. 8.79, 8.83, and 8.84 yields k_p^{app} as a function of $[\mathrm{M}^-]$:

$$k_p^{app} = k_p^{\mp} + \frac{\left(k_p^- - k_p^{\mp}\right)K^{1/2}}{[\mathrm{M}^-]^{1/2}} \tag{8.85}$$

When polymerization is carried out in the presence of excess counterion by adding a strongly dissociating salt, the concentration of free ions, depressed by the common ion effect, is given by

$$[\mathrm{P}^-] = \frac{(K[\mathrm{M}^-])}{[\mathrm{C}^+]} \tag{8.86}$$

When the added salt is strongly dissociated and the ion pairs slightly dissociated, the counterion concentration is very close to that of the added salt [CZ]:

$$[\mathrm{C}^+] \simeq [\mathrm{CZ}] \tag{8.87}$$

The concentrations of free anions and ion pairs are given by

$$[\mathrm{P}^-] = \frac{K[\mathrm{M}^-]}{[\mathrm{CZ}]} \tag{8.88}$$

$$[\mathrm{P}^-(\mathrm{C}^+)] = [\mathrm{M}^-] - \frac{K[\mathrm{M}^-]}{[\mathrm{CZ}]} \tag{8.89}$$

which are combined with Eq. 8.79 to yield

$$k_p^{app} = k_p^{\mp} + \frac{\left(k_p^- - k_p^{\mp}\right)K}{[\mathrm{CZ}]} \tag{8.90}$$

Equations 8.79 and 8.90 allow one to obtain k_p^-, $k_p^{\mp}$ and K from k_p^{app} values obtained in the absence and presence of added common ion. A plot of k_p^{app} obtained in the absence of added common ion versus $[\mathrm{M}^-]^{-1/2}$ yields a straight line whose slope and intercept are $\left(k_p^- - k_p^{\mp}\right)K^{1/2}$ and $k_p^{\mp}$, respectively. A plot of k_p^{app} obtained in the presence of added common ion versus $[\mathrm{CZ}]^{-1}$ yields a straight line whose slope and intercept are $\left(k_p^- - k_p^{\mp}\right)K$ and $k_p^{\mp}$, respectively. The combination of the two slopes and two intercepts allows the individual calculation of k_p^-, $k_p^{\mp}$ and K. (*Note*: K, $[\mathrm{P}^-]$ and $[\mathrm{P}^-(\mathrm{C}^+)]$ can also be independently determined from conductivity measurements.)

The polydispersity (PDI) of living anionic polymerized polymer can be expressed by the following depending on the mode of termination:

$$\bar{X}_n = 2p[\mathrm{M}]_\mathrm{o}/[\mathrm{I}]_\mathrm{o} \tag{8.91}$$

or

$$\bar{X}_n = p[\mathrm{M}]_\mathrm{o}/[\mathrm{I}]_\mathrm{o} \tag{8.92}$$

where the $[\mathrm{M}]_\mathrm{o}$ and $[\mathrm{I}]_\mathrm{o}$ are the initial concentrations of monomer and initiator, respectively, and the p is the fractional conversion of monomer at any time in the reaction. Low PDI can be obtained for system that has fast initiation, efficient mixing, in the absence of de-propagation, termination, and transfer reaction. The PDI is around 1.1–1.2 for many living polymerizations. The presence of termination, transfer, or side reaction will broaden the PDI. Although the bulk of propagation is carried by a small fraction of the propagating species (i.e. the free ions), this does not significantly broaden the molecular weight of polymer. Since the free ions and ion pairs are in rapid equilibrium, each polymer chain propagates as both free ion and ion pair over its lifetime and the average fractions of its lifetime spent as free ion and ion pair are not too different from any other propagating chain.

Table 8.9 shows the K and the propagation rate constants for free ions and ion pairs in styrene polymerization in THF at 25°C with various alkali metal counterions. The corresponding $k_p^{\mp}$ values in dioxane are also presented. The value of K and k_p^- in dioxane could not be obtained as conductivity measurements indicated no detectable dissociation of ion pairs to free ions in dioxane. The reactivity of the free ion is greater compared to any of the ion pairs as expected. The K values indicate that the increased solvating power affects the reaction rate primarily through an increase in the concentration of free ions. Since free ions are so much more reactive than ion pairs, their small concentration has a very large effect on the observed polymerization rate. The table shows that the dissociation constant for the ion pair decreases in going from lithium to cesium as the counterion. The order of increasing K is the order of increasing solvation of the counterion. The smaller Li^+ is solvated to the greater extent and the larger Cs^+ is the least solvated. The decrease in K has a significant effect on the overall polymerization, since there is a very significant change in the concentration of the highly reactive free ions. Thus, the free-ion concentration for polystyryl cesium is less than that of polystyryl lithium. The reactivities of the various ion pairs also increase in the same order as the K values: $\mathrm{Li} > \mathrm{Na} > \mathrm{K} > \mathrm{Rb} > \mathrm{Cs}$. The fraction of the ion pairs that are of the solvent-separated type increases with increasing solvation of the counterion. Solvent-separated ion pairs are much more reactive than contact ion pairs. The order of reactivity for the different ion pairs in dioxane is the reverse of that in tetrahydrofuran. Solvation is not important in dioxane. The ion pair with the highest reactivity is that with the weakest bond between the carbanion center and counterion.

The effect of counterion on ion-pair reactivity is different for methyl methacrylate (MMA) compared to styrene as shown in Table 8.10. The absence of solvent effect by THF for MMA polymerization is due to the presence of intramolecular solvation. The additional binding of the counterion to the polymer accounts for the low dissociation constant ($K < 10^{-9}$, MMA; compared to 10^{-7}, styrene). Smaller

Table 8.9 Effect of counterion on anionic polymerization of styrene* [3]

Polymerization in tetrahydrofuran

Counterion	$k_p^{\mp}$	$K \times 10^7$	k_p^-	$k_p^{\mp}$ for dioxane
Li^+	160	2.2	6.5×10^4	0.94
Na^+	80	1.5	6.5×10^4	3.4
K^+	60–80	0.8	6.5×10^4	19.8
Rb^+	50–80	0.1	6.5×10^4	21.5
Cs^+	22	0.02	6.5×10^4	24.5

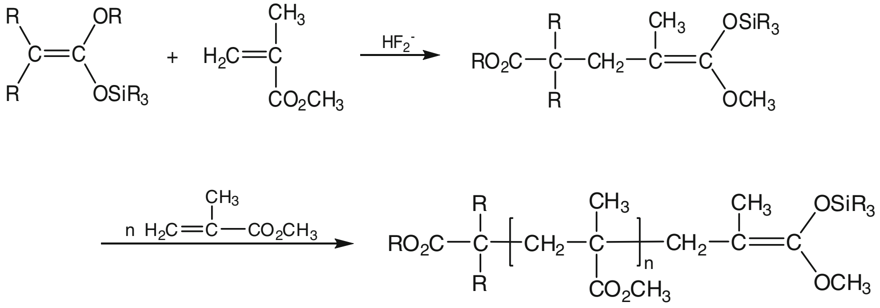
*Units of K are mole L^{-1}; rate constants are L mol^{-1} s^{-1}

counterions "fit better" into the intramolecular solvation sphere. Table 8.11 shows a comparison between anionic polymerization and cationic polymerization. The behaviors of these two polymerizations are quite different although both of them belong to ionic polymerization.

8.4 Group Transfer Polymerization

Unlike conventional anionic polymerization, group transfer polymerization (GTP) affords low-polydispersity living polymers at room temperature or above. Typically, an organosilicon compound is used to initiate the polymerization in solution in the presence of an anionic or Lewis acid catalyst. Examples of each type of compounds are given in Table 8.12.

Equation 8.93 shows an example of chemical reactions involved in the group transfer polymerization. In each propagation step, the SiR_3 group is transferred to the carbonyl oxygen of the incoming monomer, hence the name of GTP is obtained [4]. If a difunctional initiator is used, the chain propagates from each end (Eq. 8.94):



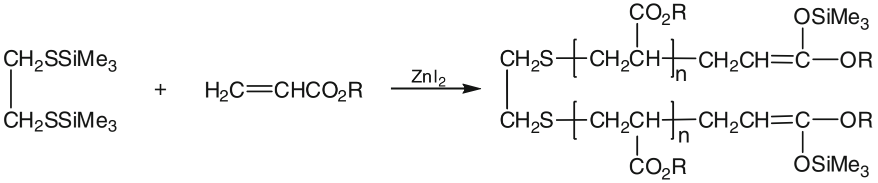
(8.93)

Table 8.10 Comparison of effect of counterion on anionic polymerization between styrene and methyl methacrylate

Cation	Styrene	Methyl methacrylate
Li^+	160	1
Na^+	80	~30–33
K^+	60–80	~30–33
Rb^+	50–80	~30–33
Cs^+	22	~30–33

Table 8.11 Comparison between cationic polymerization and anionic polymerization

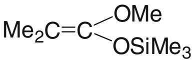
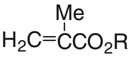
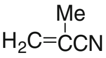
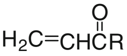
Factor	Anionic	Cationic
Propagating species	Anionic ion pair/free ions	Cationic ion pair/free ions
Difference in ion pair/free ion reactivity	Large	Small
Temperature sensitivity	Relative small	Large
$E_R = E_i + E_p - E_t$	Positive	Negative (mostly $E_t > E_i + E_p$)
Solvent	Aliphatic/aromatic hydrocarbon and ether	Prefer polar solvent
Halogenated solvent	No (facile nucleophilic substitution Rx)	Yes
Living polymerization	Most	Seldom



$$\begin{array}{c}CH_2SSiMe_3\\|\\CH_2SSiMe_3\end{array} + H_2C{=}CHCO_2R \xrightarrow{ZnI_2} \begin{array}{l} CH_2S\left[CH_2\overset{CO_2R}{\overset{|}{C}}H\right]_n CH_2CH{=}\overset{OSiMe_3}{\overset{|}{C}}{-}OR\\ | \\ CH_2S\left[CH_2\underset{CO_2R}{\underset{|}{C}}H\right]_n CH_2CH{=}\underset{OSiMe_3}{\underset{|}{C}}{-}OR\end{array} \qquad (8.94)$$

Once the monomer is consumed, a different monomer may be added, or the chain can be terminated by removal of catalyst or by protonation (Eq. 8.95) or alkylation (Eq. 8.95)

Table 8.12 Representative compounds used in group transfer polymerization [4]

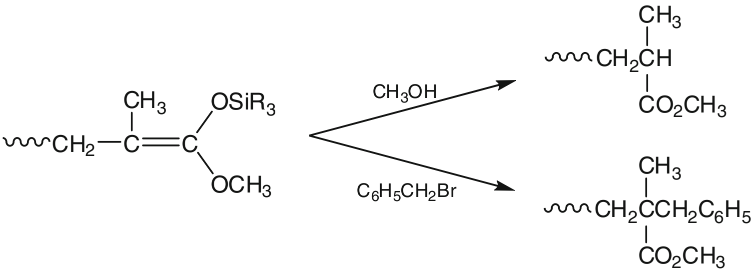
Monomers[a]	Initiators[a]	Catalysts[a]	Solvents
$H_2C{=}CHCO_2R$	 $Me_2C{=}C(OMe)(OSiMe_3)$	Anionic[b] HF_2^- CN^-	Acetonitrile 1,2-Dichloroethane[d] Dichloromethane[d]
 $H_2C{=}\overset{Me}{\overset{\mid}{C}}CO_2R$	$Me_3SiCH_2CO_2Me$	N_3^- Me_3SiF_2	N,N-Dimethylacetamide N,N-Dimethylacetamide
$H_2C{=}CHCONR_2$	Me_3SiCN	Lewis acid[c]	Ethyl acetate
$H_2C{=}CHCN$	$RSSiMe_3$	ZnX_2 R_2AlCl	Propylene carbonate Tetrahydrofuran
 $H_2C{=}\overset{Me}{\overset{\mid}{C}}CN$	$ArSSiMe_3$	$(R_2Al)_2O$	Toluene[d]
 $H_2C{=}CH\overset{O}{\overset{\Vert}{C}}R$			

[a] R = alkyl, Ar = aryl, Me = methyl, X = halogen

[b] 0.1 mol % relative to initiator

[c] 10–20 mol % relative to monomer

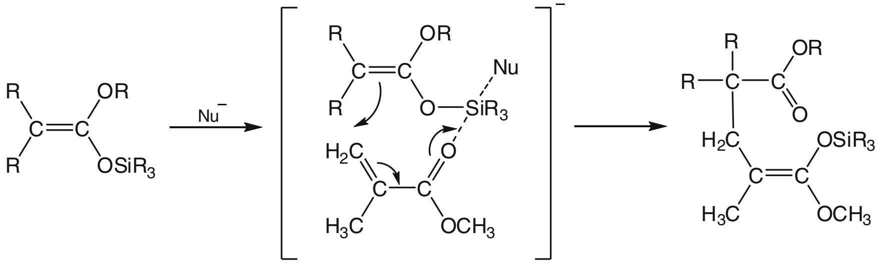
[d] Preferred with Lewis acid catalysts



(8.95)

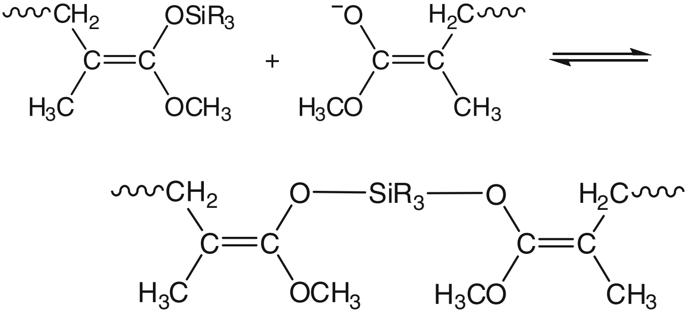
(8.96)

There are two reaction mechanisms proposed for the GTP. Equation 8.97 shows the propagating chain is completely covalent, and a hypervalent silicon intermediate is formed by activation with the nucleophilic catalyst (Nu^-). The silyl group is then transferred to the carbonyl group of an incoming monomer molecule via an eight-membered ring transition state. If Lewis acid catalysts are used, the catalyst coordinates with the carbonyl oxygen of monomer, then the monomer becomes more susceptible to nucleophilic attack by the initiator.



(8.97)

Equation 8.98 shows enolate anions and silyl ketene acetal chain ends are in rapid equilibrium with a hypervalent silicon complex. The complex thus provides a low equilibrium concentration of enolate anions for propagation and maintaining living chain ends.

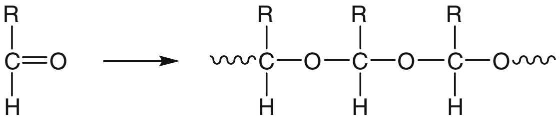


(8.98)

Group transfer polymerization (GTP) requires the absence of materials such as H_2O with active hydrogen, but O_2 does not interface with the reaction. Solvent types are wider than anionic polymerization. In anionic polymerization, dimethylformamide reacts with nucleophilic catalyst; chlorinated hydrocarbons, acetonitrile reacts with Lewis acid catalyst; ether, tetrahydrofuran and toluene are the most common solvents. The GTP lacks anionic propagation center, thus more polar solvent can be used. The concerted reaction mechanism of group transfer polymerization can reduce the side reaction problems of anionic polymerization. However, the GTP has a lower rate of propagation than that of anionic polymerization. It remains to be seen whether or not the GTP is used commercially in the near future.

8.5 Chain Polymerization of Carbonyl Monomer

The polymerization of the carbonyl group in aldehydes yields polymers, referred to as *polyacetals*, since they contain the acetal repeating structure (Eq. 8.99).



$$\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}=\mathrm{O} \longrightarrow \sim\!\sim\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-\mathrm{O}-\underset{\mathrm{H}}{\overset{\mathrm{R}}{\mathrm{C}}}-\mathrm{O}\sim\!\sim \tag{8.99}$$

Polyacetal

They have to be synthesized by either cationic or anionic polymerization at low temperatures, because they exhibit low ceiling temperature except formaldehyde as shown in Table 8.13.

8.5.1 Anionic Polymerization of Carbonyl Monomer

Formaldehyde can be polymerized by any base. Metal alkyls, alkoxides, phenolate, carboxylates, hydrated alumina, amine, phosphine, pyridine are effective in polymerizing formaldehyde. The polymerization proceeds as follows:

Initiation

$$\mathrm{H_2C=O} \longrightarrow \mathrm{A-CH_2-O^-(G^+)} \tag{8.100}$$

Propagation

$$\mathrm{A}\!\left[\mathrm{CH_2-O}\right]_n\!\mathrm{CH_2-O^-(G^+)} + \mathrm{H_2C=O} \longrightarrow \mathrm{A}\!\left[\mathrm{CH_2-O}\right]_{n+1}\!\mathrm{CH_2-O^-(G^+)} \tag{8.101}$$

Termination by chain transfer

$$\mathrm{A}\!\left[\mathrm{CH_2-O}\right]_n\!\mathrm{CH_2-O^-(G^+)} + \mathrm{ZH} \longrightarrow \mathrm{A}\!\left[\mathrm{CH_2-O}\right]_n\!\mathrm{CH_2-OH} + \mathrm{Z^-(G^+)} \tag{8.102}$$

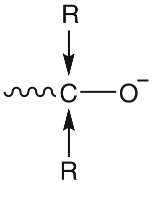
The aldehyde is initiated by anionic species A^- to form an alkoxide anion with nearby counterion G^+. Propagation proceeds in a like manner and termination occurs by transfer of a proton from ZH. The chain-transfer agent ZH can transfer a proton to the propagating alkoxide anion, such as water or alcohol. The chain-

Table 8.13 Ceiling temperatures [5]

Monomer	T_c (°C)
Formaldehyde	119
Trifluoroacetaldehyde	81
Propanol	−31
Acetaldehyde	−39
Pentanal	−42

transfer agent can have an effect on the polymerization rate if Z^- is not as effective as A^- in reinitiating polymerization.

Strong bases are required to initiate aliphatic aldehydes such as acetaldehyde and high aldehyde. The inductive effect of an alkyl substituent destabilizes the propagating anion **4** by increasing the negative charge density on oxygen. The alkyl group also decreases reactivity for steric reasons. Steric considerations are probably also responsible for low ceiling temperature as compared to formaldehyde. Alkali metal alkyls and alkoxides are required to initiate the polymerization. The presence of trace amount of water is detrimental, since the initiator reacts to form hydroxide ion, which is too weak to initiate polymerization. Ketones **4** are unreactive toward polymerization because of the steric and inductive effects of two alkyl groups. A side reaction of aldol condensation occurs with acetaldehyde and higher aldehydes containing α-hydrogens. The Aldol reaction can be extensive at ambient temperatures or higher but it can be avoided by polymerization at low temperature. The substitution of halogens on the alkyl group of an aliphatic aldehyde greatly enhances its polymerizability. Trichloroacetaldehyde (chloral) is easily polymerized by weak bases: pyridine, alkali thiocyanates, and even chloride ion. Furthermore, the polymerization of chloral by *n*-butyl lithium at −78°C can be completed in less than a second. The electron-withdrawing inductive effect of the halogens acts to stabilize the propagating anion **5** by decreasing the charge density on the negative oxygen.



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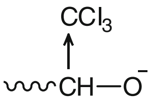
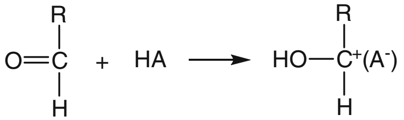


5

8.5.2 Cationic Polymerization of Carbonyl Monomer

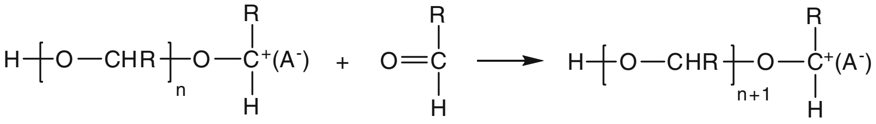
Acidic initiators can be used to polymerize carbonyl monomers, although their reactivity is lower than that in anionic polymerization. Hydrochloric acid, acetic acid, Lewis acid can be used as cationic initiator. The initiation and propagation steps are shown in the following:

Initiation



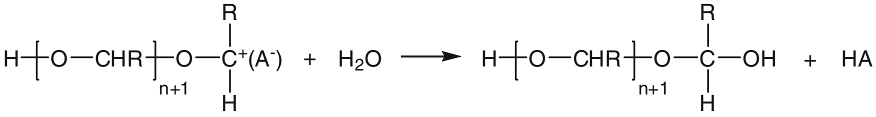
$$O{=}\overset{R}{\underset{H}{C}} + HA \longrightarrow HO{-}\overset{R}{\underset{H}{C^{+}}}(A^{-}) \tag{8.103}$$

Propagation



$$H{\left[O{-}CHR\right]}_{n}O{-}\overset{R}{\underset{H}{C^{+}}}(A^{-}) + O{=}\overset{R}{\underset{H}{C}} \longrightarrow H{\left[O{-}CHR\right]}_{n+1}O{-}\overset{R}{\underset{H}{C^{+}}}(A^{-}) \tag{8.104}$$

Termination



$$H{\left[O{-}CHR\right]}_{n+1}O{-}\overset{R}{\underset{H}{C^{+}}}(A^{-}) + H_2O \longrightarrow H{\left[O{-}CHR\right]}_{n+1}O{-}\overset{R}{\underset{H}{C}}{-}OH + HA \tag{8.105}$$

Competing side reactions in cationic polymerization of carbonyl monomers include cyclotrimerization, acetyl interchange. Acetaldehyde and higher aldehyde are reasonably reactive in cationic polymerization as compared to formaldehyde. Haloaldehydes are lower in reactivity as compared to their non-halogen counterparts due to the electron withdrawing of halogen.

8.5.3 Radical Polymerization of Carbonyl Monomer

The carbonyl double bond is difficult to be polymerized by radical initiators because of the carbonyl group being highly polarized and not prone to be attached by radical; most radicals are produced at temperatures above the ceiling temperature of carbonyl monomers [5]. There are, however, a few isolated cases of carbonyl polymerizations by radical initiators. Trifluoroacetaldehyde has been polymerized using benzoyl peroxide at 22°C. The polymerization is slow, with 18 h required to obtain 90 % conversion. However, fluorothiocarbonyl monomers such as thiocarbonyl fluoride have been polymerized at high rates by using a trialkyl boron-oxygen redox system at −78°C. Thioacetone is also polymerized by this redox system. Radical polymerizations are observed with these monomers because the electron-withdrawing substituents on the carbonyl and thiocarbonyl group decrease its polarity. The greater susceptibility of the thiocarbonyl double bond to radical polymerization is due to the lower electronegativity of sulfur compared to oxygen.

8.5.4 End-Capping Polymerization

The low ceiling temperature of polyacetal can be end capped to increase its stability. Depolymerization occurs on heating of polyoxymethylene (POM) when reactive carbanion or carbocation centers are formed by thermal bond scission at the hydroxyl end groups. The stability of POM can be improved by converting the less stable hydroxyl end groups into more stable ester groups by reaction with an anhydride [5]:

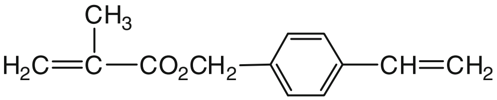
$$\mathrm{HO}{-}\left[\mathrm{CH_2O}\right]_n{-}\mathrm{CH_2OH} \xrightarrow{(\mathrm{RCO})_2\mathrm{O}} \mathrm{ROOC}{-}\left[\mathrm{CH_2O}\right]_n{-}\mathrm{CH_2COOR} \tag{8.106}$$

This reaction is referred to as *end capping* or *end blocking*. The result is that reactive carbanion or carbocation centers do not form and depolymerization does not occur at the ceiling temperature of the polymer. The polymer chains are end blocked from depolymerization. The effective ceiling temperature is increased considerably above the ceiling temperature. Acetic anhydride is the usual capping reagent.

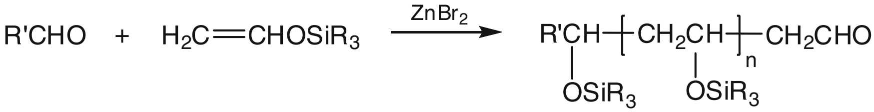
The anionic polymerization formaldehyde to POM followed by end capping is carried out commercially with a trade name of *Delrin*. The POM is highly crystalline (60–77 %) because of the ease of packing of single, polar polymer chain (T_m = 175°C). The commercial products have number-average molecular weights of 20,000–70,000 (PDI ~ 2). The POM has a good combination of properties—high strength, toughness, resistant to creep, fatigue, and abrasion; low coefficient of friction; low moisture absorption.

8.6 Problems

1. Give clear explanations for the following facts:
   a. Polymerization rate and polymer stereochemistry are more sensitive to solvent effects in ionic polymerization than in free radical polymerization.
   b. $\overline{\mathrm{DP}} = \bar{v}$ in cationic polymerization, but this is not always the case in free radical or anionic polymerization.
   c. Ethyl vinyl ether undergoes cationic polymerization faster than β-chloroethyl vinyl ether under the same conditions.
2. Predict the order of reactivity (and justify your prediction): (a) in cationic polymerization: styrene, *p*-methoxystyrene, *p*-chlorostyrene, *p*-methylstyrene; (b) in anionic polymerization: styrene, 2-vinylpyridine, 3-vinylpyridine, 4-vinylpyridine.
3. Write reactions illustrating transfer to monomer and transfer to polymer in the cationic polymerization of propylene and isobutylene. Which type of transfer would you expect to predominate in each case? Suggest a reason why propylene does not form high-molecular-weight polymer under cationic conditions. (*Note*: The order of stability of carbocations is tertiary > allylic > secondary > primary).
4. If trifluoroacetic acid is added dropwise to styrene, no polymerization occurs. On the other hand, styrene is added to the acid, however, high-molecular-weight polymer forms rapidly. Please explain.
5. What number-average molecular weight of polystyrene will be formed by polymerization of 2.0 M styrene using 1.0×10^{-3} M of sodium naphthalene in tetrahydrofuran using appropriate data from Table 8.9? If the reaction is run at 25°C, how long will it take to reach 90 % conversion?
6. Predict the structure of the soluble polymer formed from 2,6-diphenyl-1,6-heptadiene under anionic conditions. Write a mechanism for its formation.
7. Predict the structure of the polymer formed by (a) group transfer, (b) cationic, and (c) free radical polymerization of *p*-vinylbenzyl methacrylate (C. Pugh and V. Percec, *Polym. Bull.*, **14**, 109 (1985)).



