Hans Kricheldorf

Polycondensation

History and New Results

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Leo Hendrik
Baekeland 1863–1944

Wallace Hume
Carothers 1896–1937

The grandfathers of polycondensation chemistry.

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Abbreviations

DA	Donor-acceptor complex
DP	Degree of polymerization of an individual chain
DPn	Average number degree of polymerization
DPw	Average weight degree of polymerization
IMC	Initial monomer concentration
KC	Kinetically controlled (irreversible)
MWD	Molecular weight distribution
M_n	Number average degree of polymerization
M_w	Weight average degree of polymerization
$N_{a0,}N_{at}$	Number of “a” (end) groups at time zero or later
N_{b0},N_{bt}	Number of “b” (end) groups at time zero
n_c	Number fraction of all chains
n_r	Number (mole) fraction of all rings
PBT	Poly(butylene terephthalate)
PET	Poly(ethylene terephthalate)
ROP	Ring-opening polymerization
RZDP	Ruggli-Ziegler dilution principle
TC	Thermodynamically controlled (involving equilibration)
w_c	Weight fraction of all chains
w_r	Weight fraction of all rings

Chapter 1
Introduction

For three reasons polycondensation is a polymerization process, which plays a unique role in the history of chemistry in general, and in the history of polymer science in particular. Polycondensation was the first polymer forming reaction sequence which existed on the early earth before living organisms appeared. It is clear from the experiments of Stuart Miller [1, 2] and other authors that whenever organic molecules were formed on earth, α-and ß-amino acids were formed together with α-hydroxy acids, such as glycolic and lactic acid. Heating and drying of their aqueous solutions might have yielded their oligomers and polymers. The second reason for the unique role of polycondensation is the fact that the first polymer synthesized in a laboratory (although not intentionally) was poly(D,L-lactic acid) which was obtained by heating of lactic acid in vacuo (see Sect. 2.1 in Chap. 2). The third reason is the fact that the first commercialized synthetic polymers, namely Novolac and Bakelite, were polycondensates (see Chap. 2).

The main purpose of this introduction is to present and discuss the definition of the term "polycondensation", because in recent years an increasing number of authors published misleading or definitely incorrect applications of his term. The experimental and theoretical basis of step-growth polymerizations, in general, and polycondensation, in particular, was elaborated by W. H. Carothers (see Chap. 3) and by P. J. Flory (see Chap. 4). Their results and conclusions are still valid nowadays (for partial revisions see Chaps. 4, 5 and 7) and form in all textbooks the framework for chapters dealing with step-growth polymerizations. Polycondensation and polyaddition are the two branches of step-growth polymerization, which were defined by Flory via a kinetic scheme [3], which complements the kinetic definition of chain-growth polymerization (see Chap. 16). In connection with step-growth polymerizations the term polyaddition should be used instead of addition polymerization, because the latter term is frequently applied to chain-growth polymerizations of vinyl monomers and a-olefins. Polycondensation and polyaddition differ formally by the fact that each growing step of a polycondensation involves elimination of an (usually) small molecule, such as H_2O, HCl, MeOH etc. This difference does not affect the kinetic course of both polymerization processes, but it marks an enormous difference for the thermodynamic properties. A normal polycondensation of non-cyclic monomers is characterized by a reaction entropy

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(ΔS) close to zero, so that even a low reaction enthalpy suffices to promote the polycondensation. In contrast, polyaddition is characterized by a large negative reaction entropy, so that a highly exothermic reaction is needed to effect the polymerization. The requirement of a highly exothermic reaction strongly limits the number of addition reactions suited for a successful polymerization. In the case of polycondensations even a reaction enthalpy around zero may allow for the synthesis of a high molar mass polymer, when the byproduct is transferred into another phase (e.g., evaporization of CO_2 or crystallization of NaCl). From the thermodynamic point of view polycondensations of cyclic monomers represent an intermediate case, as discussed in Chap. 9.

Flory outlined [3] that the definition of polycondensation is necessarily based on kinetic aspects and not on the structure of polycondensates, because numerous polycondensates can also be prepared by ROP which usually proceeds as chain-growth polymerization. Flory's definition of step-growth polymerization is limited to polycondensations and polyadditions in the melt or in solution, and does not include solid-state polycondensations. Flory's definition of step-growth polymerizations is based on point 1.

(1) The course of a normal step-growth polymerization is characterized by the fact that monomers, oligomers and polymers can react with each other at any time This course necessarily requires that the reactivities of the functional groups does not significantly depend on the size of the molecules. This kinetic scheme has the unavoidable consequence that the molar mass distribution of the linear chains obey the most probable distribution (also called Schultz-Flory distribution), even when equilibration reactions take place. This distribution has, in turn, the consequence that the linear chains alone (cyclics not included) have a polydispersity (M_w/M_n) of 2. Slight deviations from this standard scheme are tolerable for the definition of polycondensation. For instance, the reaction of a_2 with b_2 may be slightly slower or faster than reactions with oligomers and polymers. Yet, when one monomer reacts faster with oligomers and polymers than with the second monomer, the kinetic course changes dramatically and may finally obey the definition of a chain-growth polymerization (see Chap. 8).

Theoretical and experimental research of the past 40 years allow for a more precise definition of step-growth polymerization by addition of to more points:

(2) Cyclization competes with chain growth at any monomer concentration and at any stage of the polymerization (see Chaps. 5 and 7).
(3) The molar concentration of all linear species together (monomers, oligomers and Polymers) steadily decreases with higher conversions (p in Eq. 1) [4].

The implications of this "Law of Self-Dilution" with regard to reaction rates and cyclization reactions are discussed in Chaps. 5 and 7.

$$[L]_t = [L]_0(1 - p) \tag{1}$$

$[L]_0$,$[L]_t$ = molar concentration of all linear species at time zero or later

The occurrence of condensation (elimination) steps together with points (1)–(3) yield a clearcut definition of the term polycondensation, and allow for an easy distinction from polymerizations which at first glance show similarities, but differ from the definition given above. For instance, the term polycondensation was recently misused in numerous publications [4–9] dealing with chain-growth polymerizations involving condensation steps. Such polymerizations are correctly termed “condensative chain polymerizations” according to IUPAC, and a detailed discussion is presented in Chap. 16. Confusion in the opposite direction also frequently occur. For instance, handful of papers has recently been published [10–15] on polyadditions of functional olefins or lactones under the terms “self-polycondesation” or “self-condensing polymerization”. Those polymerizations obey a step-growth kinetic, but condensation (elimination) steps are totally lacking. Such a confusion of polycondensation and polyaddition is particularly strange, as the meaning of condensation and addition reactions has been clarified in organic chemistry about hundred years ago.

Furthermore, it should be mentioned that throughout this book the following three terms coined by Flory [3] are used.

“Linear Polycondensation”. This term is used for polycondensations exclusively yielding linear reaction products. Flory originally assumed [3] that cyclization reactions do not play any role in step-growth polymerizations and used this term instead of “Two-dimensional polycondensations”.

“Two-dimensional Polycondensations” this term means polycondensations of $a - b$ and $a_2 + b_2$ polycondensations regardless, if cyclics are formed or not.

“Three-dimensional Polycondensations” this term includes polycondensations of all multifunctional monomers such as $a - b_n$ and $a_2 + b_n$ with $n > 2$

Finally, the concept of this book needs a short explanation. According to the title, this work focuses on two aspects. It is aimed at presenting an as complete as possible history of polycondensation experiments. A lot of information about Carothers work and life is available from numerous sources including the internet. Despite the outstanding work of Carothers the early history of polycondensation is not limited to his work. Information about earlier experiments is scattered over numerous original papers, patents and scarce comments in books. For example, Flory wrote a few sentences about early polycondensation experiments in his famous book “Principles of Polymer Chemistry” [16]. A broader and more detailed description of the history of polycondensation chemistry was presented by H. Morawetz in his excellent book “Polymers-The Origins and Growth of a Science” [17]. Yet, step-growth polymerization played a minor role in that work, and all the important inventions and contributions made by various polymer chemists around or after 1940 were not considered.

The second purpose of this book was the presentation of new working fields which emerged over the past fifty years. These working fields were selected under the aspect of a broader and deeper understanding of polycondensations with regard to the theoretical background and with regard to new preparative applications.

However, although the author has attempted to cite as many as possible original papers and review articles concerning these new working fields, this book was not designed as handbook of polymer syntheses.

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Part I
History

Chapter 2
Experiments Before World War I

2.1 Early Formulas and Terminology

The nineteenth century has witnessed the gradual transformation of alchemy into modern chemistry. In a simplified view of this process one may say that this evolution mainly proceeded on two tracks. Definition of elements, detection of elements, and elaboration of the periodic table represent one track. Syntheses of organic molecules in the laboratory and the elaboration of formulas allowing for a correct three-dimensional description of organic molecules represent the second track. In the first half of the nineteenth century isolation and purification of organic substances by fractionated distillation or crystallization had become standard methods. The characterization of the purified substances was performed by elemental analyses, cryoscopic determination of the molar masses (e.g., in water, benzene, or camphor), and by derivatization of functional groups. The results challenged the organic chemist to find formulas allowing for an adequate representation of chemical structures.

The confusion about structure and formulas which still existed around 1860 among the best chemists of that time is illustrated by the three formulas proposed for lactic acid [1–3] (see Formula 2.1). Two-dimensional formulas analogous to those used today were first proposed by Crum-Brown in 1863 [4] and strongly recommended by other authors [5]. These formulas were based on an important publication of Kekule (1829–1896) in which he stated [6] that carbon atoms are tetravalent and that "carbon atoms bind themselves to one another, whereby part of the affinity of one carbon is naturally engaged with an equal part of the affinity of another carbon". He also stated that "the number of H-atoms attached to n C-atoms which are linked to each other is $2n + 2$". In 1865 Kekule also "invented" the famous formula of the benzene ring [7]. Considering this progress in the "formula language" it is amazing that Kekule himself and other chemists [8] did not consider their formulas as constitutional formulas of stable molecules, where the atoms are in fixed positions relative to each other. Kekule wrote in his textbook: "which of the rational formulas should be used depends on the purpose…(they) are only transformations and not constitutional formulas….and in no

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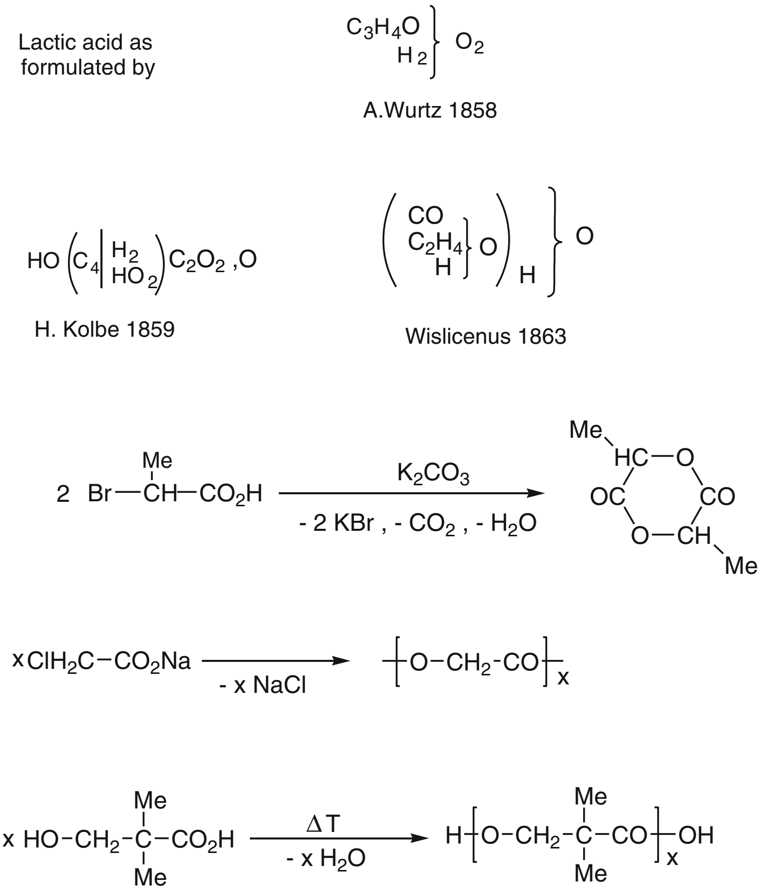
way express the positions of these atoms in the compounds". Therefore, several types of formulas coexisted in the literature for at least two decades.

A final and decisive progress was contributed by Pasteur [9–11] (1822–1895) and van t'Hoff (1852–1908) [12]. Pasteur was troubled as a student by a report that salts of tartaric acid and paratartaric acid (i.e., the racemate) differed from each other by the optical rotation of tartrate solutions and absence of optical rotation in the case of "paratartrates", although these salts had identical properties in all other aspects. Careful examination of numerous salts of racemic tartaric acid led to an extremely important discovery. In the case of sodium–potassium or sodium ammonium salts he found equal amounts of hemihedral crystals which contained either the laevorotatory or the dextrorotatory molecules. In other words, he was able to separate the optical enantiomers in their crystalline form. About 20 years later Paterno published a rarely cited paper [13] in which he presented a tetrahedral



Formula 2.1

arrangement of the four carbon valences. The genial van t'Hoff combined in 1874 (before completion of his Ph.D., thesis!), all these pieces of information in a famous paper which explained the stereochemistry of organic compounds, including their chirality, by three-dimensional formulas. Assuming a rotational barrier of the C–C double bond he also explained the different properties of fumaric and maleic acid by cis–trans isomerism. With van t'Hoff's concept all fundamental problems concerning the correlation between formulas, constitution, and properties of organic compounds were solved. In 1901, van t'Hoff was awarded with the 1st Nobel Prize of chemistry.

Long before rational and correct formulas for organic compounds were elaborated, first reports on polymerization processes were published. In 1839 E. Simon [14], a pharmacist in Berlin, distilled "storax resin" a natural product, under alkaline conditions and isolated an oil which he called "styrol" (since then the German name of styrene). He obtained correct elemental analyses, but he had no idea about the structure of his oil. Kekule's formulation of the benzene ring did not exist yet, and the correct formula of "styrol" as vinyl benzene was published by Erlenmeyer in 1866 [15]. Simon noted that "with old oil the residue that cannot be vaporized without decomposition is greater than with fresh oil undoubtedly due to a steady conversion of the oil by light and heat to a rubber-like substance". In a detailed study of styrene Blyth and Hofmann [16] confirmed Simon‘s elemental analyses and noted that this ratio was the same as that of benzene or cinnamol, an oil obtained by distillation of cinnamic acid [17]. They assumed that Simon‘s styrol and cinnamol are identical substances and they confirmed that the transition of styrol to the solid metastyrol is catalyzed by heat and sunlight and proceeds without any change of the elemental composition. This transition was discussed in 1866 by Berthelot (the most influential French chemist at that time) [18] as a polymerization which was understood as a special case of isomerism. The term isomerism was coined by Berzelius in 1832 "I suggest that substances of identical composition, but different properties, should be called isomers" [19]. One year later, Berzelius used for the first time the term "polymeric" for an isomerism which is defined by an equal elementary composition but with a different absolute number of atoms [20].

2.2 First Syntheses of Polyesters

First experiments dealing with (poly)condensations of difunctional compounds concerned aliphatic hydroxyl acids such as lactic acid, glycolic acid, or tartaric acid. In 1833, [21] GayLussac and Pelouze reported that dehydratization of (racemic) lactic acid solution at temperatures up to 140 °C yielded a non-crystalline residue with was sirupy in the heat but solid at room temperature. This residue was insoluble in water, soluble in ethanol or diethyl ether and yielded lactic acid on hydrolysis [22]. This residue was called "water free lactic acid", and the elementary formula $C_6H_5O_5$ was noted. Yet, the molar mass was not determined and no structural formula was presented, a logical consequence of the fact that even the formula of lactic acid itself was unknown at that time (see Formula 2.1) [1–3]. Synthetic route and properties of this material perfectly agree with poly(D,L-lactide) having a random stereosequence. As it became known much later, such a polylactide is an amorphous mass with a Tg of 45–50 °C (depending on the molar mass). Hence poly(D,L-lactide) represents not only the first polycondensate, but also the first synthetic polymer at all, a fact, which is largely ignored in the literature of polymer science. It is one of the numerous ironies in the history of polymer science that the usefulness of the first polycondensate was ignored for almost 150 years.

In 1849 [23] Engelhardt reported that the distillation of lactic acid yields a residue which was identical with the "water free lactic acid" of GayLussac and Pelouze. A cyclic dimeric ester called lactide was first identified by Henry in 1863 [24] who published a correct determination of its molar mass. However, the term lactide was known before and was the reason why later several authors coined the terms "glycolide" and "salicylide" for the condensation products of glycolic acid and salicylic acid, respectively. By distillation of lactic acid in a stream of air around 150 °C Wislicenus [25] found small amounts of both L,L- and racemic D,L-lactide. He did not measure their optical rotations, but he reported their different melting points: 97 and 125–126 °C, respectively. Racemic D,L-lactide was later prepared by Bischoff and Walden in two ways, namely by heating the sodium salt of a-bromo propionic acid in vacuo [26, 27] or by heating of K_2CO_3 with the anhydride of a-bromo propionic acid [28] (see Formula 2.1). A detailed study of all stereoisomers of lactide was later published by Jungfleisch and Godchot [29, 30], but nobody showed interest in polylactides before the end of World War I.

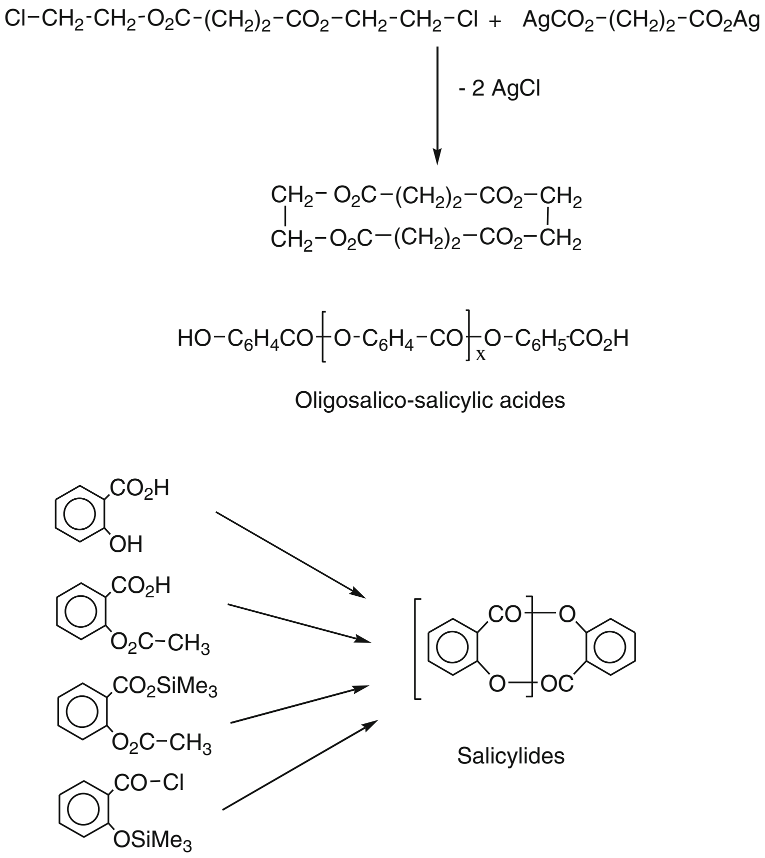
The first synthesis of a polyglycolide was reported by Desaignes in 1854 [31], who heated tartaric acid to 300 °C and obtained a crystalline high melting solid ($T_m = 220$ °C) which upon hydrolysis yielded glycolic acid. Desaignes called this product glycolide and did not recognize its polymeric structure. A few years later Kekule [32] and Norton and Tschaerniak [33] obtained a high melting polyglycolide by heating potassium or sodium chloroacetate (see Formula 2.1), and assumed again that a low molar mass polyglycolide was formed, but no molar mass measurements were performed. More than 30 years later, Anschütz and Schroeder suspected that these so-called glycolides possess a polymeric structure and began to study the (poly)condensation of glycolic acid [34–36]. Upon heating in vacuo they were able to isolate a crystalline, dimeric glycolide melting at 82–83 °C which confirmed their suspicion. Finally Bischoff and Walden [37] prepared the cyclic, dimeric glycolide by heating sodium bromoacetate in vacuo. They also observed that this glycolide yields the high melting polyglycolid upon heating with traces of water or zink chloride. Furthermore, they found, that heating of polyglycolide in vacuo allows for a depolymerization yielding the cyclic dimer. With these results the relationship between glycolide and polyglycolide was clarified, but the structure of polyglycolide with regard to end groups or cyclic character was not elucidated yet.

Meanwhile it was found that ß-hydroxy carboxylic acids eliminate water upon heating yielding unsaturated acids, whenever a proton existed in a-position. Therefore Blaise and Marcilly [38] focused their experiments on the dehydratization of ß-hydroxy pivalic acid (see Formula 2.1).Upon heating to 200 °C or upon treatment with conc. sulfuric acid at 60 °C they obtained an almost insoluble solid which was purified by washing with water and diethyl ether. They found a Tm of 165 °C and elemental analyses agreeing with the values of poly(pivalolactone). They presented formulas of linear chains having one CH_2OH and one CO_2H end group. From cryoscopic measurements in phenol they estimated a molar mass of 620 Da or a DP of 6 (presumably underestimating the real DP). Like all other researchers before Word War I these authors believed that their products were monodisperse. Polydisperse mixtures of cycles or linear chains were never taken into account. Concerning polyester of aliphatic hydroxy acids preparation and polymerization of δ-valerolactone should also be mentioned. δ-Valerolactone and the polylactone were prepared by Cloves [39] from δ-chloro valeric acid, and he also found that heating of γ-chloro-, γ-bromo-, and γ-iodo butyric acid exclusively yields γ-butyrolactone. One year later Fichte and Beiswenger [40] reported that δ-valerolactone spontaneously polymerizes when stored at room temperature and that the lactone can be recovered by heating the polylactone in vacuo.

(Poly)condensations of ethylene glycol and succinic acid were first studied by Lourenco [41–44] who heated these monomers under various reaction conditions with temperatures up to 300 °C. He isolated oligoesters having carboxylic end groups, but he also obtained a neutral polyester giving elemental analyses in agreement with those of the repeat unit. Apparently the same product ($Tm = 90$ °C) was prepared by Davidoff [45] from silver succinate and dibromoethane. Molar mass measurements were not conducted and the structure of these products remained unclear. About 8 years later polycondensations of ethylene glycol and various dicarboxylic acids were studied by Vorländer [46]. From the experiments outlined in Formula 2.2 he concluded that the neutral ethylene succinate melting at 90 °C is most likely a cyclic dimer, but he did not exclude the formation of a linear polyester.

Not only aliphatic, but also aromatic hydroxyl acids and diphenols were subjected to condensation experiments, and salicylic acid was in the focus of several research groups. In 1859, Gerhardt [47] observed that the treatment of sodium salicylate with $POCl_3$ yielded a mixture of products which was fractionated by washing and extraction with water, ethanol, and diethyl ether. An almost insoluble white powder remained the elemental analyses of which agreed with those of a repeat unit. This product was called salicylide and speculatively interpreted as analog of lactide. Yet a structural formula was not presented, and the structure of lactide was still unclear at that time.