8. Silyl vinyl ethers are polymerized in the presence of aldehyde initiators and Lewis acid catalysts to give silylated poly (vinyl alcohol):



$$\mathrm{R'CHO} + \mathrm{H_2C{=}CHOSiR_3} \xrightarrow{\mathrm{ZnBr_2}} \mathrm{R'\underset{OSiR_3}{CH}}\!-\!\left[\mathrm{CH_2\underset{OSiR_3}{CH}}\right]_n\!-\!\mathrm{CH_2CHO}$$

Propose a mechanism for the polymerization (D. Y. Sogah and O.W. Webster, Macromolecules, 19, 1775, 1986).

9. Please propose experimental approaches to determine whether the polymerization of a particular monomer is by a radical or ionic mechanism.
10. The sodium naphthalene polymerization of methyl methacrylate is carried out in benzene and tetrahydrofuran solutions. Which solution will yield the highest polymerization rate? Please discuss the effect of solvent on the relative concentrations of the different types of propagating centers.

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3. J. Brandrup, E.H. Immergut, E.A. Grulke, A. Abe, D.R. Bloch, *Polymer Handbook,* 4th edn. (Wiley, New York, 2005)
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5. G. Odian, *Principles of Polymerization*, 4th edn, Chapter 5, (Wiley Interscience, New York, 2004)
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Chapter 9
Coordination Polymerization

The coordination polymerization is invented by two Italian scientists: Karl Ziegler and Giulio Natta. They shared the nobel prize in chemistry in 1963 using Ziegler–Natta catalysts to polymerize nonpolar monomers: 1-alkene, cycloalkenes, dienes, and alkynes through coordination mechanism instead of common chain or step polymerization [1]. The polymers can exhibit stereo specificity if the monomer contains unsymmetrical carbon. Since the 1960s, both heterogeneous and homogeneous Ziegler–Natta catalysts have been developed. The heterogeneous catalysts consist of transition metal compound (e.g., titanium chloride) and organometallic compounds (e.g., aluminum alkyl halide) as cocatalyst. The homogeneous catalysts are made from transition metal metallocene and aluminum alkyl halide. The metallocene is a compound typically consisting of two cyclopentadienyl anions (Cp, which is $C_5H_5^-$) bound to a metal center (M) in the oxidation state II, with the resulting general formula $(C_5H_5)_2M$. However, the homogeneous catalysts exhibit low activity, not until 1980, W. Kaminsky found that the catalytical effects of homogeneous Ziegler–Natta catalysts can be greatly enhanced by the addition of cocatalysts derived from the reaction of aluminum alkyl with water (e.g., methylalumoxanes (MAO)) [2]. The cyclopentadienyl group of metallocenes in the homogeneous catalysts provides defined space that can control the stereo specificity of the polymer better than that of heterogeneous catalysts. Table 9.1 shows some of commercial polymers synthesized by coordination catalysts.

9.1 Heterogeneous Ziegler–Natta Polymerization

9.1.1 Catalysts

The Ziegler–Natta initiators are the only initiators that polymerize α–olefins such as propene and 1-butene which can not be polymerized by either radical or ionic initiators. Thousands of different combinations of transition and Group I-III metal

W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_9,

Table 9.1 Commercially available polymers synthesized with complex coordination catalysts [3]

Polymer	Principal stereochemistry	Typical uses
Polyethylene, high density (HDPE)	–	Bottles, drums, pipe, conduit, sheet, film, wire and cable insulation
Polyethylene, ultrahigh molecular weight (UHMWPE)	–	Surgical prostheses, machine parts, heavy-duty liners
Polypropylene	Isotactic	Automobile and appliance parts, rope, cordage, webbing, carpeting, film
Poly(1-butene)	Isotactic	Film, pipe
Poly(4-methy1-1- Pentene)[a]	Isotactic	Packaging, medical supplies, lighting
Polystyrene	Syndiotactic	Specialty plastics
1,4-Polybutadiene	trans	Metal can coatings, potting compounds for transformers
1,4-Polyisoprene	trans	Golf ball covers, orthopedic devices
Ethylene-1-alkene[b] copolymer (linear low density polyethylene, LLDPE)	–	Blending with LDPE, packaging film, bottles
Ethylene–propylene block copolymers (polyallomers)	Isotactic	Food packaging, automotive trim, toys, bottles, film, heat-sterilizable containers
Polydicyclopentadiene[c]	–	Reaction injection molding(RIM) structural plastics
1,4-Polybutadiene	cis	Tires, conveyer belts, wire and cable insulation, foot-ware
1,4-Polyisoprene	cis	Tires, foot-ware, adhesives, coated fabrics
Poly(1-octenylene) (polyoctenamer)[c]	trans	Blending with other elastomers
Poly(1,3-cyclo-pentenylenevinylene) (norbornene polymer)[c]	trans	Molding compounds, engine mounts, car bumper guards
Polypropylene(amorphous)	–	Asphalt blends, sealants, adhesives, cable coatings
Ethylene–propylene copolymer (EPM,EPR)	–	Impact modifier for polypropylene, car bumper guards
Ethylene–propylene-diene copolymer (EPDM)	–	Wire and cable insulation, weather stripping, tire side walls, hose, seals

[a] Usually copolymerized with small amounts of 1-pentene
[b] 1-Butene, 1-hexene, and 1-octene
[c] Synthesized by ring-opening metathesis polymerization of the corresponding cycloalkene

components, often together with other compounds such as electron donors, studied for use in alkene polymerizations [4].

Catalysts are prepared by mixing the compounds in a dry, inert solvent in the absence of oxygen usually at a low temperature. The mixture of aluminum compound with titanium compound is to form radical, the first of this kind catalyst being used as shown below.

Table 9.2 Variation of polypropylene isotacticity with catalyst [3]

Catalyst[a]	Stereoregularity (%)
$AlEt_3 + TiCl_4$	35
$AlEt_3 + \beta\text{-}TiCl_3$	45
$AlEt_3 + \alpha\text{-}TiCl_3$	85
$AlEt_3 + ZrCl_4$	55
$AlEt_3 + VCl_3$	73
$AlEt_3 + TiCl_4$ + P,As or Sb compounds	35
$AlEt_2X + TiCl_3$	90–99
$AlEtX_2 + \gamma\text{-}TiCl_3$ + amine	99

[a] Et = ethyl; X = halogen

$$AlR_3 + TiCl_4 \rightarrow AlR_2Cl + TiRCl_3 \tag{9.1}$$

$$AlR_2Cl + TiCl_4 \rightarrow AlRCl_2 + TiRCl_3 \tag{9.2}$$

$$AlR_3 + TiRCl_3 \rightarrow AlR_2Cl + TiR_2Cl_2 \tag{9.3}$$

$$TiRCl_3 \rightarrow TiCl_3 + R\cdot \tag{9.4}$$

$$TiR_2Cl_2 \rightarrow TiRCl_2 + R\cdot \tag{9.5}$$

Further reduction may also occur:

$$TiRCl_2 \rightarrow TiCl_2 + R\cdot \tag{9.6}$$

$$TiRCl_3 \rightarrow TiCl_2 + RCl \tag{9.7}$$

In addition, $TiCl_3$ may be formed by the equilibrium

$$TiCl_4 + TiCl_2 \rightleftharpoons 2TiCl_3 \tag{9.8}$$

The stereo regularity of the polymers depends on the type of catalysts used as shown in Table 9.2 which indicates the isotacticity of polypropylene is varied by different catalyst. Syndiotactic polypropylene has been prepared under both heterogeneous and homogeneous conditions, but only under homogeneous condition a high degree of syndiotactic placement has been achieved.

With the appropriate choice of catalyst, specific stereochemical arrangements of polymerization of diene monomer can be obtained as shown in Tables 9.3, and 9.4. The 1,3-butadiene monomer will obtain cis-1,4; trans-1,4; isotactic 1,2-, and syndiotactic 1,2-polymers. The isoprene monomer will obtain cis- and trans-1,4; 1,2-; and 3,4-polymers.

The *cis* polymer is usually formed at relative low temperature, for instance, polymerization of acetylene using an $Al(C_2H_5)_3{-}Ti(OC_4H_9 - n)_4$ catalyst yields *cis* polymer at temperatures below –78°C, but *trans* polyacetylene is formed at 150°C. The result may be due to thermal isomerization of the initially formed *cis* polymer.

Table 9.3 Catalysts for the stereospecific polymerization of butadiene [3]

Catalyst[a]	Yield (%)	Polymer structure[b]
$R_3Al + VCl_4$	97–98	trans-1,4
$R_3Al + VCl_3$	99	trans-1,4
$R_3Al + VOCl_3$	97–98	trans-1,4
$R_3Al + TiI_4$	93–94	cis-1,4
$R_2AlCl + CoCl_2$	96–97	cis-1,4
$R_3Al + Ti(OC_4H_9)_4$	90–100	1,2
$Et_3Al + Cr(C_6H_5CN)_6$;Al/Cr = 2	~100	st-1,2
$Et_3Al + Cr(C_6H_5CN)_6$;Al/Cr = 10	~100	it-1,2

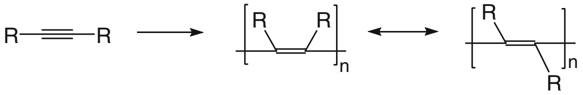
[a] Et = ethyl

[b] st = syndiotactic, it = isotactic

Table 9.4 Catalysts for the stereospecific polymerization of isoprene [3]

Catalyst[a]	Yield (%)	Polymer Structure
$R_3Al + \alpha\text{-}TiCl_3$	91	trans-1,4
$Et_3Al + VCl_3$	99	trans-1,4
$Et_3Al + TiCl_4$; Al/Ti < 1	95	trans-1,4
$Et_3Al + TiCl_4$; Al/Ti > 1	96	cis-1,4
$Et_3Al + Ti(OR)_4$	95	3,4

[a] Et = ethyl

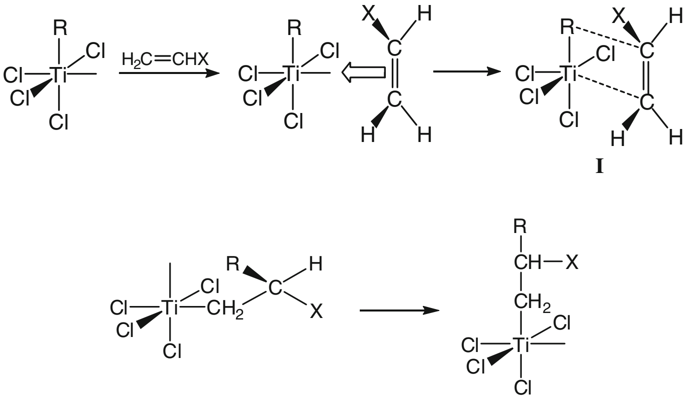


(9.9)

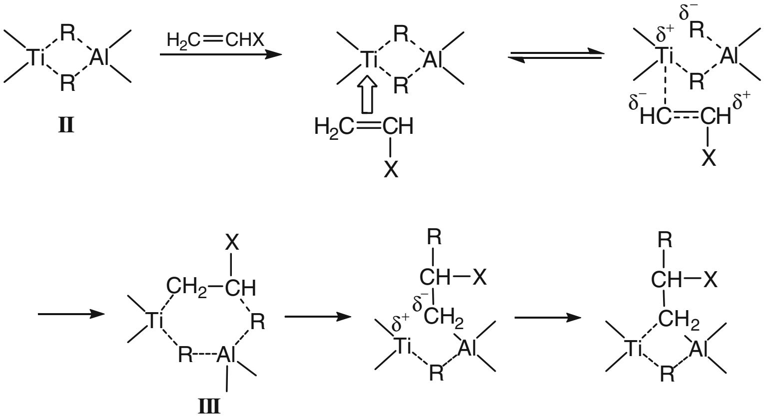
9.1.2 Reaction Mechanisms

The coordination polymerization of alkene can be preceded either by monometallic mechanism or bimetallic mechanism depending on the catalyst. Scheme 9.1 shows the reaction mechanism of substituted alkene being polymerized by using titanium compound catalyst. The double bond of alkene will undergo *cis* addition and coordinate with the empty orbital of titanium compound to form four membered ring coordinate intermediate **I**. The stereo specificity of substituted alkene is preserved via intermediate **I**. Then the bond is formed on the Ti compound catalyst. If the catalyst is made from aluminum compound and titanium compound, the polymerization will proceed through bimetallic mechanism as shown in Scheme 9.2. A bridge structure **II** is formed between two metal compounds first. Then the substituted alkene is coordinated with Ti compound to form six-membered ring coordination **III**. The stereo specificity of substituted alkene is preserved via intermediate **III**.

The polymer chain grows from the catalyst surface by successive insertion reactions of complexed monomer and the R group originally present in the



Scheme 9.1 Monometallic mechanism of Ziegler–Natta polymerization of substituted alkene



Scheme 9.2 Bimetallic mechanism of Ziegler–Natta polymerization of substituted alkene

organometallic cocatalyst ends up as the terminal group of the chain. Monomer activity decreases with increasing steric hindrance about the double bond as shown below:

$$CH_2 = CH_2 > CH_2 = CHCH_3 > CH_2 = CHCH_2CH_3 > CH_2 = CHCH_2CH(CH_3)_2 >$$
$$CH_2 = CHCH(CH_3)_2 > CH_2 = CHCH(CH_2CH_3)_2 > CH_2 = CH - C(CH_3)_3$$

The reaction has the characteristic of living anionic polymerization. The reaction is usually terminated by active hydrogen as shown in the following Eqs. 9.10–9.15. Hydrogen is the preferred transfer agent for controlling molecular weight due to low cost and clean reaction but the termination reaction is usually carried out by hydrogen containing compounds as shown in Eq. 9.15 [3].

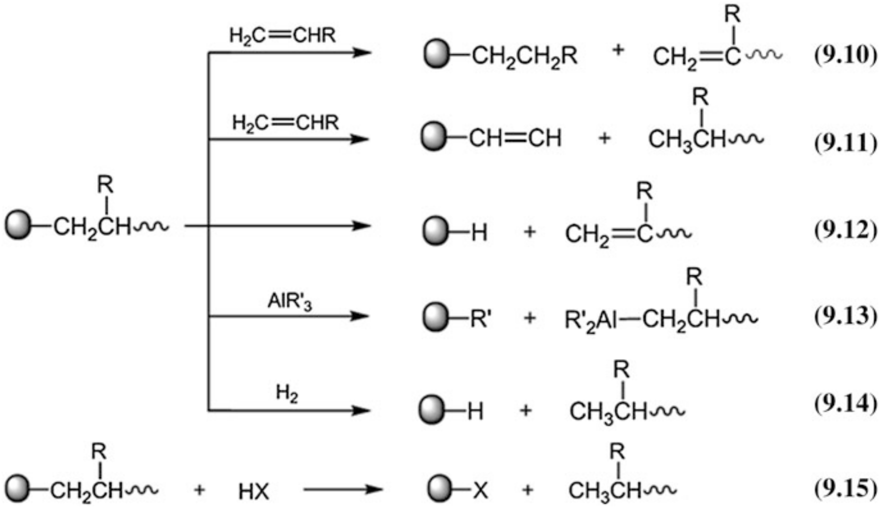
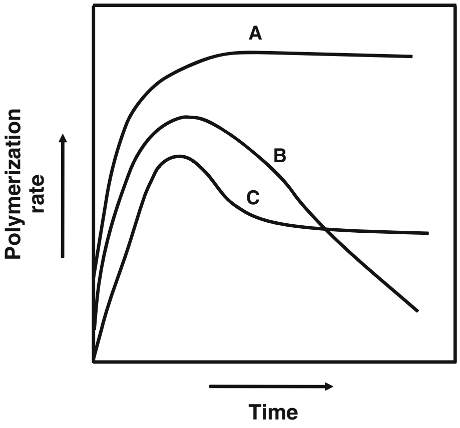


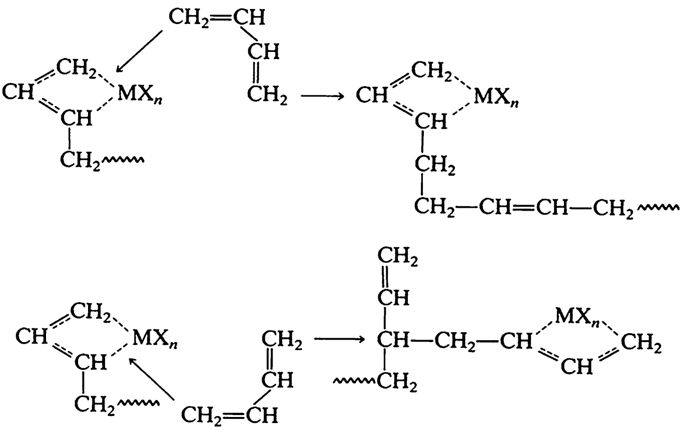
Fig. 9.1 Three types of polymerization rate observed in Ziegler–Natta polymerization: **a** constant. **b** decaying. and **c** decaying to constant [3]



The relationship between the polymerization rate and time is shown in Fig. 9.1. The decaying rate type is most common. That is due to structural changes from the reducing the number or activity of active centers. It is also due to the encapsulation of active centers by polymer which prevents approach by monomer.

Molecular weight distributions are generally broad when insoluble catalysts are used and much narrower with soluble catalysts. The board distribution may arise from the decay of catalyst activity or from the presence of sites of variable activity.

There are two theories to explain the reaction mechanisms of coordination of dienes. One theory is based on whether the catalyst coordinates one or both double bonds of the diene. Coordination of one would thus lead to 1,2-polymerization and coordination of both to 1,4-polymerization. Another theory is based on the



(9.16)

(9.17)

Scheme 9.3 Reaction mechanisms of coordination of dienes [3]

coordination of a π-allylic structure that directs the monomer approaching direction and determines the polymer structure (Scheme 9.3). If the monomer approaches the CH_2-metal (M) bond of the complex, 1,4-polymerization forms (Eq. 9.16). If it approaches the CH-metal bond, 1,2-polymerization results (Eq. 9.17). This mechanism provides no information on the geometric arrangement of the double bond or the tacticity at a stereogenic carbon.

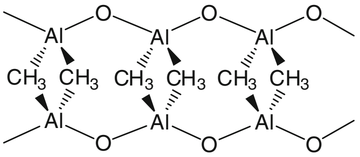
9.2 Homogeneous Ziegler–Natta Polymerization

The homogeneous Ziegler–Natta polymerization using metallocene catalysts such as bis(cyclopentadienyl)titanium dichloride **1**, and dialkylaluminum chloride **2**. Their structures are shown below.

Cp_2TiCl_2 R_2AlCl

1 **2**

Compounds **1** and **2** exhibit low catalytic activity towards ethylene and are generally unreactive toward propylene. The addition of water increases the activity substantially. The increase is the result of a reaction between the water and the alkylaluminum cocatalyst to form complex alkylalumoxanes such as methyl alumoxanes (MAO). The MAO is used in conjunction with metallocene catalysts exhibit especially high activities. MAO formed by controlled hydrolysis of trimethylaluminum that has a complex oligomeric structure with molecular weights of 1000–1500, most likely consisting of methyl-bridged aluminum atoms alternating with oxygen as shown in structures **3** and **4**. MAO is now used with a wide variety of metallocenes having the general structure **5**. Examples of catalysts are **6** and **7** which form isotactic and syndiotactic polypropylene, respectively.



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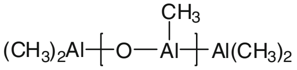
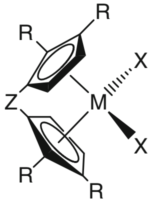


$$(CH_3)_2Al\left[O-\overset{\overset{\displaystyle CH_3}{|}}{Al}\right]Al(CH_3)_2$$

4



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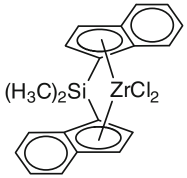

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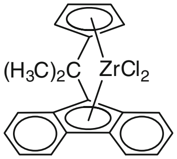
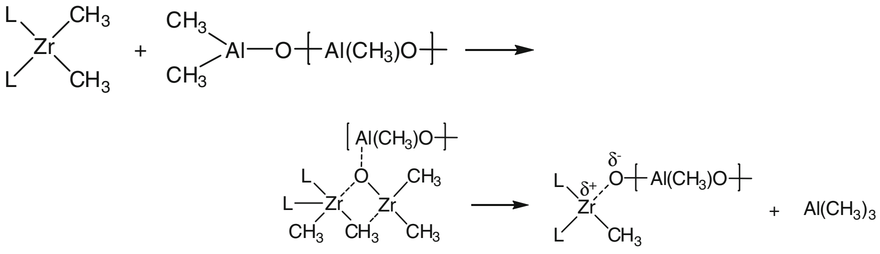


7

Metallocene has well-defined molecular structure and polymerization occurs at one position in the molecule, the transition metal atoms. Thus, the metallocene is also called *single-site catalyst* in contrast to the multi active site of heterogeneous catalyst. Scheme 9.4 shows an example of the formation of active site in a zirconium catalyst, L_2ZrCl_2 (where L represents the π ligands) which involves initial complexation between MAO and the catalyst, is followed by Cl-CH_3 exchange to



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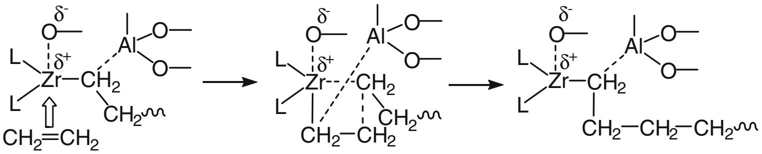
Scheme 9.4 Formation of the active site in a zirconocene catalyst

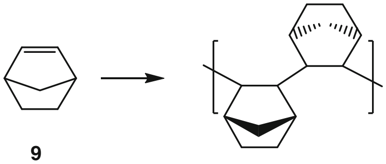


Scheme 9.5 Possible polymerization mechanism for ethylene using zirconocene catalyst

form $L_2Zr(CH_3)_2$. The methylated zirconocene reacts further with MAO to form the active species of **8**.

Scheme 9.5 shows the possible polymerization mechanisms of ethylene using zirconocene catalyst. The ethylene is *cis* added to the empty orbital of Zr site to form transition site, then is further on to precede polymerization.

The comparison between metallocene catalysts and heterogeneous catalysts for alkene polymerization is shown in Table 9.5. The metallocene out performs over the heterogeneous catalysts. Heterogeneous catalysts contain sites of variable activity that accounts for the large PDI. Metallocene catalysts differ from heterogeneous catalysts is that they are capable of polymerizing strained cyclo alkenes such as cyclobutene or norbornene **9** through the double bond to yield crystalline stereoregular polymers (Eq. 9.18). Ring-opening polymerization of cycloalkene monomers is more common with heterogeneous Ziegler–Natta catalysts.



9

(9.18)

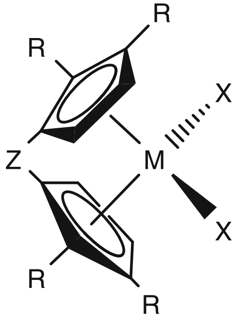
The molecular weight decreases with increasing polymerization temperature, with increasing catalyst concentration, with the addition of hydrogen to the monomer feed.

The reactivity of metallocene catalyst **10** depends on its chemical structure. The M of metallocene can be Zr, Ti or Hf. The X is Cl or alkyl; Z is an optional bridging group, $C(CH_3)_2$, $Si(CH_3)_2$, or CH_2CH_2; R is H or alkyl. For the group 4B metals, the order of activity is Zr > Ti > Hf. Alkyl groups on the cyclopentadiene rings increase catalyst activity if they are not too bulky. Large, bulky alkyl groups and electron-withdrawing groups decrease the activity. Increasing the size of the

Table 9.5 Comparison between metallocene catalysts and heterogeneous catalysts for alkene polymerization

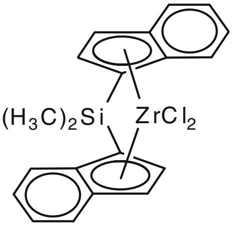
Catalyst type	PDI	Catalyst activity	Strained cycloalkene
Metallocene	2–2.5	10–100	Yes
Heterogeneous	5–6	1	No

groups attached to the atom bridging, the cyclopentadiene rings (C or Si) reduces the activity. MAO affords much higher catalyst activities than ethyl or higher alkyl alumoxane cocatalyst.



10

Achiral catalysts of $CpZrCl_2$, bridged or unbridged yield atactic polymer. Catalyst **11**(chiral) yields isotactic; **12**(achiral) yields syndiotactic polymer. The much different size of the two π ligands of **12** is assumed to play a role in the formation of syndiotactic polymer. Substitution of a methyl group on the cyclopentadiene ring of **12** results in hemi isotactic polypropylene (mixture of isotactic and atactic). Catalyst **13** can rotate between chiral and achiral geometries, with the chiral form being responsible for the isotactic blocks and the achiral form for the atactic blocks. The isotactic blocks form crystalline microdomains in the polymer matrix, the stereoblock copolymers exhibit elastomeric properties. The degree of isotacticity is sensitive to propylene pressure and reaction temperature.