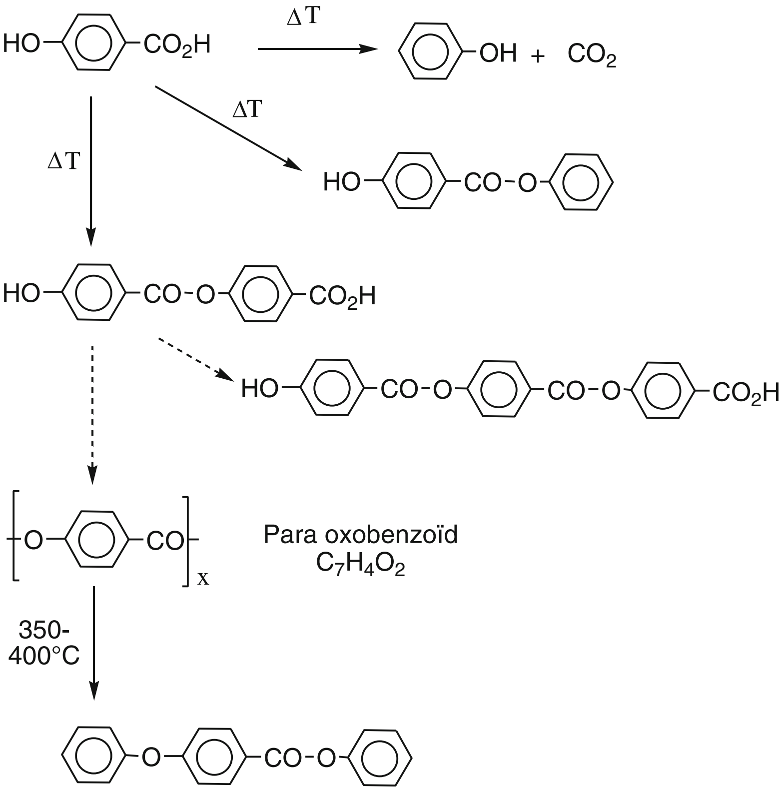
In a detailed study of salts and derivatives of salicylic acid Kraut [46] heated salicylic acid with acetyl chloride under variation of the reaction conditions. He isolated products which were interpreted as linear oligoesters called salico salicylic acid and trisalico salicylic acid (see Formula 2.2). He also reinvestigated the condensation of sodium salicylate with $POCl_3$ and interpreted the resulting salicylide as



Formula 2.2

linear heptameric oligoester (see Formula 2.2). Schiff [48] repeated the condensation of salicylic acid with $POCl_3$ and criticized the interpretation of Kraut Schiff concluded that the C_6H_4 units are connected by ether and not by ester groups. About 20 years later Anschütz [34, 49–52] launched a comprehensive study of salicylic acid derivatives and their condensation products. He synthesized salicyl chloride by means of thionylchloride (which became available after 1890), but he also performed polycondensations of salicylic acid and $POCl_3$. From his numerous results, Anschütz concluded that the main reaction products of all polycondensations are cyclic oligoesters which he called again salicylides. He believed that the crystalline α- and ß-salicylide he had isolated from several experiments were two isomers of the cyclic dimer. He also isolated a cyclic tetramer which formed a complex with chloroform, and he called a less soluble fraction of higher molar mass “polysalicylide”. In 1951, three British chemists [53] re-examined the work of Anschütz. They used various methods for reliable determination of the molar masses and they included X-ray measurements of pure crystalline substances. They reached the conclusion that the so-called α-salicylide was indeed a cyclic dimer, but ß-salicylide a cyclic trimer. The identification of the cyclic tetramer was confirmed and a cyclic hexamer was isolated from the high molar mass fraction. Their experimental work also included the new synthetic methods of Einhorn [54, 55] who had performed condensations of salicylic acid with $COCl_2$ or $POCl_3$ in pyridine, reaction conditions which favor the formation of low molar mass cyclics. Again 50 years later Kricheldorf et al. [56] examined the crude reaction products of several monomers and condensation methods (see Formula 2.2) by Fast Atom Bombardment mass spectrometry and found that cyclic oligoesters were the main reaction products of all experiments. In addition to the before mentioned rings the cyclic pentamer, heptamer, octamer, and nonamer were identified. Furthermore, it was found by means of MALDI-TOF mass spectrometry [57] that salicylic acid imparts a high cyclization tendency in copolyesters derived from m-hydroxybenzoic acid or other aromatic monomers. Hence, Anschütz's understanding of polycondensations of salicylic acid and its derivatives was eventually confirmed, and Kraut's assumption of linear oligoesters as main reaction products (favored by previous reviewers of the history of polymer science [58, 59]) was disproved. Finally, it should be mentioned that in 1862 Märker [60] reported on the pyrolysis of salicylide. A product with the elemental formula C_6H_4O was isolated. This finding was confirmed by Kraut [61] and this polymer was called phenyleneoxide, but its molar mass and structure were never characterized.

Polycondensations of m-hydroxybenzoic acid or its para isomer were less intensively studied Schiff [62] conducted polycondensations of both hydroxybenzoic acids with $POCl_3$ at 40–50 °C. The linear dimer was extracted from the reaction product of m-hydroxybenzoic acid and the insoluble reminder was considered to consist of the linear octamer, but convincing evidence for this conclusion was not presented. The only product isolated from analogous condensations of p-hydroxy benzoic acid was speculatively interpreted as tetramer. Two more research groups [62, 63] performed "dry distillations" of p-hydroxy benzoic acid, but the intractable reaction products were not characterized. A more informative study was presented by Klepl [64, 65] who analyzed the reaction products of the "dry distillation" in more detail. He observed that the melt loses phenol and carbon dioxide above 300 °C. In vacuo phenyl p-hydroxy benzoate distilled out of the reaction mixture and a solid residue was left. When the heating was stopped after 15 min, the dimer was found as the main component of the reaction mixture and a trimer was also isolated (see Formula 2.3). The insoluble and infusible residue remaining after intensive extraction with ethanol was correctly interpreted as polyester and called "paraoxibenzid". Heating of this polyester to 400 °C yielded the phenyl ester of p-phenoxy benzoic acid (see Formula 2.3). All these products were confirmed in later studies (see Chapter 14). Particularly interesting is the observation of Klepl that "paraoxibenzid" is rather stable up to 350 °C, but decomposes rapidly at higher temperatures. In later studies, it was found by DSC and X-ray measurements that poly(p-oxybenzoate) has a phase transition from a crystalline to a smectic state around 330–340 °C.



Formula 2.3

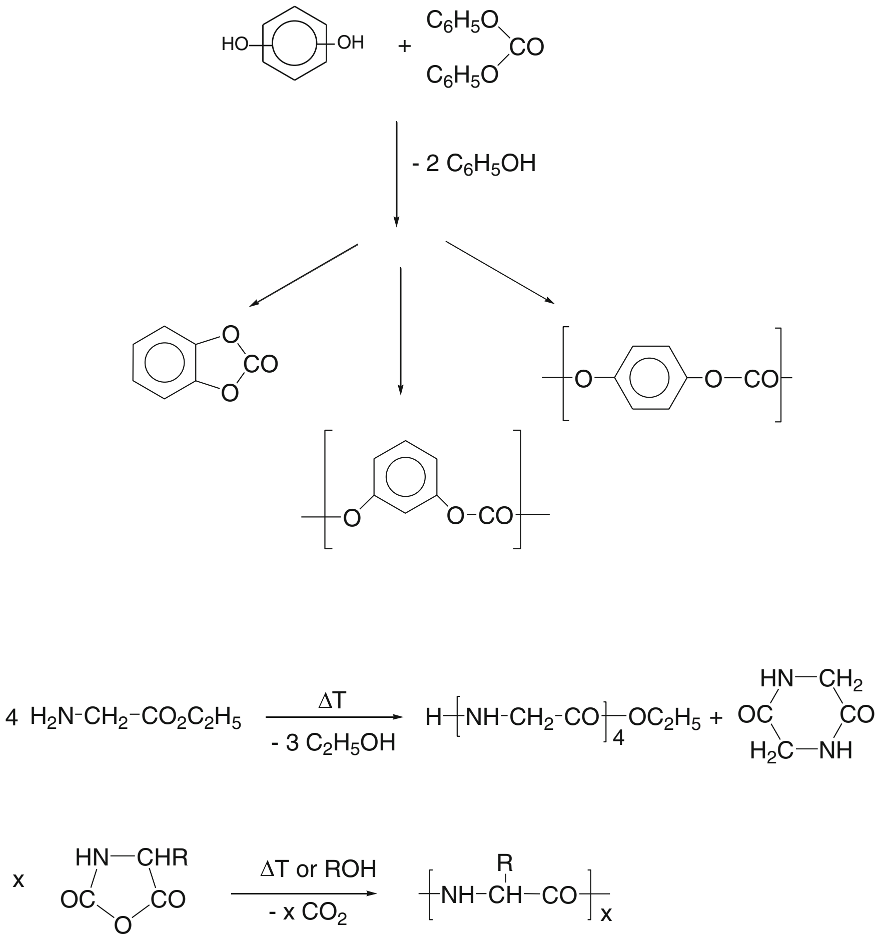
Although the smectic state is a solid phase, it is characterized by a high segmental mobility which favors chemical reactions.

Another class of aromatic polyesters, namely polycarbonates, was first prepared by Bischoff and Hedenström [66]. Those authors studied syntheses and properties of diphenyl carbonate, diphenyl oxalate and diphenyl esters of higher dicarboxylic acids. In this context, they performed polycondensations of diphenyl carbonate with catechol, resorcinol, and hydroquinone. The diphenols were heated with diphenyl carbonate up to 250 °C, and above 195 °C the liberation and distillation of phenol was observed. In the case of catechol the crystalline, monomeric, cyclic carbonate was isolated (see Formula 2.4). From resorcinol and hydroquinone insoluble, high melting residues were obtained which were purified by intensive washing with ethanol and hot diethyl phthalate. It was noted that the elemental analyses agreed with the "neutral carbonates" of the diphenols, but no comments on structure or molar mass were made. Oligomeric carbonates were also prepared by Birnbaum and Lurie [67] from resorcinol either by reaction with phosgene or by heating with cyanuric acid. A cyclic formula was presented, but molar mass measurements were not conducted.

2.3 Polypeptides and Polyamides

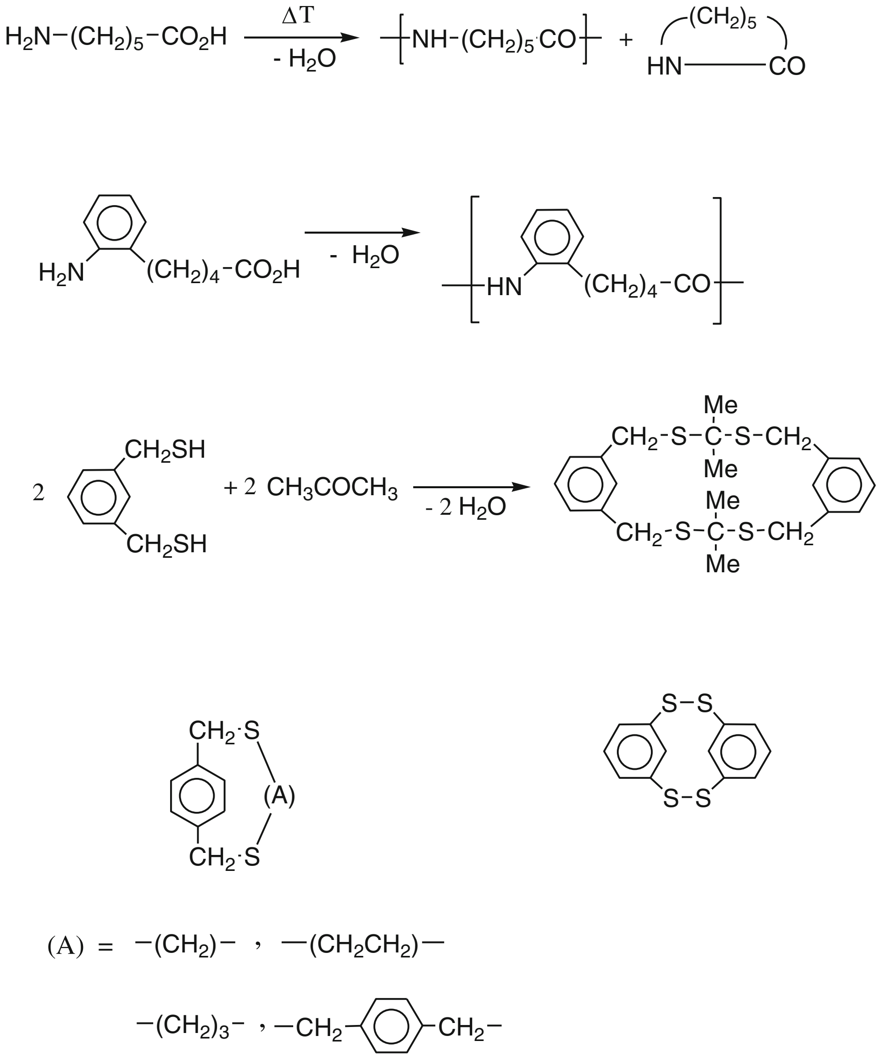
Experiments yielding oligopeptides and polypeptides were also reported before World War I. Curtius [68, 69], who systematically worked on amino acid and peptide chemistry, observed that the ethyl ester of glycine undergoes a spontaneous condensation process upon storage at room temperature. He also observed that two products were formed, the cyclic dimer (2,5-diketopiperazine) and the ethyl ester of the linear tetraglycine (see Formula 2.4). Higher oligomers were not found, seemingly, because the precipitation of the tetramer in the form of a ß-sheet structure hindered the further chain growth. He also found that for unknown reasons the presence of moisture favors the formation of the cyclic dimer at the expense of the linear tetramer. Two more research groups [70–72] obtained undefined oligoglycines by heating glycine in glycerol to 150–170 °C. However, Maillard [72] speculated that the high molar mass fraction of his reaction products mainly consisted of the cyclic octamer. High molar mass polypeptides were certainly obtained by Leuchs et al. via ring opening polymerization of a-amino acid N-carboxyanhydrides (NCAs) also called Leuchs's anhydrides [73–75]. Despite the elimination of carbon dioxide in every growing step (see Formula 2.4), the polymerization of NCAs is not a polycondensation, but a special case of chain growth polymerization labeled condensative chain polymerization according to IUPAC and is discussed in Chap. 16.

In addition to oligo- and polypeptides a several oligo- and polyamides were also prepared before World War I. (Poly)Condensations of diamines were mentioned by six research groups [76–81]. Hofmann noted in 1872 the formation of an intractable, apparently amorphous mass upon heating of 1,2-diaminoethane with diethyl oxalate [76]. Again 1,2-diaminoethane or a mixture of phenylene diamines were heated by Freund with the diethylester of malonic acid [77]. Yet, with exception of nitrogen elemental analyses he did not provide any characterization of his solid, poorly soluble reaction products. Michler and Zimmermann [78] reported that condensation of phosgene with m-diaminobenzene yielded a cyclic monomeric urea having softening temperature above 300 °C. Yet, a cyclic monomeric urea is for steric reasons impossible, and the authors certainly synthesized a mixture of cyclic and linear oligoureas. Meyer studied numerous condensations of various aromatic o-, m-, and p-diamines with esters or chlorides of aliphatic dicarboxylic acids [79]. Surprisingly he only described the isolation of crystalline cyclic monomers and dimers without mentioning polymeric byproducts. Ruggli [80] studied (poly)condensations of ω,ω'-diamino tulane with phosgene or dicarboxylic acid dichlorides. He purposely worked at low monomer concentration to favor the formation of cycles at the expense of polyamides. Fischer [81] correctly formulated formation of a polyurea prepared by heating of 1,4-diamino butane with CO_2 under pressure to 220 °C. In 1899, Gabriel and Mass [82] studied (poly)condensations of ω-amino acids. Upon heating of γ-aminobutyric acid or δ-aminovaleric acid to temperatures above 200 °C those authors



Formula 2.4

exclusively isolated the corresponding lactams, but from 6-aminohexanoic acid (called ε-leucine at that time) 20–30 % ε-caprolactam was obtained and an insoluble hard mass, a polyamide which was later called Nylon-6 or Perlon (see Chap. 6). Manasse [83] prepared shortly later Nylon-7 analogously from 7-aminoheptanoic acid and noted that in this case no lactam was detectable. Five years later von Braun [84] confirmed the results of Gabriel, Mass, and Manasse. Furthermore, he prepared a new polyamide by heating of 5-(o-aminophenyl)valeric acid (see Formula 2.5), whereas the seven-membered lactam was the main product, when 4-(o-phenyl)butyric acid was heated.



Formula 2.5

2.4 Various Polycondensates

Three research groups[85–88] worked on syntheses and characterization of oligo- and poly(ethylene glcol)s. Lourenco [85, 86] heated ethylene glycol and 1,2-dibromoethane to 120 °C for several days, and isolated oligo(ethylene glycol)s up to the hexamer by fractionated distillation. He also concluded that continuation of this series might in principle result in the formation of poly(ethylene oxide). Wurtz [87] prepared oligo(ethylene glycol)s or their acetates by heating oxirane with acetic acid or its anhydride. Yet, these polymerizations involved condensation steps only during fractionated distillation of the reaction products at temperatures up to 300 °C. Oligo(ethylene glycol)s and true poly(ethylene glycol) ($Tm = 56$ °C) were also obtained by Roithner via ring-opening polymerization of oxirane [88].

Condensation reactions yielding cyclic and/or linear oligosulfides were studied by four research groups [89–93]. In 1863, Husemann [89] prepared an intermediate by condensation of 1,2-dibromoethane with sodium sulfide. By heating he obtained the cyclic dimer, dithiane, as a volatile degradation product. Mansfeld [90] reinvestigated this reaction and interpreted the intermediate as polymer, but he speculatively assigned the formula of a cyclic trimer. Husemann also prepared poly(methylene sulphide) from dibromomethane and sodium sulfide. Furthermore, he performed condensations of dibromomethane and dibromoethane, respectively, with sodium trithiocarbonate, which was easily obtained from sodium sulfide and carbon disulfide. He isolated a five-membered cyclic ethylene trithiocarbonate, but a polymeric methylene trithiocarbonate the molar mass of which remained obscure.

In the years 1900–1909, Autenrieth, Beuttel, and Kötz [91–93] studied syntheses and reactions of the α,α-dimercaptanes of ortho-, meta-, and para-xylene. The main purpose of the condensation reactions with aldehydes, ketones, and dibromoalkanes was the isolation of cyclic compounds. For instance, oligomeric condensates were obtained when the meta dimercaptane was reacted with aldehydes, whereas a crystalline cyclic dimer was isolated with acetone as reaction partner (see Formula 2.5). In the case of the para dimercaptane crystalline dimeric cycles were also obtained with aromatic aldehydes. The condensations of the para dimercaptane with dibromoalkanes yielded several crystalline compounds which were interpreted as cyclic monomers (see Formula 2.5), although in most cases the monomeric structure is unlikely for reasons of ring strain. Another unlikely ring structure, namely a dimeric disulfide, was postulated by Zincke and Krüger [94] for the oxidation product of meta-dimercaptobenzene (see Formula 2.5).

Finally, it should be mentioned that Braun and Sobecki reported in 1911 [95] about the preparation of oligoalkanes. They extended the Grignard reaction to α,ω-dibromoalkanes. Starting out from 1,5-dibromopentane, decane, pentadecane and eicosane were isolated by fractionated distillation and characterized by elemental analyses and cryoscopy in benzene. The analogous dimer were obtained from 1,7-dibromoheptane and 1,10-dibromodecane. Twenty years later Carothers et al. [96] replaced magnesium by sodium and isolated pure alkanes up to heptakontane.

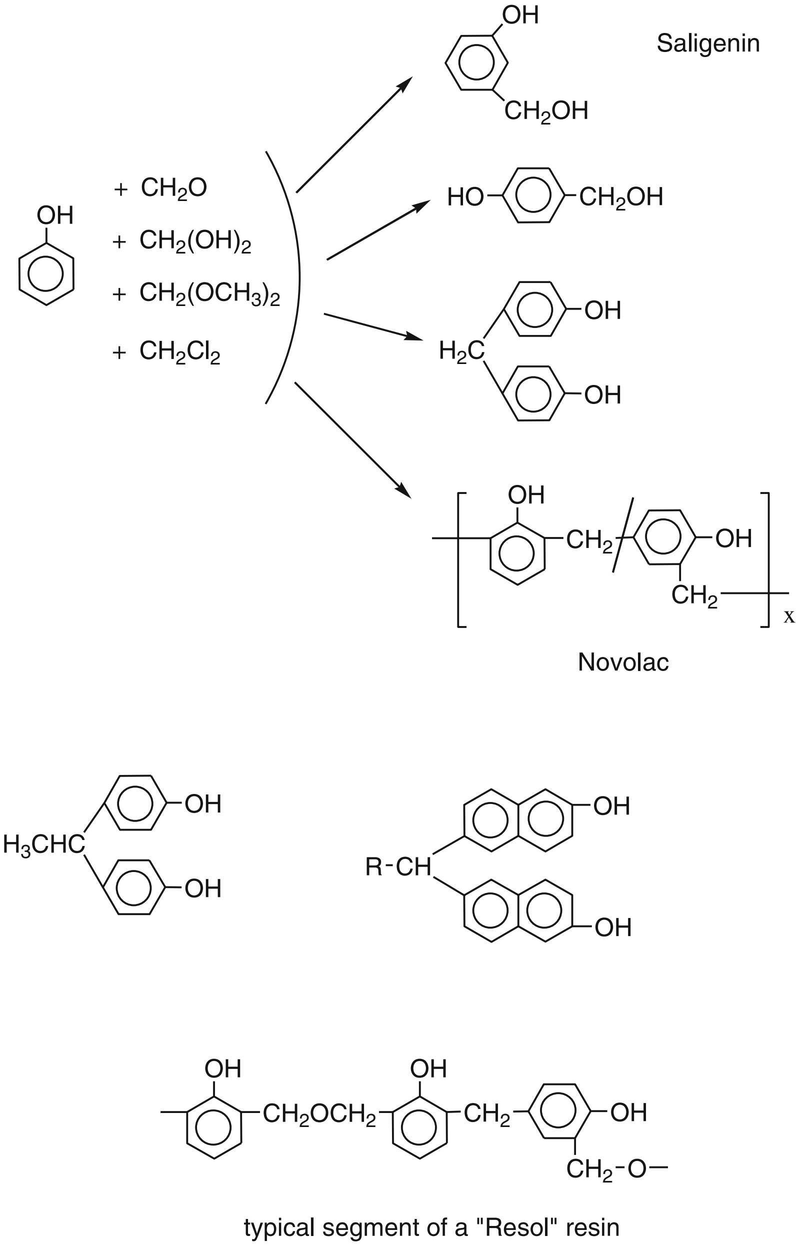
2.5 Bakelite and Related Polymers

The most intensively studied types of (poly)condensation studied before World War I were reactions between phenols and aldehydes. The interest in this field of chemistry like the interest in reactions of salicylic acid was partially motivated by the fact that extracts from the bark of willow trees have a pain-stilling effect (what was already known to the ancient Greeks). From willow trees and other plants saligenin was extracted (see Formula 2.6) which was understood as condensation product of phenol and formaldehyde. As early as 1861 Beilstein and Seelheim [97] observed that treatment of saligenin with $POCl_3$ yields a resinous product, the first synthesis of what was later called "Novolac". The first study of phenol-aldehyde condensations was published in 1872 by von Bayer [98, 99] who was professor of organic chemistry at the universities of Berlin, Staßburg and München. Because of his numerous merits in the field of synthetic organic chemistry (including the first synthesis of indigo) he was awarded with the Nobel Prize in 1905. However, his contribution to the field of phenol-aldehyde condensations was of minor importance, because he was not able to identify reaction products. von Bayer used dimethoxymethane as reaction partner of phenol, because formaldehyde was not available before 1890. Regardless, if HCl or H_2SO_4 was used as catalyst, he obtained a resin similar to that described for the condensation of saligenin with $POCl_3$ [98].

Eight more research groups performed studies of phenol-aldehyde condensations before 1895 [99–106]. Their interest was focused on the isolation and characterization of low molar mass crystalline phenol, cresol, and naphthol derivatives, such as those outlined in Formula 2.5. The formation of resins was an undesired side reaction. Particularly remarkable was the finding of Manasse [101] that not only acids, but also bases catalyze condensations of phenols and aldehydes. With the work of Manasse two different reaction mechanisms became evident. Acid catalyzed condensations are based on the enhanced electrophilicity of aldehydes (or their derivatives) resulting from protonation or complexation with Lewis acids. The bases enhance the nucleophilicity of the phenol by deprotonation, because the phenoxide anions react easily with non-activated aldehydes. The different reaction mechanisms entail somewhat different chemical structures. Acid catalyzed resins, called "Novolac", are produced from an aldehyde/phenol ratio <1.0 and contain only few ether groups (i.e., $CH_2–O–CH_2$). For base catalyzed syntheses aldehyde/phenol ratios around 1.5 are typical, and the "Resol" called resins contain a high percentage of ether groups (see Formula 2.6, bottom). Both types of resins are still used in the twenty-first century for a variety of applications [107].

After 1895 several scientists began to explore preparation, application, and commercialization of phenol-formaldehyde resins, and numerous patents were filed [108–124]. The motivation for these activities came from various sides. For wood and metal surfaces a chemically stable coating material was desired. And for the rapidly expanding application of electricity large amounts of insulating lacquers were needed. Mainly for the latter application shellac was used, a secretion of the "shellac beetle". Due to this biogenic origin shellac was a relatively rare and expensive material. The name "Novolac" indicates that the phenol-formaldehyde resins were designed as new substitutes of the "old" shellac.

Other scientists were interested in a solid plastic as substitute of wood, metal, or celluloid [115–124]. To ease the molding or shaping process, these inventors kept small amounts of the reaction medium, glycerol, or camphor in the resins before or during the curing process. Furthermore, the curing temperature was kept <100 °C


OH
+ CH_2O
+ $CH_2(OH)_2$
+ $CH_2(OCH_3)_2$
+ CH_2Cl_2
OH
CH_2OH
Saligenin
HO
CH_2OH
H_2C
OH
OH
OH
CH_2
OH
CH_2
x
Novolac
H_3CHC
OH
OH
R-CH
OH
OH
OH
CH_2OCH_2
OH
CH_2
OH
CH_2-O
typical segment of a "Resol" resin

Formula 2.6

with the consequence of a low crosslinking density. Yet, slow diffusion of the plasticizers affected the shape of the articles and rapid evaporization (e.g., in vacuo) yielded a porous material. None of these materials was useful and commercially successful.

When Baekeland stepped into this working field [120–124], he did not elaborate a new chemistry, but he developed a technical process which allowed for the production of “plastic” (the original meaning of plastic is, in principle a contradiction to the properties of a thermoset like Bakelite which does not allow any shaping under pressure after completion of the cure). The success of his work with phenol-formaldehyde resins is based on two steps. Firstly he heated the reaction mixtures to temperatures above 120 °C (up to 180 °C if necessary) to achieve a densely crosslinked material. Secondly, the cure was preformed under pressure to avoid pores. To improve handling and acceptance of his process, he developed an apparatus called “bakelizer”. He gave his name also to this first, fully synthetic commercial “plastic” which was called Bakelite. Bakelite was hard, stiff, and thermostable and resistant to any kin of solvent. Furthermore, Bakelite was an excellent electric insulator. It found hundreds of application in industry and household, because no other “plastic” could rival with its properties before World War II. For instance, amorphous polystyrene or poly(methyl methacrylate) which were commercialized around 1930 had heat-distortion temperatures (and Tg’s) below 120 °C and were soluble in many organic solvents. A standard Bakelite contained wood flour, but for special applications other components were incorporated, for instance, calcium carbonate or asbestos. A particularly remarkable application of Bakelite was the production of billiard balls which were originally made from high quality ivory. Bakelite balls had almost the same elasticity and gave the same “clicking sound” and, thus, were accepted as substitutes. In this way Baekeland saved the lives of thousands of elephants.

Finally, it should be mentioned that resinous materials quite similar to Bakelite were prepared by various research groups by heating benzyl chloride with Lewis acids or metal powders [125–135]. The first report in this direction was published by Zincke in 1869 [125], who observed evolution of HCl and formation of a yellowish resin upon heating of benzyl chloride with copper or silver. A similar result was obtained by Gladstone and Tribe [126] when benzyl chloride warmed with a Cu–Zn couple. Most research groups studied (poly)condensation reactions of benzyl chloride catalyzed by $AlCl_3$ [127–134]. As first described by Friedel and Crafts in 1885 [127] this condensation yields a brownish intractable mass, when conducted in bulk. Small amounts of anthracene were formed as byproduct and when the condensation was conducted in benzene, diphenylmethane, and dibenzylbenzenes were isolated in smaller or larger quantities depending on the monomer concentration. In this way these (poly)condensations were identified as what later was called “Friedel–Crafts Alkylation”[135].

2.6 Leo Hendrik Baekeland: Biography

Since Bakelite was the first commercial, fully synthetic polymer [136–143]. Baekeland is a particular important pioneer in the history of polycondensation, and thus, a short biography should be presented at this point. Baekeland was born on November 1863 in Ghent, Belgium. Supported by a fellowship of his hometown, he studied chemistry at the university of Ghent and received the Ph.D. in 1884 with “maxima cum laude” in the age of 21!!. He was appointed as associate professor of chemistry in 1989. He married Celine Swarts, the daughter of the head of the department and spent the honeymoon in New York. There he met R. Anthony of the E. and H. T. Anthony photographic company, who offered him a job. Baekeland emigrated to the U.S.A. and became a naturalized American in 1897.

After 2 years he quit his job and continued his career as consulting chemist. Furthermore, he continued to develop a photographic paper suitable to take good pictures at artificial light. He succeeded after 2 years of intensive work and called his invention “Velox”. Due to the economic depression in the U.S.A. at that time, he did not find investors or buyers for his photographic paper and founded together with L. Jacobi the Nepera Chemical Company in Yonkers, New York to exploit his inventions. In 1899 they sold this company to Eastman Kodak Company, and Baekeland made a net profit of US$ 215,000. He purchased a house in Yonkers and established his own, well-equipped laboratory, where he developed the Bakelite process. The first patent claim was submitted in 1907 and granted in 1909. Before and in parallel to his work on Bakelite he patented 55 inventions. In December 1909, he presented Bakelite for the first time on a meeting of the American Chemical Society and founded the General Bakelite Company in 1910. In the same year, he also founded the “Bakelit Gesellschaft” in Berlin together with J. Rütgers. Further Joint ventures in other countries followed immediately. In 1922, the Gen. Bakelite Co. was merged with Aylesworth’s Condensite Co. and with Redman’s Redmanol Chem. Products into the new Bakelite Corporation, which was finally sold to Union Carbide in 1939. L. Baekeland died in 1944 in Beacon, New York, and was buried in the Sleepy Hollow Cemetery, New York.

At that time the worldwide production of Bakelite amounted to 175,000 per year, and about 15,000 different articles were produced from this “plastic”. L. Baekeland was awarded the Franklin medal (in 1940) and he received numerous other honors. In its March issue 1999, the Time Magazin counted L. Baekeland among the 20 most important inventors and think tanks of the twentieth century.

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Chapter 3
Wallace H. Carothers: Life and Work

3.1 The Early Years

In the 100 years before World War I, numerous chemists, engineers, and employees of chemical companies had worked on isolation, modification, and application of biopolymers such as cellulose, starch, natural rubber, gutta percha, collagen, and shellac. Production and commercialization of natural rubber and cellulose derivatives had become a big business at that time. None-the-less, the scientific community had not realized that the typical properties of polystyrene and soluble biopolymers and their derivatives were the result of long polymer chains consisting of thousands of covalently connected atoms. For a variety of reasons almost all scientist believed that these materials consist of associated oligomers, although the forces which were made responsible for the strong association were not well understood. It was the German professor of organic chemistry Herman Staudinger (1881–1965), who convinced the international scientific community after a fierce scientific battle of 15 years that long covalent chains really exist [1–3]. To illustrate that even the longest chain is only one giant molecule, he coined the term "macromolecule". Among his scientific enemies were famous chemist, such as Emil Fischer (Nobel Prize 1902), Heinrich Wieland (Nobel Prize 1936), and Hermann Mark. It was for Staudinger a hard piece of work to achieve international acceptance of his concept, and it took many years until his work was awarded by the Nobel Prize Committee (1953).

As an irony of fate not only his scientific enemies adhered to a big mistake, Staudinger himself made also an important mistake. He believed like many other (polymer)chemists at that time that the reactivity of end groups dramatically decreases with increasing length of oligomers. In the years before 1930, the European chemists were divided into two groups. One group considered Staudinger as fool, whereas the other group considered him as scientific hero. Under these conditions neither group had a motivation to study step-growth polymerizations. Therefore, it was a logic consequence that experimental and theoretical studies of step-growth polymerizations were performed outside Europe. The man

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who elaborated the scientific basis of step-growth polymerization was the American chemist Wallace Hume Carothers [4–8].

Carothers was born in April 27, 1896 in Burlington Iowa as the first child of Ira Hume Carothers and his wife Mary. In 1914 he entered the Capital City Commercial College in De Moins, Iowa, where his father was teacher. Yet, in 1915 he moved to Tarkio, Missouri, to study chemistry. He gained the bachelor degree in 1920 and continued afterwards his studies at the University of Urbana, Illinois. After gaining the Master degree in 1921 he taught chemistry for one year at the University of South Dakota, returned to Urbana and obtained the Ph.D. in 1924 under the supervision of Prof. R. Adams. After two years as assistant professor in Urbana he moved to Harvard, where he taugh experimental and theoretical organic chemistry.

In 1926 Ch. Stine became director of the Central Chemical Department of DuPont. In 1927 the Executive Committee decided to finance a research group with the objective to discover new scientific facts mainly in the field of catalysis, colloid chemistry, and polymerization. At first DuPont tried to hire established professors, such as R. Adams or H. Gilman, as leaders of the new research group, but without success. Finally, they hired E. O. Kraemer (Univ. of Wisconsin) for the colloid group and W. H. Carothers for the polymerization group. When Carothers received the first offer from DuPont, he was reluctant to accept it, because he was mainly interested in fundamental research and enjoyed at Harvard "the freedom of academic research". To justify his negative response he mentioned health problems: "I suffer from neurotic spells of diminished capacity which might constitute a much more serious handicap there than here". However, a DuPont executive traveled to Harvard and persuaded him to accept a new offer which doubled his salary and permitted him to concentrate on fundamental research also at DuPont.

3.2 The Time at DuPont

Carothers began to work at the "Experimental Station" in Delaware in February 1928. His primary goal was syntheses of polymers having molar masses above 4,000 Da, the maximum mass achieved by E. Fischer in Berlin by the stepwise synthesis of polysaccharides. Most of Carothers activities in the following nine years may be subdivided into the following five groups:

1. Halogenated synthetic rubbers
2. Syntheses of high molar mass aliphatic polyesters
3. Preparation, characterization, and polymerization of cyclic esters
4. Cyclic and polymeric anhydrides of aliphatic dicarboxylic acids
5. Syntheses and fiber spinning of aliphatic polyamides.

His work will be discussed below along the above given order. Carothers published around 60 patents and more than 60 papers (including three review articles [9–11]) part of which will be cited below [9–51].

In 1928 and 1929, Carothers team consisted of a handful of Ph.D. chemists and two advisors: Prof. Adams and Prof. C. S. Marvel (both from the Univ. of Illinois). The advisers had their own laboratory at the Experimental Station nicknamed "Purity Hall". No success was achieved until the end of 1929. In January 1930, E. K. Bolton became the new boss of Carothers, he advised Carothers group to focus part of their activities on the preparation of synthetic rubbers starting out from acetylene. At that time a Belgian immigrant, J. A. Nieuwland (1878–1936), who was working at the "Notre Dame" university (Indiana) had already synthesized a couple of interesting monomers, such as vinylacetylene and divinylacetylene. By addition polymerization with S_2Cl_2 the latter monomer was transformed into a low molar mass rubber. DuPont financially supported his work, but until 1930 no technically useful rubber was obtained. Vinylacetylenen has disgusting property to undergo spontaneous, explosion-like polymerizations. Carothers proposed to add a small amount of HCl as stabilizer. His coworker A. M.Collins discovered the addition of HCl across the double bond and isolated a new monomer, 2-chloro-1,3-butadiene (Chloroprene). Its radical polymerization yielded a high molar mass rubber, later called Neoprene [12–16] which was commercialized by DuPont after 1932. This new synthetic rubber differed from natural rubber, from poly(cis-1,4-butadiene) and from poly(cis-2,3-dimethyl-1,4-butadiene) by the predominance of trans double bonds. Furthermore, it was more stable against oxidation and against the attack of warm motor oils. Therefore, it was (and is still) used for elastic tubes and cables in the neighborhood of hot engines. Carothers group studied a variety of halogenated dienes, their syntheses, reactions, and polymerizations [17–23]. Yet, either due to high costs or poorer properties nothing better than Neoprene was found, and Neoprene is still produced in the twenty-first century.

In 1930 J. W. Hill, a coworker and friend of Carothers, began to explore the preparation of polyesters by polycondensation of aliphatic diols and dicarboxylic acids in the melt (Formula 3.1). The four synthetic methods outlined in Formula 3.1 were, in principle, known, but any systematic study was still lacking, and even polyesters having Mns in the range of 3,000–5,000 Da were still unknown. Carothers's group focused its work on polycondensations of diols and dicarboxylic acids, because this route was the least expensive approach and because it opened the access to a broad variety of polyesters. Previous studies were not successful, because Mns above 5,000 Da were not achieved [24–27]. End group analyses based on chemical modifications revealed that the reactive end groups (CH_2OH and CO_2H) were still there when the polycondensations were stopped. Hence, it was concluded that the diffusion and evaporation of the liberated water was the limiting factor for the progress of the polycondensation. This conclusion was confirmed when a new reactor, called "molecular still", was used which enabled a more efficient removal of water from the reaction mixture [27]. Now several polyesters having Mns up to 12,000 Da were obtained and called "superpolyesters" [28–30]. By working up the reaction mixtures it was immediately observed that these polyesters allowed for drawing fibers from the melt It was the first promising success in direction of synthetic textile fibers. Unfrotunately it turned out, that the melting temperatures of the aliphatic polyesters ($Tm < 110$ °C) were too low for any application, and later it was also found that the sensitivity to hydrolytic degradation was too high for applications as textile fibers. None-the-less, the success with superpolyesters prompted Bolton and Carothers to study syntheses and properties of aliphatic polyamides more intensively.

In connection with the work on linear polyesters the Carothers group explored syntheses and properties of monomeric and dimeric cyclic esters in much detail [31–38]. Beyond academic curiosity these activities were motivated by two aspects

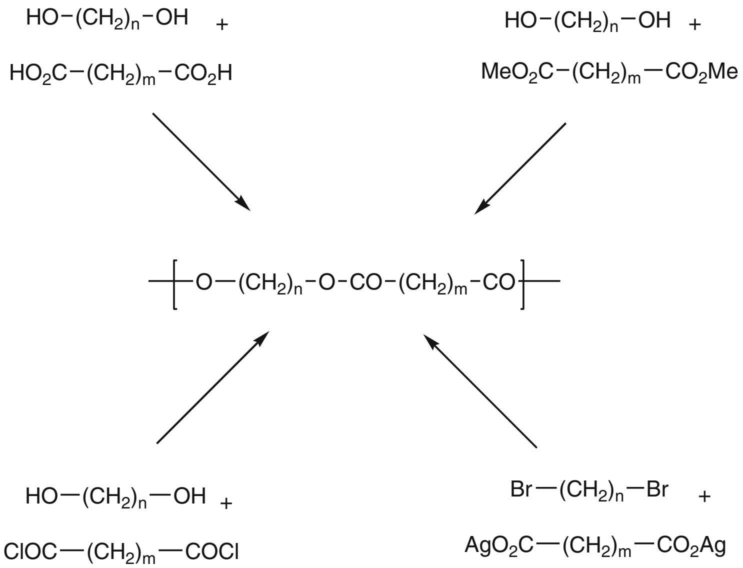
1. usefulness as monomers for ring-opening polymerization,
2. usefulness as components of perfumes and fragrances depending on the odor.

"Neopren"

Poly(trans-2-chloro-1,4-butadiene)

Methyl rubber

Poly(cis-2,3-dimethyl-1,4-butadiene)



Formula 3.1

The second aspect was based on the well-known fact that 15–17 membered cyclic ketones which were difficult to prepare at that time possess a strong musk odor.

A new synthetic approach was elaborated, namely the depolymerization of low molar mass polyesters in vacuum at temperatures above 230 °C. The catalysts were optimized for different types of polyesters, and finally more than 60 new cyclic monomers and dimer were isolated. Correlations between chemical structure and ring size, on the one hand, and yields, Tm's, density or odor, on the other, were elaborated. For several macrocyclic esters consisting of 15–17 atoms in the ring musk-like odors were indeed found.

The same synthetic approach was used for the preparation of cyclic anhydrides [39–43]. It was known before that succinic and glutaric acid form cyclic anhydrides which do not polymerize (see Formula 3.1, bottom). Hill and Carothers studied the reactions of higher dicarboxylic acids with acetyl chloride or acetic anhydride. In all cases, polymeric anhydrides were obtained which were supposed to possess mixed anhydride end groups containing acetyl residues. The sensitivity to hydrolysis alcoholysis and phenolysis prevented exact molar mass measurements. However, a reliable distinction from monomeric cyclic anhydrides was achieved by reaction with aniline, because cyclic anhydrides can only yield one reaction product. When the polymeric anhydrides were heated to 150 °C in vacuum they degraded almost completely by "back-biting". In this way 10 new cyclic anhydrides were isolated. These cyclic anhydrides underwent rapid polymerization in contact with traces of moisture.

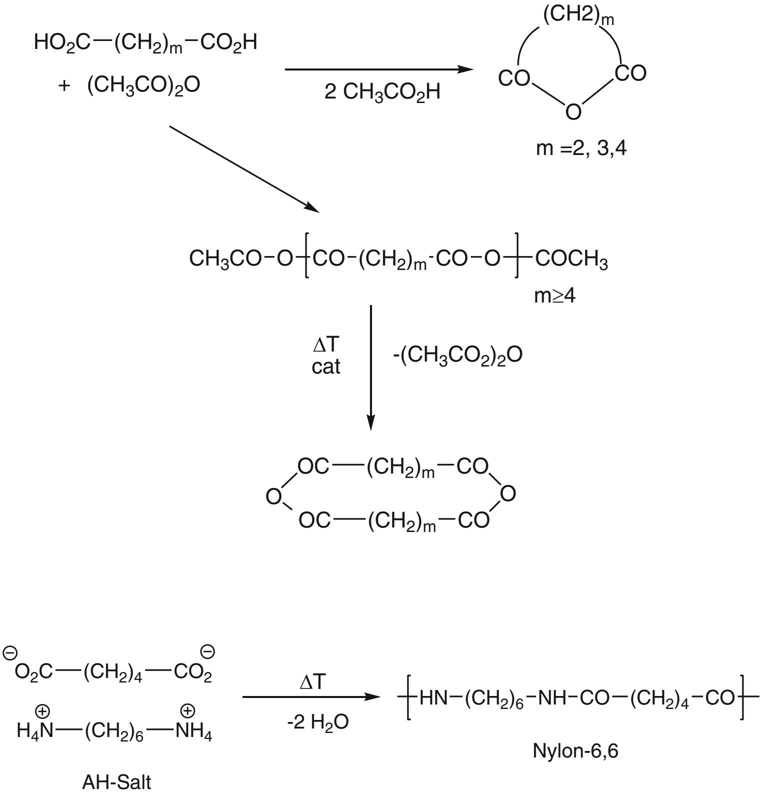
A systematic exploration of aliphatic polyamides was launched in 1934. W.R. Peterson, D. Coffman, and (later) G. Berchet were the active researchers in this field. After several fiber-forming and high-melting polyamides were obtained in small scale experiments, K. Bolton decided to concentrate all further efforts on the polyamide later called Nylon-6,6. For the development of a commercial textile fiber, a new team was installed with G. Graves as leader. In 1935 the first pound of nylon-6.6 was prepared and used for fundamental studies of fiber spinning. The technical production began in 1938, and in 1939 and 1940 a worldwide PR-campaign for the first man-made fiber was launched. Nylon stockings for women was the first commercial hit. Yet, under the influence of World War II most of DuPont's Nylon production was reserved for military purposes, above all for the production of parachutes. In both areas, stockings and parachutes, the Nylon fiber replaced the silk which was imported before from Japan. After World War II the success story of Nylon-6,6 continued, although it was finally found that it is not an ideal textile fiber for everyday clothes. However, it is an ideal fiber for any sport activities and in the twenty-first century the most important application was the production of carpets.

If Bolton's decision to select G. Graves as leader of the Nylon project was a serious disappointment for Carothers or a relief is seemingly not clear. It had at least two advantages for him, he could continue to concentrate on fundamental research and he had less stress in his private life. Carothers was well aware of the fact that he suffered from depressive moods. In 1931 he moved to a house in

Wilmington, which he shared with three other DuPont scientists. He wrote to a close friend: “There does not seem to be much to report concerning my experiences outside of chemistry. I’m living out in the country with three other bachelors, and they being socially inclined have all gone out in tall hats and white collars, while I after my ancient custom sit sullenly at home.” When he had to present a talk outside DuPont he drank considerable amounts of alcohol before to fight the nervousness. In 1933 and 1934 his psychic problems worsened. He bought a house near Wilmington and moved to it with his parents. However, his parents strongly criticized his affair with a divorced woman. Due to this permanent stress under the same roof, his parents returned to De Moins, and Carothers had to spend several months in a hospital for psychiatric treatment. After his return to the laboratory he began to date Helen Sweetman, an employee of DuPont working on patent applications. They married in February 1936 and several months later his wife became pregnant. On April 30 1936, Carothers was elected to the National Academy of Sciences, a very high honor. Carothers was the first industrial organic chemist who received this honor. None-the-less, his depression worsened and prevented him most of the year from working at the Experimental Station. His psychiatrist, Dr. Appel, informed his friends about a high risk of suicide.

On January 8, 1937, Carothers’s sister Isabel died of pneumonia, and he and his wife traveled to Chicago and De Moins to attend her funeral and burial. He returned to Philadelphia to consult again his psychiatrist. On April 28 he went to the Experimental Station to work as usual. The following day he checked in at a hotel in Philadelphia and committed suicide by drinking a solution of potassium cyanide in lemon juice. It was a particular tragedy that he died before his daughter was born and before the big success of his invention, Nylon-6,6, became evident. Due to the dramatic increase of depressions after 1934 and his sudden death, Carothers published little [44] about polyamides [39]. Yet, after his death DuPont filed numerous patents with his name [45–51].