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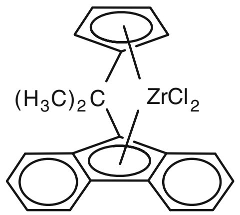

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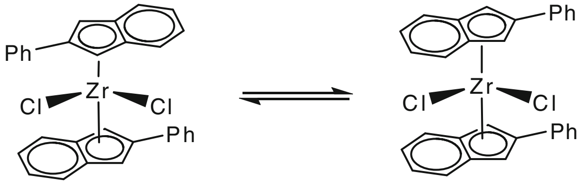
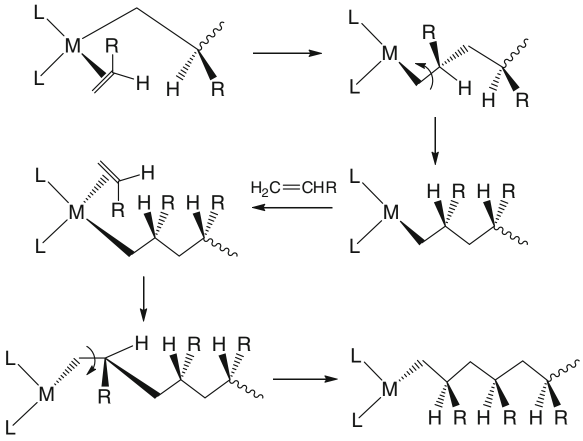


13 **14**

Scheme 9.6 A mechanism for isotactic placement with a metallocene catalyst [3]



What are the reaction mechanisms for the stereospecificity of metallocene catalyzed polymerization? Most models take into account steric interactions involving the π ligands attached to the metal atom and the last inserted monomer unit of the polymer chain, as the incoming monomer inserts itself into the constrained active site. Scheme 9.6 describes the isotactic placement for **11**. Optically active isotactic polymer will form from pure enantiomer of **11**. The larger fluorenyl group restricts the approach of the propylene molecule such that one side of the coordination site is enantioselective to one face of the monomer, and the other side of the coordination site shows the opposite enantioselectivity. Thus as the coordination site moves from side to side, syndiotactic polymer is formed. A methyl group on the cyclopentadiene ring presumably interferes with the selectivity on one side only. Since only one side of the coordination site is then stereoselective, a hemi-isotactic polymer forms.

Dow Chemical Company is using metallocene catalysis to produce its new Questra syndiotactic polystyrene (SPS). Dow has transformed polystyrene—an amorphous, low melting point, relatively brittle plastic—into a tough crystalline material with a melting point of 270°C (conventional is 250°C) for electronics, automotive under-the-hood, engineered films, and medical applications. Therefore polystyrene can be either low cost common plastic or high performance engineering plastics.

9.3 Ziegler–Natta Copolymerization

Random copolymers of ethylene and 1-alkenes are obtainable with Ziegler–Natta catalyst. The most important ones are ethylene with 1-alkene (LLDPE) and ethylene with ethylene propylene monomer (EPM) or ethylene-propylene-diene monomer (EPDM). Table 9.6 summarizes the reactivity ratio of Ziegler–Natta

Table 9.6 Representative reactivity ratios of Ziegler–Natta copolymerization [3]

Monomer 1	Monomer 2	Catalyst[a]	r_1	r_2
Heterogeneous				
Ethylene	Propylene	$TiCl_3/AlR_3$	15.72	0.110
Ethylene	Propylene	VCl_3/AlR_3	5.61	0.145
Ethylene	1-Butene	VCl_3/AlR_3	26.90	0.043
Propylene	1-Butene	VCl_3/AlR_3	4.04	0.252
Homogeneous				
Ethylene	Propylene	Cp_2ZrMe_2	31	0.005
Ethylene	Propylene	$[Z(Ind)_2]ZrCl_2$	6.6	0.060
Ethylene	1-Butene	Cp_2ZrMe_2	55	0.017
Ethylene	1-Hexene	Cp_2ZrMe_2	69	0.020

[a] $R = C_6H_{13}$; Cp = cyclopentadiene; Me = methyl; $Z = CH_2CH_2$; Ind = indene

copolymerization. The reactivity ratio is the rate constant ratio of monomer toward itself and toward other monomer and expressed as $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$. The determination of reactivity ratio will be discussed in Chap. 10.

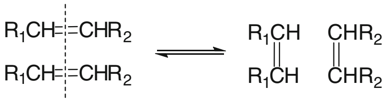
Ethylene is more reactive than higher alkenes with both heterogeneous and homogeneous catalysts. In most instances, r_1r_2 is close to unity. With hetero geneous catalysts, a wide range of compositions is generally obtained, possible because different active sites may give rise to different reactivity ratios, or because of decay of activity. A more homogeneous polymer composition is obtained with soluble catalysts, particularly if monomer composition is carefully controlled to remain relatively constant during polymerization.

There is serious question as to whether the compositions also include significant amounts of homopolymer. The problem arises with uncertainties over the lifetimes of propagating chains, which may become detached from catalyst by chain transfer, thereby leaving the catalyst still active to initiate homopolymerization of a second monomer. Thus Ziegler–Natta method is inferior to anionic polymerization for synthesizing carefully tailored block copolymers.

Kodak’s polyallomers and Uniroyla’s TPR are block copolymer of ethylene and propylene. They are high impact plastics exhibiting crystallinity characteristics of both isotactic polypropylene and linear polyethylene. They contain homopolymers in addition to block copolymers. The conventional random copolymers of ethylene and propylene are elastomeric nature.

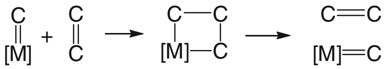
9.4 Metathesis Polymerization

Alkenes undergo a double bond redistribution reaction (Eq. 9.19) called olefin metathesis in the presence of certain complex coordination catalysts. Bond redistribution involves cleavage of the double bonds (trans-alkylidenation). Scission of the single bonds adjacent to the double bonds (trans-alkylation) has been ruled out as a possibility from deuterated alkene experiments. Tungsten compounds are particularly effective for olefin metathesis. The catalysts are formed by the reaction of tungsten hexachloride (WCl_6) with alcohol and ethylaluminum dichloride ($C_2H_5AlCl_2$). Other transition metals, notably Ru, Mo, Rh, and Ti are also effective.



(9.19)

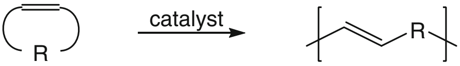
The reaction mechanisms of metathesis polymerization are shown in Eq. 9.20.



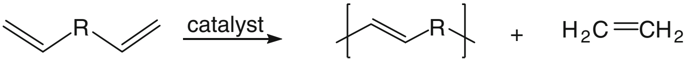
15 **16**

(9.20)

Equations 9.21 and 9.22 show two examples of metathesis polymerization. A double bond containing polymer can be obtained through metathesis polymerization. The method developed in 1970, now it is recognized as a particularly convenient way to make polymers containing precisely spaced carbon–carbon double bonds in the polymer backbone.



(9.21)



(9.22)

The Grignard metathesis reaction has been used to synthesize conducting polymer extensively such as poly(3-hexyl thiophene) as shown in Fig. 5.6 where the catalyst of Ni(dppp)Cl_2 was used [5, 6].

9.5 Problems

1. Explain (a) how sites of variable activity in a heterogeneous catalyst might result in a polymer of high polydispersity, (b) why molecular hydrogen is useful for controlling molecular weight in Ziegler–Natta polymerization, and (c) why only coordination catalysts are effective for polymerizing propylene and higher 1-alkenes. They cannot be polymerized by free radical polymerization.
2. Explain how LDPE and LLDPE differ in terms of structure, synthesis, and properties.

3. Assuming only head-to-tail polymerization and *cis* double-bond opening occurs, give the structure and stereochemical designation of all stereoregular polymers obtainable in principle by stereospecific polymerization of (a) 2-methyl-1-butene, (b) trans-2-pentene, (c) isoprene, and (d) propyne.
4. What are the mechanisms for syndiotactic and isotactic placement in propene polymerization? Please describe the reaction conditions which are favored either syndiotactic placement or isotactic placement.
5. Please discuss the use of homogeneous versus heterogeneous reaction conditions for the coordination polymerizations of propene, isoprene, styrene, methyl methacrylate, and n-butyl vinyl ether.
6. Crystalline-crystalline block copolymer of regioregular poly(3-hexyl thiophene) and polyethylene can be prepared by ring-opening metathesis polymerization (Eq. 9.21). Please write out the reaction mechanism to show how the copolymer is being synthesized [7].

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Chapter 10
Chain Copolymerization

Copolymers [1, 2] contain two or more repeating monomer structures in the polymer chain. The copolymer can be synthesized by chain polymerization using two or more type of monomers. It is called chain copolymerization. The process can be depicted as

$$M_1 + M_2 \rightarrow \sim\sim M_1M_2M_2M_1M_2\,M_1\,M_1M_2\sim\sim \tag{10.1}$$

The amount of each monomer in the copolymer is determined by their relative concentration and reactivities. The simultaneous chain polymerization can also be carried out with more than two type of monomers. Such polymerizations are generally referred to as *multicomponent copolymerizations*; the term *terpolymerization* is specifically used for systems of three kind of monomers.

Copolymerization allows the synthesis of an almost unlimited number of different products by variations in the chemical structure and relative amounts of two monomer units or higher in the copolymer product. Thus, polymer can be tailor made into product with specifically desired properties. Most of commercial polymers are copolymers. Copolymers are different from polymer blends. Polymer blends are that polymers mixed physically without chemical bonds. Whereas copolymers are that polymers contain more than one kind of monomer repeating unit.

There are three different types of copolymer structures—alternating, block, and graft. The *alternating* copolymer (I) contains the two monomer units in equimolar amounts in a regular alternating distribution:

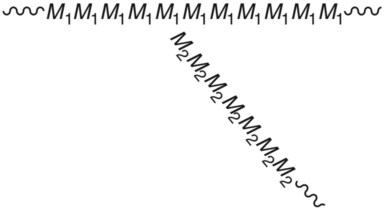
$$\sim\sim M_1M_2\;\;M_1M_2\;\;M_1M_2\sim\sim \tag{I}$$

Copolymers are named by following the prefix *poly* with the names of the two repeating units. The copolymer is specified by inserting -*alt*- for alternate, -*stat*- for statistic, or -*ran*- for random in between the names of the two repeating units, but -*co*- is used for nonspecific copolymer. A block copolymer (II) is a linear copolymer with one or more long uninterrupted sequences of each polymeric species.

W.-F. Su, *Principles of Polymer Design and Synthesis*,
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_10,

$$\sim\!\sim M_1M_1M_1M_1 \sim\!\sim M_2M_2M_2\sim\!\sim \tag{II}$$

While a *graft* copolymer (III) is a branched copolymer with a backbone of one kind of monomer to which are attached one or more side chains of another monomer,



(III)

10.1 Reaction Kinetics of Free Radical Copolymerization

The reaction kinetics of free radical copolymerization is similar to the homopolymerization. However, one needs to consider the variations in reactivity between reacting species [3]. Copolymerization of the two monomers leads to two types of propagating species—one with M_1 and the other with M_2 at the propagating end and. These can be represented by $M_1\cdot$ and $M_2\cdot$. If one assumed that the reactivity of the propagating chain is dependent only on the monomer unit at the end of the chain, four propagation reactions are then possible. Monomers M_1 and M_2 can each add either to a propagating chain ending in M_1 or to one ending in M_2, they are

$$M_1^{\cdot} + M_1 \xrightarrow{k_{11}} M_1^{\cdot} \tag{10.2}$$

$$M_1^{\cdot} + M_2 \xrightarrow{k_{12}} M_2^{\cdot} \tag{10.3}$$

$$M_2^{\cdot} + M_1 \xrightarrow{k_{21}} M_1^{\cdot} \tag{10.4}$$

$$M_2^{\cdot} + M_2 \xrightarrow{k_{22}} M_2^{\cdot} \tag{10.5}$$

where k_{11} is the rate constant for a propagating chain ending in M_1 adding to monomer M_1, k_{12} is for a propagating chain ending in $\mathrm{M_1}$ adding to monomer M_2, and so on. The active center of propagating chain is added to same monomer (i.e., reactions in Eqs. 10.2 and 10.5) is referred to as *homopropagation* or *self-propagation*; if it is added to other monomer (reactions in Eqs. 10.3 and 10.4) is referred to as *cross-propagation* or a *crossover* reaction. To derive the reaction kinetic equations of copolymerization, we assume the chemical reactivity in a copolymerization is dependent only on the identity of the monomer unit at the growing end and independent of the chain composition preceding the last monomer unit. All propagation reactions are irreversible.

Monomer M_1 disappears by reactions in Eqs. 10.2 and 10.4, while monomer M_2 disappears by reactions in Eqs. 10.3 and 10.5. The rates of disappearance of the two monomers are given by

$$-d[M_1]/dt = k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1] \tag{10.6}$$

$$-d[M_2]/dt = k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] \tag{10.7}$$

Dividing Eq. 10.6 by Eq. 10.7 yields the ratio of the rates at which the two monomers enter the copolymer, that is, the copolymer composition, as

$$\frac{d[M_1]}{d[M_2]} = \frac{k_{11}[M_1\cdot][M_1] + k_{21}[M_2\cdot][M_1]}{k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2]} \tag{10.8}$$

In order to remove the concentration terms in $M_1\cdot$ and $M_2\cdot$ from Eq. 10.8, a steady-state concentration is assumed for each of the propagating chains $M_1\cdot$ and $M_2\cdot$ separately. For the concentrations of $M_1\cdot$ and $M_2\cdot$ remain constant, their rates of interconversion must be equal. In other words, the rates of reactions in Eqs. 10.3 and 10.4 must be equal:

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \tag{10.9}$$

Equation 10.9 can be rearranged and combined with Eq. 10.8 to yield

$$\frac{d[M_1]}{d[M_2]} = \frac{\frac{k_{11}k_{21}[M_2\cdot][M_1]^2}{k_{12}[M_2]} + k_{21}[M_2\cdot][M_1]}{k_{22}[M_2\cdot][M_2] + k_{21}[M_2\cdot][M_1]} \tag{10.10}$$

Dividing the top and bottom of the right side of Eq. 10.10 by $k_{21}[M_2\cdot][M_1]$ and combining the result with the parameters r_1 and r_2, which are defined as

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21} \tag{10.11}$$

One finally obtains

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1](r_1[M_1] + [M_2])}{[M_2]([M_1] + r_2[M_2])} \tag{10.12}$$

Equation 10.12 is known as the *copolymerization equation* or the *copolymer composition equation*. The copolymer composition, $d[M_1]/d[M_2]$, is the molar ratio of the two monomer units in the copolymer which is related to the concentrations of the two monomers in the feed, $[M_1]$ and $[M_2]$, and the parameters r_1 and r_2. The parameters r_1 and r_2 are called the *monomer reactivity ratios*. Each r defines as the ratio of the rate constant for a propagating chain adding its own type of monomer to the rate constant for its addition of the other monomer. The tendency of two monomers to copolymerize is expressed by r values between zero and unity.

A r_1 value greater than unity means that $M_1\cdot$ preferentially adds M_1 instead of M_2, while an r_1 value less than unity means that $M_1\cdot$ preferentially adds M_2. A r_1 value of zero would mean that M_1 is incapable of undergoing homopolymerization.

The copolymerization equation can also be expressed in terms of mole fractions instead of concentrations. If f_1 and f_2 are the mole fractions of monomers M_1 and M_2 in the feed, and F_1 and F_2 are the mole fractions of M_1 and M_2 in the copolymer, then

$$f_1 = 1 - f_2 = [M_1]/([M_1] + [M_2]) \tag{10.13}$$

and

$$F_1 = 1 - F_2 = d[M_1]/(d[M_1] + d[M_2]) \tag{10.14}$$

Combining Eqs. 10.13 and 10.14 with Eq. 10.12 yields

$$F_1 = \left(r_1 f_1^2 + f_1 f_2\right) / \left(r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2\right) \tag{10.15}$$

The copolymerization equation has been experimentally verified in numerous co-monomer systems. The copolymerization equation is equally useful to radical and ionic chain copolymerizations, although the r_1 and r_2 values for any particular co-monomer pair can be drastically different depending on the mode of initiation. Thus the r_1 and r_2 values for the co-monomer pair of styrene (M_1) and methyl methacrylate (M_2) are 0.52 and 0.46 in radical copolymerization, 10 and 0.1 in cationic polymerization, and 0.1 and 6 in anionic copolymerization [1]. Figure 10.1 shows that these different r_1 and r_2 values give rise to large differences in the copolymer composition depending on the mode of initiation. The ionic copolymerizations are expected to be more selective than radical copolymerization. Methyl methacrylate shows increased reactivity in anionic copolymerization and decreased reactivity in cationic copolymerization, while the opposite is observed for styrene. Thus, for an equimolar styrene—methyl methacrylate feed the copolymer is approximately a 1:1 copolymer in the radical polymerization but

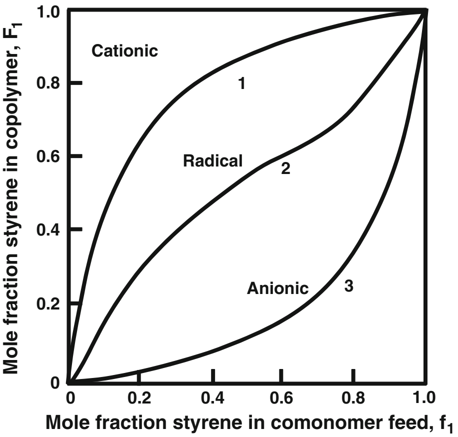


Fig. 10.1 Dependence of the instantaneous copolymer composition F_1 on the initial co-monomer feed composition f_1 for styrene-methyl methacrylate in cationic (plot 1), radical (plot 2), and anionic (plot 3) copolymerizations initiated by $SnCl_4$, benzoyl peroxide, and Na/liquid NH_3, respectively [1]

is mostly styrene in the cationic copolymerization and mostly methyl methacrylate in the anionic copolymerization.

Radical copolymer is more useful than cationic or anionic copolymer, because about all the monomers are reacted in the radical copolymer. Since termination and initiation rate constants are not involved in the copolymer composition equation, the copolymer composition is independent of difference in the rates of initiation and termination. Thus, the particular initiation system used in a radical copolymerization has no effect on copolymer composition. The copolymer composition is also independent on the absence or presence of inhibitions or chain transfer agents. Therefore, under a wide range of conditions, the copolymer composition is independent of the degree of polymerization.

10.1.1 Types of Copolymerization Behavior

Different types of copolymerization behavior are observed depending on the reactivity ratios of monomers [4]. Copolymerizations can be classified into three types: (1) $r_1r_2 = 1$, (2) $r_1r_2 < 1$, (3) $r_1r_2 > 1$. When the r_1r_2 product is unity, the reaction is called ideal copolymerization. Ideal copolymerization occurs when the two types of propagating chains $M_1\cdot$ and $M_2\cdot$ show the same preference for adding one or the other of the two monomers. Under these conditions

$$k_{22}/k_{21} = k_{12}/k_{11} \text{ or } r_2 = 1/r_1 \tag{10.16}$$

and the relative rates of incorporation of the two monomers into the copolymer is independent of the identity of the unit at the end of the propagating chains. Thus, by combination Eq. 10.16 with Eqs. 10.12 or 10.15 reduces the copolymerization equation to

$$d[M_1]/d[M_2] = r[M_1]/[M_2] \tag{10.17a}$$

or

$$F_1 = r_1f_1/(r_1f_1 + f_2) \tag{10.17b}$$

Most of ionic copolymerizations are ideal type. When $r_1r_2 = 1$, the two monomers show equal reactivity toward both propagating chains. The copolymer composition is the same as the two monomers along the copolymer chain. This behavior is called *random* or *Bernoullian*. For the case, where the two monomer reactivity ratios are different, that is, $r_1 > 1$ and $r_2 < 1$ or $r_1 < 1$ and $r_2 > 1$, one of the monomers is more reactive than the other toward both propagating chains. The copolymer will contain a larger proportion of the more reactive monomer in random placement. Figure 10.2 shows the variation in the copolymer composition as a function of the co-monomer feed composition for different value of r_1. When, for example, $r_1 = 10$, $r_2 = 0.1$, copolymer cannot contain appreciable amounts of M_2. Thus, a co-monomer feed composition of 80 mol% $M_2 (f_2 = 0.8)$ would yield

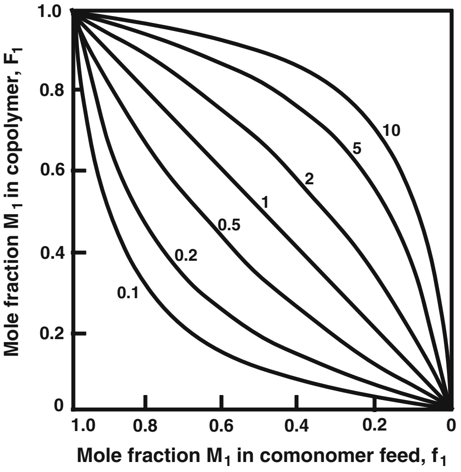


Fig. 10.2 Dependence of the instantaneous copolymer composition F_1 on the initial co-monomer feed composition f_1 for the indicated values of r_1 where $r_1 r_2 = 1$ [1]

a copolymer containing only 18.5 mol% $M_2 (f_2 = 0.185)$. It is only $r_1 \approx r_2$, a large range of co-monomer feed compositions which gives copolymer contain appreciable amount of both monomers.

The term ideal copolymerization does not mean it is a desirable process. It is used to explain the process becomes processively more difficult to produce copolymers containing appreciable amounts of both monomers as the difference in r_1 and r_2 increases. For example, $r_1 = 10$ and $r_2 = 0.1$, the *extreme ideal behavior* occurs when r_1 and r_2 are very different, the obtained copolymers do not contain appreciable amounts of M_2. To yield copolymers containing appreciable amounts of both monomers, a larger range of co-monomer feed compositions, can be used only for r_1 and r_2 do not differ markedly (e.g., $r_1 = 0.5$, $r_2 = 2$).

When $r_1 r_2 = 0$, the two monomers enter into the copolymer in equimolar amounts in a nonrandom, alternating arrangement along the copolymer chain. This type of copolymerization is referred to as *alternating copolymerization*. Each of the two types of propagating chains preferentially adds to the other monomer, that is, $M_1 \cdot$ adds only M_2 and $M_2 \cdot$ adds only M_1, the copolymerization equation reduces to

$$d[M_1]/d[M_2] = 1 \tag{10.18a}$$

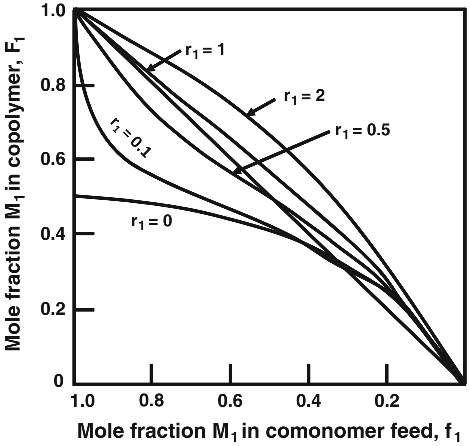
or

$$F_1 = 0.5 \tag{10.18b}$$

The copolymer has the alternating structure irrespective of the co-monomer feed composition. The behavior of most co-monomer systems lies between the two extremes of ideal and alternating copolymerization.

As the $r_1 r_2$ product decreases from unity toward zero, there is an increasing tendency toward alternation. Perfect alternation will occur when r_1 and r_2 become progressively less than unity. The range of behaviors can be seen by considering the

Fig. 10.3 Dependence of the instantaneous copolymer composition F_1 on the initial co-monomer feed composition f_1 for the indicated values of r_2 being constant at 0.5 [1]



situation where r_2 remains constant at 0.5 and r_1 varies between 2 and 0. Figure 10.3 shows the copolymer composition as a function of the feed composition in these cases. The curve for $r_1 = 2$ is ideal copolymerization. As r_1 decreases below 2, there is an increasing tendency toward the alternating behavior with each type of propagating chains preferring to add to the other monomer. The increasing alternation tendency is measured by the tendency of the product $r_1 r_2$ to approach zero. When $r_1 r_2$ is very small or zero, the alternation tendency is very large and the range of copolymer compositions that can be obtained is again limited. In the extreme case, only the 1:1 alternating copolymer can be produced for $r_1 r_2 = 0$.

For values of $r_1 r_2 < 1$, the F_1 versus f_1 curves are across the line of $F_1 = f_1$. At these intersections or *crossover points* the copolymer and feed composition are the same. The copolymerization occurred without a change in the feed composition is called "*azeotropic copolymerization*". The copolymerization Eq. 10.12 can be reduced to

$$d[M_1]/d[M_2] = [M_1]/[M_2], \text{ as}$$

$$[M_1]/[M_2] = (r_2 - 1)/(r_1 - 1) \tag{10.19a}$$

or

$$f_1 = (1 - r_2)/(2 - r_1 - r_2) \tag{10.19b}$$

For the special case of $r_1 \gg r_2$ (i.e. $r_1 \gg 1$ and $r_2 \ll 1$), both types of propagating chains preferentially add to monomer M_1. There is a tendency toward "*consecutive homopolymerization*" of the two monomers to form block copolymer. For example, the radical polymerization of styrene and vinyl acetate with monomer reactivity ratios of 55 and 0.01 produces block copolymer.

For all copolymerizations except azeotropic copolymerization, the co-monomer feed and copolymer compositions are different. There is a drift in the co-monomer composition toward the less reactive monomer as the degree of conversion increases. Skeist [5] developed a useful method to analyze copolymer composition as a function of conversion. Consider a system initially containing a total of M moles of the two monomers and in which the copolymer formed is richer in monomer M_1 than is the feed (that is, $F_1 > f_1$). When dM moles of monomers have been copolymerized, the polymer will contain $F_1 dM$ moles of monomer 1 and the feed will contain $(M - dM)$ $(f_1 - df_1)$ moles of monomer 1. A material balance for monomer 1 requires that the moles of M_1 copolymerized is equal to the difference in the moles of M_1 in the feed before and after reaction, or

$$Mf_1 - (M - dM)(f_1 - df_1) = F_1 dM \tag{10.20}$$

Equation 10.20 can be rearranged and converted to the integral form

$$\int_{M_0}^{M} \frac{dM}{M} = \ln \frac{M}{M_0} = \int_{(f_1)_0}^{f_1} \frac{df_1}{(F_1 - f_1)} \tag{10.21}$$

where M_0 and $(f_1)_0$ are the initial values of M and f_1.