In almost all comments on Carothers life and work, the invention of nylons is hailed as his biggest success. Another, perhaps even more important result is ignored or underestimated. As mentioned in the beginning of this chapter, Staudinger and many other (polymer) chemists of that time believed that the reactivity of end groups strongly decreases with higher DPs of oligomers. With the syntheses of superpolyesters by a more efficient removal of liberated water Carothers and Hill unambiguously demonstrated that the progress of a polycondensation is not limited by decreasing reactivity of the end groups. An important contribution to this point came from P. J. Flory who became member of Carothers group in the age of 24. He was mainly interested in theoretical aspects of step-growth polymerizations, and he analyzed both the kinetic course and the molar mass distribution of the polyester syntheses. His analyses and calculations confirmed that the reactivity of end groups does not decrease with increasing conversion and increasing DPn: These results not only paved the way to the invention of Nylon-66 fibers, they paved the way for any successful step-growth polymerization. From the viewpoint of the author this is the most important outcome of Carothers’s work.



Formula 3.2

Finally, it should be mentioned that Carothers formulated the first quantitative description of step-growth polymerizations (Eq. 4.2). This so-called Carothers-Equation correlates the average degree of polymerization (DP) with the conversion (p). Although this equation is not quite correct (see Chap. 7), it is an useful approximation to the course of step-growth polymerizations for conversions <98 %. It highlights that step-growth polymerizations in contrast to chain-growth polymerizations require conversions >99 % to yield polymers having Mn's > 10,000 Da.

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Chapter 4
Paul J. Flory and the Classical Theory of Polycondensation

4.1 Introduction and Biography

Paul J. Flory was born on June 19, in Sterling, Illinois, as the sixth generation of European immigrants born in America [1–3]. His father, Ezra Flory, was clergyman-educator and his mother, Martha, was school-teacher. Both parents were descendents of farmers and were the first of their families, who attended college. Paul Flory graduated in 1931 from Manchester College, Indiana, where his interest in chemistry was stimulated by Prof. C. W. Holt. This teacher encouraged him to enter the Graduate School of the Ohio State University, where he became interested in physical chemistry. He accomplished his Ph.D. in 1934 under the guidance of Prof. H. L. Johnston.

After completion of the PD he joined the Central Research Dept. of E. I. DuPont, where he was assigned to the research group of Carothers. His supervisor inspired him to explore the fundamentals of polycondensation and of the structural characteristics of polymeric substances. In 1938 (i.e. after the death of Carothers in 1937) he joined the Basic Science Research Laboratory of the University of Connecticut, the beginning of a long and successful academic career.

After 2 years, the out brake of World War II forced him to return to industry. At that time the U.S.A. needed badly a rapid development of a technical production of synthetic rubber, because the supply of natural rubber was endangered by the occupation of south Asia by Japanese troops. After 3 years in the Esso Laboratories of the Standard Oil Company he moved to the research Laboratories of the Goodyear Tire and Rubber Co. In spring 1948 he was hired by the Chemistry Department of Cornell University for a lectureship which had two important consequences. First, his lectures formed the basis for his famous book "Principles of Polymer Chemistry" [4] which was published by Cornell University Press in 1953. Second, he was offered a professorship, which he accepted in autumn 1948.

In 1957 Flory moved with his family to Pittsburgh to establish a broad program of fundamental research at the Mellon Institute, but part of the promised financial support was withdrawn later. Therefore, he accepted a professorship in the Chemistry Department of Stanford University in 1961. This move let him to

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reshape the concept of his future research activities. To use his own words [1]: "Two areas have dominated the interests of my coworkers and myself in 1961. The one concerns the spatial configuration of chain molecules and the treatment of the configuration dependent properties by rigorous mathematical methods, the other constitutes a new approach to an old subject, namely the thermodynamics of solutions. Our investigation in the former area have proceeded from foundations laid by Prof. M. V. Volkenstein and his collaborators in the Soviet Union and were supplemented by major contribution of the late Prof. K. Nagai in Japan" The success of this work was summarized in another important book entitled "Statistical Mechanics of Chain Molecules", which was published in 1969 [5].

P. J. Flory was married since 1936 with the former Emily Catherine Tabor. They had three children. The daughter Susan was married with Prof. Springer (Department of Mechanical Engineering University of Michigan), and Melinda was married with Prof. D. E. Groom (Department of Physics, University of Utah). They also had a son, Dr. Paul Flory, Jr., who pursued an academic career in medicine. From both daughters P. J. Flory had four grandchildren. Flory died on September 8. 1985, and his son died in the same year by a heart attack.

In addition to the working fields mentioned above by Flory himself, the following areas of interest and achievement should be mentioned.

(1) Fundamentals of step-growth polymerization (mainly before 1952) [6] and the formulation of the classical theory of polycondensation.
(2) The role of excluded volume effects, above all, their influence on the configuration of polymer chains.
(3) The formulation of the hydrodynamic constant "theta" and the definition of the "Theta Point," where excluded volume effects are neutralized. These results were particularly important, because they allow a rational interpretation of physical measurements of dilute polymer solutions.

Flory's published work comprises more than 400 papers in addition to the aforementioned books. In 1985 Stanford University Press published the book "Selected Works of Paul J. Flory." Among the numerous awards and honors he received (e.g., Priestley Medal 1974, Perkin Medal 1977, Elliot H. Cresson Medal 1971), the Nobel Prize awarded in 1974 was the most prestigious one. Flory used his prestige and this award to campaign for international human rights, mainly with regard to the treatment of scientists in the former Soviet block.

4.2 The Classical Theory of Two-dimensional Polycondensations

Flory's fundamental concept of step-growth polymerizations is based on two premisses. First. The reactivities of functional involved in the polymerization process are independent on the size of the molecules. Second, end-to-end cyclization (end-biting) does not play any role. Flory's mathematical treatment of step-growth polymerization started out from his experience with the syntheses of polyesters and polyamides performed in Carother's research group. Any mathematical treatment of a polymerization process requires at first a definition of the conversion (the letter "*p*," was used in Flory's and Stockmayers work and is also used in this book). In contrast to organic and inorganic chemistry, polymer chemistry requires at least three different definitions of conversion, namely for chain-growth polymerization, for step-growth polymerization and for ring–ring (or polymer–polymer) equilibration. In the case of step-growth polymerization p is defined by the consumption of functional groups according to Eq. (4.1). This equation may be found in textbooks and review articles, but it was not formulated by Flory. He said in connection with syntheses of polyesters (Ref. [6], p. 156): "the extent of reaction, *p*, defined as the fraction of functional groups which has been esterified…" He discussed several times he consequences of $p = 1$, meaning 100 % conversion, without noticing the inconsistency with the second premisse of his theory. Whereas $p = 1$ means total absence of functional end groups ($N_{at} = 0$ in Eq. (4.1)), the final result of a perfectly linear polycondensation is one giant chain having two end groups. This inconsistency has interesting implications and will be discussed together with other problems of Flory's theory in the last subchapter.

$$p = N_{ao} - N_{at}/N_{ao} \text{ or } p = N_{bo} - N_{bt}/N_{bo} \tag{4.1}$$

$N_{a0,}$ N_{at} = number of "*a*" groups at time 0 or later

The next point discussed by Flory was the relationship between $\mathrm{DP_n}$ (Flory frequently used x as symbol) and conversion. He formulated Eq. (4.2), later called "Carother's equation," but he also formulated Eq. (4.3). As will be shown below, Eqs. (4.2) and (4.3) do not give the same result under all circumstances. Anyway Eq. (4.2) demonstrates that syntheses of high molar mass polymers via polycondensation requires extremely high conversions (>98 %) in contrast to chain-growth polymerizations. On the basis of Eq. (4.2), Mn was defined according to Eq. (4.4).

$$DP_n = 1/1 - p(= x) \tag{4.2}$$

$$DP_n = \text{average number of units/number of molecules} \tag{4.3}$$

$$Mn = M_0 DPn = M_0/(1 - p) \tag{4.4}$$

with M_0 = mass of a repeat unit in the case of *a*–*b* monomers or

$M_0 = M_{rp}/2$, with M_{rp} = mass of the repeat unit in the case of $a_2 + b_2$.

At this point it should be emphasized that $\mathrm{DP_n}$ or x count the repeat units in the case of $a - b$ monomers, but the sum of units resulting from a_2 and b_2 monomers and not the repeat units.

Flory then considered the influence of a monofunctional additive (chain terminator) on the $\mathrm{DP_n}$ (Eq. 4.5). In the case of $a_2 + b_2$ polycondensations stoichiometric imbalance has the same consequence for $\mathrm{DP_n}$ as addition of a monofunctional chain terminator (Eqs. 4.5–4.9), But the consequences are different from the preparative point of view. When the conversion of the monomer used in lower concentration (e.g. a_2) is quantitative, telechelic oligomers, or polymers exclusively terminated by "*b*" groups will be obtained, and many research groups later prepared telechelic blocks on the basis of Flory's calculations. After defining

"r" and "p_{a}": $r = N_{a0}/N_{b0}$

p_{a} = fraction of "a" groups, which have reacted at a given stage of the polycondensation

Flory calculated the number of repeat units:

$$(N_{a0} + N_{b0})/2 = N_{a0}(1 + 1/r)/2 \tag{4.5}$$

And the total number of end groups:

$$2N_{a0}(1-p) + (N_{b0} - N_{a0}) = N_{a0}[2(1-p) + (1-r)/r] \tag{4.6}$$

For the DP_n he obtained:

$$DP_n = (1 + r)/2r(1-p) + 1 - r \tag{4.7}$$

And for quantitative conversion ($p = 1$):

$$DP_n = (1 + r)/(1 - r) \tag{4.8}$$

$$DP_n = (\text{moles bifunctional units excl. of stabilizers})/(\text{moles stabilizer units}) \tag{4.9}$$

Equation (4.8) is also applicable to the addition of a monofunctional stabilizer (st), when "r" is redefined according to Eq. (4.10)

$$r = N_{a0}/(N_{a0} + 2N_{st}) \tag{4.10}$$

To avoid misunderstandings, it should be emphasized that the $\mathrm{DP_n}$'s calculated via Eqs. (4.1) and (4.6–4.9) represent the sum of $\mathrm{a_2}$ and $\mathrm{b_2}$ based units and not repeat units.

Flory then calculated number (frequency) distribution (n_x) and mass distribution (w_x) of linear, two-dimensional polycondensations as follows (citation from Ref. [6], pp 174–175): "Consider for example, the polyester produced from a *w*-hydroxy acid. The probability that the carboxyl group of the first unit is esterified is equal to p. The probability of that the carboxyl group of the second unit is esterified, this probability being independent of whether or not linkage 1 has been formed, is likewise equal to p. The probability that this sequence continues for x–1 linkages is the product of these separate probabilities, or p^{x-1}. This is the probability that the molecules contain at least x–1 ester groups or at least x units. The probability that the xth carboxyl group is unreacted, thus limiting the chain to exactly x units is 1–p. Hence the probability the molecule in question is composed of exactly x units is given by Eq. (4.11).

$$n_x = p^{x-1}(1-p) \tag{4.11}$$

Obviously, the probability n_x that any molecule selected at random is composed of x units must equal the mole fraction of x-mers. The total number of x-mers is given by:

$$N_x = N(1-p)p^{x-1} \tag{4.12}$$

When N is the total number of molecules of all size, letting N_0 present the total number of units, it follows that

$$N = N_0(1-p) \tag{4.13}$$

$$N_x = N_0(1-p)^2 p^{x-1} \tag{4.14}$$

If the added weight of the end groups is neglected, the molecular weight of each species is directly proportional to x. Hence, the weight fraction (w_x) be written as

$$w_x = xN_x/N_0 \tag{4.15}$$

Combining with Eq. (4.14) yields the weight distribution

$$w_x = x(1-p)^2 p^{x-1} \tag{4.16}$$

Figures 4.1 and 4.2 illustrate the dependence of number and mass distribution on the conversion [6].

About M_n Flory wrote “The number average is given by:

$$M_n = \Sigma M \times N_x/\Sigma N_x \tag{4.17}$$

where M_x is the molecular weight of an x-mer and the summations are overall species from $x = 1$ to infinity. The weight average molecular weight is defined as

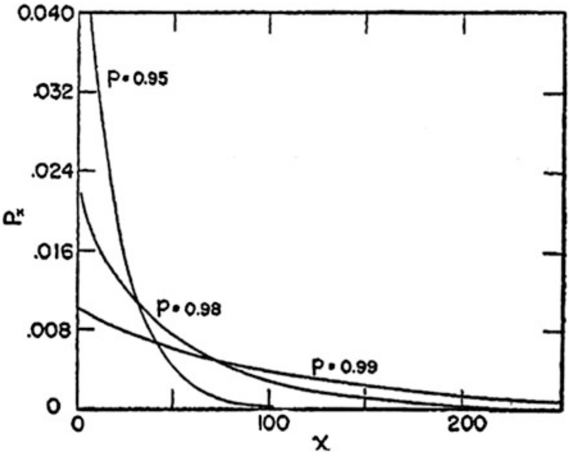
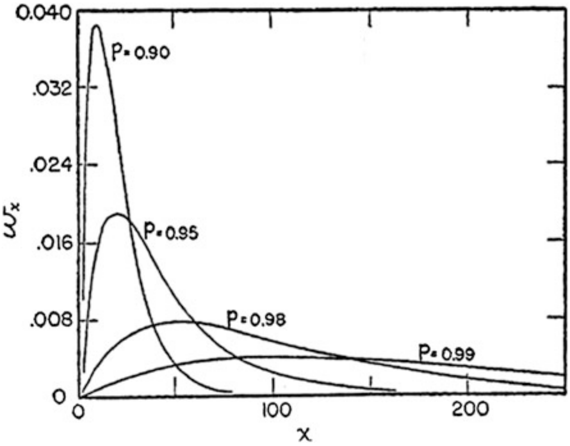


Fig. 4.1 Number (mole) fraction of linear chains versus degree of polymerization (x = DP) according to Eq. (4.11); from Ref. [6] with permission (Copyright 1946 American Chemical Society)

Fig. 4.2 Weight fraction of linear chains versus degree of polymerization (x = DP) according to Eq. (4.16); from Ref. [6] with permission (Copyright 1946 American Chemical Society)



$$M_w = \Sigma M_x w_x / \Sigma w_x \tag{4.18}$$

With $Mx = xM_0$, where M_0 Is the molecular weight of a repeat unit, Flory derived Eqs. (4.19) and (4.20) from a combination of Eqs. (4.12) and (4.17):

$$M_n = M_0 \Sigma \left[x p^{x-1} (1 - p)^2 \right] \Big/ \left[\Sigma \left[p^{x-1} (1 - p)^2 \right] \right] \tag{4.19}$$

$$M_n = M_0 / (1 - p) \tag{4.20}$$

Analogously combinations of Eqs. (4.16) and (4.18) yielded Eqs. (4.21) and (4.22):

$$M_w = M_0 \Sigma \left[x^2 p^{x-1} (1 - p)^2 \right] \Big/ \Sigma \left(x p^{x-1} (1 - p)^2 \right] \tag{4.21}$$

$$M_w = M_0 (1 + p) / (1 - p) \tag{4.22}$$

From the quotient of Eqs. (4.22) and (4.20) the dispersity "D" was derived as

$$D = [M_0 (1 + p) / (1 - p)] / [M_0 (1 - p)] = 1 + p \tag{4.23}$$

For high molar mass polymers the syntheses of which requires conversions >99 % the maximum D equals 2.

Flory emphasized that Eqs. (4.12) and (4.16) are valid for both, KC linear polycondensations and for the fraction of linear polymers in TC polycondensations. Flory's equations and this conclusion were reinvestigated and debated by other authors [7–20], but a consensus was reached saying that Flory was correct [21]. However, it must be kept in mind that Flory's equations and the cited contributions of other authors do not provide an adequate description of real polycondensates containing cyclic oligomers and polymers (Chap. 7).

Finally, it should be mentioned that Flory's mathematical treatment of two-dimensional polycondensations also included a kinetic analysis of the polyester syntheses performed in Carother's group. Polycondensations conducted in the presence or absence of protic catalysts, such as H_2SO_4 or 4-toluene sulfonic acid, were compared. Several decades later Costa and Villermaux [22–24] presented a detailed kinetic study of polyester syntheses based on tri(ethylene glycol) and adipic acid.

4.3 Three-dimensional Polycondensations of ab_f (ab_n) Monomers

Whereas the discussion of three-dimensional polycondensations in Flory's first review article [6] is limited to $a_3 + a_2 + b_2$ monomer combinations, his book "Principles of…." [4] also includes a detailed theoretical description of polycondensations based on ab_f monomers (Ref. 4 pp. 361–383). Flory postulated and (theoretically) demonstrated for the first time that polycondensations of ab_f monomers free of side reactions necessarily results in randomly branched (hyperbranched = *hb*) polymers, and that regardless of the conversion no gelation occurs. He defined "f" as the number of "b" groups in the monomer, p_a as the conversion of "a" groups and "x" as DP of individual chains (as before). Regardless of x, all hb polymers can only have one "a" end group, and the number of unreacted "b" is correlated with x according to $(f–2)\ x–1$. He then introduced the branching probability "α" which equals p_b, the fraction of "b" groups reacted:

$$p_b = p_a/(f-1) \tag{4.24}$$

$$\alpha = pa/(f-1) \tag{4.25}$$

With N_0 as the total number of units, the total number of molecules is $N_0(1–p)$ and the DP_n obeys Eq. (4.26):

$$DP_n = 1/(1-p) = 1/[1-\alpha(f-1)] \tag{4.26}$$

For calculation of the MWD Flory defined ω_x as the total number of configurations (meaning isomers of branching; Ref. [4] p. 365). He then formulated Eqs. (4.27) and (4.28) as the number (frequency) distribution, where n_x is the mole fraction of an x-mer in analogy to linear polymers:

$$n_x = \omega_x \alpha^{x-1}(1-\alpha)^{fx-2x+1} \tag{4.27}$$

$$n_x = [(1-\alpha)/\alpha]\omega_x \beta^x \qquad \text{with } \beta = \alpha(1-\alpha) \tag{4.28}$$

On the basis of numerous assumptions and mathematical operations (not presented here) the mass distribution was formulated according to:

$$\mathrm{w_x} = [(1-\alpha)/\alpha][1-\alpha(\mathrm{f}-1)] \times \omega_\mathrm{x}\beta^\mathrm{x} \tag{4.29}$$

$$x_n = \Sigma x n_x \tag{4.30}$$

$$x_w = \Sigma x^2 n_x / \Sigma x n_x \tag{4.31}$$

$$x_w / x_n = \left[1 - \alpha^2(f-1)\right] / [1 - \alpha(f-1)] \tag{4.32}$$

From the number average degree of polymerization (Eq. 4.30) and from the weight average (Eq. 4.31) Flory calculated the polydispersity according to Eq. (4.32) and gave the following comments: The broadening of the distribution as the reaction proceeds toward completion is also shown by the expressions for the number and weight average degrees of polymerization. Both go to infinity as *a*—*ac* (with $\alpha_c = 1/(f–1)$ see below), of course, but x_w gets there faster—so much, so that the ratio of x_w/x_n (i.e. *D*) goes to infinity also. However it turned out in the decades after 1990 that Flory's conclusion is far from the experimental reality as discussed in the last subchapter.

4.4 Three-dimensional Polycondensations of $a_3 + b_2$ Monomers and the Formation of Networks

Flory developed a fundamental theory of $a_3 + a_2 + b_2$ polycondensations mainly with the purpose to formation and structure of networks. He considered his theory as an approximation based on two assumptions: First, "*a*" groups do not react with each other, and second, intramolecular condensation steps do not play a significant role. In order to avoid misunderstanding of his knowledge and intention, his own words should be cited (Ref. [4], pp 348 and 349). "to examine the significance of this approximation further, it should be noted that a highly branched polymer molecule" retains many unreacted functional groups which offer a number of opportunities for reactions between pairs on the same molecule. That intramolecular reaction between them proceeds to appreciable degree in competition with intermolecular polycondensation is shown by Kienle and coworkers [25, 26] in the condensation of glycerol with dibasic acids. If esterification were exclusively intermolecular, the number of molecules should decrease by one for each ester group formed. Kienle and coworkers observed that the cryoscopically determined number of particles decreased less than the extent of esterification; the discrepancy amounted to about 5 % of the total esterification. With less highly branched molecules the discrepancy presumable should be smaller. It is convenient to consider that the assumption of an exclusively intermolecular condensation fails to eliminate from consideration the fraction of condensation which is "wasted" on the formation of intramolecular connections which do not increase the molecular weight or, rather, do not decrease the number of molecules. The error so introduced is generally is small. To take account of the intramolecular condensation would complicate the theory without adding materially to its content beyond improvement in numerical agreement with experiment."

The purpose of the following treatment is to define the conditions under which indefinitely large chemical structures, or infinite networks, will occur. To this end we seek the answer to the question: Under what conditions is there a finite probability that an element of the structure selected at random occurs as part of an infinite network? …. First of all, it is necessary to determine the branching coefficient α which is defined as the probability that a given functional group of a branching unit leads via chain of bifunctional units to another branch unit.

Flory outlined the above given reaction scheme (here "I" may have any value from 0 to infinity) as basis for his further considerations: "…the probability that the first "*a*" group of the chain shown on the right, has reacted is given by p_a, the fraction of all "a" groups which have reacted; similarly, the probability that the "*b*" group on the right of the first *b–b* unit has reacted, is given by p_b. Let ρ present the ratio of "*a*" s (reacted and unreacted) belonging to branch units to the total number of "*a*" s in the mixture. Then the probability that a "*b*" group has reacted with a branch unit is $p_b\rho$; the probability that it is connected to a bifunctional *a–a* unit pb(1–ρ). Hence, the probability that the "*a*" group of a branch unit is connected to the sequence of units shown in the preceding formula is given by":

$$p_a[p_b(1-\rho)p_a]^i p_b\rho$$

"The probability a that the chain in a branch unit regardless of the number "*i*" of pairs of bifunctional units is given by the sum of each expression having $i = 0$, 1, 2, 3….etc., respectively. That is":

$$\alpha = \Sigma[p_a p_b(1-\rho)]^i p_a p_b \rho \tag{4.33}$$

or

$$\alpha = p_a p_b \rho / [1 - p_a p_b(1-\rho)] \tag{4.34}$$

"If we let the ratio of "*a*" to "*b*" groups initially present be presented by "*r*," as in the case of "ii" type linear polymers (i.e. polymers based on $a_2 + b_2$ monomers), then; $p_b = rp_a$

Substitution in Eq. (4.33) to eliminate either p_b or p_a":

$$\alpha = rpa^2\rho / \left[1 - rp_a^2(1-\rho)\right] \tag{4.35}$$

or

$$\alpha = p_b^2\rho / \left[r - p_b^2(1-\rho)\right] \tag{4.36}$$

Flory then mentions that *r* and ρ can experimentally be determined via the feed ratio and the titration of end groups. Furthermore, he considered three special cases:

(1) When there are no a_2 units, $r = 1$ and

$$\alpha = rp_a^2 = p_b^2/r \tag{4.37}$$

(2) When "a" and "b" groups are present in equimolar quantities, $r = 1$, $p_a = p_b = p$ and:

$$\alpha = p^2 r / \left[1 - p^2(1 - \rho)\right] \tag{4.38}$$

(3) When b_2 monomers are absent and a_2 monomers can react with multifunctional $\mathrm{R}{-}a_f$ monomers:

$$\alpha = p\rho / [1 - p(1 - \rho)] \tag{4.39}$$

Flory in Ref. [4] p. 48:

"If the branch units is other than trifunctional, the same equations for the calculation of α can be employed, r and ρ have been so defined as to preserve these equations independent of the functionality of the branching unit". And on p. 49:

"The critical value of α at which the formation of infinite networks becomes possible can be deduced as follows. If the branching unit is trifunctional, each chain which terminates in a branch unit is succeeded by two more chains. If both of these terminate in branch units, four more chains are reproduced and so on. If $a < ½$, there is less than an even chance that each chain will lead to a branch unit, and thus, to two more chains.... Under these circumstances the network cannot possibly continue indefinitely. When $\alpha > ½$, a growing chain has better than an even chance to reproduce two new chains. Two such chains will on the average reproduce 4α new chains and so on; n chains can be expected to lead to $2n\alpha$ new chains, which is greater than n, when $a > ½$. Unlimited structures, or what we have called infinite networks, are then possible. Hence $a = ½$ presents the critical condition for incipient formation od infinite networks in a trifunctional branched system".

As a general formula for polycondensations of $\mathrm{R\text{-}a_f}$ monomers, Flory then defined the critical α value according to:

$$\alpha_c = 1/(f - 1) \tag{4.40}$$

For equifunctional polycondensations of $\mathrm{R\text{-}a_f}$ branch monomers with $\mathrm{b_2}$ monomers follows:

$r = 1$ and $\rho = 1$, so that Eqs. (4.37) and (4.38) are reduced to

$$\alpha = p^2 \tag{4.41}$$

Under these simplified conditions Eq. (4.41) allows for calculation of the critical conversion p_c, at which the gel point is reached. For $f = 3$, p_c amounts to 70.8 % conversion and for $f = 4$, $p_c = 57.8$ %. Experiments of Kienle with glycerol [25, 26], of Stockmayer et al. with pentaerythritol [27] and of Flory with tricarballylic acid [6, 28] yielded slightly higher p_c values (+ 4–5 %)which were ascribed to a small extent of cyclization reactions. Flory also pointed out that the average number degree of polymerization is relatively low up to the gel point, and he presented Eq. (4.42) for the calculation of $\mathrm{DP_n(x_n)}$. For the appearance of gelation it suffices, when only a small number of the largest molecules react with each other: “If the primary molecules are large, the proportion of cross-linkages required for gelation becomes remarkably small; a ratio of one cross-linkage for two primary molecules is sufficient for onset of formation of infinite structures (gel).”

$$DP_n = [f(1-\rho+1/r)+2\rho]/[f(1-\rho+1/r-2p_a)+2\rho] \tag{4.42}$$

4.5 Contribution of Other Authors

In the 50 years after the appearance of Flory’s book “Principles…”numerous authors published contributions to the theory of step-growth polymerization covering the following aspects:

(I) Completion of Flory’s theory.
(II) Reinvestigation of certain aspects of Flory’s theory.
(III) Theoretical treatment of polycondensations deviating from Flory’s premisses:

  (a) because cyclization reactions play an important role,
  (b) because non-symmetrical monomers are used or because the reactivities of the monomers deviate from those of oligomers and polymers.

(IV) Extension of Flory’s theory toward syntheses of copolymers.
(V) Kinetic analyses and modeling of individual polycondensations.
(VI) Modeling of individual polycondensation reactions.
(VII) Modeling of technical polycondensation processes.
(VIII) Analyses and modeling of branching and crosslinking reactions.

In the year 2004, S. Kuchanov, H. Slot and A Stork [29] published a comprehensive review article entitled “Development of a quantitative theory of polycondensation” with 462 references (incl. a handful papers of Flory). A particular quality and advantage of this review is the fact that all the pertinent Russian literature is included. It is, of course beyond the scope of this chapter to comment on all these references. However, a few topics are discussed in this and other chapters. For instance examples concerning point (II) were mentioned above [7–20]. The various aspects of cyclization reactions (IIIa) are discussed in Chaps. 5, 7, and 12. The literature dealing with theory and modeling of branching reactions is mentioned in Chaps. 10 and 11, and publications concerning points (IIIb) and (IV) are shortly presented in the following text.

Polycondensations violating Flory’s premisse that the reactivity of all functional groups is independent of the size of the molecules (IIIa) were subjected to kinetic analyses and computer modeling by numerous authors. In the review article of Kuchanov et al. [29]. The relevant papers are subdivided into two categories: papers dealing with electronic or steric short-range effects and papers dealing with long-range effects. This subdivision is maintained in the following text. Short-range effects means that in the case of an a_2 monomer the reactivity of one “a” group changes when the other “a” group has reacted with b_2 or “b” functions. Long-range effects summarizes electronic interactions of functional groups with the delocalized electrons of the neighboring units, so that the reactivity of the end groups depends on the lengths of oligomers. Another kind of long-range effects concerns mutual interactions of end groups and active centers (e.g. electric charges) separated by numerous repeat units. The mutual interaction occurs, when both groups come in close vicinity due to conformational rearrangements of the chain segment between the groups [30].

Experimental studies of the short-range effect are typical for monomers, such as aldehydes, ketones, CH_2Cl_2 or CH_2Br_2 (see. Chap. 8) and cyclic dicarboxylic anhydrides (see. Chap. 9). The first theoretical work on short-range effects was published by Case [31] on the basis of the FSSE model. Polycondensations of an a_2 monomer showing substitution dependent reactivity with a b_2 monomer the reactivity of which was independent were analyzed. The MWD of polymers formed by such a monomer combination was described by the extended Flory distribution, analogous to that of an ideal polycondensation involving a non-symmetrical *a–a*’ monomer with a symmetrical b_2 monomer. The term “quasi-ideal” was coined by Kuchanov for such polycondensations [32]. Most publications dealing with short-range effects were focused on irreversible (KC) polycondensations [33–38]. They include systems combining two monomers having substitution dependent reactivities of their functional groups. None of these papers considered the role of solvation or long-range volume effects or an influence of cyclization reactions.

Concerning long range-effects, several authors tried to calculate the influence of solvent and dilution on the MWD in TC polycondensations of $a-b$ monomers [39, 40] and in KC polymerizations [41–50]. In the latter case, cyclization was again ignored, and part of the authors obtained contradicting results. Papers presenting a theoretical treatment of polycondensations involving polymers where the reactivity of an end group depends on long-range mesomeric effects were not found by the author, but experimental studies including mechanistic discussions are presented in Chap. 8.

Finally, papers dedicated to theoretical studies of copolycondensations should be mentioned. From the experimental point of view it is convenient to characterize different sequences by a “microheterogeneity parameter” (C_h) which may be defined according to Eq. (4.43). The frequency of the three possible dyads in a binary system can be determined from the intensities of the dyad signals in ^{1}H NMR or ^{13}C NMR spectra. A first mathematical treatment of such a copolycondensation was published by Shtrikhman in 1959 [51]. Many more studies were presented later by other research groups [52–83], part of which focused on KC polycondensations [52–60], whereas another part concentrated on TC polycondensations [62–83]. Relatively few papers deal with copolycondensations of non-symmetrical monomers [34, 64, 84–88]. The first study in this direction was apparently published by Korshak et al. [84]. Again it should be mentioned that cyclization reactions were not taken into account. This aspect is of interest, because it was demonstrated by

Kricheldorf et al. [89]. using MALDI-TOF mass spectrometry that syntheses of copolycarbonates with high conversion exclusively yielded cyclic oligomers and polymers in the observable mass range. These cyclic possess all possible compositions and include a considerable fraction of cyclic homopolymers.

4.6 Critical Comments

Flory's classical theory of step-growth polymerizations is based on the assumption that end-to-end cyclization does not play a significant role. There were two reasons which let Flory reach this erroneous conclusion. Firstly, in the years 1910–1940 syntheses of macrocycles consisting of 10–20 ring-atoms was an important working field in organic chemistry, and it was demonstrated by numerous chemist that it is extremely difficult to prepare macrocycles of that size in acceptable yields. Secondly, Flory has the immense historical merit having introduced statistical conformational analyses into polymer science. His calculations had, for instance the purpose to predict typical physical properties of polymer solutions and to predict cyclization probabilities. Yet, with regard to cyclization probabilities his calculations were misleading, and in his first review he concluded [6, p. 149]: "However, in ordinary bifunctional condensations (no diluent) the primary product from monomers (or dimmers) of fifteen or more members is almost exclusively linear polymer. This results from the statistical improbability that the ends of long chains of atoms connected by valence bonds about there is free rotation, will meet." He cited the calculations of Guth and Mark [90] and Kuhn [91], but he did not consider the "Law of Self-dilution" (Eq. 1.1) [92]. In his book "Principles…." [4] he accepted the formation of cyclic oligomers by "back-biting" equilibration according to the Jacobson-Stockmayer theory, but, as cited in Chap. 5, he remained reluctant to accept end-to-end cyclization (end-biting) of polymer chains.

Ignoring a permanent competition of intra- and intermolecular condensation steps causes problems for the interpretation of Flory's formulas regardless, if KC or TC polycondensations are concerned. These problems begin with the definition of conversion, p, (Eq. 4.1), because a quantitative conversion ($p = 1$) cannot be achieved in a perfectly linear polycondensation. For the end of a linear polycondensation a $DP_{\max}$ may be defined which equals the number of monomers initially present in the reaction mixture and thus, also equals the number of "a" groups regardless, if $a–b$ or $a_2 + b_2$ monomers are polymerized (Eq. 4.44).

This definition is also valid for polycondensations of ab_f monomers.

$$DP_{\max} = N_{a0} \tag{4.44}$$

Equation 4.1 may be combined with all other equations of Flory when the limitation $Nt > 2$ is added. Without this limitation $p = 1$ inserted into the "Carothers equation" (4.2) has the consequence that DP_n goes to infinity. Insertion of $p = 1$ into the equations of number and mass distributions (4.12) and (4.16) has the consequence that all linear species disappear. The only reasonable interpretation is the to postulate that cyclic species were exclusively formed in contradiction to Flory's premisse of perfectly linear polycondensations. A third example demonstrating that Flory's equations are inconsistent with $p = 1$ is given by Eqs. (4.7) and (4.8). Flory derived Eq. (4.8) from (4.7) with $p = 1$, but for an equimolar feed ratio ($r = 1$) DP_n Goes to infinity. In contrast, Eq. (4.7) yields correct results for all conversions with $p_{\max} = N_{a0}-2/N_{a0}$.

Another problem results from Flory's calculations of polydispersities, Eqs. (4.23) and (4.32). Even Flory's concept of cyclization-free step-growth polymerizations are taken seriously, Eq. (4.23) does not give a satisfactory description of the DP_n–p correlation, because the final state of a linear polycondensation is one giant chain. This means $D = 1$, whereas Flory's equation yields $D = 2$, regardless, if the maximum conversion is defined by $p = 1$ or N_{a0}–$2/N_{a0}$. When the formation of cyclic oligomers and polymers is taken into account, Eqs. (4.23) and (4.32) are useless for the calculation of the dispersities of virgin reaction products. For various KC polycondensations the author has found Ds in the range of 3–15 [93–96], and members of E. I. DuPont found for the TC syntheses of Nylon-6, Nylon-6,6, and PET dispersities in the range of 3–13 [97] (for the linear chains alone a D around 2 was found). The experimental dispersities reported for several ab_f (ab_n) polycondensations also fall into the range of 5–15, whereas according to Eq. (4.32) the dispersity approaches infinity for $p = 1$. These results are a consequence of the fact that end-to-end cyclization causes opposite trends for the dispersities of two-dimensional and three-dimensional polycondensations. In the former case the presence of cyclics enhances the number of oligomers above the values predicted by Flory (Eq. 4.3) and thus, enhances the D, whereas in three-dimensional polycondensation the limitation of the chain growth due to cyclization also limits the increase of D.

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Chapter 5
W. H. Stockmayer and the Role of Equilibration

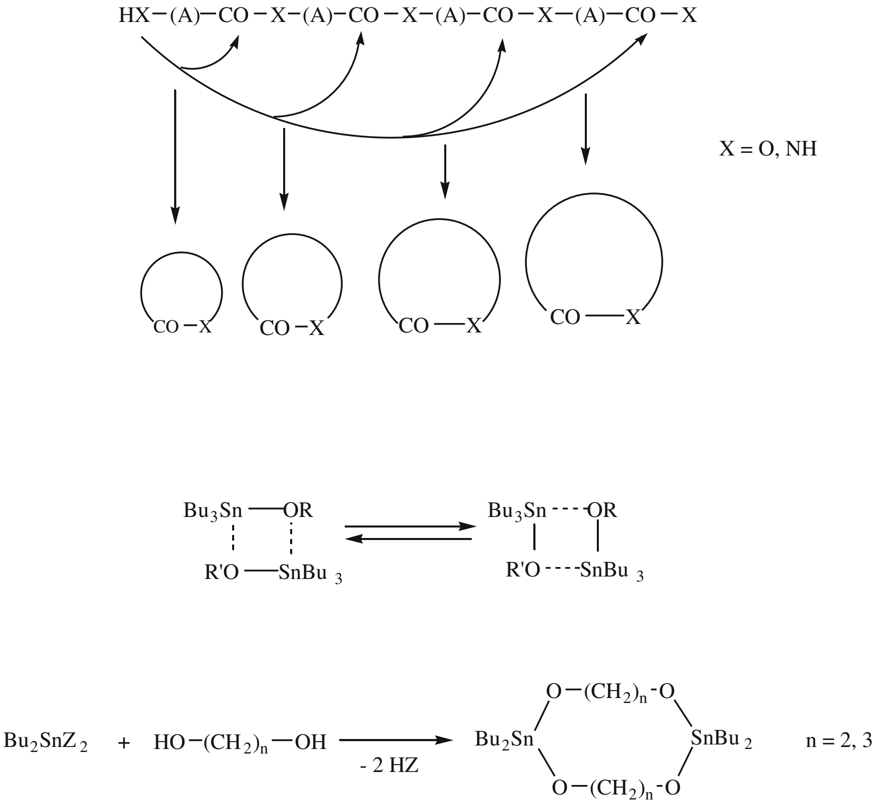
5.1 Introduction and Biography

Like all other chemical reactions, polymer syntheses may be subdivided into two categories, namely into kinetically controlled (KC) polymerizations and thermodynamically controlled (TC) polymerizations. KC polymerizations are characterized by irreversible reaction steps, equilibration reactions are absent, and the reaction products may be thermodynamically stable or not. TC polymerizations involve rapid equilibration reactions, above all formation of cyclics by "back-biting" of a reactive chain end (see Formula 5.1), and the reaction products represent the thermodynamic optimum at any stage of the polymerization process. Borderline cases also exist, which means that a rapid KC polymerization is followed by slow equilibration. This combination is typical for many Ring-opening polymerizations (ROPs).

Polymerizations of unsaturated monomers, such as olefins, vinyl monomers, or acetylenes, exclusively proceed as KC reaction sequences. With exception of crystalline polyethylene, the resulting polymers are thermodynamically unstable, because the corresponding cyclohexanes or benzenes are more stable, but equilibration catalysts do not exist. As soon as polymer backbones include heteroatoms, equilibration reactions become possible, and many polymers may be prepared by KC and by TC polymerizations. An interesting case is synthesis and polymerization of oxiranes. Their synthesis from β-bromoalcohols and their polymerization via anionic or coordination insertion catalysts represent KC reactions. Yet, heating of oxiranes or poly(alkylene oxides)s with strong protic acids yields the thermodynamically more stable 1,4-dioxanes.

Carothers work included both, KC and TC polymerization, but neither he nor his coworker Flory realized and discussed this difference. Under the conditions used by Carothers, the syntheses of polyesters and polyamides were TC polycondensations, whereas the syntheses of polyalkanes from 1,10-dibromodecane and sodium metal were perfect KCPs (see Chap. 3). In 1950, Stockmayer and coworkers published two papers [1, 2] which dealt with the formation of cylics in ring-chain equilibria during synthesis or thermal degradation of polymers. The first paper was focused on the calculation of distribution functions of the cyclic oligomers, whereas the second

H. Kricheldorf, *Polycondensation*, DOI: 10.1007/978-3-642-39429-4_5,



Formula 5.1

paper described syntheses and reversible degradation of poly(1,10-decamethylene adipate). With these two papers Stockmayer et al. implanted two new, important concepts into the theory of step-growth polymerization, namely (a) the formation of cycles as integral part of a polycondensation process, and (b) the differentiation between KC and TC polymerizations

Walter Stockmayer was born in Rutherford, New Jersey, on April 7, 1914 [3, 4]. His father was organic chemist and stimulated his interest in chemistry. As undergraduate student of the Massachusetts Institute of Technology, MIT (1933–1935) he became interested in the mathematical aspects of physical chemistry. From 1935 to 1937, a Rhodes Scholarship allowed him to work at the university of Oxford on gas kinetics with D. L. Chapman. After returning to the MIT he was teaching fellow for 1 year, and completed his studies with the Ph.D. in 1940. He continued his academic career at MIT as Research Fellow until 1941, when he moved to Columbia University as instructor for 2 years. Afterwards, he returned to MIT as Assistant Professor until 1946, and was appointed as the Associate Professor until 1952. He was entitled Professor of Physical Chemistry and worked in this position at MIT until 1961. He moved to Dartmouth College as a Full Professor of Chemistry, and was Chairman of the Chemistry Department in the years 1963–1967 and 1973–1976. His official career ended as Professor Emeritus in 1979.

Stockmayers work is documented in approximately 200 publications. He founded the ACS journal “Macromolecules” and received numerous honors and awards, for instance, the Polymer Physics Award of the American Chemical Society. At the time of his death, he was the only non-German scientist awarded with the Hermann Staudinger Prize (in 1999). He died on May 9, 2004 at Norwich, Vermont. His wife Sylvia predeceased him in 2002. They left two sons and one daughter and eight grand children.

5.2 The Jacobson–Stockmayer (JS) Theory

The JS theory had two aims. First, it should describe the course of TC polycondensations with regard to quantity and Molecular weight distribution (MWD) of linear and cyclic species. Second, the distribution function of cyclics should be derived from the configurational and conformational properties of the linear chains. The JS theory is based on the following assumptions and restrictions.

(1) The reactivities of the functional groups is independent on the size of the molecules.
(2) The elementary steps in polycondensation are completely reversible.
(3) Only flexible aliphatic chains (including polysiloxanes) obeying a Gaussian statistics of the average end group distances are considered.
(4) For the distribution function only those cycles the ring closure of which does not involve enthalpic interactions, so that only entropic changes had to be considered were included.

J + S discussed three types of monomers:

(I) a_2: e.g., dimethylsilanol;
(II) a–b: e.g., 11-hydrocyundecanoic acid;
(III) $a_2 + b_2$: e.g., 1,10-decanediol + adipic acid

The calculation of Figs. 5.1, 5.2, and 5.3 and the experimental work of J + S are exclusively based on case III. J + S used the following definitions and correlations.

N = all monomers (N' = monomers in the ring fraction)
M = all molecules (cyclic and linear species)
I = all rings
C_n = molecular size distribution of chains
R_n = molecular size distribution of rings

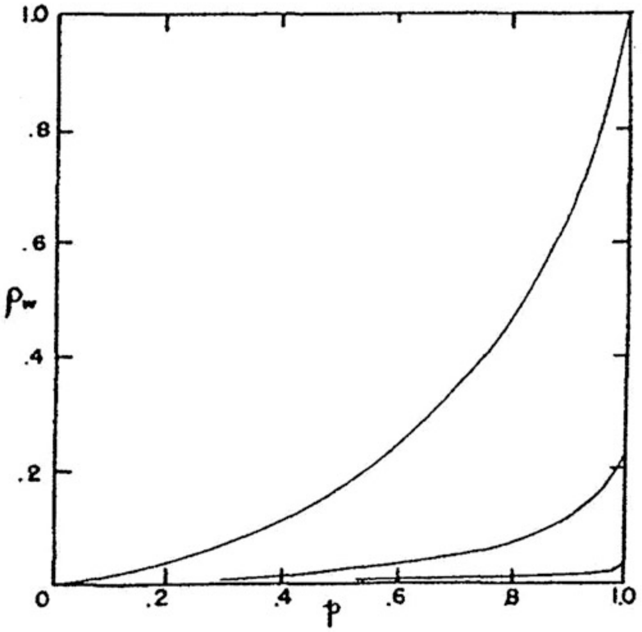


Fig. 5.1 Weight fraction of rings, ρ_w, as a function of the extent of reaction, p, for a Case IIIa polymer at three dilutions. *Upper curve* $B'/c = 0.5$; *middle curve* $B'/c = 0.05$; *lower curve* $B'/c = 0.005$. Reproduced from Ref. [1] with permission (copyright 1950, American Institute of Physics)

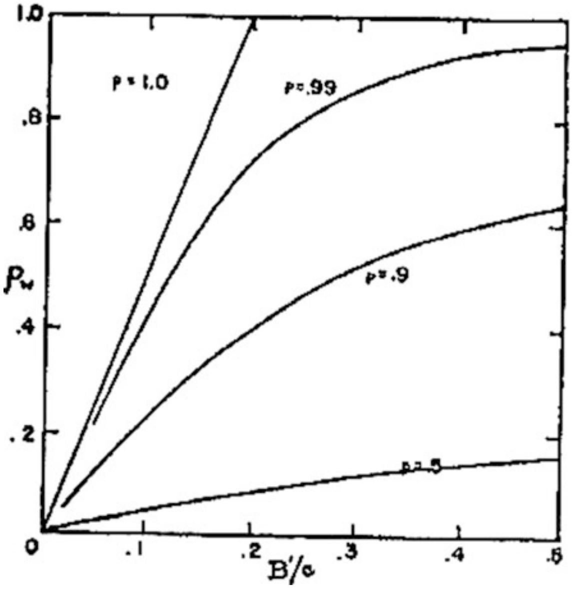


Fig. 5.2 Weight fraction of rings, ρ_w, as a function of dilution, B'/c, for a Case IIIa polymer at various extents of reaction p. Reproduced from Ref. [1] with permission (copyright 1950, American Institute of Physics)

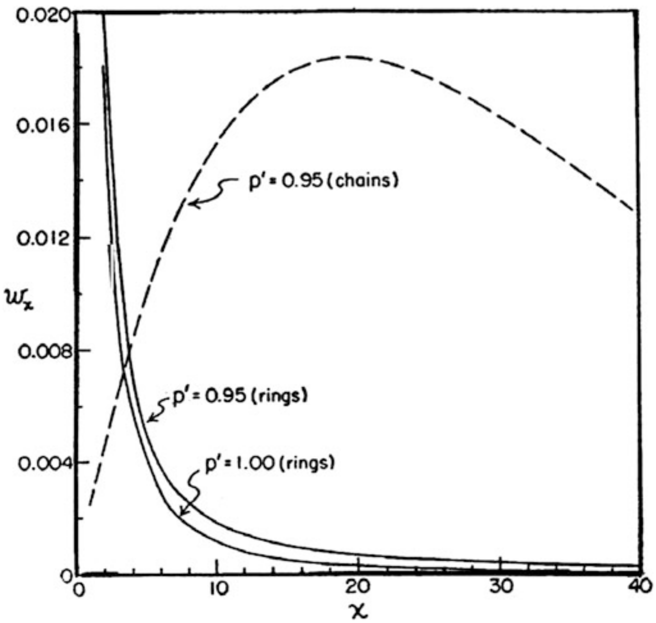


Fig. 5.3 Weight fraction distribution of cyclic polymers for a type ii polymer with $B'M_0/c = 0.01$ (g./cc.)$^{-1}$ as calculated from Eq. (5.16) for $p' = 0.95$ and 1.00 (*solid curves*); only even integral values of x apply. The chain distribution for $p' = 0.95$ is shown or comparison by the *broken curve* calculated from Eq. (5.19). Reproduced from Ref. [3] with permission (ii-polymers means $a_2 + b_2$ polycondensates) (copyright 1953, Cornell University Press)

$$\Sigma_n(C_n + R_n) = M \tag{5.1a}$$

$$\Sigma_n n(C_n + R_n) = N \tag{5.1b}$$

$$\Sigma_n R_n = I \tag{5.1c}$$

In the Appendix of Ref. [1], J + S calculated R_n from structural and conformational properties of the chains and obtained the distribution functions:

$$R_n = BV(p')^n n^{-5/2} \quad \text{or} \tag{5.2a}$$

$$\text{with } B = [3/2\pi v)]^{3/2}/2b^3 \tag{5.3}$$

Insertion of Eqs. (5.2a) and (5.2b) in (5.1c) gave Eq. (5.2b)

$$\Sigma(p')^n n^{-5/2} \tag{5.2b}$$

Equations (5.2a), (5.2b), and (5.3) are based on the following definitions:

V = Volume of the system

v = chain atoms per monomer or repeat unit (ζ in Flory's contribution [5], see next Sect. 5.3)

p' = fraction of reacted groups in the linear chains. J + S used the symbol x, but x has a different meaning in Flory's work and in other chapters of this book, hence Flory's symbol p' was used in this chapter.

b = effective link length of polymer chain, correlated with bond length l according to Eq. (5.4) and with the end-to-end distance of a coiled chain according to Eq. (5.5).

$$b^2 = l^2(1+\cos\alpha)/(1-\cos\alpha) \tag{5.4}$$

$$\left(L^2\right)_{\text{av}} = vnb^2 \tag{5.5}$$

From experimental data, [2] J + S obtained via Eq. (5.3) $b = 4.4$. A for poly(ecamethylene adipate) and speculated that this relatively high value might indicate partially hindered rotations.