Equation 10.15 allows the calculation of F_1 as a function of f_1 for a given set of r_1 and r_2 values. These can then be employed as $(F_1 - f_1)$ to allow the graphical or numerical integration of Eq. 10.21 between the limits of $(f_1)_0$ and f_1. In this manner, one can obtain the variations in the feed and copolymer compositions with the degree of conversion as shown in Eq. 10.22.

$$1 - \frac{M}{M_0} = 1 - \left[\frac{f_1}{(f_1)_0}\right]^{\alpha} \left[\frac{f_2}{(f_2)_0}\right]^{\beta} \left[\frac{(f_1)_0 - \delta}{f_1 - \delta}\right]^{\gamma} \tag{10.22}$$

The zero subscripts indicate initial quantities and the other symbols are given by

$$\alpha = \frac{r_2}{(1 - r_2)} \tag{10.23a}$$

$$\beta = \frac{r_1}{(1 - r_1)} \tag{10.23b}$$

$$\gamma = \frac{(1 - r_1 r_2)}{(1 - r_1)(1 - r_2)} \tag{10.23c}$$

$$\delta = \frac{(1 - r_2)}{(2 - r_1 - r_2)} \tag{10.23d}$$

Equation 10.22 or its equivalent has been used to correlate the drift in the feed and copolymer compositions with conversion for a number of different copolymerization systems.

Fig. 10.4 Variations in feed and copolymer compositions with conversion for styrene (M_1), methyl methacrylate (M_2) with $(f_1)_0 = 0.80$, $(f_2)_0 = 0.20$ and $r_1 = 0.53$. $r_2 = 0.56$ [1]

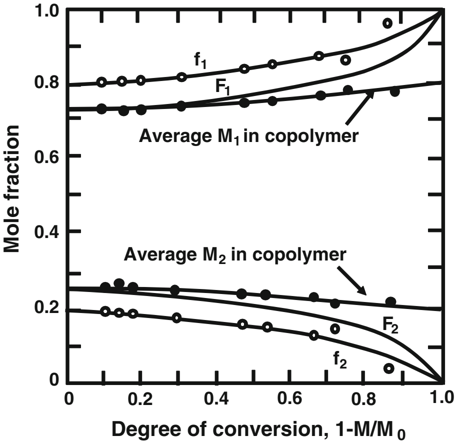


Figure 10.4 shows the variations in feed and copolymer composition with conversion for styrene and methyl methacrylate. The average composition of the copolymer is slightly richer in methyl methacrylate than the feed, because methyl methacrylate has a slightly larger monomer reactivity ratio than styrene. The feed becomes richer in styrene with conversion which leads to an increase in the styrene content of the copolymer with conversion. The average copolymer composition becomes richer in styrene than methyl methacrylate, but less so than the instantaneous copolymer composition.

10.1.2 Effect of Reaction Conditions on Radical Copolymerization

Monomer reactivity ratios are generally (but not always) independent of the reaction medium in radical polymerization. For nonhomogeneous conditions, sometime, the reaction medium affects the monomer reactivity ratio. For instance, the emulsion polymerization of styrene and acrylonitrile, co-monomer feed composition at the reaction site is different from that in the bulk of the reaction system [1]. Deviations are also observed in some copolymerization where the formed copolymer is poorly soluble in the reaction medium. For the copolymerization of methyl methacrylate (M_1) and *N*-vinyl carbazole (NVC) (M_2), $r_1 = 1.80$, $r_2 = 0.06$ in benzene but $r_1 = 0.5$, $r_2 = 0.75$ in methanol. The propagating copolymer chains are completely soluble in benzene, but are marginal in methanol. NVC is preferentially absorbed by the copolymer compared to methyl methacrylate, so NVC enters the copolymer to a greater extent than expected based on the feed composition. The viscosity of solution has effect on r value. Copolymerization of styrene (M_1) and methyl methacrylate (M_2) in bulk leads to a copolymer containing less styrene than that is carried out in benzene solution. The gel effect in bulk polymerization decreases the mobility of styrene resulting in a decrease in r_1 and an increase in r_2 [6].

Copolymerization involving the combination of polar M_1 and nonpolar M_2 monomers often shows different behavior depending on the polarity of the reaction medium. The copolymer composition is richer in the less polar monomer for reaction in a polar solvent compared to nonpolar solvent for the copolymerization of styrene with acrylamide, acrylonitrile, 2-hydroxyethyl methacrylate, respectively. The result is due to the feed composition in the domain of the growing polymer radical being richer in the less polar monomer. The polar solvent complexes with the polar monomer thus reduces its reactivity [1].

The r_1 and r_2 are relatively insensitive to temperature, for example, the r_1 and r_2 values for styrene and 1,3-butadiene are 0.64 and 1.4 at 5°C, and 0.60 and 1.8 at 45°C, respectively. The r_1 and r_2 values for styrene and methyl methacrylate are 0.52 and 0.46 at 60°C, and 0.59 and 0.54 at 131°C [7]. The monomer reactivity ratio is the ratio of two propagation rate constants, and its variation with temperature will depend on the difference in propagation activation energies according to

$$r_1 = k_{11}/k_{12} = A_{11}/A_{12} \ \exp\left[(E_{12} - E_{11})/\mathrm{RT}\right] \tag{10.24}$$

where E_{11} and A_{11} are the propagation activation energy and frequency factor for M_1 radical adding M_1 monomer, respectively, and E_{12} and A_{12} are the corresponding values for M_1 radical adding M_2 monomer. The effect of temperature on r is not large, since the activation energies for radical propagation are relatively small and fall in a narrow range such that $E_{12} - E_{11} \ll 10$ kJ/mol for most pairs of monomers. An increase in temperature results in a less selective copolymerization as the two monomer reactivity ratios of a co-monomer pair each tends toward unity with decreasing preference of either radical for either monomer. Temperature has large effect on those systems, r deviates markedly from unity: especially for ionic polymerization [1].

The pressure effect [1] on the monomer reactivity ratio can be expressed by

$$d \ln r_1/dP = -\left(\triangle v_{11}^{\ddagger} - \triangle v_{12}^{\ddagger}\right)\Big/\mathrm{RT} \tag{10.25}$$

where $\triangle v_{11}^{\ddagger}$ and $\triangle v_{12}^{\ddagger}$ are the propagation activation volumes for radical M_1 adding monomers M_1 and M_2, respectively. Although propagation rates increase considerably with pressure, r is less sensitive to pressure, since $(\triangle v_{11}^{\ddagger} - \triangle v_{12}^{\ddagger})$ is smaller than either $\triangle v_{11}^{\ddagger}$ or $\triangle v_{12}^{\ddagger}$. The effect of pressure tends to decrease the direction of selectivity of ideal copolymerization. For example, the r_1r_2 product for the copolymerization of styrene and acrylonitrile changes from 0.026 at 1 atm to 0.077 at 1000 atm, while r_1r_2 for the copolymerization of methyl methacrylate and acrylonitrile changes from 0.16 to 0.91. The ideal copolymerization remains so regardless the change of pressure.

10.1.3 Reactivity and Composition of Free Radical Copolymerization

Table 10.1 shows the monomer reactivity ratios of monomers in radical copolymerization [1]. With the same monomer, such as acrylic acid, its r_1 can be varied from 0.25 to 8.7 by changing reaction with styrene radical to vinyl acetate radical. The data are useful for a study of the relation between structure and reactivity in radical addition reactions. The reactivity of monomer toward a radical depends on the reactivities of both of the monomers and radicals. The relative reactivities of monomers and their corresponding radicals can be obtained from an analysis of the monomer reactivity ratios. The reactivity of a monomer can be seen by considering the inverse of the monomer reactivity ratio ($1/r$). The inverse of the monomer reactivity ratio gives the ratio of the rate of reaction of a radical with another monomer to its rate of reaction with its own monomer.

Table 10.2 shows $1/r$ values calculated from the data in Table 10.1. The data in each vertical column show the *monomer reactivities* of a series of different monomers toward the same reference polymer radical. Thus the first column shows the reactivities of the monomers toward the butadiene radical, the second column shows the reactivities of the monomers toward the styrene radical, and so on. It is important to note that the data in Table 10.2 cannot compare the reactivity by horizontal row.

Table 10.2 is organized according to the general decrease order of monomer reactivity in each column. The order of monomer reactivities is approximately the same in each vertical column irrespective of the reference radical. There are few exceptions where the strong alternating tendency of certain co-monomer pairs is present. The data [1] show the substitution effect on the reactivity of monomer toward radical attack in a general order of

$$-\phi, -\mathrm{CH}=\mathrm{CH_2} > -\mathrm{CN}, -\mathrm{COR} > -\mathrm{COOH}, -\mathrm{COOR} > -\mathrm{Cl} > -\mathrm{OCOR}, -\mathrm{R} > -\mathrm{OR}, -\mathrm{H}$$

The order of monomer reactivities corresponds to the order of increased resonance stabilization by the particular substituent of the radical formed from the monomer. The order of *radical reactivity* can be obtained by multiplying the $1/r$ by the appropriate propagation rate constants of homopolymerization (k_{11}) that is equal to k_{12}, reaction rate of radical-monomer combination. The k_{12} values in any vertical column in Table 10.3 give the order of monomer reactivities as shown in Table 10.2.

Table 10.3 gives the order of radical reactivities toward a reference monomer in the horizontal row. The order of substituent in enhancing radical reactivity is the opposite of their order in enhancing monomer reactivity. A substituent on the monomer can increase or decrease its reactivity depends on the ability of substituent to stabilize or destabilize the corresponding radical. For example, vinyl acetate radical is about 100–1000 times more reactive than styrene radical toward a given monomer, while styrene monomer is only 50–100 times more reactive than

Table 10.1 Monomer reactivity ratios in radical copolymerization [1]

M_1	r_1	M_2	r_2	T (°C)
Acrylic acid	0.24	*n*-Butyl methacrylate	3.5	50
	0.25	Styrene	0.15	60
	8.7	Vinyl acetate	0.21	70
Acrylonitrile	0.86	Acrylamide	0.81	40
	0.046	1,3-Butadiene	0.36	40
	0.69	Ethyl vinyl ether	0.060	80
	0.98	Isobutylene	0.020	50
	1.5	Methyl acrylate	0.84	50
	0.14	Methyl methacrylate	1.3	70
	0.020	Styrene	0.29	60
	5.5	Vinyl acetate	0.060	70
	3.6	Vinyl chloride	0.044	50
	0.92	Vinylidene chloride	0.32	60
	0.020	2-Vinylpyridine	0.43	60
	0.11	4-Vinylpyridine	0.41	60
Allyl acetate	0	Methyl methacrylate	23	60
	0	Styrene	90	60
	0.70	Vinyl acetate	1.0	60
1,3-Butadiene	0.75	Methyl methacrylate	0.25	90
	1.4	Styrene	0.58	50
	8.8	Vinyl chloride	0.040	50
Diethyl fumarate	0	Acrylonitrile	8.0	60
	0.070	Styrene	0.30	60
	0.44	Vinyl acetate	0.011	60
	0.48	Vinyl chloride	0.13	60
Diethyl maleate	0	Acrylonitrile	12	60
	0	Methyl methacrylate	20	60
	0.010	Styrene	6.1	70
	0.040	Vinyl acetate	0.17	60
	0.046	Vinyl chloride	0.90	70
Ethylene	0	Acrylonitrile	7.0	20
	0.010	*n*-Butyl acrylate	14	150
	0.38	Tetrafluoroethylene	0.10	25
	0.79	Vinyl acetate	1.4	130
Fumaronitrile	0.019	*n*-Dodecyl vinyl ether	0.004	60
	0	Methyl methacrylate	6.7	79
	0.006	Styrene	0.29	65
Maleic anhydride	0	Acrylonitrile	6.0	60
	0.045	n-Butyl vinyl ether	0	50
	0.012	Methyl acrylate	2.8	75
	0.010	Methyl methacrylate	3.4	75
	0.08	*cis*-Stilbene	0.07	60
	0.03	*trans*-Stilbene	0.03	60
	0.005	Styrene	0.050	50
	0	Vinyl acetate	0.019	75
	0	Vinyl chloride	0.098	75

(continued)

Table 10.1 (continued)

M_1	r_1	M_2	r_2	T (°C)
Methacrylic acid	2.4	Acrylonitrile	0.092	70
	0.60	Styrene	0.12	60
	24	Vinyl chloride	0.064	50
	0.58	2-Vinylpyridine	1.7	70
Methacrylonitrile	0.46	Ethyl methacrylate	0.83	80
	0.25	Styrene	0.25	80
	12	Vinyl acetate	0.01	70
Methyl acrylate	0.84	Acrylonitrile	1.5	50
	0.070	1,3-Butadiene	1.1	5
	3.3	Ethyl vinyl ether	0	60
	2.8	Maleic anhydride	0.012	75
	0.40	Methyl methacrylate	2.2	50
	0.80	Styrene	0.19	60
	6.4	Vinyl acetate	0.030	60
	4.4	Vinyl chloride	0.093	50
	0.17	2-Vinylpyridine	1.7	60
	0.20	4-Vinylpyridine	1.7	60
Methyl methacrylate	0.36	Acenaphthylene	1.1	60
	0.46	Styrene	0.52	60
	9.0	Vinyl chloride	0.070	68
	2.4	Vinylidene chloride	0.36	60
α-Methylstyrene	0.14	Acrylonitrile	0.030	75
	0.040	Maleic anhydride	0.080	60
	0.27	Methyl methacrylate	0.48	60
	0.14	Styrene	1.2	60
Methyl vinyl ketone	0.35	Styrene	0.29	60
	8.3	Vinyl chloride	0.10	70
	1.8	Vinylidene chloride	0.55	70
Styrene	90	Ethyl vinyl ether	0	80
	42	Vinyl acetate	0	60
	15	Vinyl chloride	0.010	60
	1.8	Vinylidene chloride	0.087	60
Vinyl acetate	3.4	Ethyl vinyl ether	0.26	60
	0.24	Vinyl chloride	1.8	60
	0.030	Vinylidene chloride	4.7	68

vinyl acetate monomer toward a given radical as summarized in Table 10.4. Thus, styrene has higher reactivity than vinyl acetate toward same radical. However, its corresponding radical has lower reactivity toward same monomer.

The interaction of radical reactivity and monomer reactivity in determining the rate of a radical-monomer reaction can be illustrated by potential energy changes accompanying the radical-monomer reaction as a function of the separation between the atoms forming the new bond as shown in Fig. 10.5.

Table 10.2 Relative reactivities (1/*r*) of monomers with various polymer radicals[a][1]

Monomer	Polymer radical						
	Butadiene	Styrene	Vinyl acetate	Vinyl chloride	Methyl methacrylate	Methyl acrylate	Acrylonitrile
Butadiene	–	1.7	–	29	4	20	50
Styrene	0.7	–	100	50	2.2	5	25
Methyl methacrylate	1.3	1.9	67	10	–	2	6.7
Methyl vinyl ketone	–	3.4	20	10	–	–	1.7
Acrylonitrile	3.3	2.5	20	25	0.82	1.2	–
Methyl acrylate	1.3	1.3	10	17	0.52	–	0.67
Vinylidene chloride	–	0.54	10	–	0.39	–	1.1
Vinyl chloride	0.11	0.059	4.4	–	0.1	0.25	0.37
Vinyl acetate	–	0.019	–	0.59	0.05	0.11	0.24

[a] 1/*r* values calculated from data of Table 10.1

Table 10.3 Rate constants (k_{12}) for radical-monomer reactions [1, 2]

Monomer (M_2)	Polymer radical						
	Butadiene	Styrene	Methyl methacrylate	Acrylonitrile	Methyl acrylate	Vinyl acetate	Vinyl chloride
Butadiene	100	280	2,060	98,000	41,800	–	319,000
Styrene	70	165	1,130	49,000	10,045	230,000	550,000
Methyl methacrylate	130	314	515	13,100	4,180	154,000	110,000
Acrylonitrile	330	413	422	1,960	2,510	46,000	225,000
Methyl acrylate	130	215	268	1,310	2,090	23,000	187,000
Vinyl chloride	11	9.7	52	720	520	10,100	11,000
Vinyl acetate	–	3.4	26	230	230	2,300	6,490

[a] k_{12} values calculated from data in Table 10.2

Table 10.4 The reactivity comparison between monomer and its corresponding radical

Reactant	Reactivity	Toward
Vinyl acetate radical	100–1,000 x	Same monomer
Styrene radical	1	Same monomer
Styrene monomer	50–100 x	Same radical
Vinyl acetate monomer	1	Same radical

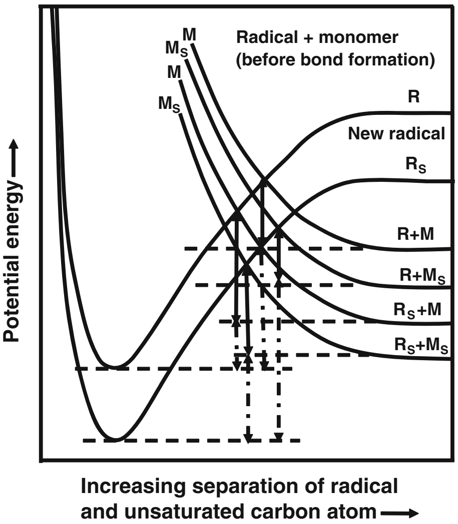


Fig. 10.5 Reaction coordination diagram for the reaction of a polymer radical with a monomer. The dependence of the potential energy of the system (radical + monomer) on the separation between the radical and the unsaturated carbon atom of the monomer is shown. The subscript *s* indicates the presence of a substituent that is capable of resonance stabilization. Activation energies are represented by the *solid-line arrows*; heats of reaction by the *broken-line arrows* [1]

These energy changes are shown for four possible reactions between resonance-stabilized and nonstabilized monomer and radicals are

$$R\cdot + M \rightarrow R\cdot \tag{10.26a}$$

$$R\cdot + M_s \rightarrow R_s\cdot \tag{10.26b}$$

$$R_s\cdot + M_s \rightarrow R_s\cdot \tag{10.26c}$$

$$R_s\cdot + M \rightarrow R\cdot \tag{10.26d}$$

where the presence or absence of the subscript s indicates the presence or absence, respectively, of a substituent that is capable of resonance stabilization. Vinyl acetate and styrene monomers are examples of M and M_s, respectively; vinyl acetate and styrene radicals are examples of $R\cdot$ and $R_s\cdot$, respectively. There are two sets of potential energy curves in Fig. 10.5. One set of four repulsion curves represents the energetic approach of a radical to a monomer; the other set of two Morse curves represents the stability of the bond finally formed. The intersections of the curves represent the transition states for the monomer-radical reactions. The

Table 10.5 Rate constants (k_{12}) for radical-monomer reactions involving chlorine substituted ethylenes [1]

Monomer	Polymer radical		
	Vinyl acetate	Styrene	Acrylonitrile
Vinyl chloride	10,000	9.7	725
Vinylidene chloride	23,000	89	2,150
cis-1,2-Dichloroethylene	365	0.79	–
trans-1,2-Dichloroethylene	2,320	4.5	–
Trichloroethylene	3,480	10.3	29
Tetrachloroethylene	338	0.83	4.2

order of reaction rate constants for the various monomer-radical reaction is the following which is the opposite order of activation energy of reaction.

$$R_s\cdot + M < R_s\cdot + M_s < R\cdot + M < R\cdot + M_s$$

This order of reactivity is consistent with the data in Tables 10.2 and 10.3 as well as many homopolymerization data. The monomers without stabilizing substituents (e.g., vinyl chloride or vinyl acetate) will self-propagate faster than those with stabilizing substituents. Copolymerization will occur primarily between two monomers with stabilizing substituents or between two monomers without stabilizing substituents.

The rates of radical-monomer reactions are also affected by the presence of steric hindrance [1]. Table 10.5 shows the k_{12} values for the reactions of various chlorine substituted ethylenes with vinyl acetate, styrene, and acrylonitrile radicals. The k_{12} of vinylidene chloride is two times higher as compared with vinyl chloride toward vinyl acetate polymer radical which is due to more resonance structure available from vinylidene chloride. The k_{12} of *trans*-1,2-dichloroethylene is six times higher as compared with *cis*-1,2-dichloroethylene toward vinyl acetate polymer radical which is due to the less steric hindrance from the *trans*-1,2-dichloroethylene reacting with vinyl acetate polymer radical. The k_{12} of trichloroethylene is higher than *trans*-1,2-dichloroethylene toward vinyl acetate polymer radical, because the trichloroethylene can provide more resonance structure after the reaction. The trend is similar for the polymer radical of styrene and acrylonitrile.

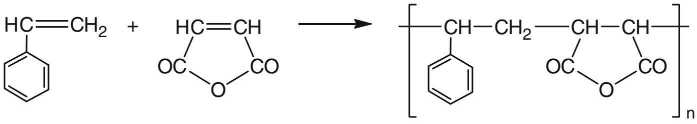
Table 10.6 lists the monomers in order of their r_1 r_2 value with other monomers. The further apart two monomers are, the greater is their tendency toward alternation. Thus, acrylonitrile undergoes ideal copolymerization with methyl vinyl ketone ($r_1r_2 = 1.1$) and alternating copolymerization with butadiene ($r_1r_2 = 0.006$).

The order of monomers in Table 10.6 is based on polarity of the double bond. Monomers with electron-donating substituents are located at the top (left) of the table and those with electron-withdrawing substituents at the bottom (right). The r_1r_2 value decreases progressively as one considers two monomers further apart in the table. Monomers on the left are less polar monomers, on the right are more polar. The tendency toward alternation increases as the difference in polarity

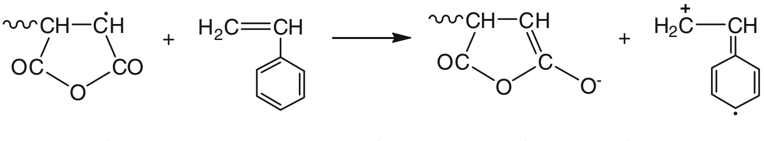
Table 10.6 Values of r_1r_2 in radical copolymerization [1]

	n-Butyl vinyl ether (-1.50)	Butadiene(-0.50)	Styrene(-0.80)	Vinyl acetate(-0.88)	Vinyl chloride(0.16)	Methyl methacrylate(0.40)	Vinylidene chloride(0.34)	Methylvinyl ketone(1.06)	Acrylonitrile(1.23)	Diethyl fumarate(2.26)
Butadiene(-0.50)										
Styrene(-0.80)		0.78								
Vinyl acetate(-0.88)			0.55							
Vinyl chloride(0.16)		0.31	0.34	0.39						
Methyl methacrylate(0.40)		0.19	0.24	0.30	1.0					
Vinylidene chloride(0.34)		<0.1	0.16	0.6	0.96	0.61				
Methylvinyl ketone(1.06)			0.10	0.35	0.83		0.99			
Acrylonitrile(1.23)	0.0004	0.006	0.016	0.21	0.11	0.18	0.34	1.1		
Diethyl fumarate(2.26)	~0		0.021	0.0049	0.056		0.56			
Maleic anhydride (3.69)	~0.002		0.006	0.00017	0.0024	0.13				

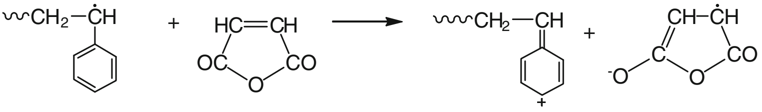
between the two monomers increases. Maleic anhydride, diethyl fumarate (Et–OOC–C=C–COOEt), and fumaronitrile (HOOC–C=C–C≡CN) do not homopolymerize. However, they will form alternating copolymer with electron-donor monomers such as styrene, vinyl ethers, and NVC. The copolymerization (Eq. 10.27) takes place even though neither monomer undergoes appreciable homopolymerization.


(10.27)

Two mechanisms [1] have been proposed to explain the strong alternation tendency between electron-donor and electron-acceptor monomers. One mechanism considers the interaction between an electron-acceptor radical and an electron-donor monomer or an electron-donor radical and an electron-acceptor monomer leads to a decrease in the activation energy for cross-propagation. The transition state is stabilized by partial electron transfer between the electron-donor and electron-acceptor species such as the reactions between styrene monomer and maleic anhydride radical as below


(10.28)

or the reactions between styrene radical and maleic anhydride monomer.



(10.29)

The second mechanism suggests the formation of a 1:1 complex between donor and acceptor monomers first, then the complex undergoes homopolymerization to obtain alternating copolymer.

$$M_1 + M_2 \overset{K}{\rightleftharpoons} M_1M_2(\text{complex}) \tag{10.30}$$

$$\sim M_1M_2 + M_1M_2 \xrightarrow{k} \sim M_1M_2M_1M_2\cdot \tag{10.31}$$

The reactions have been studied by the UV and NMR. The results indicate the formation of charge transfer complexes between electron-donor and electron-acceptor monomers which supports the second mechanism.

Various attempts have been made to place the radical–monomer reaction on the quantitative aspects of the correlation between structure and reactivity. Alfry and Price proposed Q-e Scheme [8] that is a useful correlation. The rate constant for a radical-monomer reaction $M_1\cdot$ and M_2 can be expressed by

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \tag{10.32}$$

where P_1 and Q_2 are measures of the resonance stabilization of $M_1\cdot$ radical and M_2 monomer, respectively, and e_1 and e_2 are measures of their polarities. By assuming that the same e value applies to both a monomer and its corresponding radical, one can write expression of k_{11}, k_{22}, k_{21} similar to Eq. 10.32. These can be appropriately combined to yield the monomer reactivity ratios in the forms as below

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \tag{10.33}$$

$$r_2 = Q_2/Q_1 \exp[-e_2(e_2 - e_1)] \tag{10.34}$$

which correlate monomer–radical reactivity with the parameters Q_1, Q_2, e_1, and e_2. The reactivity of monomers is described by a resonance factor "Q" and polar factor "e". Table 10.7 lists the Q, e values of some monomers. Therefore, we can use the Q-e Scheme to predict monomer reactivity ratios. Values of Q and e have been assigned to monomers based on their r values. For styrene, $Q = 1$, $e = -0.80$ are assigned. The accurately quantitative prediction of monomer reactivity ratio using Q-e scheme is limited to the copolymerization that has been experimentally carried out before. Therefore, it is a semi-experimental prediction. The precision of the predicted value, sometime is questionable, if the experimental data of known reactivity ratio are not accurate. The Q, e values do not consider the steric effect.