For the calculation of the weight fraction of rings (ρ_w in Ref. [1], w_r in Ref. [5]). J + S presented the following definitions and equations:

$$C_{m+n} \rightarrow C_m + R_n \quad \text{(no byproduct involved)} \tag{5.6}$$

$$C_{m+n} \rightarrow C_m + C_n \quad \text{(byproduct needed)} \tag{5.7}$$

$$C_n \rightarrow R_n \quad \text{(byproduct eliminated)} \tag{5.8}$$

Commenting on poly(decamethylene adipate) [2] J + S noted that the role of water in Eqs. (5.6) and (5.7) was ignored, because it does not show up in the sum of all three equations.

The mass action product was formulated according to Eq. (5.9):

$$K_1 = C_m + R_n/C_{m+n} = R_n/(p')^n \tag{5.9}$$

Taking into account the definitions (5.10) and (5.11), Eqs. (5.12) and (5.13) were formulated correlating the weight fraction of rings with experimental data, such as the monomer concentration (IMC) and conversion p'.

$$c = N/(N_oV); \quad \text{the “ground molar concentration”} \tag{5.10}$$

with N_o = Avogadro's number

$$B' = B/N_o \tag{5.11}$$

$$\rho_w = w_r = (B'/c)\left(\sum_{n=1}^{\infty} (p'n^{-3/2}\right) \quad \text{for } A_2 \text{ monomers} \tag{5.12}$$

$$\rho_w = w_r = 2(B'/c)\left(\sum_{n=1}^{\infty} (p'n^{-3/2}\right) \quad \text{for } a_2 + b_2 \text{ monomers} \tag{5.13}$$

From Eq. (5.13) J + S calculated Figs. 5.1 and 5.2. These diagrams illustrate that w_r increases with conversion and with dilution. Yet, 100 % rings can only be achieved at $p = 1$, below a critical IMC corresponding to $B' = 0.19$ (Fig. 5.2). Above the critical IMC (typical for polycondensations in bulk) only a few percent of cyclics will be formed even at $p = 1$. The main reaction product containing 95–98 % of all monomer units is then one giant chain. For reasons discussed below, this conspicuous result will be called "Bose–Einstein" (B–E) phenomenon.

Concerning the experimental work, it should be noted that J + S studied two types of poly(decamethylene adipate) as starting materials.

(a) The "equivalent" polyesters which were prepared by polycondensation of equimolar amounts of both monomers, with variation of the conversion (and thus DP).
(b) The "100 % polyester" which was prepared with a 5 % excess of 1,10-decanediol and long reaction time to achieve 100 % conversion of the CO_2H groups.

In both cases, relatively low DPs (< 41) were prepared and studied. A weak point in that work is the fact that J + S were not able to prove that their starting materials contained only negligible amounts of cyclics, as it was hoped for.

5.3 Flory's Contribution

In his book "Principles of Polymer Chemistry" [5] Flory accepted the JS theory and discussed the formation of cyclic oligomers as a result of equilibration reactions, but he remained reluctant to accept the formation of higher cyclic oligomers and polymers via end-to-end cyclization (p. 99): "It can be shown from statistical considerations that the probability of the two ends of a very long chain will occupy positions adjacent to each other varies approximately as the inverse three-halves power (exp-3/2) of the chain length or number of chain atoms The probability that the end group of a given molecule is adjacent to the end group of another will vary with their concentration, and hence, inversely to the first power of the chain length. Consequently, intramolecular reaction gradually becomes increasingly improbable as the length of the bifunctional species increases, as in fact is indicated by the data… for the formation of rings with more than eighteen members."

Flory elaborated the JS theory in more detail: (a) with regard to the B–E phenomenon and (b) with regard to the MWD of equilibrated polymers. In his equations, he used most of the symbols published by J + S, but the following differences need to be taken into account.

ρ_w (J + S) = w_r (Flory): weight fraction of all cyclics

n (J + S) = x (Flory): DP of individual cyclic or linear species

v (J + S) = ζ (Flory): number of chain atoms or skeletal bonds in a repeat unit

x (J + S) = p' (Flory): virtual conversion of the chain fraction correlated with the total conversion p by Eq. (5.14)

$1/c$ (J + S) = M_0/c (Flory): c in mol/L (J + S), but c in g/cm^3 (Flory) with M_0 as mass of the repeat unit in g.

$$(1 - p') = (1 - p)/(1 - w_r) \tag{5.14}$$

In the text below the original symbols of Flory were used. For the calculation of w_r, Flory formulated Eq. (5.15) concerning $a - b$ (i) monomers and Eq. (5.16) concerning $a_2 + b_2$ (ii) polymers.

$$\begin{gathered} w_r = \Sigma w_{\mathrm{rx}} = (2B'/M_0/c)\Sigma(p')^x x^{-3/2} \\ \text{with } w_{\mathrm{rx}} \text{ as weight fraction of rings having identical } x \end{gathered} \tag{5.15}$$

$$\begin{gathered} w_r = \ (2B'M_0/c)\Sigma(p')^x/(x/2)^{3/2} \\ \text{in the text } \phi\left(p'^2,\ 3/2\right) \text{ is used as abbreviation for the second term} \end{gathered} \tag{5.16}$$

With regard to the B–E phenomenon he discussed aliphatic polyesters and polyamides derived from dicarboxylic acids (ii -polymers) assuming the following parameters: $\zeta = 10$–20 and $l = 4 \times 10^{-8}$ cm. He concluded: "Of greatest interest is the range of high extents of reactions ($p > 0.95$ perhaps), where the average degree of polymerization for chains is not uninterestingly low. If the weight fraction of rings is not too large, $1 - p'$ is not very different from $1 - p$ (see Eq. (5.14)), hence p′ is also near unity. The function $\phi(p'2, 3/2)$ increases from 1.6 to 2.6 as p' increases from 0.90 to 1.00. The increase in w_r as the condensation nears completion is correspondingly small, since according to Eq. (5.16) w_r is equal to the product of $B'M_0/c$ and ϕ. For values of $B'M_0$ given above, w_r at $p' = p = 1$ should amount to only 2.5 % at $c = 1$ g/cm^3. Thus, the work of J + S predicts that the proportion of cyclic polymers will be small, but not negligible in undiluted systems. In type i-polymers (ω-hydroxy- or ω-aminoacids), w_r should be about twice as great for the same value of z and other parameters".

With regard to the MWD of equilibrated polymers, Flory mainly discussed the mass distributions. He started out from the equations of number and weight distributions (5.17) and (5.18) already presented in Chap. 4.

$$n_c = p^{x-1}(1 - p) \quad \text{number distribution of linear chains} \tag{5.17}$$

$$w_c = xp^{x-1}(1 - p)^2 \quad \text{mass distribution of linear chains} \tag{5.18}$$

With $B'M_0/c = 0.01$ (e.g., polycondensation in bulk) and with $p' = 0.95$ ($w_r = 0.0324$) and $p' = 1.00$ ($w_r = 0.0522$) he calculated from Eq. (5.15) the solid curves in Fig. 5.3 and gave the following comment: "Unlike the distribution of open chain polymers, the curves decrease monotonically with increase in (ring) size. Of even more significance is the virtual confinement of the distribution to the very low range and the comparative lack dependence on the extent of reaction (p) except in the range of large size. The amount of cyclic polymer of low x greatly exceeds that of open chain polymer of the same size (compare broken curve)…. The number average degree of polymerization of cyclic species exceeds 4 for ii ($a_2 + b_2$) polymers or 2 for i-(a–b) polymers, regardless of the extent of reaction…. For complete rigor, the distributions (equations) previously presented for linear polymer chains (e.g., Eqs. (5.17) and (5.18)) should be modified through substitution of p' for the overall extent of reaction. Thus, for example Eq. (5.18) for the weight fraction of chains should be replaced by Eq. (5.19)"

$$w_{cx} = (1 - w_r)x(p')^{x-1}(1 - p)^2 \tag{5.19}$$

w_{cx} is the weight fraction of chains x-mer referred to the mixture of chain and ring species, and p', the conversion of the chains alone, is correlated with p according to Eq. (5.14).

"Likewise, p in other formulas given in the preceding sections (e.g., Eq. (5.16)) of the present chapter should be replaced by p'. For polymers formed (or equilibrated) in the absence of diluent, p' will be only slightly less than p, hence the revision is usually scarcely significant. The dashed curve shown in Fig. 5.3 has been calculated from Eq. (5.19).In order to obtain the complete size distribution, including both, ring and chain species, the curves for the latter should be added to the dashed curve. This revision would greatly increase the portion of very low polymers over the amounts previously considered, and it would cause the combined distribution for chains and rings to pass through a minimum at a low value of x… Although, the proportion of rings in equilibrium in an undiluted polymer may be scarcely significant on a weight basis, they may make a relatively large contribution to the total number of molecules, and hence, markedly lower the DP. This will be particularly true if p is large and the number of chains is small."

In 1966, Flory and Semlyen [6] described an improved version of the JS approach to the calculation of cyclization equilibrium constants (K_x in all papers of Flory and Semlyen) and said about their intention: "The cyclization for larger rings may in principle, serve as measure for the statistical configuration of chain molecules… The theory of J + S requires minor amendment in order to achieve a close comparison with recent configuration studies on this polymer (PMDS). Their treatment was set forth in terms of the hypothetical, freely jointed or random flight chain model, a model which has been used extensively despite its unrealistic failure to take account of the correlations of directions of successive bonds imposed by bond angles and by hindrance of bond rotation. Realization of the full potential of their theory as a basis for relating macrocyclization equilibria to chain configuration statistics requires that it be recast in terms relevant to real molecular chains. This we attempt below. The basic assumption underlaying their method will be examined critically as well. Then the results of Brown and Slusarzuk will be compared with theory, and implications of the comparison will be pointed out"

$$-M_y - M_{y-x} - \; + c - M_x \tag{5.20}$$

$$K_x = \left[-M_{y-x}-\right][c - M_x]/\left[-M_y-\right] \tag{5.21}$$

$$K_x = (3/2\pi)^{3/2}/2^{5/2} < h^2 > {}^{3/2} N_A x \tag{5.22}$$

$$K_x = (3/2\pi)^{3/2}/2^{5/2} C_{cr}^{3/2} x^{5/2} N_A \tag{5.23}$$

with: $< h2>$ 0 mean square end-to-end distance

Na = Avogadros number

x = DP of rings

The “characteristic ratio” C_{cr} was defined as $C_{cr} = \langle h^2 \rangle_0 / 2xl^2$ where l is the bond length (1.64×10^{-8} cm for PDMS)

For the calculation of K_x Flory and Semlyen started out from the mass action Eqs. (5.20) and (5.21) like J + S, but then introduced a probability ($W(\mathbf{0})$) for chain conformations bringing the chain ends in close neighborhood to each other with vectors of the functional groups allowing for immediate ring closure. Finally, they arrived at Eqs. (5.22) and (5.23) which were, in turn, used for the calculation of K_x’s. The calculated values were in good agreement with the experimental results for cyclosiloxanes with DP > 15 (30 skeletal bonds).

In 1976, Flory et al. [7–9] returned to the problem of macrocyclization equilibria, presenting a new mathematical approach called “Direction Correlation Factor” theory, to improve the agreement between calculated and experimental data for rings of DP < 15. Cyclization equilibrium constants (K_x) for the formation of cyclic poly(dimethyl siloxane)s, PDMS, were calculated for $6 < x < 31$ and compared with experimental data. Similar calculations were performed for cyclic oligomers of Nylon-6, but the agreement with the experimental data was not satisfactory for the smaller rings. Remarkably, Flory presented a positive citation of two papers of Andrews and Semlyen (see below) who reported that equilibrated Nylon-6 contains around 12 % of cyclic species in the melt at 500–560 K. Unfortunately, he did not comment, how this relatively large value fits in with the much lower values he had previously calculated from the J + S theory (see text above and p. 328 in Ref. [5]).

5.4 Contributions of Other Research Groups

Almost all contributions of other research groups may be subdivided into the following three categories:

(I) Theoretical studies of chain conformations and their relationship to cyclization probabilities. For access to the numerous publications which have appeared in this field the reader is referred to three review articles [10–12].

(II) Syntheses (and characterization) of cyclic oligomers by equilibration (depolymerisation) in solution.

(III) Elaboration of the weight distribution of cyclic oligomers and calculation of equilibrium constants (K_c).

Studies of the depolymerisation of polymers with the purpose to isolate and characterize cyclic oligomers were already reported by Carothers et al. as mentioned in Chap. 3. However, Carothers used depolymerisation in the melt at high temperatures combined with distillation of the cycles in vacuo. In this way he obtained more than 60 new cyclic oligomers in yields around 10–25 %. Yet, he also performed depolymerisation of aliphatic polyesters in solution [13–15].

Further studies of equilibration reactions of aliphatic polyesters in solution catalyzed by titanium alkoxides were contributed by Billmeyer et al. [16–18]. Semlyen et al. [19] used a dibutyltin salt for the preparation of cyclic oligomers by depolymerization of poly(tetraethyleneglycol succinate). Extraction and characterization of cyclic oligo(alkylene isophthalate)s and oligo(alkylene terephthalate)s [20–24] beg an in 1954 with the work of Ross et al. [20], who isolated the cyclic trimer from PET. A detailed study of 13 different polyesters was reported by Wick and Zeigler [25]. Semlyen et al. [26] were particularly interested in the depolymerisation of polyesters derived from tetra(ethyleneglycol) and phthalic, isophthalic and terephthalic acidacid, whereas Montaudo et al. [27] studied other polyesters of terephthalic acid.

Depolymerization of PET and PBT in solution with the purpose to prepare cyclic oligomers in high yields (up to 90 %) was also studied by four research groups [28–34]. A first patent in this direction was claimed by a Japanese company [28] followed by extensive work of Brunelle and other members of General Electric [29–32]. Based on their work, a small company named “Cyclics” was founded, which prepared cyclic oligoPETs and PBTs in several tons per year. Almost at the same time preparative depolymerisation of PET [33] and PBT [34] in solution was also investigated by Semlyen et al. Depolymerization of poly (ethylene 2,6-naphthoate) in solution was later reported by McKnight et al. [35], who used the isolated cyclic oligomers as monomers for ROP.

Preparation of cyclic oligo(ether sulfone)s by cesium fluoride-catalyzed depolymerisation in aprotic solvents was reported by Colquhoun et al. [36, 37]. The fluoride ion cleaves the C–O bonds at temperatures > 140 °C and the resulting phenoxide ions attack the neighboring ether groups forming cyclics by “backbiting”. Several cyclic oligoethers up to the pentamer were isolated and characterized by X-ray crystal structure analyses.

Much more work was invested by numerous research groups [38–53] into the extraction and characterization of cyclic oligoamides. Most of the work was focused on Nylon-6. With exception of the results reported by Kricheldorf et al. [51, 52], all papers agree, in that the weight fraction of the cyclics did not exceed 12 %, and the DP of the isolated or identified cycles never exceeded 9. Furthermore, all those papers have in common that hot water or methanol was used for extraction and the conversion and thus, the DP of the polyamide was never varied over a broad range. Apparently, all those authors believed that all cyclics were extracted, when the eluent was bare of cyclics. Furthermore, the absence of cyclics from the imsoluble remainder was never checked. Using long reaction times, Kricheldorf et al. [50, 51] prepared high molar mass Nylon-6 (Mn around 45,000 Da by SEC with triple detection)and a Nylon-6,8/Nylon-7 copolymer. These polyamides were either extracted four times with different solvents or reprecipitated and extracted. Upto 28.5 % of the polyamides were removed in this way, and MALDI-TOF spectra confirmed that the extracted fractions exclusively consisted of cyclics. Cyclic nylon-6 having masses up to 11,000 Da corresponding to a DP near 100 were detected. Furthermore, the mass spectra of the remainder exclusively displayed peaks of cycles indicating that the remainder still contained a large fraction of cyclic polyamides. These results allow three important conclusions. First, the weight fractions of cyclic oligoamides reported by other research groups underestimated the total weight fraction of all cyclics in the virgin polyamides. Second, a separation of higher cyclic oligomers and polymers from linear chains by extraction alone is not feasible. Third, when the conversion is pushed toward 100 %, the polyamides mainly consist of cyclic species including high molar mass cyclic polymers. The only example of a depolymerisation of a polyamide in solution was reported by Colquhoun et al., who prepared the cyclic dimer from poly(*m*-phenylene isophthalamide) by means of sodium benzanilide-catalyzed transamidation in DMSO at 150 °C [52].

Further studies of detection, preparation, and characterization of cyclic oligomers and polymers concerned equilibrated poly(dimethyl siloxane)s, PDMSs. In 1946, three papers dealt with thermal degradation [54] or acid catalyzed equilibration [55, 56] of PDMS, but the resulting cyclosiloxanes were not quantified. About 20 years later research groups of DowCorning [57–61] and General Electric [62] performed comprehensive studies of base-catalyzed equilibrations of PDMS or cyclotetrasiloxane. From this time on almost all papers dealing with equilibration of PDMS and other polymers included experimental determination and/or computation of equilibrium constants (K_x) of cyclic oligomers.

Carmichael et al. [55–61] developed a theoretical model for the calculation of K_x and measured K_x values of cyclosiloxanes having DP's < 11. The experimental K_x values were found to be independent of the reaction medium and to disagree with their own model and also with the JS theory.

Brown and Slusarczuk [62] equilibrated octamethylcyclotetrasiloxane in bulk or in toluene at 110 °C using a concentration of 3 mol/L of ($SiMe_2O$) units. Large quantities were equilibrated and the K_x values of cyclosiloxanes up to DP's around 200 were determined. In agreement with Carmichael, a maximum was found for DP 4 and 5 and a broad minimum between DP 9 and 14. Above DP 15, a monotonous decrease with ring size was observed up to DP 200 with a slope of -2.85. As mentioned above [6], Flory and Semlyen had calculated a slope of -2.55 with a refined version of the JS equation.

Based on this procedure Semlyen et al. [63–73] performed extensive studies of isolation and characterization of cyclosiloxanes using improved GL, HPLC, and preparative SEC methods. In addition to isolation and characterization of individual cyclosiloxanes, narrow fractions of cyclic polysiloxanes containing cycles up to DPs of 500 were prepared. Linear chains which were also present in the high molar mass fractions were effectively separated from the rings. In this way the first synthesis of cyclic polymers was achieved [63, 64]. Furthermore, perdeuterated PDMS was analyzed [65, 66], polysiloxanes based on (SiMePhO) [67] or (SiHMeO) [68] units, and a so-called "paraffin-polysiloxane" [69] were studied. Roovers [70] contributed a study of poly(methyl vinyl siloxane). The entire work of Semlyen et al. on cyclic polysiloxanes is described in more than 30 publications and summarized in several book chapters [71–75].

Semlyen also extended determination and computation of K_x to other polymers, such as aliphatic polyesters [76, 77] and to PET [78], whereas as K_x' values of cyclic oligo(butylene terephthalate)s were determined by Hubbard et al. [79]. K_x of cyclic oligomers of poly(1,3-dioxolane)s [80] of aliphatic polymides [81, 82] and of elemental sulfur [83] were again studied by the Semlyen group. As expected, a poor agreement with the JS theory was found for relatively small cyclic oligomers (e.g., DP < 6) but the agreement improved with increasing ring size.

$$\begin{gathered} K_x = \left(3/2\pi\left\langle h_x^2\right\rangle\right)^{3/2}\left(1/\mathrm{N_A}\sigma_{\mathrm{Rx}}\right) \\ \text{with}\, \sigma_{Rx} = \text{ symmetry number of an x - meric ring} \end{gathered} \tag{5.24}$$

For all the afore-mentioned computations of K_x values Semlyen et al. used Eq. (5.24). The unperturbed mean square end-to-end distance of the linear precursors were calculated via the matrix algebraic methods of Flory and Jernigan [84, 85] using rotational isomeric state models based on detailed structural information [86]. However, Semlyen et al. [62, 63] also improved and applied another mathematical approach to the calculation of K_xs, the so-called “Direct Computational Method”. The JS theory is limited to polymers obeying Gaussian statistics and cycles, free of enthalpic interactions. The “Direct Computational Method” does not need such restrictions [87–90]. The distances between terminal atoms of chains are calculated for all discrete conformations defined by the rotational isomeric state model. Any correlation between the directions of terminal bonds involved in the cyclization process can be investigated and their effect on K_x assessed. It can take into account favorable and unfavorable correlations between the directions of terminal bonds, as well as any excluded volume effect. Semlyen demonstrated [62, 63, 72] that the “Direct Computational Method” yields more realistic K_x values for small cyclic oligomers.

Finally, it should be noted that the concept of ring-chain equilibria and their interpretation via the JS theory was also applied to ROPs of various cyclic monomers. A recent review covering this working field was published by Szymanski [91].

5.5 Comments on the Critical Initial Monomer Concentration

The papers of J + S brought three important results. First, the demonstration that certain polycondensations, the TC polycondensations, involve rapid equilibration including the formation of cyclics by “back-biting”. Second, a mathematical approach allowing for the calculation of ECs and MWD distribution of the cyclics. Third, the existence of the Bose–Einstein (B–E) phenomenon in the mathematical treatment of ring-chain equilibria, saying that above a critical IMC the maximum yield of cyclics decreases with increasing IMC, so that at $p_{\max}$ ($p = 1$ is impossible above the critical conc.) one giant chain is formed having a weight fraction in the range of 95–98 % depending on the monomer structure.

Whereas points one and two were studied and confirmed by numerous research groups, the crIMC phenomenon requires a critical discussion, because any experimental evidence is lacking. On p. 1601 in Ref. [1] J + S say: “Qualitatively, as would be expected, the yield of rings in a polymer system is predicted to increase with dilution. A less trivial and more interesting feature of the theory rests in the mathematical coincidence of the ring distribution equation with those expressing the thermodynamic properties of the perfect Bose–Einstein gas. Thus, a critical phenomenon arises which is normally analogous to the well known B-E condensation: there is a critical concentration, below which the condensing system can be converted into rings, but above which this is not possible [16]”.

Unfortunately, neither Stockmayer nor Flory contributed any study to this problem. Despite the numerous studies of equilibrated PDMS also Semlyen did not discuss this point. Since equilibration of cyclic monomers or very long chains are equivalent to a TC polycondensation with high conversion (> 99.9 %), results obtained from equilibration of cycles above the critical concentration are of great interest with regard to the crIMC. About the KOH catalyzed equilibration of cyclotetrasiloxane, first reported by Brown et al. [62], Semlyen made the following comment [74]: “The last authors reported large scale ring-chain equilibration reaction for PDMS in solution in toluene (at a siloxane concentration of 222 g/L) and in bulk. In the 5 L solution equilibrate cycles are present as 95 % of the total siloxane, so that the chains constitute about 1 % of the solution as a whole”. The molar ($SiMe_2$–O–) concentration corresponded to 3 mol/L, but Semlyen did not say, if this high concentration was below or above the critical concentration. A recent calculation of Szymanski showed [92] that 3 mol/L is very close to the crIMC, but not above. For the equilibration in bulk no information about the content of cycles was given. Carmichael [59] mentioned in a review article that the fraction of cyclosiloxane in PDMS equilibrated in bulk amounts to 15 %. However, his analytical method did not allow for a quantification of higher cyclic oligomers and polymers, and thus, his data are meaningless.

$$[La]_p = [La]_0(1 - -p) \quad \text{with } [La] = \text{molar concentration of all linear species} \tag{5.25}$$

At this point the afore-mentioned results of Kricheldorf et al. [46, 47] concerning cyclic polyamides come into play. These syntheses of Nylons were conducted in bulk at an IMC, around 10 mol/L, corresponding to the conditions used by J + S for the calculation of the lowest curve in Fig. 5.1 (calculated with $B'/c = 0.005$) and in perfect agreement with the conditions used by Flory for his calculations (2.5 weight % of cycles) presented in Sect. 4.3. After optimization of the conversion, around 30 % of the virgin reaction products were removed by repeated extraction and reprecipitation. Furthermore, the MALDI-TOF spectra evidenced that the insoluble remainder still contained a large fraction of cyclic polyamides. This means that the weight fraction of cyclic species was at least by a factor 10 more likely by a factor 20 higher than calculated by J + S and Flory for an aliphatic $a_2 + b_2$ polycondensate. Moreover, the best mass spectrum of Nylon-6 exclusively displayed peaks of cyclics upto masses around 11 000 Da corresponding to a DP (x) around 100. These results are far outside any margin of error in the calculations of J + S or Flory and cast serious doubts on the existence of the crIMC phenomenon.

Furthermore, the role of end-to-end cyclization and the role of self-dilution [93] (Eq. (5.25)) of the linear active species La must be taken into account (both aspects were neither discussed by J + S nor by Flory). At first, it should be emphasized, that cyclization via "back-biting" is not a hindrance for cyclization via "end-biting". The rings formed by "end-biting" will, of course, not maintain their ring size, because they will be involved in the equilibration process. Yet, cyclization by "end-biting" has a strong influence on the course of the polycondensation, because it consumes end groups in contrast to "back-biting." Therefore, "end-biting" lowers the concentration of linear chains and their reduced concentration favors, in turn, cyclization due to the RZDP.

Furthermore, it may be helpful to compare two hypothetical polycondensation experiments. In experiment (A) the IMC is 1 mol/L and slightly below the critical conversion, while in experiment (B) the IMC is 4 mol/L and above the critical conversion. Close to 100 % conversion the difference in the concentration of linear species has almost vanished, and only a handful of long chains has survived in both experiments (see also Fig. 7.2). Their concentration is around 10^{-23} mol/L, and thus, the RZDP plays a decisive role. According to the JS theory the chains in experiment (A) will cyclize when the conversion goes to completion, and at $p = 1$ all reaction products will be cycles. In experiment (B) the chains are not allowed to cyclize and form one giant chain at $p_{\max}$ (in addition to the much smaller weight fraction of rings). Hence, the question arises, where do the chains in experiment (B) know from that they are not allowed to cyclize, although concentration and reactivity of the end groups are the same as in experiment (A). Of course, the DPn of the chains in experiment (B) may be slightly higher, and the fraction of the cycles slightly lower than in experiment (A), but this difference is negligible considering the extremely low concentration of the chains.

The same problem may be considered from another perspective.

The kinetic probability of end-to-end cyclization is the same in KC and TC polycondensations because it depends on the same parameters: structure and conformations of the chains and their molar concentration. Using three different mathematical approaches Gordon et al. [94] and Stepto et al. [95] have shown that even the longest chains cyclize at high conversions, and at $p = 1$ all reaction products are necessarily rings. No influence of a critical IMC was detected.

In this context the experiments of Höcker et al. [96], Rempp et al. [97], Roovers et al. [98]. and other research groups [99] should be recalled. Those authors obtained high yields of cyclic polymers from preformed difunctional polymers (e.g., bisanionic polystyrene) by polycondensation with difunctional reaction partners at an IMC of 10^{-5} mol/L. The final concentration of chains in experiments (A) and (B) are by a factor 10^{-18} lower, and chain growth without any cyclization is absolutely unlikely: In summary, the existence of the critical IMC is unproven, it is in contradiction to the results of Kricheldorf et al. [46, 47], it is in conflict with the calculations of Gordon et al. or Stepto et al. (see Chap. 7), and it is in conflict with the law of self-dilution combined with the RZDP:

In discussions, the author was confronted with the following objection. When the linear chains and their end groups vanish, the rate of equilibration slows down and finally vanishes, the resulting 100 % cycles do not equilibrate anymore, and thus, are outside the JS theory. For three reasons this argumentation is not helpful. First, when a polycondensation in bulk with 99.999999 conversions is considered, end groups and equilibration still exist. Now the question is in principle the same as for 100 % conversion. Does the reaction mixture mainly (in terms of weight fraction) consist of rings, or is their weight fraction in the range of 2.4–2.5 % as calculated by J + S and Flory. Second, this objection also concerns polycondensations below the critical conversion, where J + S have admitted as part of their theory that 100 % cycles will be formed at $p = 1$. Unfortunately, neither J + S nor Flory explained if the rings formed at $p = 1$ are in equilibrium with each other or not. Third, not all ring–ring equilibria require end groups as catalyst. It is well-known from NMR experiments [100] that tributyltin alkoxides rapidly exchange their alkoxide groups via strong DA-interactions (Formula 5.1). This exchange also occurs (for electronic and steric reasons even more rapidly) in the case of dibutyltin alkoxides. Therefore, polycondensations of dibutyltin derivatives with 1,2-ethanadiol or 1,3-propanediol yield the cyclic dimers (see Formula 5.1), but the cyclic monomer with 1,4-butanediol, regardless which derivatives and which reaction conditions are used [101–103]. The thermodynamically most stable products are formed under all circumstances. Strong DA-interactions are also known from other metal alkoxides, so that the tin alkoxides are not exceptions.

Finally, it should be mentioned that J + S garnished their statement about the BE phenomenon with a footnote (labeled 16) saying: “A trivial case, the condensation of the entire system into a single giant ring is possible at all concentrations”. This statement is pretty strange, because the formation of a single giant ring is absolutely unlikely from a kinetic point of view and impossible when equilibration occurs.

In summary, it remains to say that TC polycondensations are not fully understood as long as the problem of the crIMC phenomenon is not definitely solved. This problem is particularly important because technical polycondensates such as Nylon-6, Nylon-6,6, PET, and PBT are produced at an IMC clearly above the crIMC.

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Chapter 6
Important Polycondensates

While the origins of Bakelite and Nylon-6,6 are reported in Chaps. 2 and 3 respectively, the history of other important commercial polycondensates invented and developed after the death of Carothers in 1937 should shortly be described in this Chapter. Due to the success of Nylon-6,6, DuPont and, later, other chemical companies concentrated their research activities at first on the field of aliphatic polyamides.

6.1 Nylon-6 and Other Aliphatic Polyamides

Although the "Nylon group" of DuPont way focused on the technical production and commercialization of Nylon-6,6 its research activities covered a broad range of aliphatic polyamides based on various a,ω -diamino alkanes and dicarboxylic acids [1–3]. After World War II only Nylon-6,10 was commercialized in small quantities, a little later followed by Nylon-6,12 which replaced Nylon-6,10 to a large extent. It is mainly used as engineering plastic, for example as fishing lines and as tooth brush bristles, but it is difficult to dye [2]. After 1970 a Japanese company offered Nylon-6,9. All these polyamides have in common that their Tm's are 40–60 °C lower than that of Nylon-6,6 (see Table 6.1) [3–5], so that processing (incl. spinning) from the melt is easier and less costly. Furthermore, the absorption of moisture is lower (see Table 6.2) [6], and thus, all properties, above all, the dimensional stability is less sensitive to the presence of moisture. A disadvantage is the lower heat deflection temperature. However, it should be mentioned at this point that, whenever a polymer is designed and marketed as engineering plastic, chemical companies usually offer several modifications. For instance, a higher strength, stiffness, and heat deflection temperature can be achieved by incorporation of glass fiber. A higher impact strength results from incorporation of a finely dispersed rubber phase, and further variations of the properties are obtained by blending with other polymers or by syntheses of block-copolymers.

Nylon-6,6 was and is mainly used as a fiber [1], above all, for the production of carpets and sports goods including clothes for outdoor activities. However,

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Table 6.1 Melting temperatures (Tm's) of various Nylons

Nylon-X,Z	Tm[a] (°C)	Nylon-Y	Tm[b]
Nylon-4,4	280	Nylon-6	214 220[c]
Nylon-4,5	233	Nylon-7	225
Nylon-4,6	300	Nylon-8	185
Nylon-6,4	250	Nylon-9	194
Nylon-6,6	265	Nylon-10	177
Nylon-6,8	235	Nylon-11	187 198[c]
Nylon-6,10	215[d] 240[c]	Nylon-12	190 200[c]
Nylon-6,12	218[d]		
Nylon-12,8	192		

[a] Data taken from Ref. [3]
[b] Data taken from Ref. [4]
[c] Data taken from Ref. [5]
[d] Data taken from Ref. [6]

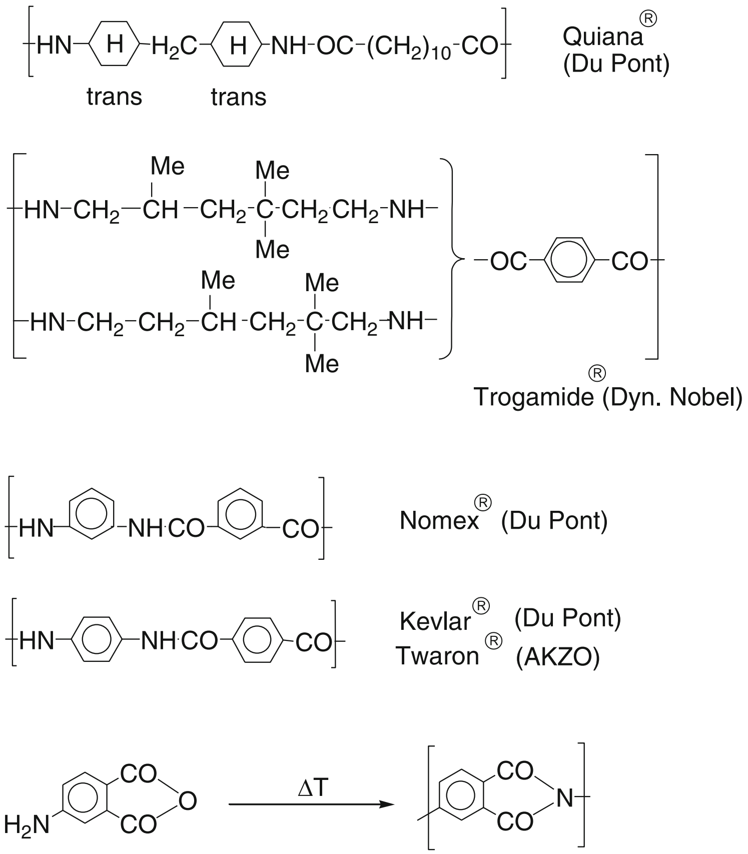
Table 6.2 Absorption of water by Nylons at 50 or 100 % relative humidity[a]

Nylon	Absorbed in water in weight %	
	50 % r. h.	100 % r. h.
Nylon-6	2.7	9.5
Nylon-6,6	2.5	8.0
Nylon-6,10	1.5	3.5
Nylon-6,12	1.3	3.0
Nylon-11	0.8	1.0
Nylon-12	0.7	1.4

[a] Date taken from Ref. [6]

Nylon6,6 is not well accepted as textile fiber for everyday clothes. Therefore, DuPont developed in the 1960 s a better textile fiber which was commercialized in 1968 under the trademark Quiana [1] (see Formula 6.1). The Tm of 275 °C still allows spinning from the melt and the high Tg (145 °C vs. 65 °C for Nylon-6,6) together with a low absorption of water entails a higher form stability. Furthermore, Quiana looks like silk and feels like silk, but it is difficult to dye and the costs of the monomers are considerably higher than those of Nylon-6,6 and have prevented a large-scale production.

Another high melting polyamide fiber, Nylon-4,6; was commercialized after 1990 by DSM in Europe under the trademark "Stanyl". The attractive properties of this polymer were known since the days of Carothers [6–9], but due to the high Tm (around 300 °C) it proved to be impossible to prepare a high molar mass polymer without discoloration by polycondensation in the melt. In the 1970s Gaymans et al. [10]. elaborated a successful, two-step procedure. At first a prepolymer is produced in water under pressure at 200–215 °C. The second step



Formula 6.1

consists of solid state polymerization of the prepolymer at 290 °C [11]. The relatively high heat deflection temperature and strength are of interest for electronic articles, tire cords, and for airbags.

None of the afore-mentioned polyamides could rival with Nylon-6,6 in terms of commercial success. The only successful competitor appeared quite early on the scene, namely Nylon-6, which was developed by Paul Schlack in 1938 [12–16]. Schlack was born on December 1897 in Stuttgart, where he grew up and attended the high school. He served in the German army during World War I and survived without being seriously wounded. He studied chemistry at the Technical University of Stuttgart and gained the Ph.D. in 1924. Afterwards he was hired by Agfa which at that time was member of the I. G. Farben. From 1926 to 1946 he was leader of the fiber research center in Berlin-Lichtenberg working on modification of cellulose acetate fibers and on synthetic fibers based on vinyl polymers, polyesters, or polyamides. In 1935, he was sent to DuPont to learn more about the "superpolyesters" developed by Carothers' group (see Chap. 3). At that time he was not informed about the first successful preparation of Nylon-6,6 fibers, and he was not informed about Carothers failure to prepare high molar mass Nylon-6 from ε-caprolactam. Schlack had himself performed unsuccessful experiments with this lactam before, and knowing about the failure of Carothers experiments would have prevented him from resuming new experiments with ε-caprolactam, as he told later. In 1937, Schlack got information about DuPonts success with Nylon-6,6, and this information prompted him to conduct new experiments with ε-caprolactam. Within a few months he succeeded to prepare Nylon-6 having a molar mass sufficient for spinning useful fibers. In 1938, representatives of DuPont appeared in his institute showing Nylon-6,6 stockings and offering a license. The DuPont delegates were greatly surprised to see another Nylon of similar quality in the hands of Schlack, and they had to learn that the German patents did not violate the patents of DuPont. In 1939, DuPont and I. G. Farben founded a cartel sharing the world markets for both Nylons.

Early in 1945 Schlacks research center was moved from Berlin to Bobingen (a small city in South-West Germany, where a plant producing cellulose-based fibers existed) to save it from Russian troops and from air raids of the Royal Air Force. After the war, Schlack was head of the fiber production in Bobingen and in 1955, he became head of the fiber research activities of Frabwerke Hoechst AG. In 1961, he was honored by the technical university of Stuttgart with the title “professor” and received later several more honors and awards. He died on August 1987 in Leinfelden-Echterdingen (South-West Germany).

Schlacks successful syntheses of high molar mass Nylon-6 in January 1938 was based on heating the pure lactam with water or 6-aminohexanoic acid as initiators/catalysts, and both compounds are still used for this purpose in the twenty-first century. Immediately after the first successful “lab-experiments” two small pilot plants were built up in Berlin-Lichtenberg, and the first Nylon-6 stocking were produced in 1939. However, the Nazis did not allow for commercialization and kept the invention secret. The German military forces consumed all Nylon-6 under the code-name “Perluran” for military purposes. A large-scale production of textile fibers (mainly needed for parachutes) began in 1943, in a new plant in Landsberg/Warthe (east of Frankfurt-Oder, now in Poland). This plant was conquered by Russian troops in 1945 and the entire plant was transported to St. Petersburg. The German chemist and engineers were forced to move to St. Petersburg to establish a production of Nylon-6 in Russia. From 1946 until the end of the “Cold War” the world of nylons was subdivided into two hemispheres. All communistic countries had to produce Nylon-6 on the basis of the Russian technology, whereas in the western hemisphere Nylon-6,6 was the dominant polyamide for many years. The production of Nylon-6 in West Germany began slowly after 1949 under the trademark “Perlon”. In the USA Allied Chemical Corporation started a large-scale production of Nylon-6 in 1955. In the twenty-first century Nylon-6 and Nylon-6,6 are produced worldwide in similar quantities.

Two more polyamides based on ω-amino acids were introduced into the markets after 1955, namely Nylon-11 (1955) and Nylon-12 (1966) [17]. Nylon-11 is produced by melt polycondensation of 11-amino undecanoic acid, which is prepared from the oil of castor beans [17, 18]. Hence Nylon-11 is the only polyamide based on natural resources. Nylon-11 was first commercialized by the French company Alkema under the trademark “Rilsan”. Nylon-12 was first produced in Germany by Marl-Hüls AG via ROP of ω-laurin lactam, the synthesis of which starts out from the trimerization of butadiene (via cyclododecanone and Beckmann rearrangement of the oxime) [17, 19]. The properties of Nylon-11 and 12 are similar Their strengths and elastic moduli are lower than those of Nylon-6 or -6,6. The water absorption is also lower and the dimensional stability and resilience is higher. Both Nylons are mainly processed by extrusion and injection moulding and rarely by fiber spinning (for properties see Ref. [19]).

All the polyamides mentioned before have in common that they are semicrystalline and their crystallinity is decisive for the mechanical properties and various applications. After 1960 a quite different group of polyamides was developed, namely amorphous, transparent materials having Tg’s in the range of 120–180 °C. The first representative of this group was invented by a research group of W. R. Grace Co around 1960 [20, 21]. The production was licensed to the Dynamit Nobel AG (Germany) and commercialized in 1967 under the trademark “Trogamide-T” [22] (see Formula 6.1). Trogamide-T modified with glass fibers or flame retardant additives was offered in the USA by Kay Fries Inc. LNP Corp. and Fiberfil. After 1967, a dozen of chemical companies began to market a broad variety of amorphous polyamides These polyamides were exclusively used as engineering plastics competing with polycarbonates (PCs) and poly(ether sulfone)s (PESs). The polyamides are less sensitive to alkaline solutions than PCs and less sensitive to organic solvents than both, PCs and PESs. The absorption of water is low, and thus, the dimensional stability is independent of a moist environment. However, the production costs are higher than those of poly(bisphenol-A carbonate).

6.2 Aromatic Polyamides (Polyaramides)

The working field of polyaramides was opened in 1862 with a short notice of Harbordt [23] who heated m-amino benzoic acid to 200 °C in the presence of HCl and obtained an intractable mass. Characterization and processing of a polyaramide was, of course, outside the reach of the scientists at that time. Systematic research on polyaramides began about 100 years later in the laboratories of DuPont and AKZO. According to the American Federal Trade Commission polyamides may be named “aramide fibers” when at least 85 % of the amide groups are connected to two aromatic rings. This definition explains, why polyaramides produced by several chemical companies are not necessarily homopolymers. However, the first two polyaramides introduced into the markets were indeed homopolymers, namely:

(1) poly(-phenylene isophthalamide), see Formula 6.1, and
(2) poly(p-phenylene terephthalamide), see Formula 6.1

Research on polyaramides began at DuPont after 1950, and a first patent appeared in 1958 [24]. The first technical product was the "m-polyaramide", which was commercialized as a fiber in 1967 under the name "Nomex". Due to a Tm of 290–295 °C, combined with high thermostability, Nomex allows for faster sewing and weaving than Nylon-6,6, and it has a higher form stability. Particular important for most applications is its low flammability (see below) Mainly responsible for this success was Wilfred Sweeney (1926–2011), who earned in 2002 the Lavoisier Medal for his life work as researcher [25, 26]. Sweeney had worked at DuPont for 38 years, and he had also contributed to the development of the "Dacron" polyester fiber. The Lavoisier medal is the highest honor of science excellence awarded by DuPont.

As evidenced by numerous patents [27–32] the main driving force behind the research on polaramides was Stephanie Kwolek. Her big success came with the commercialization of the "p-polyaramide" under the trademark "Kevlar" in 1973. Kwolek was born in July 1923 in New Kensington, Pennsylvania, and studied chemistry at the Carnegie Mellon University. She intended to make a medical career, and just to earn money she accepted in 1946 a temporary job at the DuPont facilities in Buffalo, New York State [33, 34]. She found her work so interesting that she abandoned to pursue a medical career and continued to work for DuPont. She moved to the headquarters in Wilmington in 1950 and started to work on polyaramides in 1964. She observed that solutions of poly(p-benzamide) and Kevlar were cloudy, opalescent, and had a low viscosity when stirred. In other words, she observed lyotropic solutions, which were not well understood at that time and thrown away. However, she persuaded a technician operating a spinneret to make a spinning test, and surprisingly, she obtained a fiber, which was stronger than Nylon-6,6. From this moment on her supervisor supported further research on these unusual materials. After almost 40 years of research work for DuPont she retired in 1986. She received several honors and awards, and in 2003 she was added to the National Women's Hall of Fame [33, 34].

In 1976, the Teijin Co. began with production of a copoly(p-aramide) containing a smaller amount of 4,4′-diamono diphenyl ether in addition to p-phenylene diamine. The incorporation of the second diamine slightly reduced the strength of the fiber, but it also had two benefits, first, only one solvent was needed for the synthesis (see below) and second, a patent war with DuPont was avoided. Later Teijin also acquired the "Twaron" production from the Dutch AKZO. "Twaron" is the trademark of a "Kevlar"- like poly(p-aramide) developed by AKZO in the years 1968–1978 [35, 36]. It was commercialized in 1978 under the name "Arenka" and later renamed.

Regardless of chemical structure, the synthetic method is, in principle, the same for all polyaramides [37–39]. The diamine is reacted with isophthaloyl- or terephthaloyl chloride in dry N-methylpyrrolidone (NMP) at −10 °C in the presence of $CaCl_2$, LiCl, or mixtures of both salts. The solvent plays the role of HCl acceptor and it strongly solvates the cations, thereby enhancing the basicity of the chloride anions. The Cl anions react, in turn, as acceptors of H-bonds and prevent association and precipitation of the polyaramide chains. The resulting viscous solution can directly be used for fiber spinning, and the expensive solvent can be recovered from the spinning process. This combined process was way elaborated and patented by Leo Vollbracht of AKZO before 1970 and this procedure formed the basis for the production of “Twaron” with the consequence that after 1980 a patent war with DuPont broke out. Originally, DuPont used the carcinogenic and expensive hexamethyl phosphorous triamide, HPTA, as solvent, but Kevlar precipitates from this solvent or HPTA mixtures at relatively low molecular weights. The solubility in NMP/$CaCl_2$ solutions is better, so that Mn’s up to 20 kDa can be obtained without posttreatment. Therefore, DuPont adopted later the AKZO procedure for the production of “Kevlar”. Regardless of the reaction mixture, it turned out hat for the spinning of high strength fibers spinning of the “p-polyaramide” from a solution in water-free sulphuric acid is best suited. Depending on concentration and temperature this solution has a liquid-crystalline (lyotropic) character with two benefits. First, the viscosity is relatively low during the spinning process, and second, the poly(p-aramide) chains reach a high level of parallel alignment which optimizes strength and elastic modulus of the fiber. Depending on the degree of orientation, which may be improved by a post-treatment, the elasticity modulus of “Kevlar”/“Twaron” fibers fall into the range of 60–150 kN/m^2 compared to 10 kN/m^2 for “Nomex”.