Table 10.7 *Q* and *e* values for various monomers [1]

Monomer	Q	e
Acenaphthalene	0.720	−1.88
Ethyl vinyl ether	0.018	−1.80
Propene	0.009	−1.69
N-Vinylpyrrolidone	0.088	−1.62
n-Butyl vinyl ether	0.038	−1.50
i-Butyl vinyl ether	0.030	−1.27
p-Methoxystyrene	1.53	−1.40
Isobutylene	0.023	−1.20
Allyl acetate	0.24	−1.07
Vinyl acetate	0.026	−0.88
α-Methylstyrene	0.97	−0.81
Styrene	1.00	−0.80
Indene	0.13	−0.71
p-Bromostyrene	1.30	−0.68
Allyl chloride	0.026	−0.60
Isoprene	1.00	−0.55
1,3-Butadiene	1.70	−0.50
2-Vinylpyridine	1.41	−0.42
Ethylene	0.016	0.05
Vinyl chloride	0.056	0.16
m-Nitrostyrene	2.19	0.20
Vinylidene chloride	0.31	0.34
Methyl methacrylate	0.78	0.40
Acrylamide	0.23	0.54
Methacrylic acid	0.98	0.62
Methyl acrylate	0.45	0.64
Methacrylonitrile	0.86	0.68
Vinyl fluoride	0.008	0.72
4-Vinylpyridine	2.47	0.84
n-Butyl acrylate	0.38	0.85
Acrylic acid	0.83	0.88
1-Hexene	0.035	0.92
Methyl vinyl ketone	0.66	1.06
Diethyl maleate	0.053	1.08
Acrylonitrile	0.48	1.23
Tetrafluoroethylene	0.032	1.63
o-Chlorostyrene	2.66	1.57
Diethyl fumarate	0.25	2.26
Fumaronitrile	0.29	2.73
Maleic anhydride	0.86	3.69

The assumption of same *e* value for monomer and radical is inadequate. However, the *Q*-*e* Scheme still useful prediction tool for the structure-reactivity relationship. It can be used to give a general idea of the behavior to be expected from a co-monomer pair that has not been studied.

10.1.4 Rate of Polymerization of Free Radical Copolymerization

The rate of copolymerization depends on the rate of initiation, termination, and propagation. Two different approaches have been used to derive expressions for the rate of copolymerization basis on how the termination reactions are proceeded: (1) by chemical control [4] or (2) by diffusion control [9]. For the first approach, the copolymerization consists of four propagation reactions and three termination reactions

Propagation

$$M_1\cdot + M_1 \xrightarrow{k_{11}} M_1\cdot \tag{10.35}$$

$$M_1\cdot + M_2 \xrightarrow{k_{12}} M_2\cdot \tag{10.36}$$

$$M_2\cdot + M_2 \xrightarrow{k_{22}} M_2\cdot \tag{10.37}$$

$$M_2\cdot + M_1 \xrightarrow{k_{21}} M_1\cdot \tag{10.38}$$

Termination

$$M_1\cdot + M_1\cdot \xrightarrow{k_{t11}} \text{dead polymer} \tag{10.39}$$

$$M_2\cdot + M_2\cdot \xrightarrow{k_{t22}} \text{dead polymer} \tag{10.40}$$

$$M_1\cdot + M_2\cdot \xrightarrow{k_{t12}} \text{dead polymer} \tag{10.41}$$

The overall rate of copolymerization from the rate of propagation is

$$\begin{aligned} R_p &= -(d[M_1] + d[M_2])/dt \\ &= k_{11}[M_1\cdot][M_1] + k_{12}[M_1\cdot][M_2] + k_{22}[M_2\cdot][M_2] + k_{21}[M_2\cdot][M_1] \end{aligned} \tag{10.42}$$

To eliminate $[M\cdot]$ in Eq. 10.42, a steady-state concentration is assumed for each type of radical,

$$k_{21}[M_2\cdot][M_1] = k_{12}[M_1\cdot][M_2] \tag{10.43}$$

The overall rate of copolymerization from the rate of termination is

$$R_t = 2k_{t11}[M_1\cdot]^2 + 2k_{t12}[M_1\cdot][M_2\cdot] + 2k_{t22}[M_2\cdot]^2 \tag{10.44}$$

By combining Eq. 10.42 with Eqs. 10.43 and 10.44, then using r_1, r_2 definitions, one can obtain the rate of copolymerization as

$$R_p = \left(r_1[M_1]^2+2[M_1][M_2]+r_2[M_2]^2\right)R_t^{1/2}/ \left\{\left(r_1^2\delta_1^2[M_1]^2\right)+(2\phi r_1 r_2\delta_1\delta_2[M_1][M_2])+\left(r_2^2\delta_2^2[M_2]^2\right)\right\}^{1/2} \tag{10.45}$$

where

$$\delta_1 = (2k_{t11}/k_{11}^2)^{1/2} \tag{10.46a}$$

$$\delta_2 = (2k_{t22}/k_{22}^2)^{1/2} \tag{10.46b}$$

$$\phi = k_{t12}/2(k_{t11}k_{22})^{1/2} \tag{10.46c}$$

The δ_1 and δ_2 values are obtained from homopolymerization and the r_1 and r_2 from copolymerization data. The rate of copolymerization is experimentally determined, then the ϕ is calculated from Eq. 10.45. Table 10.8 shows the values of ϕ and r_1r_2 of several monomer pairs. There is a general trend of ϕ values greater than unity that indicates the cross-termination is favored. When the ϕ increases with r_1r_2 approaching zero, the tendency toward cross-termination is in parallel with the tendency toward cross-propagation. This leads to the conclusion that polar effects are responsible for the tendency toward cross-termination. The reaction between radicals of dissimilar polarity is enhanced because of stabilization of the transition state for termination by electron-transfer effects.

Alternating copolymerization proceeds with enhanced propagation (r_1 and $r_2 < 1$) and enhanced termination ($\phi > 1$). The rate composition plot will depend on the values of ϕ, r_1 and r_2. Figure 10.6 shows two plots of R_p versus feed for the copolymerization of styrene and methacrylonitrile using ϕ values of 1 and 6 for calculation. The experimental data follow the plot for $\phi = 6$ quite well. The copolymerization of styrene ($r_1 = 42$) and vinyl acetate ($r_2 = 0$) presents a typical example of this case. The value of r_2 is very small and Eq. 10.45 can be reduced to

$$R_p = ([M_1]+2[M_2]/r_1)R_t^{1/2}\Big/\delta_1 \tag{10.47}$$

Table 10.8 Values of ϕ and r_1r_2 in radical copolymerization of several monomer pairs [1]

Comonomer	ϕ	r_1r_2
Styrene-butyl acrylate	150	0.07
Styrene-methyl acrylate	50	0.14
Methyl methacrylate-*p*-methoxystyrene	24	0.09
Styrene-methyl methacrylate	13	0.24
Styrene-methacrylonitrile	6	0.16[c]
Styrene-methoxystyrene	1	0.95

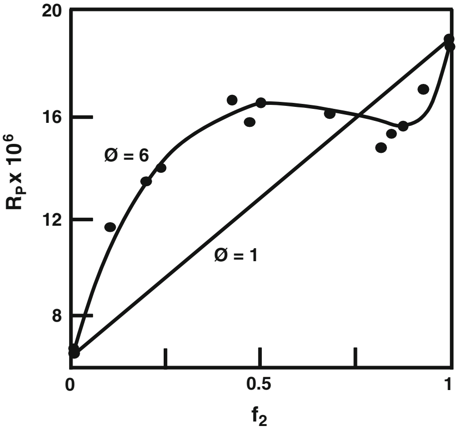


Fig. 10.6 Dependence of the rate of radical copolymerization of styrene-methacrylonitrile at 60 °C on the co-monomer feed composition. The two plots are the theoretical plots calculated for ϕ values of 1 and 6; the *circles* represent the experimental data [1]

The addition of very small amount of styrene to vinyl acetate, styrene inhibits the polymerization of vinyl acetate. Vinyl acetate radicals are rapidly converted to styrene radicals. The styrene radicals react very slowly with vinyl acetate monomer. The net effect is an almost complete cessation of polymerization. R_p is very small according to Eq. 10.47.

For the second approach, diffusion controlled termination, the following reactions are considered to obtain the kinetic expression for the rate of copolymerization

$$\begin{aligned} &M_1\cdot + M_1\cdot \\ &M_1\cdot + M_2\cdot \xrightarrow{k_{t(12)}} \text{dead polymer} \\ &M_2\cdot + M_2\cdot \end{aligned} \tag{10.48}$$

where the termination rate constant $k_{t(12)}$ is a function of the copolymer composition. The condition for the steady state for the total concentration of radicals can be expressed by Eq. 10.49 instead of Eq. 10.44.

$$R_t = 2k_{t(12)}([M_1\cdot] + [M_2\cdot])^2 \tag{10.49}$$

By combining Eqs. 10.42, 10.43, and 10.49 with the definitions of r_1 and r_2, one obtains the rate of copolymerization as

$$R_p = \frac{\left(r_1[M_1]^2 + 2[M_1][M_2] + r_2[M_2]^2\right)R_t^{1/2}}{k_{t(12)}^{1/2}\left\{\left[\frac{r_1[M_1]}{k_{11}}\right] + \left[\frac{r_2[M_2]}{k_{22}}\right]\right\}} \tag{10.50}$$

In the ideal situation, one would expect the termination rate constant $k_{t(12)}$ to be a function of the termination rate constants for the corresponding two homopolymerizations as the following:

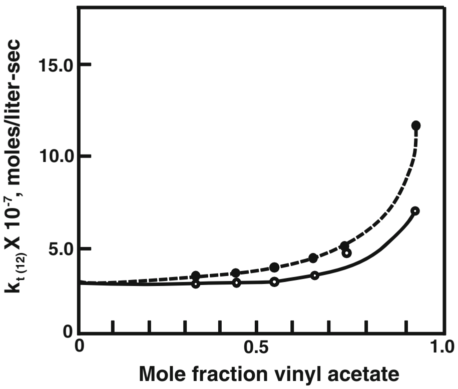


Fig. 10.7 Dependence of the termination rate constant $k_{t(12)}$ on the mole fraction of vinyl acetate in the radical copolymerization of vinyl acetate-methyl methacrylate. The *solid-line* plot and *open circles* represent calculations by Eq. 10.51; the *broken-line* plot and *solid circles* represent calculations by Eq. 10.50 [1]

$$k_{t(12)} = F_1 k_{t11} + F_2 k_{t22} \tag{10.51}$$

where $k_{t(12)}$ is the average of k_{t11} and k_{t22} each weighted on the basis of the copolymer composition in mole fractions. Equations 10.50 and 10.51 have been validated by experimental data as shown in Fig. 10.7. The lines are calculated data and circles are experimental data. They are fitted quite well except the slight deviation obtained from Eq. 10.51 calculation. The result indicates the weighting the k_{t11} and k_{t22} values directly with the copolymer composition may not be correct.

10.2 Cationic Copolymerization

The reactivity of monomer in cationic copolymerization [1] will be increased by (1) increasing the electron density on the double bond and (2) resonance stabilization on the carbocation from the substituent on the monomer. However, it will be affected by the reaction conditions, e.g., solvent, counterion, temperature, and so forth. The relative reactivities of various substituted styrenes have been correlated by the Hammett sigma-rho ($\rho\sigma$) relationship

$$\log(1/r_1) = \rho\sigma \tag{10.52}$$

For example, log $(1/r_1)$ values for a series of *meta*- and *para*-substituted styrenes copolymerized with styrene were plotted against the sigma substituent constants to yield a straight line with slope ρ of negative sign. The sigma value of a substituent is a quantitative measure of the total electron-donating or electron-withdrawing effect of substituent. Electron-withdrawing and electron-donating substituents have positive and negative sigma constants, respectively. A negative value of ρ means $1/r_1$ is increased by electron-donating substituents as expected for cationic polymerization. Substituents increase the reactivity of styrene in the following order of

Table 10.9 Steric effects in copolymerization of α- and β-methylstyrenes (M_1) with *p*-chlorostyrene (M_2) [1]

M_1	r_1	r_2
Styrene	2.31	0.21
α-Methylstyrene	9.44	0.11
trans-β-Methylstyrene	0.32	0.74
cis-β-Methylstyrene	0.32	1.0

$$p\text{-OCH}_3(-0.27) > p\text{-CH}_3(-0.17) > p\text{-H}(0.00) > p\text{-Cl}(0.23) \\ > m\text{-Cl}(0.37) > m\text{-NO}_2(0.71)$$

The Hammett-type approach is very useful for the quantitative correlation of monomer reactivity with structure semi-experimentally, but it is applicable only to substituted styrenes. The generally observed order of monomer reactivity is

$$\text{vinyl ether} > \text{isobutylene} > \text{styrene, isoprene}$$

which is the order expected on the basis of the electron-donating ability of various substituents. Monomers with electron-withdrawing substituent such as acrylonitrile, methyl methacrylate, and vinyl chloride show negligible reactivity in cationic copolymerization. Steric effect is also important in cationic copolymerization. Table 10.9 shows the effect of methyl substituents in the α- and β-positions of styrene. The reactivity of α-methylstyrene is higher than that of styrene due to the presence of electron-donating group of methyl group at α-position to have stabilized cationic propagating chain. On the other hand, the reactivity of β-methylstyrene is lower than that of styrene due to the presence of methyl group at β-position to have steric hindrance effect to retard the copolymerization with *p*-chlorostyrene. The steric effect is to outweigh the electronic effect of methyl group on the double bond. The *trans*-β-methylene is higher reactivity than *cis*-β-methylene as expected from the retardation of the later, although the amount is not large. It is interested to note that the 1,2-disubstituted alkene have some finite reactivity ratio which is zero in free radical copolymerization. Furthermore, the 1,2-disubstituted alkene can self propagate in cationic copolymerization but it is negligible in free radical reaction.

The effect of solvent or counterion on the monomer reactivity ratios is expected as we have observed in the cationic homopolymerization [1]. Actually, the effects are more complicated and difficult to predict than the homopolymerization, since changes in solvent or counterion often result in alternations in relative amounts of different types of propagating center, each of which may be differently affected by solvent. Table 10.10 illustrates these kind of effects for the copolymerization of isobutylene and *p*-chlorostyrene. The $AlBr_3$ initiated copolymerization shows $r_1 = 1.01$, $r_2 = 1.02$ in hexane but $r_1 = 14.7$, $r_2 = 0.15$ in nitrobenzene. Because the polar characteristic of *p*-chlorostyrene, the calculation of r values using the bulk comonomer feed composition results in a lower value of r_1 together with a

Table 10.10 Effect of solvent and initiator on *r* values in cationic polymerization [1]

$r_1 = k_{11}/k_{12}$ isobutylene	$r_2 = k_{22}/k_{21}$ *p*-chlorostyrene	Solvent	Initiator
1.01	1.02	n-$C_6H_{14}(\varepsilon 1.8)$	$AlBr_3$
14.7	0.15	C_6H_5–$NO_2(\varepsilon 36)$	$AlBr_3$
8.6	1.2	C_6H_5–NO_2 (ε 36)	$SnCl_4$

Table 10.11 Effects of solvent and counterion on copolymer composition in the copolymerization of styrene and *p*-methylstyrene[1]

Initiator system	% Styrene in copolymer[a]		
	Toluene (ε 2.4)	1,2-Dichloroethane (ε 9.7)	Nitrobenzene (ε 36)
$SbCl_5$	46	25	28
AlX_3	34	34	28
$TiCl_4$, $SnCl_4$, $BF_3 \cdot OEt_2$, $SbCl_3$	28	27	27
Cl_3CCO_2H	–	27	30
I_2	–	17	–

[a] Co-monomer feed = 1:1 styrene and *p*-methylstyrene

higher value of r_2. By changing the polarity of solvent, the *r* value is varied. In the nonpolar solvent, hexane, the polar monomer *p*-chlorostyrene solvates the propagating center, so the r_2 is increased. However, in the polar solvent, nitrobenzene, the propagating center is solvated by solvent which makes the reaction of polar monomer decreased with a reduced r_2. The solvent effect cannot be considered independent of counterion effect. The $AlBr_3$ is a stronger initiator than $SnCl_4$ that produces a higher concentration of propagating center. Thus, a stronger solvent effect is observed for polar *p*-chlorostyrene with an order decrease in r_2 (1.2 vs. 0.15) using $AlBr_3$ initiator.

Table 10.11 illustrates another example of the effects of solvent and counterion on the copolymerization of styrene with *p*-methylstyrene. The data indicate the copolymer composition to be (1) insensitive to the type of initiator for high polarity solvent such as nitrobenzene or 1,2-dichloroethane and (2) insensitive to solvent polarity for any initiator except the strongest $SbCl_5$. The styrene content decreases with decreasing initiator strength for the low-polarity solvent of toluene. In the poor solvent, the monomers compete, against the solvent, with each other to solvate the propagating center. The more polar *p*-methylstyrene preferentially solvates the propagating chains, so it is preferentially incorporated into the copolymer. For the polar solvent, the counterion does not appreciably influence the reaction, because the monomer cannot compete with the solvent to solvate the propagating chain. For the strong initiator of $SbCl_5$, the concentration of propagating center is high, the less polar monomer of styrene can be incorporated more into copolymer when the reaction is in the less polar solvent of toluene.

Temperature has a greater influence on monomer reactivity ratios in cationic copolymerization than in radical copolymerization because of the greater spread of propagation activation energies for the ionic process [10]. The ratio of any two rate constants is expected to toward unity when temperature increases. Since the smaller rate constant (larger activation energy) will increase faster with increasing temperature than the larger rate constant (smaller activation energy).

10.3 Anionic Copolymerization

The reactivity of anionic copolymerization is enhanced by electron-withdrawing substituent that decreases the electron density on the double bond and resonance stabilizes the formation of carboanion [1]. The reactivity is generally increased by the increasing of electron-withdrawing power of the substitute as the following:

$$-\mathrm{CN} > -\mathrm{CO_2R} > -\phi, -\mathrm{CH{=}CH_2} > -\mathrm{H}$$

There is a tendency toward ideal behavior in most anionic copolymerizations. Steric effects give rise to an alternating tendency for certain co-monomer pairs. Thus the styrene-*p*-methylstyrene pair shows ideal behavior with $r_1 = 5.3$, $r_2 = 0.18$, $r_1r_2 = 0.95$, while the styrene-α-methylstyrene pair shows a tendency toward alternation with $r_1 = 35$, $r_2 = 0.003$, $r_1r_2 = 0.11$, respectively. The steric effect of the additional methyl substituent in the α-position hinders the addition of α-methylstyrene to α-methylstyrene anion and results in lower reactivity ratio.

Monomer reactivity ratios and copolymer compositions of anionic copolymerizations are also altered by changes in the solvent or counterion. Table 10.12 shows data for styrene-isoprene copolymerization at 25°C by *n*-butyl lithium. As in the case of cationic copolymerization, the effects of solvent and counterion cannot be considered independently of each other. For the tightly bound lithium counterion, there are large effects due to the solvent. In a poor solvent such as benzene, the copolymer is rich in the less reactive isoprene (contains 15 % styrene), because isoprene is preferentially complexed by lithium ion. In a good

Table 10.12 Effect of solvent and counterion on copolymer composition in styrene-isoprene copolymerization [1]

Solvent	% Styrene in copolymer for counterion	
	Na^+	Li^+
None	66	15
Benzene	66	15
Triethylamine	77	59
Ethyl ether	75	68
Tetrahydrofuran	80	80

solvent triethylamine, preferential solvation by monomer is much less important and the inherent greater reactivity of styrene presents high concentration of 59 % in the copolymer.

10.4 Copolymerization Involving Dienes

Diene monomers contain two double bonds that are used in the copolymerization to have crosslinkable functionality, so a cross-linked polymers can be obtained. The reaction is similar to the step polymerization where tri or tetra functional reactants are used. The cross-linking reaction occurs early or late in the copolymerization depends on the relative reactivities of the two double bonds of the diene. The extent of cross-linking depends on (1) the reactivity of the two double bonds of the diene and (2) the amount of diene relative to the other monomer. Therefore, there are usually three types of copolymerization between monomer and diene that are discussed in the following.

The first type is the copolymerization of monomer A with diene BB where all of the double bonds have the same reactivity [1]. Methyl methacrylate-ethylene glycol dimethacrylate (EGDM), vinyl acetate-divinyl adipate (DVA), and styrene-*p*- or *m*-divinylbenzene (DVB) are examples of this type of copolymerization system. Since $r_1 = r_2$, $F_1 = f_1$. At the extent of reaction p, there are $p[A]$ reacted A double bonds, $p[B]$ reacted B double bonds, and $p^2[BB]$ reacted BB monomer units. $[A]$ and $[B]$ are the concentrations of A and B double bonds, $[BB]$ is the concentration of BB, and $[B] = 2[BB]$. The number of cross-links is simply the number of BB monomer molecules in which both B double bonds are reacted that is, $p^2[BB]$. The number of polymer chains is the total number of A and B double bonds reacted divided by the weight average degree of polymerization, $([A] + [B])p/\overline{X}_w$. The critical extent of reaction at the gel point p_c occurs when the number of cross-links per chain is 1/2 and thus is given by

$$p_c = \frac{[A] + [B]}{[B]\overline{X}_w} \tag{10.53}$$

Table 10.13 Cross-linking in the copolymerization of styrene-divinylbenzene [1]

Mole fraction DVB	Gel point (p_c)	
	Calculated from Eq. 10.53	Observed
0.004	0.210	0.160
0.008	0.100	0.140
0.020	0.042	0.076
0.032	0.026	0.074
0.082	0.010	0.052
0.300	0.004	0.045

The equation holds best for systems containing low concentrations of the diene monomer. With increasing diene concentration, the equation predicts gel points at conversions that are increasingly lower than those found experimentally as shown in Table 10.13. This general behavior has been attributed to the wastage of the diene monomer due to (1) intramolecular cyclization, and (2) the reactivity of the second double bond in *BB* is decreased on reaction of the first double bond as a consequence of its presence in a polymer chain [1].

A second case is the copolymerization of *A* and *BB* with reactivities r_1 and r_2, respectively [1]. In the case, the critical extent of reaction at gelation is given by

$$p_c = \frac{\left(r_1[A]^2 + 2[A][B] + r_2[B]^2\right)^2}{\overline{X}_w[B]([A] + [B])(r_2[B] + [A])^2} \tag{10.54}$$

If $[A] \gg [B]$, then

$$p_c = \frac{[A]r_1^2}{[B]\overline{X}_w} \tag{10.55}$$

When the double bonds of the diene are more reactive than that of the other monomer ($r_2 > r_1$), cross-linking occurs in the early stages of the copolymerization. Cross-linking is delayed until the later stages if $r_1 > r_2$.

The third case is the copolymerization of a monomer *A* with the diene *BC* where groups *A* and *B* have equal reactivity, but group *C* has a much lower reactivity [1]. The copolymerization of methyl methacrylate(*A*)-allyl(*C*)-methacrylate(*B*) is an example. If *r* is the reactivity ratio of *C* and *B* groups, then the rate constant for *A* and *B* will have the following relationship:

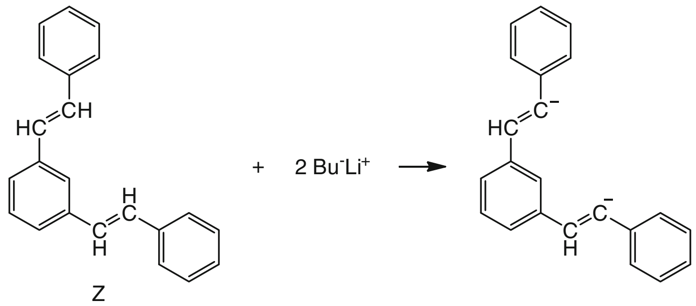
$$r = k_{AC}/k_{AA} = k_{AC}/k_{AB} = k_{BC}/k_{BA} = k_{BC}/k_{BB} \tag{10.56}$$

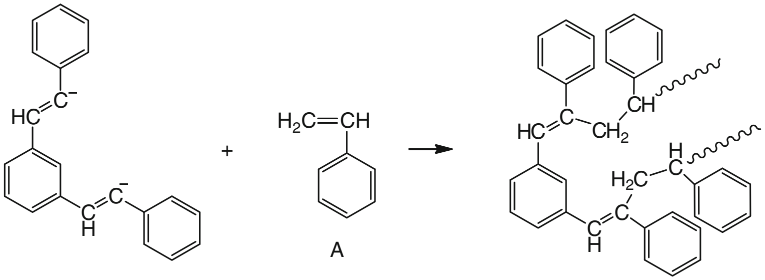
The copolymer will consist of copolymerized *A* and *B* groups with pending *C* groups that will react later into cross-linking. The critical extent of reaction at gelation is given by

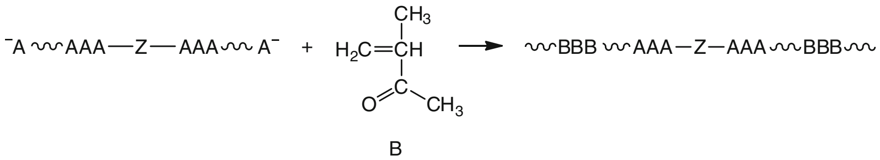
$$p_c = 1 - \exp\frac{-1}{2q\overline{X}_w r} \tag{10.57}$$

where *q* is the mole fraction of the diene in the initial co-monomer feed.

From the discussion above, one can control the gelation of diene copolymerization and the extent of cross-linking by reducing the amount of diene, the degree of polymerization by using chain transfer agents, proper choice of the reactivity of diene.







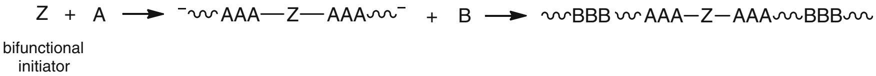
10.5 Block Copolymers

Block copolymers offer the potential to have product having desired and balanced properties of two or more homopolymers. The block copolymer can be synthesized via sequential monomer addition and then terminates with water using anionic polymerization as following

$$A \xrightarrow{RLi} R\sim\sim AAA^- \xrightarrow{B} R\sim\sim AAA\sim\sim BBB^- \xrightarrow{H_2O} R\sim\sim AAA\sim BBBH \tag{10.58}$$

However, the additional sequency of monomer is very important to determine the success of this kind copolymerization. For example, polystyryl carbanion will initiate polymerization of methyl methacrylate, but the reverse does not occur due to the reactivity difference in carbanion. Sequencing is not a problem in synthesizing block copolymers of styrene with isoprene or 1,3-butadiene due to similar reactivity of the monomer. The length of each segment in the block copolymer is determined by the amount of each monomer added relative to the amount of initiator. The overall properties of the product are various with the block lengths of the different monomers.

Difunctional initiators such as sodium naphthalene can be used to synthesize ABA, BABAB, CABAC, and other symmetrical block copolymers. Difunctional initiators can also be prepared by reacting a diene with two equivalents of *s*- or *t*-butyl lithium.



(10.59)

Triblock copolymer is able to be prepared using a difunctional initiator to initiate the first monomers and result in a homopolymer with two head carbanions. Following by introducing the second monomers and then the ABA triblock copolymer such as methyl methacrylate–styrene-methyl methacrylate is formed as following:

Triblock copolymers such as styrene-isoprene-styrene and styrene-1,3-butadiene-styrene are useful thermoplastic elastomers. They behave as elastomers at ambient temp. However, they are thermoplastic at elevated temperature. Styrene is a hard segment, and butadiene is soft. Diblock copolymers do not show good elastomer behavior but the triblock copolymer with the hard blocks at both ends of the polymer chain bearing rubbery behavior. Higher level block structures do not offer any performance advantage over triblock copolymer.

10.6 Commercial Copolymers

Many commercial copolymers are synthesized basis on polystyrene. Polystyrene itself is brittle and low impact resistance, but it can be copolymerized with rubber-based polymer to have both properties of strength and impact resistance [1]. Examples of styrene copolymers are styrene butadiene rubber (SBR) for tire which contains 25 % styrene, 75 % 1,3-butadiene; Latex paint which has 50–70 % styrene, 30–50 % 1,3-butadiene. Carboxylated SBR is a backing material for the usage of carpets and styrene/divinyl benzene is used for size-exclusion chromatography. The copolymer containing 50–90 % styrene, 10.40 % acrylonitrile (SAN) is widely used in houseware and packaging. The ABS consists of a glassy polymer (SAN) dispersed in a rubbery matrix (grafted rubber) for houseware, housing. The HIPS (high impact polystyrene) is produced by polymerization of styrene in the presence of a rubber of poly-1,4-butadiene.

Other important commercial copolymers are based on polyethylene. Ethylene polymer has the properties of crystallinity, high glass transition temperature, high T_m, high chemical resistance and vinyl acetate polymer has the properties of optical clarity, impact and stress crack resistance, flexibility, and adhesion. By copolymerization of ethylene with vinyl acetate (2–18 %), the merits of both polymers can be achieved. They are called EVA and widely used in food packaging, stretch and shrink film, drum liner, and so on. The copolymers of ethylene/ methyl methacrylate (15–30 %) or ethyl, butyl, methyl acrylates exhibit improved thermal stability, low temperature flexibility. Ethylene-acrylate-alkenoic acid (small amount crosslinker) elastomer has excellent oil resistance and stability over a wide temperature range (−50 to 200°C). The copolymer of ethylene-acrylic acid (15–20 %) has improved adhesion, abrasion resistance, toughness, and low temperature flexibility.

10.7 Problems

1. Define the reactivity ratios r_1 and r_2 and indicate their values for (a) ideal, (b) alternating, (c) azeotropic, and (d) block copolymerization.
2. Derive the copolymer equations, stating the assumptions used.
3. Consider the following monomer reactivity ratios for the copolymerization of various pairs of monomers:

Case	r_1	r_2
1	0.1	0.2
2	0.1	10
3	0.1	3
4	0	0.3
5	0	0
6	0.8	2
7	1	15

   What is the composition of the copolymer that would be formed at low conversion from equimolar mixtures of the two monomers in each case? What kind of copolymer will be formed for each case?
4. Using the r_1 and r_2 values from Table 10.1, construct plots showing the initial copolymer composition as a function of the co-monomer feed composition for the radical copolymerizations of methyl acrylate-methyl methacrylate and styrene-maleic anhydride. Are these examples of ideal or alternating copolymerization?
5. Consider the radical copolymerization of a benzene solution that is 1.5 M in styrene and 3.0 M in methyl acrylate.
   a. What is the initial copolymer composition if the polymerization is carried out at 60 °C using benzoyl peroxide at a concentration of 5.0×10^4 M? How is the copolymer composition affected if 3.0×10^3 M benzoyl peroxide is used?
   b. How will the presence of 5.0×10^5 M *n*-butyl mercaptan affect the initial copolymer composition?

6. Using the *Q* and *e* values in Table 10.7, calculate the monomer reactivity ratios for the co-monomer pairs styrene-butadiene and styrene-methyl methacrylate. Compare the results with the r_1 and r_2 values in Table 10.1.
7. Discuss qualitatively the course of the radical copolymerization for each of the following co-monomer pairs in terms of the degree of reaction at which gelation would be expected to occur:

   a. Styrene-divinylbenzene
   b. Methyl methacrylate-allyl methacrylate
   c. Vinyl acetate-EGDM
   d. Methyl methacrylate-DVA
   e. Styrene-butadiene

8. Carbonyl monomers can be copolymerized with either carbonyl monomer or alkene. Please write the chemical reactions, reaction condition and reaction products of acetaldehyde copolymerized with chloral, formaldehyde and styrene, respectively. What kind of copolymer of each monomer pair, random, alternate, or block will be obtained for each copolymerization? Explain your answer.
9. 1,3-Butadiene is copolymerized with the following monomers by radical, cationic and anionic initiation, respectively. Please discuss the expected qualitatively copolymer composition in order of their increasing butadiene content and what kind of copolymer would be formed for each of the comonomer pairs using those three different initiation conditions respectively. a. n-Butyl vinyl ether, b. methyl methacrylate, c. methyl acrylate, d. styrene, e. maleic anhydride, f. vinyl acetate, and g. acrylonitrile
10. Discuss the general effects of temperature, solvent, and catalyst on the monomer reactivity ratios in radical copolymerization; compare the differences between the radical copolymerization and ionic copolymerization with the corresponding effects.

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Chapter 11
Ring-Opening Polymerization

Polymers can be synthesized by polymerizing monomers with ring structure as shown in Table 11.1. The polymerization of these compounds has some aspects of both chain and step polymerizations as far as kinetics and mechanisms are concerned. The ring-opening polymerization has been used in the polymerization of commercial important polymers such as curing of epoxy resin from 3-membered ring cyclic ethers (epoxides), polyesters from cyclic ester (lactones), polyamides from cyclic amides (lactams), polysiloxanes from cyclic siloxanes, and so on. We will discuss the reaction mechanisms and kinetics of ring-opening polymerization in depth using epoxide, lactam, and cyclic siloxane as examples.

11.1 Reactivity of Cyclic Monomers

The ease of polymerization of a cyclic monomer depends on both thermodynamic and kinetic factors [2]. The single most important factor that determines whether a cyclic monomer can be converted to linear polymer is the thermodynamic factor, i.e., the relative stabilities of the cyclic monomer and linear polymer structure. The thermodynamic stability of the monomer is dependent on the strain in the ring structure. The strain in cyclic structure is very high for the 3- and 4-membered rings, decreases sharply for 5-, 6-, and 7-membered rings, increases for 8–13 membered rings, and then decreases again for larger rings. There are two types of strain: angle strain and conformational strain. Ring structures of less than five atoms are highly strained due to the high degree of angle strain, i.e., the large distortion of their bond angles from the normal tetrahedral bond angle. Bond angle distortion is virtually absent in rings of five or more members. For rings larger than five atoms, the strain due to bond angle distortion becomes too excessive to have planar rings. Therefore, rings larger than five atoms exist in more stable, nonplanar forms. The differences in strain among 5-membered ring or larger are due to differences in conformational strain. The 5- and 7-membered rings are somewhat strained in comparison to the 6-membered ring because of the torsional strain arising from eclipsed conformations on adjacent atoms of the ring. Rings of 8 or

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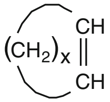
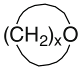
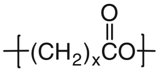
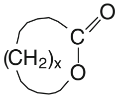
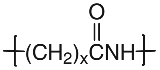
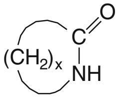
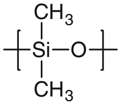
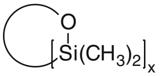
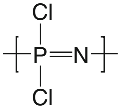
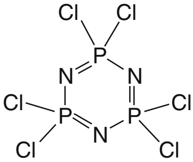
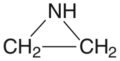
Lecture Notes in Chemistry 82, DOI: 10.1007/978-3-642-38730-2_11,

Table 11.1 Examples of polymers prepared by ring-opening polymerization [1]

Polymer type	Polymer repeating group	Monomer structure	Monomer type
Polyalkene	$-[CH{=}CH(CH_2)_x]-$		Cyclic alkene
Polyether	$-[(CH_2)_xO]-$		Cyclic ether[a]
Polyester[b]	 $-[(CH_2)_xC({=}O)O]-$		Lactone
Polyamide	 $-[(CH_2)_xC({=}O)NH]-$		Lactam
Polysiloxane	 $-[Si(CH_3)_2{-}O]-$		Cyclic siloxane
Polyphosphazene	 $-[PCl_2{=}N]-$		Hexachloro-cyclotriphosphazene[c]
Polyamine	$-[CH_2CH_2NH]-$		Aziridene[d]

[a] Epoxide ($x = 2$); oxetane ($x = 3$)

[b] Ring opening of cyclic oligomers has also been developed

[c] Phosphonitrilic chloride trimer

[d] Also called alkyleneimine

more members have transannular strain arising from repulsive interactions between hydrogens or other groups which are forced into crowd positions in the interior of the ring structure. Transannular strain nearly disappears for rings larger than 13 members, because the ring becomes sufficiently large to accommodate substituents without transannular repulsions. The general order of thermodynamic stability of different sized rings of cycloalkene is given by 3,4 $\ll$ 5,7–13 $<$ 6,14 and larger. The same order is observed for a variety of ring structures such as ethers, lactones, or lactams. It has been observed that substituents on the ring generally increase its stability relative to the linear structure as repulsive interactions between substituents are less severe in the ring structure.

Table 11.2 shows the semiempirical enthalpy, entropy, and free energy changes for the conversion of cycloalkanes to the corresponding linear polymer. The denoting liquid–crystal (lc) subscripts of ΔH, ΔS, and ΔG indicate that the values are those for the polymerization of liquid monomer to crystalline polymer. ΔH_{lc} is the major factor

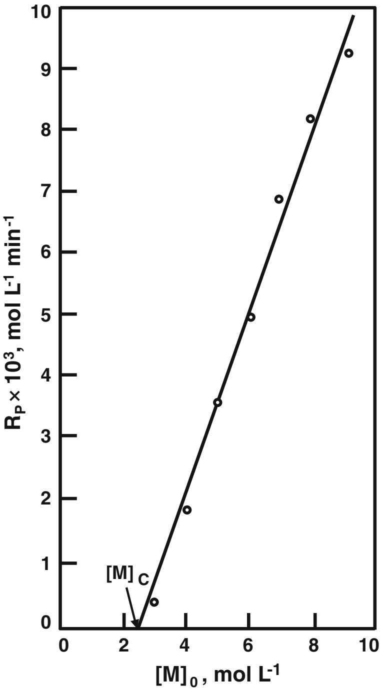
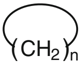


Fig. 11.1 Determination of the equilibrium monomer concentration $[M]_c$ for the $(C_2H_5)_3O^+(BF_4)^-$ initiated polymerization of tetrahydrofuran in dichloroethane at 0°C [2]

Table 11.2 Thermodynamics of polymerization of cycloalkanes at 25°C[2]

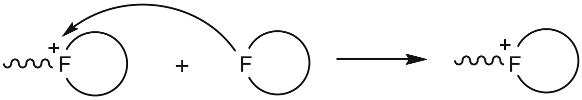
 n	ΔH (KJ/mol)	ΔS (J/mol K)	ΔG (KJ/mol)
3	−113.0	−69.1	−92.5
4	−105.1	−55.3	−90.0
5	−21.2	−42.7	−9.2
6	+2.9	−10.5	+5.9
7	−21.8	−15.9	−16.3
8	−34.8	−3.3	−34.3

in determining ΔG_{lc} for 3- and 4-membered rings, while ΔS_{lc} is very important for the 5- and 6-membered rings. The enthalpy and entropy factors ΔH_{lc} and ΔS_{lc} contribute about equally for larger sized rings. Since both ΔH_{lc} and ΔS_{lc} are negative, ΔG_{lc} becomes less negative with increasing temperature. Above ceiling temperature, ΔG_{lc} becomes positive, and polymerization is no longer favorable. For all size rings, the presence of substituents decreases thermodynamic feasibility for polymerization. Interactions between substituents are more severe in the linear polymer than in the cyclic monomer, ΔH_{lc} is less negative, while ΔS_{lc} is more negative.

Although ring-opening polymerization is thermodynamically favored for all except the 6-membered cycloalkane, polymerization of cycloalkanes has been achieved in very few cases, almost exclusively with cyclopropane derivatives, and only oligomers are obtained. This point out that thermodynamic feasibility does not guarantee the actual polymerization of a cyclic monomer. Polymerization requires that there is a kinetic pathway for the ring to open and undergo reaction. The cycloalkanes do not have a bond in the ring structure that is easily to be attacked by an initiator. On the other hand, the lactams, lactones, cyclic ethers and acetals, and other cyclic monomers can be polymerized. The presence of a heteroatom in the ring provides a site for nucleophilic or electrophilic attack by initiator species, resulting in initiation and subsequent propagation by ring opening. Thus, these type monomers are both kinetically and thermodynamically favored to be polymerized. In general, the polymerizability is higher for rings of 3, 4, and 7–11 members, lower for rings of 5 members, and much lower for rings of 6 members. However, there are exceptions. For instance, 6-membered rings with two or more heteroatoms in the ring undergo polymerization. The 6-membered lactam undergoes polymerization as well.

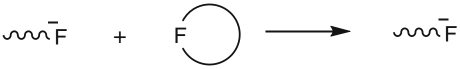
11.2 General Aspects of Mechanisms and Kinetics

Ring-opening polymerization is generally initiated by the same types of ionic initiators used in the polymerization of monomers containing carbon–carbon and carbon–oxygen double bonds [2]. Most cationic ring-opening polymerization involves the formation and propagation of oxonium ion centers. Reaction involves the nucleophilic attack of monomer on the oxonium ion:



(11.1)

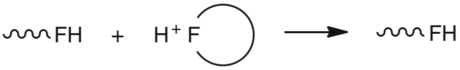
where F represents a functional group such as O, NH, Si–O, C(=O)–O, and C(=O)–NH in ethers, amines, siloxanes, esters, and amides, respectively. The typical anionic ring-opening polymerization involves the formation and propagation of anionic centers. Reaction proceeds by nucleophilic attack of the propagating anion on monomer:



(11.2)

where F^- represents an anionic propagating center, such as alkoxide or carboxylate, derived from the cyclic monomer. Ionic ring opening-polymerization exhibits similar behaviors as the ionic polymerization of carbon–carbon and carbon–oxygen double bonds discussed in Chap. 8.

Some ring-opening polymerization proceeds by a different route called *activated monomer polymerization*. The reaction involves a cationic or anionic species derived from the monomer. For example, cationic activated monomer polymerization does not proceed with monomer, but with protonated monomer that reacts with the neutral functional end group of the propagating polymer.



(11.3)

Ring-opening polymerization is like a chain polymerization, consisting of a sequence of initiation, propagation, and termination. On the other hand, only monomer adds to the growing chains of propagation that is similar to step polymerization. However, unlike step polymerization, monomer and larger sized species do not generally react themselves or with each other in ring-opening polymerization. Many ring-opening polymerizations proceed as living polymerization. Block copolymer can be synthesized by this way. The propagation rate constants of ring-opening polymerizations are generally similar to the rate constants in most step polymerizations which make them several orders of magnitude lower than those in typical chain polymerizations. Thus, the buildup of polymer molecular weight is slower for ring opening polymerization as compared to chain polymerizations.

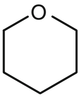
Polymerization–depolymerization equilibria are more often encountered in ring-opening polymerization than in the chain polymerizations. Ring-opening polymerization offers an alternate to step polymerization for the synthesis of many polymers. Thus, polyesters can be produced either by ring-opening polymerization of lactones as well as step polymerization of diacids with diols. The ring-opening polymerization has the advantage over step polymerization for high molecular weight polymer. The molecular weight of ring-opening polymerization depends on conversion and the monomer: initiator ratio. However, the monomers of ring-opening polymerization are not as readily available as the monomers of step polymerization. On the other hand, the molecular weight of step polymerization depends on the conversion and stoichiometric balance which is more difficult to control as compared with ring-opening polymerization.

11.3 Cyclic Ethers

The carbon–oxygen bond in ethers is a strong bond, and the ether oxygen is a Lewis base [2]. Thus, the ring-opening polymerization of cyclic ethers is initiated only by cationic species except for epoxides. The 3-membered ring of epoxide is highly strained which can be initiated by either cationic or anionic initiators.

The polymerization of simple cyclic ethers has been generally limited to those of 3, 4, and 5 ring members, although some works have been done with the 7-membered ring. The study of larger sized rings has been carried out mostly with cyclic acetals. The reactivity of different sized cyclic ethers follows the generally expected order. Cyclic ethers of less than 5 members or more than 6 members are relatively easily polymerized. The 5-membered cyclic ethers polymerize with more difficulty.

Substituted 5-membered cyclic ethers are usually unreactive, although some cyclic acetals undergo polymerization. The 6-membered cyclic ethers such as tetrahydropyran **1** and 1,4-dioxane **2** are unreactive under a wide range of reaction conditions, but the 6-membered cyclic acetal, trioxane **3**, undergoes polymerization.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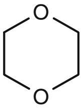
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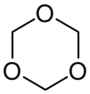
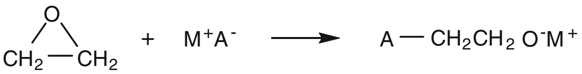

3

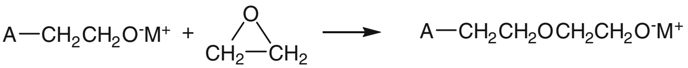
11.3.1 *Anionic Polymerization of Epoxides*

The anionic polymerization of epoxides such as ethylene and propylene oxides can be initiated by strong base such as metal hydroxide, alkoxide, oxide, amine, metal alkyls, and aryls (e.g., sodium naphthalene).

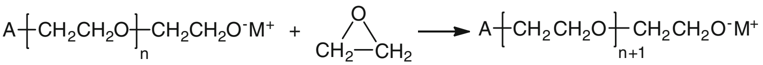
11.3.1.1 Reaction Mechanisms

The reaction mechanisms of ethylene oxide initiated by M^+A^- can be shown in the following [2]:

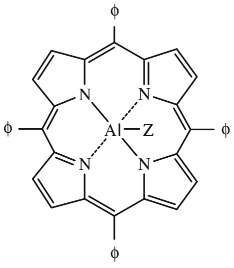

(11.4)


(11.5)

Equation 11.4 is the initiation reaction and Eq. 11.5 is the propagation reaction. The overall reaction can be expressed in the following:


(11.6)

Some initiators polymerize epoxides through an anionic coordination mechanism. Metalloporphyrin derivatives of aluminum and zinc (**4** with Z = Cl, OR, R, OOCR, SR) are commonly used as initiators.



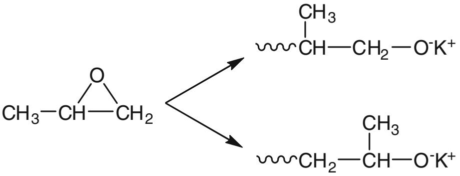
4

Propagation with the anionic coordination initiator **4**, involves covalent propagation in which the epoxide monomer is inserted into a metal–oxygen bond as shown in Eq. 11.7.

(11.7)

The propagation is a kind of anionic coordination process that involves the formation of an alkoxide anion on metal and then the cleavage of the metal–oxygen bond at the propagation center. The metalloporphyrin-initiated polymerizations are accelerated by sterically hindered Lewis acids. The Lewis acid coordinates with the oxygen of monomer that weakens the C–O bond for a facile nucleophilic attack. The Lewis acid must be sterically hindered to prevent the acid reacting with the propagating center attached to the porphyrin structure. Thus, aluminum ortho-substituted phenolates such as methyl aluminum bis (2,6-di-t-butyl-4-methyl phenolate) accelerate the polymerization very high in the order of 10^3. The aluminum phenolates without ortho substitutes and other less sterically hindered Lewis acids are much less effective.

The polymerization of an unsymmetric epoxide, propylene oxide, involves two possible reaction sites (at carbon 1 or carbon 2) on the epoxide ring for the nucleophilic ring-opening reaction. Thus, two different propagating species can be formed as below:



(11.8a)

(11.8b)

The propagation occurs almost exclusively by attacking at the carbon 2—less sterically hindered site, i.e., an S_N2 attack (Eq. 11.8b), so the polymer has a predominantly head-to-tail structure. As expected, more steric hindered propylene oxide and other substituted epoxides polymerize more slowly than does ethylene oxide. Most anionic polymerizations of epoxides proceed as living polymerization, so the block copolymer can be formed by successive monomer addition.

11.3.1.2 Kinetics

The expressions for the rate and degree of polymerization of ring-opening polymerization are essentially the same as used to describe living chain polymerizations [2]. For instance, the polymerization rate of sodium methoxide initiated polymerization of ethylene oxide can be expressed in the following:

$$R_p = k_p^{app}[M^*][M] \tag{11.9}$$

where $[M^*]$ is the total concentration of free ion and ion pairs. The effect of reaction media on R_p are similar to the ionic polymerization discussed in Chap. 8. Changes in solvent and counterion affect reaction rates and the observed rate expressions by altering the relative amounts of free ion and ion-pair propagating species, and the extent of association of initiator and propagating species.

The degree of polymerization can be expressed by

$$\overline{X}_n = \frac{p[M]_0}{[I]_0} \tag{11.10}$$

which is the same expressions for living radical and ionic polymerizations, p is the fractional conversion of monomer at a specific time of reaction. The total number of propagating chains per initiator molecule should be counted to determine $[I]_0$. For example, aluminum porphyrin initiator, $[I]_0$ is the concentration of the aluminum porphyrin since there is one propagating chain per aluminum atom. However, for aluminum isopropoxide, $[I]_0$ is three times the concentration of aluminum isopropoxide because each aluminum atom carries three propagating chains that is, each isopropoxide group is an initiator.

11.3.1.3 Exchange Reaction

Exchange side reactions are involved in the polymerization of epoxide which takes place in the presence of protonic substances such as water or alcohol [2]. For example, the polymerization initiated by metal alkoxides and hydroxides requires the presence of water or alcohol to produce a homogeneous system by solubilizing the initiator. In the presence of alcohol, the exchange reaction between a propagating chain and the alcohol can be expressed by

$$\mathrm{R}-(\mathrm{OCH_2CH_2})_n-\mathrm{O^-Na^+}+\mathrm{ROH}\rightleftharpoons \mathrm{R}-(\mathrm{OCH_2CH_2})_n-\mathrm{OH}+\mathrm{RO^-Na^+} \tag{11.11}$$

Similar exchange reaction is possible between the newly formed polymeric alcohol in Eq. 11.11 and other propagating chains:

$$\mathrm{R-(OCH_2CH_2)}_n\mathrm{-OH+R-(OCH_2CH_2)}_m\mathrm{-O^-Na^+} \rightleftharpoons$$

$$\mathrm{R-(OCH_2CH_2)}_n\mathrm{-O^-Na^+ + R-(OCH_2CH_2)}_m\mathrm{-OH} \quad (11.12)$$

These exchange reactions lower the polymer molecular weight. Thus, the number-average degree of polymerization is reduced by including the concentration of alcohol.

$$\overline{X}_n = \frac{p[M]_0}{[I]_0 + [ROH]_0} \quad (11.13)$$

Each alcohol molecule contributes equally with initiator to determine the size of propagating chains. The exchange reactions look like chain-transfer reactions, but they are not. The obtained polymeric alcohol via exchange is not dead but simply dormant. All alcohol and alkoxide molecules are in dynamic equilibrium in the reaction. Each polymer chain alternates between the active propagating alkoxide and dormant alcohol, so the exchange reaction places an upper limit on the polymer molecular weight. For example, ethylene oxide polymerizations initiated by alkoxides or hydroxides in alcohol, very few reports described the achievement of more than 10,000 molecular weight.

This alcohol exchange side reaction does not occur in the polymerizations initiated by alkoxides and hydroxides in aprotic polar solvents. This limitation also does not observe in the polymerizations initiated by the other initiators such as metal alkyls and aryls and various coordination initiators, since those initiators are soluble in benzene or tetrahydrofuran. Molecular weight as high as 10^5–10^6 has been achieved. However, the addition of alcohol or other protonic substance can serve to control polymer molecular weight. Equation 11.13 allows one to calculate the amount of alcohol or other substance required to be added to achieve the desired number-average molecular weight.

If the added alcohol ROH is more acidic than the polymeric alcohol, it will react with the first-formed propagating species as shown in below:

$$\mathrm{ROCH_2CH_2O^-Na^+ + ROH \rightarrow ROCH_2CH_2OH + RO^-Na^+} \quad (11.14)$$

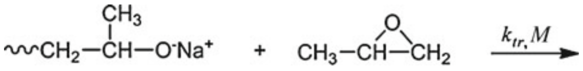
Reinitiation by $\mathrm{RO^-Na^+}$ is slow, since ROH is relatively acidic. This results in a decreased polymerization rate and a broadening of the polymer molecular weight. The rate of polymerization will not be affected much if the ROH is less acidic than the polymeric alcohol. Exchange will occur in the later stages of reaction with a broadening of the molecular weight distribution. Other protonic compound such as HCl or RCOOH present in the reaction, the inhibition, or retardation will occur because the anion such as $\mathrm{Cl^-}$ or $\mathrm{RCOO^-}$ does not have nucleophilicity. Reinitiation cannot occur. The polymeric alcohols are no longer dormant but dead. In this case, both polymerization rate and polymer molecular weight decrease along with a broadening of the polymer molecular weight.

The above discussed initiators are not strong enough to open the ring of cyclic ethers larger than three. However, they can be polymerized in the presence of

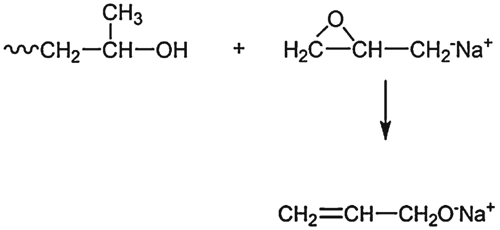
Lewis acid. For example, the oxetane cannot be polymerized by porphyrin alone, but the reaction proceeds with the addition of Lewis acid. The tetrahydrofuran can be polymerized by the combination of aluminum alkoxide and Lewis acid. The Lewis acid complexes with the ether oxygen that results in weakened carbon–oxygen bond and enhanced nucleophilic attack.

11.3.1.4 Chain Transfer to Monomer

The molecular weight of propylene oxide polymerized by anionic polymerization is rather low (<6,000), because there are large amount of chain transfer to monomer. This involves proton abstraction from the methyl group on the epoxide ring then followed by rapid ring cleavage to form the ally alkoxide anion **5**, which isomerizes partially to the enolate anion **6**. Species **5** and **6** reinitiate polymerization of propylene oxide. The monomer chain-transfer constant is larger by factors of 10^2–10^4 than the usual monomer transfer in ionic chain polymerization [3]. Equations 11.15–11.17 describe the chain-transfer reaction to monomer. Chain transfer to monomer is in the less extent for polymerizations using anionic coordination initiators and higher polymer molecular weight have been obtained [4].



(11.15)



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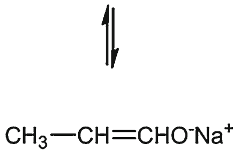
(11.16)



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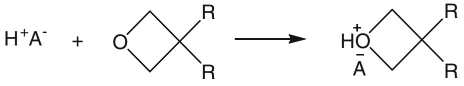
(11.17)

11.3.2 Cationic Polymerization of Epoxides

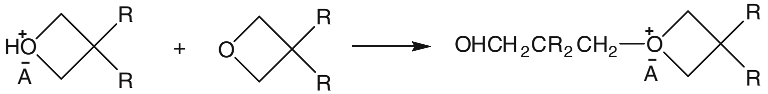
The epoxide is cationic polymerized through tertiary oxonium ion-propagating species using cationic initiators.

11.3.2.1 Initiation

A variety of cationic initiator systems used in polymerization of alkene can be used for cyclic ether to generate tertiary oxonium ion-propagating species [2]. Strong protonic acids such as trifluoroacetic, fluorosulfonic, and trifluoromethanesulfonic (triflic) acids initiate polymerization by the formation of a secondary oxonium ion initially (Eq. 11.18) which then reacts with a second monomer molecule to form the tertiary oxonium ion (Eq. 11.19) as shown below. This type of initiation is limited by the nucleophilicity of the anion A^- derived from the acid. For acids other than the very strong acids such as fluorosulfonic and triflic acids, the anion is sufficiently nucleophilic to react with monomer, secondary and tertiary oxonium ions. Thus, only very low molecular weight products are produced. The presence of water can also directly disrupt the polymerization, since its nucleophilicity allows it to react with monomer rather than the formation of the propagating oxonium ions.



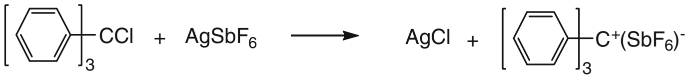
(11.18)



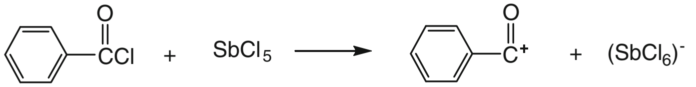
(11.19)

Lewis acids, such as BF_3 and $SbCl_5$ need in conjunction with water or some other protogen, initiate polymerization of cyclic ethers. The initiator and coinitiator form an initiator–coinitiator complexes [e.g., $BF_3 \cdot H_2O$, $H^+(SbCl_6)^-$] to act as a proton donor. Cationic photopolymerizations are achieved when similar proton donors are formed by the photolysis of diaryliodonium or triarylsulfonium salts.

The use of cationogen such as an alkyl or acyl halide with a Lewis acid generates carbocations and acylium ions, either in situ or as isolate salts, which can initiate polymerization as shown below:

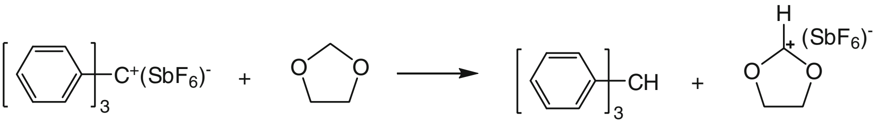


(11.20)



(11.21)

The initiation with some carbocations, especially trityl, does not involve direct addition to monomer. The carbocation abstracts a hydride ion from the alpha carbon of monomer and the newly formed carbocation initiates polymerization. The hydride ion abstraction is very facile with 1,3-dioxolane, so it can be used to produce stable 1,3-dioxolan-2-ylium salts (**7**), then used subsequently as initiators as shown below:



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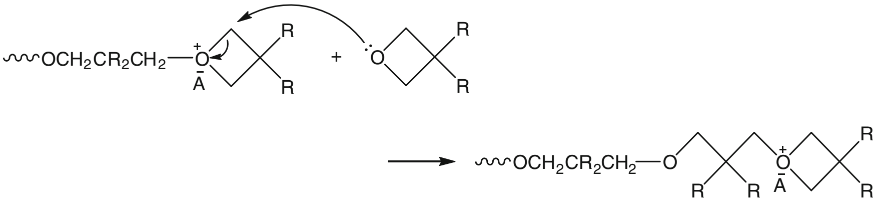
(11.22)

A more reactive cyclic ether such as oxirane or oxetane has been used in combination with Lewis acid, protogen, or cationogen to initiate the polymerization of less reactive cyclic ethers such as tetrahydrofuran. The formation of the secondary and tertiary oxonium ions of the more reactive cyclic ether can act as initiators for polymerization of the less reactive cyclic ether. The reactive cyclic ethers are called promoter which is used in relative small amounts to the cyclic ether being polymerized. The promoter increases the ability of the less reactive cyclic ether to form the tertiary oxonium ion.

11.3.2.2 Propagation

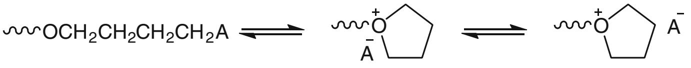
The propagation of cationic polymerization of cyclic ethers is proceeded by a tertiary oxonium ion, as shown below, where A^- is counter ion [2].



(11.23)

The alpha carbon of the oxonium ion is electron-deficient because of the adjacent positively charged oxygen. Propagation occurs at the alpha carbon of the oxonium by S_N2 reaction. However, S_N1 ring opening has been suggested for a monomer with two alkyl substituents at the alpha-position. Most cationic ring-opening polymerizations are highly regioselective with the formation of head-to-tail structures, only few cases contain head-to-head and tail-to-tail structures are found in some systems.

The cationic ring-opening polymerizations contain three species in equilibrium: Covalent ester **8**, ion pair **9**, and free ion **10** in equilibrium. The relative amounts of each species depend on the monomer, solvent, temperature, and other reaction conditions similar to the cationic polymerization of alkene.



8 **9** **10**

(11.24)

There is usually little or no difference in reactivity between free ions and ion pairs as observed in the cationic chain polymerization. The presence of covalent species has been identified by NMR and other methods, but whether they are reactive or dormant is not very clear. The covalent propagating involves two steps as shown in Eqs. 11.25 and 11.26. The covalent propagation has been confirmed in the polymerization of THF by triflic esters. A mixture of oxonium ion and macroester is obtained when methyl triflate is mixed with THF. Covalent propagation is slower than ionic propagation by a factor of 10^2–10^3 or more. In most of cationic polymerization of cyclic ethers, the covalent species are present predominately. In the polymerization of THF by methyl triflate, covalent species account for about 95 % of species in CCl_4 solution. Ionic species increased to 95 % in the very polar solvent CH_3NO_2. When covalent species are the major species, they are dormant species because of their lower reactivity as compared to ionic species. This slows down the propagation and also allows sufficient time to complete the initiation. That results in a living polymerization by reversible deactivation of ionic propagation species as described in the living free radical polymerization, and shown below:

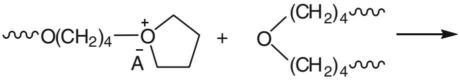
$$\sim\sim OCH_2CH_2CH_2CH_2A \rightleftharpoons \sim\sim O(CH_2)_4OCH_2CH_2CH_2CH_2{}^{+}A^{-} \qquad (11.25)$$

$$\rightleftharpoons \sim\sim O(CH_2)_4OCH_2CH_2CH_2CH_2A \qquad (11.26)$$

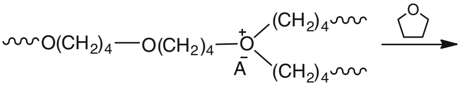
11.3.2.3 Termination and Transfer Processes

The cationic ring opening polymerization of cyclic ethers can proceed as living polymerization when irreversible chain-transfer reactions are absent [2]. These conditions can be achieved when an appropriate initiator is used to generate reversible covalent and ionic exchange propagating species. The suitable initiators are acylium and 1,3-dioxolan-2-ylium salts containing very stable counterions such as AsF_6^-, PF_6^-, and $SbCl_6^-$ or with very strong acids (fluorosulfonic and trifluoromethane sulfonic acid) or their esters.

The chain transfer to polymer resulted in the propagation chain is terminated but the kinetic chain is unaffected. The reaction is similar to that of cationic polymerization of alkene as discussed in Chap. 8. The reaction involves the propagating chain being nucleophilic attacked by the ether oxygen of polymer chain, the same type of reaction involved in propagation to form the tertiary oxonium ion **11**. Subsequently, nucleophilic attack on **11** by monomer yields **12** and regenerates the propagating species as shown in Eqs. 11.27–11.29. The overall effect is a broadening of the molecular weight distribution. The molecular weight distribution in some reaction system is close to the distribution expected for a step polymerization (about 2). Chain transfer to polymer also occurs as an intramolecular reaction as well intermolecular reaction. The intramolecular reactions (back-biting reaction) results in the formation of cyclic oligomers instead of linear polymer. In other words, the chain ends in **11** are connected to each other. The competition between propagation and chain transfer to polymer depends on many factors. For instance, propagation is favored on steric grounds since attack by monomer is less hindered than attack by the ether oxygen of polymer chain. The relative nucleophilic activities of ether oxygens from monomer and polymer are important that vary considerably depending on monomer ring size. Toward the end of polymerization, intramolecular (not intermolecular) chain transfer to polymer becomes progressively more important at lower monomer concentrations.



(11.27)



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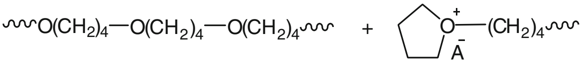
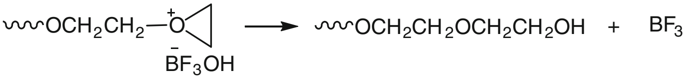
(11.28)



12

(11.29)

Termination reactions occur by combination of the propagating oxonium ion with either the counterion or an anion derived from the counterion as shown in Eq. 11.30. It is known that the use of protonic acids as initiators is limited by the nucleophilicity of the anion of the acid. Transfer of an anion from the counterion, for example, occurs to varying degrees depending on the stability of the counterion. Thus, counterions such as $(PF_6)^-$ and $(SbCl_6)^-$ have little tendency to bring about termination by transfer of a halide ion, while counterions of aluminum and tin have appreciable transfer tendencies; others such as $(BF_4)^-$ and $(FeCl_4)^-$ are intermediate in behavior.

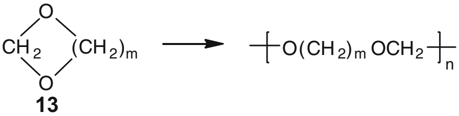


(11.30)

Termination may also occur by chain transfer with the initiator (e.g., alcohol or water) or with chain-transfer agent. The termination has been deliberated to carry out to produce polymers with specific molecular weights or telechelic polymers with specific end groups. For example, hydroxyl and amine end groups are obtained by using water and ammonia as chain-transfer agents; carboxyl-ended telechelics can be obtained by termination with ketene silyl acetal then followed by hydrolysis with base. The insolubility of polymer will also terminate the reaction because the active site is not accessible.

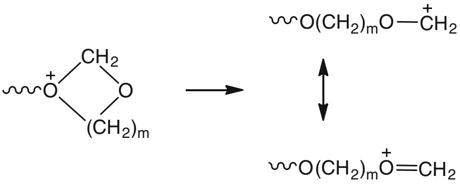
11.3.3 Polymerization of Cyclic Acetals

The cyclic structure of cyclic acetals contains at least one 1,1-dialkoxy grouping [$(RO)_2CH_2$ or $(RO)_2CHR$] [2]. They can be easily polymerize by cationic initiation. Various 1,3-dioxocycloakanes **13** are commonly used such as 1,3-dioxolane ($m = 2$), 1,3-dioxepane ($m = 4$), and 1,3-dioxocane ($m = 5$) are commonly used. The polymers of cyclic acetal can be considered as copolymers of the $O(CH_2)_m$ and OCH_2 units. The 6-membered ring cyclic acetal, 1,3-dioxane ($m = 3$), is too stable to be polymerized. The polymerization reaction of cyclic acetal is shown below:



(11.31)

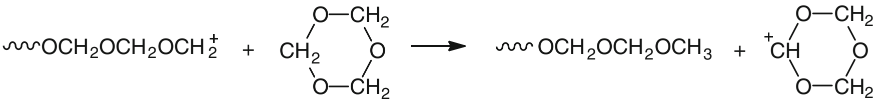
Two kinds of propagating chains were proposed for the reaction mechanisms of cyclic acetal polymerization as shown in Eq. 11.32. Both experimental and computational data indicate that more than 99.9 % of the propagating species are oxonium ions for unsubstituted 1,3-dioxocycloalkanes. Since oxonium ions are 100-fold lower in reactivity toward propagation than oxycarbocations, propagation is predominately carried by oxonium ions [5]. However, the propagation by oxycarbocations is significant for 2-alkyl-1,3-dioxocycloalkanes. The 2-alkyl substitudent provides the additional stabilization of positive charge center and the steric hindrance that lead the propagation through oxonium ions.



(11.32)

1,3,5-trioxane, the cyclic trimer of formaldehyde, by cationic ring opening polymerization yields the same polymer, polyoxymethylene, as the cationic polymerization of formaldehyde (Sect. 8.5.2). This polymerization has been carried out in industry using boron trifluoride etherate in the presence of water. The 1,3,5-trioxane polymerizes in spite of containing 6-membered ring, because the polymerization occurs with simultaneous precipitation of crystalline polymer. The heat of crystallization makes the process an exothermic polymerization. The polymerization of 1,3,5-trioxane proceeds with the formation of polymer-formaldehyde equilibrium. Thus, the reaction involves an induction period for the build-up of the equilibrium concentration of formaldehyde. This induction period also corresponds to a built-up in 1,3,5,7-tetroxocane by the insertion of formaldehyde into 1,3,5-trioxane. Polymer is not formed until both formaldehyde and 1,3,5,7-tetroxocane appear. Formaldehyde (a lesser extent) and 1,3,5,7-tetroxocane decrease the induction period by increasing the rate of propagation to have the crystalline polymer precipitated out. Then, the polymerization is accelerated by converting 1,3,5-trioxane monomer to crystalline polymer directly. The polymerization is usually carried out in bulk or at high monomer concentration to depress cyclic oligomer formation via chain-transfer reaction.

The reaction of transfer and termination of cyclic acetals are similar to the cyclic ether. Chain transfer to polymer (both inter- and intramolecular) is faster in cyclic acetal polymerizations as compared to cyclic ethers because acetal oxygens in the polymer chain are more basic than the corresponding ether oxygens. The trioxane polymerization exhibits an additional termination reaction by chain transfer. The propagating chain with monomer via hydride ionic transfer to form methoxy terminated polymer and carbocation **14**. The **14** can reinitiate the polymerization.



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(11.33)

11.3.4 Kinetic Characteristics

The reaction kinetics of cationic ring-opening polymerization depend on its reaction mechanism [2]. Some polymerizations can be described the same as the cationic polymerization of carbon–carbon double bonds. If the polymerizations are with little or no termination, the kinetic expressions of living polymerization can be followed. The cationic ring-opening polymerizations of larger sized ring (≥ 4) take place without terminations and are reversible. The propagation-depropagation equilibrium can be expressed by

$$M_n^* + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} M_{n+1}^* \tag{11.34}$$

The polymerization rate can be expressed by

$$R_p = \frac{-d[M]}{dt} = k_p[M^*][M] - k_{dp}[M^*] \quad (11.35)$$

At the equilibrium, the polymerization rate is zero, then

$$k_p[M]_c = k_{dp} \quad (11.36)$$

where $[M]_c$ is the equilibrium monomer concentration.

Combining Eqs. 11.35 and 11.36, give the polymerization rate as

$$\frac{-d[M]}{dt} = k_p[M^*]([M] - [M]_c) \quad (11.37)$$

Integrate Eq. 11.37 and yield

$$\ln\left(\frac{[M]_0 - [M]_c}{[M] - [M]_c}\right) = k_p[M^*]t \quad (11.38)$$

where $[M]_0$ is the initial monomer concentration.

The equilibrium monomer concentration $[M]_c$ is obtained by direct analysis or by determining the intercept of a plot of polymerization rate versus initial monomer concentration as shown in Fig. 11.1. The polymerization data are then plotted according to Eq. 11.38 as shown in Fig. 11.2. A straight line is obtained and its slope is $k_p[M^*]$. Since $[M^*]$ can be obtained from measurements of the number-average molecular weight of living polymer, one can determine the propagation rate constant. The concentration of the propagating chain is reciprocal to the concentrations of initiator and coinitator (living polymerization equation). For the case, the concentration of propagating centers changes with time, integration of Eq. 11.38 yields

$$\ln\left(\frac{[M]_1 - [M]_c}{[M]_2 - [M]_c}\right) = k_p \int_{t_1}^{t_2} [M^*]t \quad (11.39)$$

where $[M]_1$ and $[M]_2$ are the monomer concentrations at times t_1 and t_2, respectively.

The quantitative dependence of the degree of polymerization on various reaction parameters has been described by an equilibrium polymerization involving initiation

$$I + M \overset{K_i}{\rightleftharpoons} M^* \quad (11.40)$$

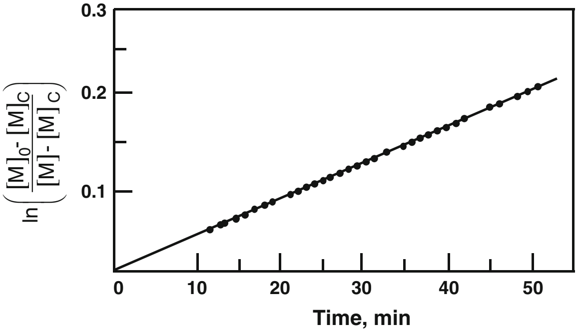


Fig. 11.2 Disappearance of monomer in the polymerization of tetrahydrofuran by $(C_6H_5)_2CH^+(SbCl_6)^-$ at 25°C; a plot of Eq. 11.38 [2]

followed by propagation (Eq. 11.34). The degree of polymerization is then given by

$$\overline{X}_n = \frac{[M]_0 - [M]_c}{[I]_0 - [I]_c} \tag{11.41}$$

where $[M]_c$ and $[I]_c$ are the unreacted monomer and initiator concentrations at equilibrium. The polymer molecular weight increases with decreasing $[I]_0$ and increasing $[M]_0$. Larger values of k_p, (the equilibrium constant for Eq. 11.34) and smaller values of K_i yield higher polymer molecular weights by decreasing $[M]_c$ and increasing $[M]_o$, respectively.

11.3.5 Thermodynamic Characteristics

The temperature effect on the rate of polymerization of cyclic ethers and acetals is dependent on types of monomers, solvents, initiators, and coinitiators [2]. The effect is generally similar to those observed in ionic polymerizations of alkenes. The rate of polymerization is almost always increased with increasing temperature, so the E_{Rp} is positive. Typical values of E_{Rp} are in the range 20–80 kJ mol^{-1} with most of values in the upper range.

The effect of temperature on the degree of polymerization is more complex [2]. For most polymerization, increasing the temperature decreases the polymer molecular weight because of increased rates of transfer and termination relative to propagation. Table 11.3 shows this effect for the polymerization of oxetane by boron trifluoride through the intramolecular chain transfer to polymer, the formation of cyclic tetramer is increased with increasing temperature. In other polymerizations, the propagating rate is increased with increasing temperature, but the termination and transfer reactions may not be appreciably affected. That results in an increase in polymer molecular weight. Figure 11.3 shows this example observed in the polymerization of tetrahydrofuran. The molecular weight of

Table 11.3 Effect of temperature on polymerization of oxetane [2]

Temperature (°C)	Intrinsic viscosity of polymer (dLg^{-1})	Ultimate conversion of monomer (%)	Proportion of tetramer (%)
−80	2.9	95	4
0	2.1	94	10
50	1.3	64	66
100	1.1	62	62

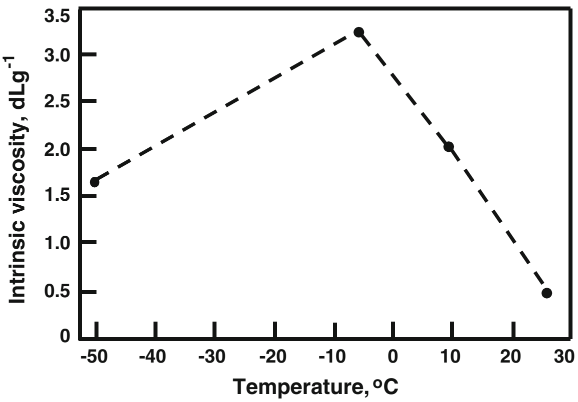


Fig. 11.3 Effect of temperature on polymer molecular weight in the BF_3 polymerization of tetrahydrofuran. [2]

polymer increases initially with increasing temperature up to about −5°C and then subsequently decreases at higher temperatures. The rate of termination is relatively unaffected at the lower temperatures but increases with temperature at the higher temperatures.

The enthalpies and entropies of polymerization of different cyclic ethers and acetals are summarized in Table 11.4. The data of carbonyl monomer, formaldehyde, are included for the purpose of comparison. As compared with the enthalpies and entropies of alkene polymerization (Table 7.16), the ΔH values of 3- and 4-membered ring are comparable to those of alkenes. Both values are appreciably larger than the value of formaldehyde. The conversion of a carbonyl π bond to a σ bond is not as exothermic as the corresponding conversion of an alkene π bond. The ΔH values of the larger sized cyclic monomers are much lower than those of alkenes. The ΔS values of most cyclic monomers are considerably smaller as compared to those of the alkenes and carbonyls. The results indicate that the cyclic monomers, having less degree of freedom to begin with, the loss in disorder on polymerization (ΔS) are less than for noncyclic monomers. Ethylene oxide is an exception because of its highly strained 3-membered ring. The ΔS values for few of the cyclic monomers, tetrahydrofuran, and 3,3-bis(chloromethyl)oxetane, are similar to the lowest values observed for alkene monomers. The ΔH values of different cyclic ethers and acetals follow closely to the order expected from the relative stability of the ring size. The 3- and 4-membered cyclic monomers undergo the most exothermic polymerizations that are decreasing fast with large

Table 11.4 ΔH and ΔS of polymerization of cyclic ethers [2]

Monomer	Ring size	$-\Delta H$ (KJ/mol)	$-\Delta S$ (J/mol K)
Ethylene oxide	3	94.5	174
Oxetane	4	81	–
3,3-Bis(chloromethyl) oxetane	4	84.5	83
Tetrahydrofuran	5	23.4	82.4
1,3-Dioxolane	5	17.6	47.7
4-Methyl-1,3-dioxolane	5	13.4	53.1
Trioxane	6	4.5	18
1,3-Dioxepane	7	15.1	48.1
2-Methyl-1,3-dioxepane	7	8.8	37.2
4-Methyl-1,3-dioxepane	7	9.2	38.9
1,3-Dioxocane	8	18.3	–
1,3,6-Triocane	8	13.0	21.3
2-*n*-Butyl-1,3,6-trioxocane	8	7.9	16.3
1,3,6,9-Tetraoxacycloundecane	11	8.0	6.2
Formaldehyde	–	31.1	79.2

sized ring. For example, trioxane, the 6-membered ring monomer has a ΔH very close to zero. Due to the steric hinderence, substituents on a ring structure decrease the tendency to polymerize and the ΔH value is lowered. For instance, the ΔH values of the substituted 1,3-dioxlane, 1,3-dioxepane, and 1,3,6-trioxocane monomers are lower than that of the corresponding unsubstituted monomers. Substituted oxetanes are an exception to this generalization, the strain effect is overweight the substitution effect.

11.3.6 Commercial Applications of Polymers of Cyclic Ether

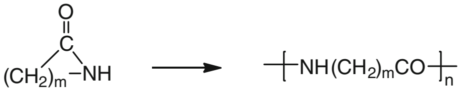
One of the most important industrial applications of polymers of cyclic ether is to make polyether macrodiols for polyurethane industry. They are telechelic polyethers having hydroxy terminal groups. They are synthesized from the polymerizations and copolymerizations of ethylene and propylene oxides as well as polymerization of tetrahydrofuran. The commercial macrodiols in the molecular weight range of 500–6,000 and are used to produce polyurethane and polyester block copolymers including the thermoplastic polyurethane and polyester elastomers. The polyether macrodiols are also referred to as polyether glycols or polyols (trade names: Carbowax, Jeffox, Polyglycol, Polymeg, and Terathane). The medium molecular weight (~20,000) of ethylene oxide and propylene oxide polymers and copolymers are used as hydraulic fluids and lubricants, additives in cosmetics, and binders in ceramic and powder metallurgy by taking the advantage of their hydrophilic properties. The high molecular weight (10^5–10^6) of ethylene oxide polymers are used in flocculation, denture adhesives, packaging films, thickening agent in paints, and so on.

The copolymers made from epichlorohydrin with ethylene oxide and allyl glycidyl ether are useful elastomers. These materials (trade names: Epichlomer, Herclor, and Hydrin) have good resistance to fuel, oil, ozone, and heat. They also exhibit low temperature flexibility and high permeation resistance toward air and vapors of hydrocarbons and fluorocarbons.

Epoxy resin [6, 7] contains 3-membered oxirane terminal groups that can be ring opening polymerized with either multifunctional base or acid to form cross-linked polymers. They exhibit excellent adhesive strength and chemical resistance, high thermal resistance, and mechanical strength. They have been used extensively in electronic industry as bonding adhesive, electrical insulations for large power equipment, composites for aerospace industry, baking enamels for appliances and cars, and so on. The photo initiated cationic ring opening polymerization of epoxy resin has been utilized in electronics, printing, and coating.

11.4 Lactams

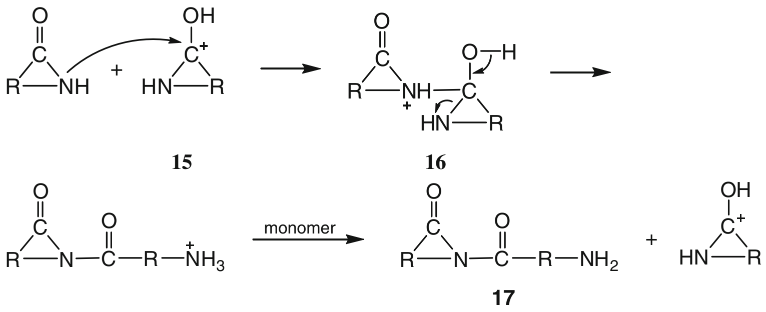
The polymerization of lactams (Eq. 11.42) can be initiated by bases, acids, and water. Initiation by water is the most often used method for polymerization of lactams in industry [2]. Anionic initiation is also used in industry to produce objects directly in molds through bulk polymerization. Cationic initiation is not useful, because the conversions and polymer molecular weights are low. Nylon 6 is produced commercially which accounts for almost one–third of all polyamides. Nylons 11 and 12 are specialty polyamides which are used in the applications requiring high moisture resistance and hydrolytic stability.



$$\overset{\displaystyle \overset{O}{\|}}{C}\text{—}(CH_2)_m\text{—}NH \longrightarrow \text{—}[NH(CH_2)_mCO]_n\text{—} \tag{11.42}$$

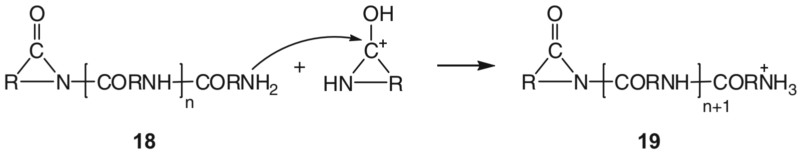
11.4.1 Cationic Polymerization

A various of protonic and Lewis acids can initiate the cationic polymerization of lactame. The reaction follows the mechanism of acid-catalyzed nucleophilic substitution reactions of amides as shown in Eq. 11.43. Initiation occurs by nucleophilic attack of monomer on protonated monomer **15** to form an ammonium salt **16** that subsequently undergoes proton exchange with monomer to yield **17** and protonated monomer.



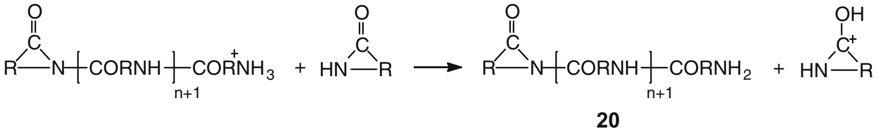
(11.43)

Propagation proceeds in a similar manner as a nucleophilic attack by the primary amine end group of a growing polymer chain **18** on protonated monomer to yield **19** as shown in Eq. 11.44.



(11.44)

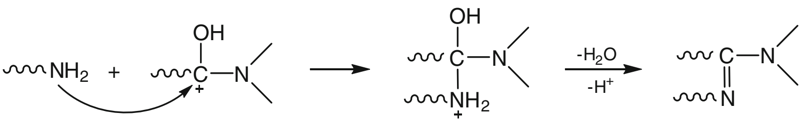
Then **19** undergoes proton exchange with monomer as below:



(11.45)

20 is an AB type of monomer which can be self propagated through the reaction between amine and lactam end groups. Actually, the lactam end groups are protonated prior to reaction. The reaction is similar to Eq. 11.44. Although this reaction is only a minor contribution to the overall conversion of lactam to polymer, it determines the final degree of polymerization. There are intermolecular nucleophilic attack of amine on amide linkages within a polymer chain which result in cyclic oligomer formation. Overall, the molecular weight distribution of the polymer is close to the Flory most probable distribution.

Various side reactions greatly limit the conversions and polymer molecular weights of cationic polymerization of lactams. The highest achievable molecular weights are 10,000–20,000. The most significant side reaction is amidine **21** formation as shown in Eq. 11.46. Propagation of the polymer chain and amidine formation proceed through the common intermediate **20** formed by attaching an amine group to the protonated carbonyl of any amide group. The formation of amidine formation decreases the concentration of amine groups in the reaction system which leads to a slower rate of reaction. The water released during the formation of amidine can initiate polymerization but at a slower rate. Furthermore, amidine groups react rapidly with acidic initiators to generate relatively unreactive salts that decreases the rate and degree of polymerization.



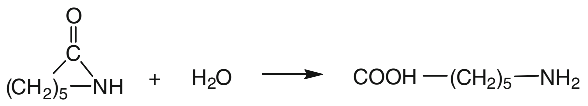
21

(11.46)

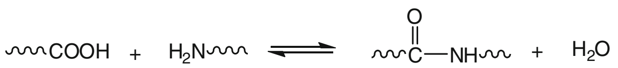
Both the hydrolytic and anionic routes described below require that a lactam have a hydrogen on the nitrogen. Therefore, the N-alkylated lactams can only be polymerized by cationic route. The commercial applications for N-alkylated polyamides are limited, because they are low in melting points from the lack of hydrogen bonding.

11.4.2 Hydrolytic Polymerization

When water initiator is used to polymerize the lactam, the polymerization is called hydrolytic polymerization [2]. It is a special case of cationic polymerization. This reaction has been used extensively in the production of Nylon 6 from ε-caprolactam commercially. Several equilibria are involved in the polymerization. These are hydrolysis of the lactam to ε-amino-caproic acid (Eq. 11.47), step polymerization of the amino acid with itself (Eq. 11.48), and the initiation of ring-opening polymerization by the amino acid obtained from Eq. 11.47.



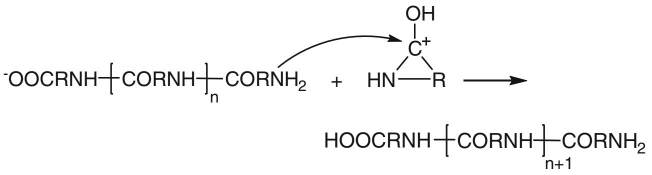
(11.47)



$$\sim\!COOH + H_2N\!\sim \rightleftharpoons \sim\!\overset{O}{\overset{\|}{C}}\!-\!NH\!\sim + H_2O \qquad (11.48)$$

The COOH group of the amino acid protonates the lactam to form cationic active species that can be nucleophic attacked by amine to initiate the reaction.

The propagation process follows the same manner in the cationic polymerization as shown in Eq. 11.49. The product subsequently protonates lactam and propagation continues.



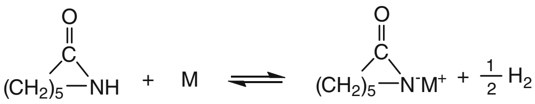
(11.49)

The overall rate of conversion of ring-opening polymerization of ε-caprolactam (Eq. 11.47) is higher than the step polymerization of ε-amino-caproic acid (Eq. 11.48) by more than an order of magnitude. The self polymerization of ε-amino-caproic acid accounts only a few percent of the total polymerization of ε-caprolactam. The polymerization is acid catalyzed as shown in Eq. 11.49, amines and water are poor initiators. The polymerization rate in the presence of water is first-order in lactam and second-order in COOH terminated molecule.

Although the self polymerization of ε-amino-caproic acid is only a minor contribution to the overall conversion to polymer, it determines the final degree of the polymerization at equilibrium since the polymer undergoes self-condensation. Usually, most of the water used to initiate polymerization is removed after about 80–90 % conversion in order to drive the reaction to high molecular weight. Thus, the molecular weight polymer can be controlled by the initial amount of water, monomer concentrations, and the addition of small but specific amount of monofunctional acid. The molecular weight distribution is followed the statistic probability distribution proposed by Flory. The amidines formed in hydrolytic polymerization of lactam do not limit the molecular weight, because the carboxyl end groups of growing chain are quite reactive toward amidine groups.

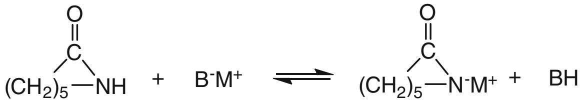
11.4.3 Anionic Polymerization

Strong bases such as alkali metals, metal hydrides, metal amides, metal alkoxides, and organometallic compounds are used to initiate the polymerization of a lactam [2]. The lactam anion is forming using metal as shown in Eq. 11.50.



(11.50)

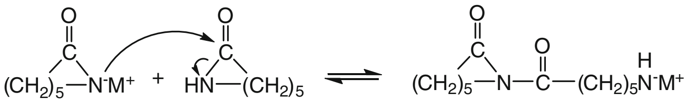
or with a metal derivative as shown in Eq. 11.51.



(11.51)

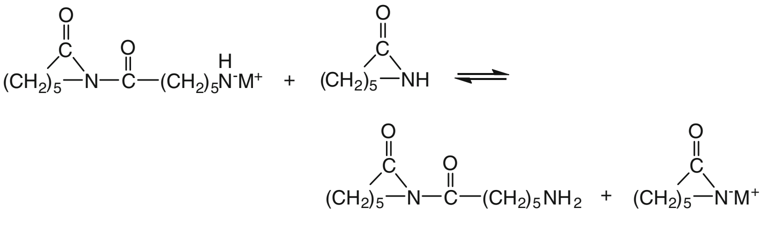
The use of an alkali metal or metal hydride gives a high concentration of lactam anion, but side reactions contaminate the product with amines and water that destroy reactive initiating and propagating species. The use of weaker bases produces a lower concentration of lactam anion unless the equilibrium is pushed to the right of the chemical reaction equation. The use of most bases contaminates the system with the conjugate acid (BH) of the base that also destroys reactive species. The preferred method of initiation consists of generating and purifying the lactam anion first, then the purified anion is used to initiate the polymerization.

The lactam anion reacts with monomer in the second step of the initiation process by a ring-opening trans-amidation to form primary amine anion as below:



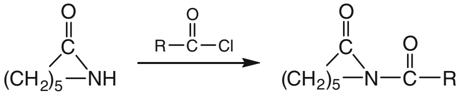
(11.52)

The lactam anion is not stabilized by conjugation with a carbonyl group. It is highly reactive and rapidly abstracts a proton from monomer to form the imide dimer and regenerate the lactam anion.



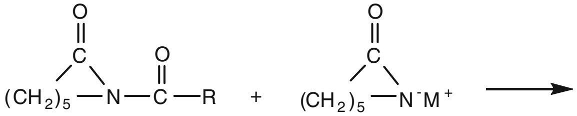
(11.53)

The lactam polymerization is limited by using strong base alone. There are the induction periods as discussed before and the reaction is only limited to more reactive lactams such as ε-caprolactam and 7-heptanolactam. The less reactive lactams such as 2-pyrrolidinone and 2-piperidinone, are much sluggish toward polymerization by strong base alone. The formation of the imide dimer is difficult from these relatively unreactive lactams. The limitations can be overcome by forming an imide by reacting lactam with an acylating agent such as acid chloride, anhydride, isocyanate, monocarbodiimide, and others (11.54). The N-acyl lactam can be synthesized in situ or preformed and then added to the monomers for polymerization. The use of an acylating agent is advantageous even for the more reactive lactam as induction periods are absent, polymerization rates are higher and lower reaction temperature can be used.

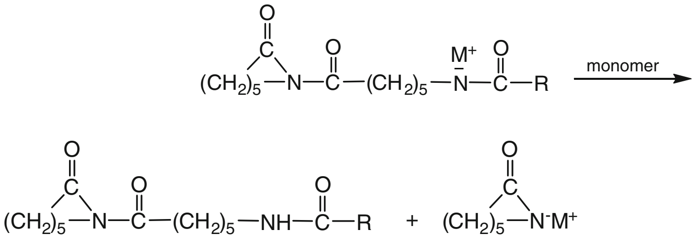


(11.54)

The initiation of N-acyl lactams involves it reacts with activated monomer followed by fast proton exchange with monomer as below:

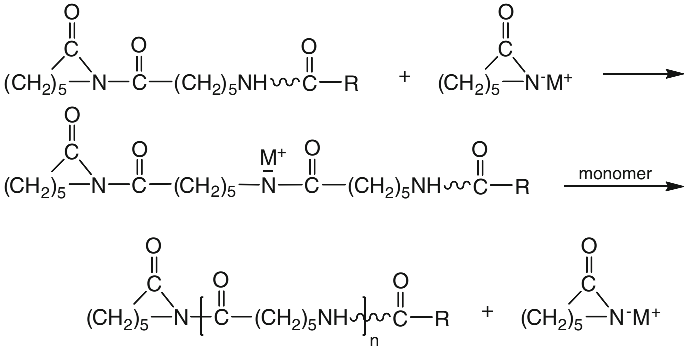


(11.55)



(11.56)

The propagation follows the same manner as in the strong base initiation process except that the propagating chain has an acylated end group instead of the amine end group:



(11.57)

The polymerization rate is dependent on the concentrations of base and N-acyl lactam, which determine the concentrations of activated monomer and propagating chains, respectively. The degree of polymerization increases with conversion and monomer concentration but decreases with N-acyl lactam concentration. These characteristics are qualitatively similar to those of living polymerization, but lactam polymerization is not living polymerization. Due to the side reactions, the decay of activated monomer and propagating chain concentration is very rapid. The side reactions include hydrogen abstraction from C–H bonds α- to amide carbonyls to form β-ketoimides and β-ketoamides and then subsequently to generate side products through Claisen-type condensation reactions. The latter reaction yields water as a product which decreases the concentrations of activated monomer and N-acyl lactam.

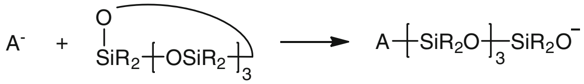
The molecular weight distribution (MWD) is usually broader than the most probable distribution as a result of branching at the later stages of reaction. The polymeric amide anion attacks the lactam end group of another polymer chain to form branching. Further branching will occur through Claisen condensation. The MWD is considerably broader when an N-acyl lactam is not used because the initiation is slow. The high PDI is also due to the polymer chains initiated early, grow for longer times than those initiated later.

11.4.4 Reactivity of Lactam

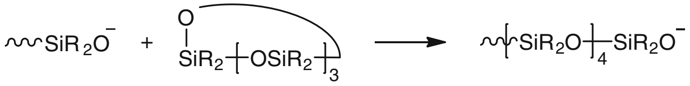
The polymerization reactivity of lactam depends on ring size and type of initiation. The reactivity of cationic and hydrolytic polymerizations is wider spread than does anionic polymerization due to their lower reactivity. The 6-membered lactam can undergo polymerization in anionic polymerization, whereas most of 6-membered cyclic monomers are unreactive toward ring-opening polymerization. The substituted lactams exhibit lower reactivity than that of unsubstituted lactams due to the steric hindrance effect at the reaction site.

11.5 Cyclosiloxanes

The high molecular weight polysiloxane is synthesized by either cationic or anionic ring opening polymerization of trimer or tetramer of cyclic siloxanes [2]. The anionic polymerization of cyclic siloxanes can be initiated by alkali metal hydroxides, alkyls, and alkoxides, silanolates such as potassium trimethylsilanoate, $(CH_3)_3SiOK$, and bases. Both initiation and propagation involve a nucleophilic attack on monomer similar to the anionic polymerization of epoxides as shown below:



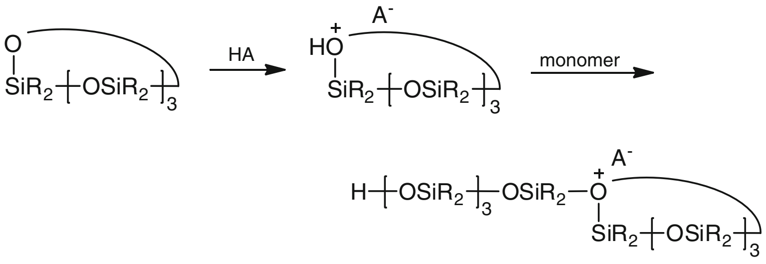
(11.58)



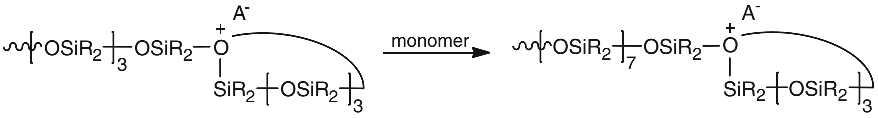
(11.59)

It is interesting to note that the enthalpy of polymerization of cyclic siloxanes, ΔH, is nearly zero and entropy ΔS is positive by 6.7 J mol^{-1} K^{-1} [8, 9]. The driving force of this polymerization is the increase in entropy on polymerization. The positive ΔS values for the cyclic siloxane probably result from the high degree of flexibility of the linear polymer chains and the large sized atoms of Si. This flexibility leads to greater degrees of freedom in the linear polymer compared to the cyclic monomer.

The cationic process is more complicated and less understood than the anionic process. Various protonic and Lewis acids are used to initiate cationic polymerization of cyclic siloxanes. Most of the cationic polymerization proceeds by simultaneously step polymerization and ring-opening polymerization. The initiation starts with the protonation of monomer then followed by subsequent reaction with monomer to form the tertiary oxonium. The propagation step follows the similar nucleophilic attack of monomer on the tertiary oxonium ion as shown below:



(11.60)



(11.61)

Polysiloxane (silicone) is a very important commercial polymer. It possess an unusual combination of properties which can sustain a wide temperature range (−100 to 250°C). It exhibits very good low temperature flexibility because its low Tg of −127°C. Silicone is very stable to high temperature, oxidation, and chemical and biological environments because its strong and long Si–O bond and wide Si–O–Si bond as compared with carbon–carbon bond. It has been used widely in our daily life such as sealants, coatings, medical implants, and so on.

11.6 Copolymerization

Considerable ring-opening copolymerizations have been performed either using similar type cyclic monomers (e.g., two kind cyclic ethers or two kind lactams) or using different type cyclic monomers (e.g., cyclic ether with lactam) [2]. The copolymerizations between cyclic monomers with alkene and other compounds are also extensively studied. Ring-opening copolymerization is very complicated. For copolymerization proceeds by the *activated monomer* mechanism such as cyclic ether and lactams, the actual monomers are the activated monomers. The concentration of two activated monomers may be different from the comonomer feed. Calculations of monomer reactivity ratios using the feed composition will introduce errors. Most of ring-opening copolymerizations involve propagation–depropagation equilibria which need to handle the experimental data very carefully to determine the reactivity ratio of each monomer.

The situation is more complicated when there are additional equilibria between polymer and cyclic oligomer or by intermolecular chain transfer to polymer which result in reshuffling of monomer units. It is possible to avoid or minimize the reshuffling equilibria by using mild initiators, low conversions, and highly reactive monomers. However, reactions of near-complete reshuffling of monomer units have been observed in industrial practice. For instance, the anionic copolymerization of octamethyl cyclotetrasiloxane (M_1) and 1,3,5,7-tetramethyl-1,3,3,7-tetravinyl cyclotetrasiloxane (M_2) (feed ratio 9:1) by potassium silanolate at 130 °C. The initial copolymer is very rich in M_2, and this monomer is exhausted early. Further reaction results not only in conversion of M_1 but also redistribution of the M_2 units. Silicon 29 NMR shows the M_2 units to be in blocks at short reaction times but statistically distributed at long reaction times. Similar results have been observed in the cationic copolymerization of methyl glyoxylate and 1,3-dioxolane [2].

Counterion effects similar to those in ionic chain copolymerizations of alkenes are present. Monomer reactivity ratios are also sensitive to solvent and temperature. Some ring-opening polymerizations proceed two different mechanisms, simultaneously. The monomer reactivity ratios for any co-monomer pair are unlikely to be the same for the two different propagations. Any experimentally determined *r* values are the combination of two different *r* values.

The selection of adequate initiator is extremely important for copolymerizations between monomers containing different polymerizing functional groups. Basic differences in the propagating centers (oxonium ion, amide anion, carbocation, etc.,) for different types of monomer may exclude some kind of copolymerizations. Even when two different types of monomers have similar propagating centers, they may not have completely compatible two crossover reactions. For example, oxonium ions initiate cyclic amine polymerization, but ammonium ions do not initiate cyclic ether polymerization.

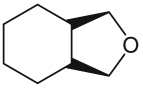
The copolymerization of cyclic ether with acetal discussed previously produces commercial important product (Sect. 11.3.3). Copolymerization is used extensively for silicone polymers. Varying amounts of substituents such as phenyl or vinyl are introduced into the basic poly(dimethyl siloxane) structure to modify properties of the final product. Phenyl groups improve the low-temperature flexibility of silicone polymers by decreasing their low-temperature crystallinity. Their high-temperature performance and miscibility with organic solvents are also improved. Vinyl groups allow more efficient crosslinking by either hydrosilation or peroxides.

A wide range of different block copolymers has been synthesized by using the sequential ring-opening polymerization. These include various copolymers made from two different cyclic monomers containing the same functional group such as two cycloalkenes, cyclic ethers, lactams, lactones, etc. There are very few reports of block copolymers of lactams or cyclic siloxanes produced by sequential addition which may be due to the exchange reactions occurred in the polymerization.

Furthermore, many block copolymers can be obtained by sequential polymerization of a cyclic monomer and an alkene monomer such as the combination of methyl methacrylate with epoxide, polystyrene with ethylene oxide or hexamethyl cyclotrisiloxane, etc. Actually, it is easier to obtain block copolymers from these combinations than to obtain the corresponding statistical copolymers. Synthesis of a statistical copolymer requires that various homo- and cross-propagation rates are similar. Synthesis of a block copolymer by sequential addition requires that the system be living with one or the other and the cross-propagation proceeding at a reasonable rate. Thus, anionic copolymerization of styrene with ethylene oxide does not occur because the addition of alkoxide ion to the carbon–carbon double bond and homopropagation of polystyryl anion are less favored as compared to the addition of polystyryl anion to ethylene oxide and homopropagation of alkoxide anion. However, block copolymerization is easily achieved by adding ethylene oxide to living polystyrene. Triblock polymers can be obtained in some system using appropriate difunctional initiators.

11.7 Problems

1. Discuss why cyclic alkane monomer does not undergo ring-opening polymerization as readily as cyclic ether or cyclic amide from the aspects of thermodynamic and kinetic point of view. Write out the reaction mechanism to explain your answers.
2. Please compare and discuss the polymerizability of following two monomers to undergo ring-opening polymerization.



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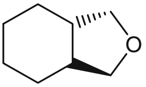
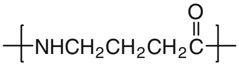
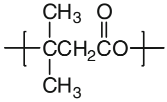


II

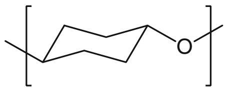
3. Compare and discuss the differences in rate of polymerization and degree of polymerization among free radical polymerization, step polymerization and ring-opening polymerization.
4. Give structures of cyclic monomers, initiators, and reaction conditions that might be used to prepare the following polymers:

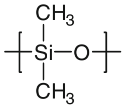
(a) 

$\left[\mathrm{NHCH_2CH_2CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\right]$

(b) 

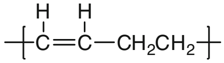
$\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\mathrm{CH_2}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\right]$

(c) 

(d) 

$\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-\mathrm{O}\right]$

(e) $\left[\mathrm{OCH_2CH_2OCH_2}\right]$

(f) 

$\left[\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-\mathrm{CH_2CH_2}\right]$

5. Please explain why anionic polymerization of propylene oxide is usually limited to produce a relatively low molecular weight polymer.
6. The molecular weight of ring-opening polymerization of ethylene oxide initiated by sodium methoxide in alcohol is limited to 10,000. Please explain why. How would you change the polymerization condition to obtain the polymer to have molecular weight higher than 50,000?
7. Please explain the following observations:
   (a) A small amount of epichlorohydrin greatly increases the rate of the polymerization of tetrahydrofuran by BF_3 even though epichlorohydrin is much less basic than tetrahydrofuran.
   (b) The addition of small amounts of water to the polymerization of oxetane by BF_3 increases the polymerization rate but decreases the degree of polymerization.
8. What are the roles of an acylating agent and activated monomer in the anionic polymerization of lactams?

9. The monomer reactivity ratios of anionic copolymerization (using an acetylated initiator) of ε-caprolactam (M_1) and α-pyrrolidinone (M_2) can be calculated using standard copolymerization equation to be $r_1 = 0.75$ and $r_2 = 5.0$ with the conclusion that ε-caprolactam is eight times more reactive than α-pyrrolidinone. However, the experimental data show reversed reactivity behavior. Please propose the reaction mechanism to explain the observation [10].
10. Please explain why the epoxy resin usually exhibits better adhesive strength than acrylate resin. The epoxy resin usually made from bisphenol A with epichlorohydrin in presence of base. Please write the chemical reaction involved in this synthesis. Explain why the oxirane ring of epoxy resin can be opened either by acid or base and write out their reaction mechanisms.

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