All polyaramides possess the following properties [38–40]:

(a) Low flammability.
(b) Short-term thermostability up to 500 °C.
(c) Low electric conductivity.
(d) Prone to electrostatic built up (unless finished).
(e) Good resistance to abrasion (like Nylons).
(f) Good resistance to organic solvents.
(g) Relatively high sensitivity to salts and acids.
(h) Sensitivity to UV light.

The poly(p-aramide)s possess the following additional advantages:

(i) Outstanding strength-to-weight properties of the fibers.
(j) High elastic (Young’s) modulus.
(k) High tenacity.
(l) Low creep.
(m) Low melting temperature.

“Nomex” is used in sheet form, but mainly as fiber [25, 38, 39]. The Nomex sheet is calendered paper mostly used for electric insulating purposes. Honeycomb structures combined with a phenolic resin are widely used as fire-proof components in aircraft construction. However, the most important application of “Nomex” results from the combination of low flammability, thermostability, and flexibility of its fabrics. These fabrics and clothes are worn by fire fighters, pilots of racing cars, pilots and crews of military air planes. Their heat resistant clothing (one or more layers) includes shoes, socks, balaclavas, gloves, and hoods.

“Nomex” was and still is widely used in the U.S. space programs, for instance, in the form of airbags for the Mars-Pathfinder and Mars-Exploration-Rover missions.

Since important properties of the poly(p-aramide)s are quite different from those of “Nomex”, most applications are also different. Characteristic are applications as “bullet-proof” body armor, cut-fast gloves, substitute of asbestos, and as reinforcing component in concrete. They are also used as fibers in high performance tires for airplanes and racing cars, or as laminates for the construction of boat hulls. Furthermore, poly(p-aramide)s are used for the production of sports articles, drum heads, brake pads, turbo hoses, optical fiber cables, or electrical–mechanical cables. Their fabrics serve as hot air filters and in combination with “Nomex” for the production of protective clothing and helmets. The total production of polyaramides amounts in 2008 to 60,000 tons.

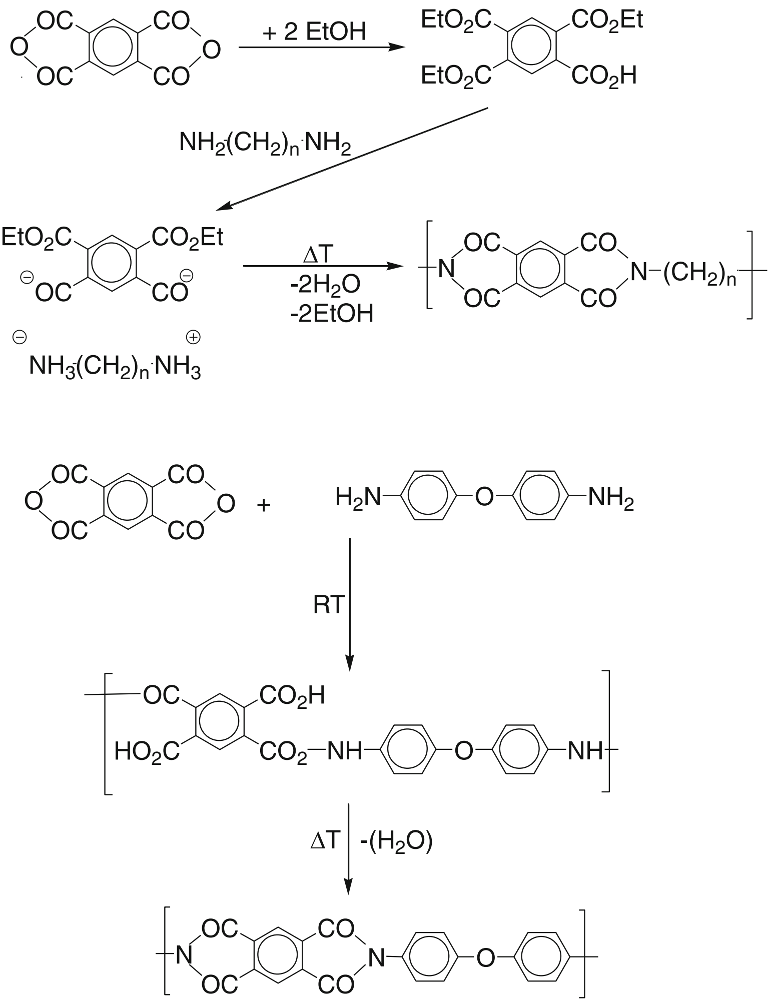
Other heat- and fire resistant fibers were reviewed by Kwolek et al. [40].

6.3 Polyimides

The history of polyimides begins in 1908 with a short note of Bogert and Renshaw [41] who heated 4-aminophthalic anhydride to 200 °C and obtained an intractable material. Systematic and extensive research activities started at DuPont after the end of World War II [42]. W. M. Edwards and somewhat later C. E. Scroog were the leaders of this project [43–48]. The first experiments were based on pyromellitic anhydride (PyAh) and aliphatic diamines and followed the reaction pathway elaborated by Carothers for the preparation of Nylons (see Chap. 3). At first, PyAh was reacted with ethanol and the resulting dicarboxylic acids (two isomers) were combined with the diamines. The resulting diammonium salts eased purification of the monomers and optimized the stoichiometry. Upon heating to the molten state amide groups were formed immediately followed by imidization (see Formula 6.2, top).

This procedure is not well suited for aromatic diamines, because their basicity is 5–6 orders of magnitude lower than that of aliphatic diamines. This problem prompted the elaboration of a new approach which became the standard procedure for the technical production of polyimides (see Formula 6.2, bottom). At first the diamine is directly reacted with the dianhydride yielding a polyamic acid which in most cases is soluble in the reaction medium (e.g., dimethyl acetamide or NMP) [43, 47, 48]. This solution which is useful for casting films, may be stored at − 10 °C for several months. Heating of poly(amic acid)s to 200 °C or better to 250–300 °C promotes the inmidization process the progress of which increases with time and temperature. Structure and thermal properties of several polyimides prepared by the DuPont group before 1964 are compiled in Table 6.3.

The few properties listed in this table illustrate the main advantage of these aromatic polyimides, namely an outstanding thermostability combined with low sensitivity to oxidation. These properties come close to the limits of soluble organic polymers. Probably the most widely used representative of this class of polyimides is poly(4,4′-diaminodiphenyl ether pyrromellitimide), which was



Formula 6.2

commercialized by DuPont as fiber, tape, or lacquer under the name "Kapton"[49]. "Kapton" is used for various purposes in space projects, and for construction of war ships, military airplanes, and rockets. It also serves for various purposes in scientific research, for instance, as X-ray window, because it combines high chemical stability with good transparency for X-ray radiation.

A third synthetic approach which came up in the years 1967–1970 was polycondensation of diisocyanates with tetracarboxylic anhydrides (Formula 6.4, top). Syntheses of phthalimides from phthalic anhydride and isocyanates were known since 1900 [50], but it took more than six decades until this reaction was adopted to the preparation of polyimides [51–55]. This approach is flexible, because it is

Table 6.3 Properties of selected poly(pyromellit imide)s[a]

Diamine	Solubility	Zero strength temperature (°C)	Thermal stability in air	
			275 °C	300 °C
1.3-Diaminobenzone	Conc. H_2SO	900	>1 year	>1 month
1.4-Diaminobenzone	Conc. H_2SO_4	900	>1 year	>1 month
4.4′-Diaminobiphenyl	Fuming HNO_3	>900	–	1 month
4.4′-Diaminodiphenyl methane	Conc. H_2SO_4	800	–	7–10 days
4.4′- Diaminodiphenyl ether	Fuming HNO_3	850	>1 year	>1 month

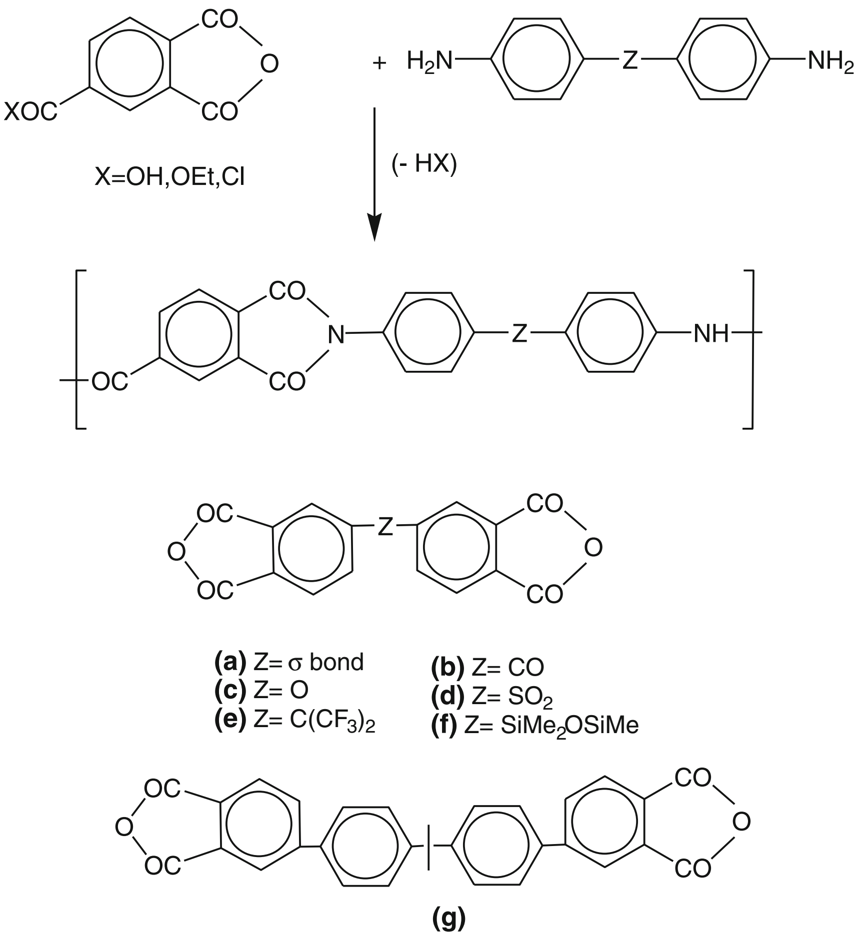
[a] Date taken from Ref. [46]

suited for both, aliphatic and aromatic diisocyanates, and because it may be performed in solution and in the melt. The results depend very much on the structure of the diisocyanates and on the nature of the catalyst, but high molar mass polyimides are difficult to obtain.

In the wake of the pioneering work of DuPont several chemical companies developed polyímides. Thereby, the structure varied over a broad range, either by variation of the diamine or by variation of the dianhydride (see Formula 6.3a–f). Furthermore, various divalent groups were incorporated into the polymer backbone. The three most important classes of modified polyimides are: poly(amide imide)s, poly(ester imide)s, and poly(ether imide)s. The first technical production of a poly(amide imide) was developed by Amoco Co. and a product based on trimellitic acid and p-phenylene diamine was commercialized under the trademark "Torlon"[56]. A family of products with variation of diamine, molecular weight, and additives was finally produced. For application as engineering plastics these poly(amide imide)s are prepared by polycondensation of the diamine with the acid chloride of trimellitic anhydride. Yet, polycondensation of trimellitic anhydride with 4,4′-diisocyanatodiphenyl methane in an inert, aprotic solvent is advantageous, when application as coating or insulating lacquer is intended.

A family of highly thermostable poly(ether imide)s allowing for processing from the melt was commercialized by General Electric in 1982 under the family name "Ultem" [57]. The most widely used member of the Ultem family is seemingly derived from m-phenylene diamine and the dianhydride (g) in Formula 6.3. In addition to the neat poly(ether imide) glass-fiber reinforced composites are offered as engineering plastics. Furthermore, solutions in organic solvents are available for application as lacquers, coatings, and for the casting or extrusion of films. Dozens of poly(ester imide)s with broad variation of their chemical structure were developed and in several cases commercialized as insulating lacquers. A review of this working field was previously published by Lienert in Ref. [58]. Further reviews dealing with a broad variety of polyimides are presented in Refs. [58–66].

Finally, it should be mentioned that the aromatic polyimides were the forerunners of a diversified group of thermostable polymers having heterocyclic moieties in their repeat units, for example, poly(benzimidazole)s, poly(benzoxazole)s, poly(benzthiazole)s, poly(benzobisthiazole)s, poly(1,3,4-oxadiazole)s,



Formula 6.3

poly(1,2,4-triazole)s, and poly(quinoxaline)s. Numerous reviews, book chapters, and books were dedicated to these materials, and the Refs. [38, 62–68] only represent a selection. Furthermore, it should be mentioned that the journal "High Performance Polymers" is focused on syntheses and characterization of polymers having outstanding thermal and mechanical properties.

6.4 Poly(alkylene terephthalate)s

In his papers and patents on aliphatic polyesters Carothers mentioned terephthalic acid as potential reaction partner of α,ω-alkanediols, but a description of a concrete experiment or polyester was never published. Therefore, it is correct that

John R. Whinfield is honored for the invention of poly(ethylene terephthalate), PET [69–71]. Whinfield was born in Sutton, Surrey, UK, in February 1901. He attended Merchant Taylor's School and Caius College in Cambridge studying natural science and chemistry. Afterwards he worked for 1 year without pay in the laboratory of Ch. F. Cross and E. J. Bevan, who had invented the "viscose reaction" for the production of rayon fibers from raw cellulose in 1892. In 1924, Whinfield was hired as a research chemist by the Calico Printers Association in Manchester. He had to care about dying and finishing of fabrics mainly based on cellulose fibers, but beyond his daily duty he had a great interest in synthetic fibers He followed closely the work of Carothers looking for a new fiber that could rival with Nylon-6,6. Since the Tm's of all aliphatic polyesters prepared by Carothers were too low for any application, it was evident that an aromatic or cycloaliphatic monomer was needed as reaction partner. In 1940, he and his assistant James T. Dickson mastered the synthesis of poly(ethylene terephthalate) having a molar mass high enough for fiber spinning. From the properties of the first fibers it was immediately learned that the PET fiber could indeed rival with Nylon-6,6 in terms of Tm, strength, and resilience. A patent was filed in July 1941, but not officially registered. The invention was kept secret, because of its potential utility for the British war industry [70].

The Calico printers Association sold their patent rights to ICI which registered the patent in 1946 [72]. Since October 1929 ICI and DuPont had an agreement to exchange information about patents and research development. On this basis DuPont purchased patent rights from ICI, filed two additional patents in 1949 [73, 74] and commercialized PET fibers under the trademark "Dacron". Whinfield went to work for ICI in 1947 and supervised the development of the "Terylene" fiber. Whinfield was honored as "Commander of the Order of the British Empire" in 1954, he obtained the honorary fellowship of the textile Industry in 1953 and the Perkin Medal in 1956. He died in Dorking, Surrey, in July 1966.

After 1946 the usefulness of PET was not only explored with regard to its fiber properties, but also as a film-forming material and also as engineering plastic [75–77]. Annealed, highly crystalline PET is a hard and rather brittle material, but the rate of crystallization is low. By rapid cooling from the melt elastic more or less transparent films may be obtained containing only small (nano) crystallites. Such PET films were and are used for electric insulation, for magnetic recording tapes, for photographic films and for packaging purposes. Furthermore, highly transparent, high strength films were developed by ICI (trademark "Melinex") and by DuPont (trademark "Mylar") applying a biaxial drawing process. However, in the beginning of the twenty-first century only 10 % of the worldwide PET production goes into film applications, whereas 60 % is used for textile fibers. The remaining 30 % is processed to a broad variety of bottles, which in the case of soft drinks and mineral water have largely replaced the traditional glass bottles. An application of PET as engineering plastic was explored by the Dutch AKZO NV and by the German Hoechst AG after 1960. In 1966–1967 injection-moldable PET was commercialized under the name "Arnitel" and "Hostadur". However, due to the relatively slow crystallization this project was unsuccessful, and the much faster

Table 6.4 Properties of PET, PBT and PPT[a,b]

Property	PET	PBT	PPT
Melting temperature (Tg in °C)	260–265	220–225	225–230
Glass-transition (Tm in °C)	75	40	45
Tensile strength (MPa)	72.5	67.6	56.5
Flexural modules (GPa)	3.11	2.76	2.34
Heat distortion temperature (°C)	65	59	54
Notched impact strength (J/m^2)	37	48	53
Dielectric constant at 1 MHz	0.407	0.393	0.296

[a] Determined by DSC with heating rate at 20 °C/min and depending on the content of ether groups

[b] Data taken from Ref. [79]

crystallizing poly(butylene terephthalate), PBT, proved better suited as engineering plastic.

When the "Whinfield-Dickson patents" expired, numerous chemical companies started with development and commercialization of PBT as an "injection-moldable" engineering plastic [78]. The rapid crystallization of PBT results from rapid conformational changes around the CH_2–CH_2 bonds. This rotation is hindered in PET by unfavorable electronic interactions of the neighboring CO groups. Owing to a lower Tm and Tg (see Table 6.4) the mechanical properties of PBT are inferior to those of PET, but for injection molding the faster crystallization is a decisive advantage. In addition to neat PBT numerous composites (e.g., containing glass fibers), block-copolymers and blends were commercialized. Furthermore, PBT blocks proved to be well suited as hard segments of thermoplastic elastomers.

Although, poly(1,3-propylene terephthalate), PPT, was synthesized by Whinfield and Dickson in 1941, successful commercialization was delayed until 1998 [79]. The main reason for this delay was the high prize of 1,3-propanediol. New technologies of Shell and DEGUSSA (now Evonik, Germany) allowed for a sufficiently cheap production after 1980 and paved the way for the production of PPT. The "Shell polyester" was marketed under the name "Conterra", while DuPont called its polyester Sorona 3GT. Table 6.4 presents a comparison of physical and mechanical data of PET, PBT, and PPT.

6.5 Polycarbonates

First experiments yielding cyclic or oligomeric aromatic carbonates were described in 1898 as reported in Chap. 2. It took more than five decades until high molar mass polycarbonates were invented, but then this invention happened independently in two places within 8 days. Responsible for the first synthesis of poly(bisphneol-A carbonate), PAC, were Hermann Schnell and his coworker Ludwig Bottenbruch, who worked for the Bayer AG in Krefeld-Uerdingen.

H. Schnell was born in Gaienhofen (Baden, Germany) on September 8, 1916 [80]. He studied chemistry at the university of Freiburg i.Br., and gained his Ph.D. under H. Staudinger. After being hired by Bayer AG he worked as researcher for several years in the main laboratory in Leverkusen. In 1953 he became head of a research group at the central laboratory Uerdingen. Only 2 months later he synthesized PAC, which was patented in 1955 and commercialized in 1960 under the trademark "Makrolon". This success was not trivial, because he had to fight for many months and years against the prejudices and enviness of his colleagues, who believed that the chemical, thermal, and mechanical stabilities of PAC do not suffice for long-term applications. Yet, he brought his invention to commercial success and told later: "it is not enough to make an invention, you have to fight to get your invention accepted in the face of all subsequent obstacles." Schnell became later head of the entire polymer research activities of Bayer AG. At the end of his career he was (co)author of more than 400 patents. He earned the "H. Staudinger Medal" in 1970 and the Swinburne Award in 1976. Nine years after his death (September 1999) he was awarded in the USA by introduction into the Plastics Hall of Fame [81].

The second inventor of PAC was Daniel Fox [82]. He graduated with a Ph.D. from the University of Oklahoma in 1952, and was hired by General Electric as a research chemist for the laboratories in Schenectady. At this time his new colleagues were looking for a novel insulating material, but had problems with the hydrolytic stability of their polyesters. Fox had learned during his studies at the university that the carbonate of gujacol was insensitive to hot water. Remembering this experience he began to elaborate a procedure for the preparation of PAC. At first neither Fox nor his colleagues nor his boss were aware of the interesting properties of this new material, but several months later they learned that PAC was unbreakable and filed a patent. From a routine patent search program Fox discovered that surprisingly the Bayer AG had submitted a similar patent. Since neither patent had yet been granted, both companies negotiated the situation and signed an agreement which allowed both companies to produce polycarbonates regardless which company was granted legal priority.

Bayer was able to document that Schnell had made his invention 1 week before Fox. General Electric had to pay royalties until the Bayer patent expired. Nonetheless, Fox received several honors, and in Pittsfield, Massachusetts the Dan Fox drive is named after him [82].

Soon after the first synthesis of PAC the research group of Bayer began to elaborate three different synthetic methods [83–88]:

(1) Interfacial phosgenation of bisphenols (see Chap. 8) [83–85].
(2) Transesterification of bisphenols with excess diphenylcarbonate in the melt around 300 °C [86, 87].
(3) Synthesis of cyclic oligocarbonates by phosgenation in dilute solution followed by ring-opening polymerization in the melt [88].

Characteristic advantages of the first method are colorless products and easy variation of the molar mass over a wide range. Disadvantageous are the use of poisonous phosgene and large amounts of sodium chloride as byproduct. The second method avoids phosgene when diphenylcarbonate is produced from CO or CO_2, but disadvantageous are a high risk of discoloration and branching. The third method is particularly suitable for reaction-injection molding, but it is expensive. A less expensive variant avoiding isolation of individual macrocycles has recently been developed by researchers of General Electric [89].

According to information disclosed by researchers of Bayer AG to the author more than 300 bisphenols were transformed into polycarbonates, but none of these polymers showed a better balance of low costs and useful properties than the polycarbonate of bisphenol-A. Several modifications of PAC were commercialized. Incorporation of bulkier bisphenols, such as 3,3′5,5′-tetramethyl bisphenol-A or 1,1-bis(4-hydroxyphenyl)cyclohexane raises the Tg above 150 °C and reduces the sensitivity to hydrolysis, it also reduces the unusually high impact strength of the parent homopolymer. In corporation of 3,3′5,5′-tetrabromobisphenol-A lowers the flammability and modification of end groups influences the rheological properties.

Characteristic for PAC is a high impact strength, which results from group motions which occur even below 0 °C and transform the impact energy into heat. A consequence of this useful property is applications, such as safety glasses, protective helmets, and unbreakable lenses. Yet, for applications as lenses or visors PAC needs to be coated to reduce its sensitivity to scratches and organic solvents. Numerous physical properties and applications are compiled in Refs. [84, 85, 90, 91].

Finally, it should be mentioned that even before H. Schnell was elected to the plastic Hall of Fame, a former coworker, Dieter Freitag had received this Honor. D. Freitag invented a polycarbonate suited for rapid injection moulding, and on the basis of this invention billions of compact discs were produced worldwide. Another achievement was the development of aromatic poly(ester carbonate)s, APECs. D. Freitag was born in Offenbach (Germany) were he grew up. He studied chemistry in Freiburg i.Br. and Frankfurt a. M., where he received the doctor’s degree in 1967. Immediately afterwards he started his career at Bayer AG, where he spent over 30 years. His career proceeded from the role of Group Leader to the Director of Research and development of the Plastic Business and ultimately to the Head of Bayers material Research Department. After his retirement in 2001, he joined the Triton Systems (USA) as Chief Technical Officer and developed with his new team the technical production of Polyphosphonates, an extremely flame retardant class of engineering plastics and additives which is now produced in more than six countries. He received numerous honors and awards, for instance, the Otto Bayer Medal and the Herrmann Mark Medal [92, 93].

6.6 Aromatic Polyethers

6.6.1 Poly(phenylene oxide)s

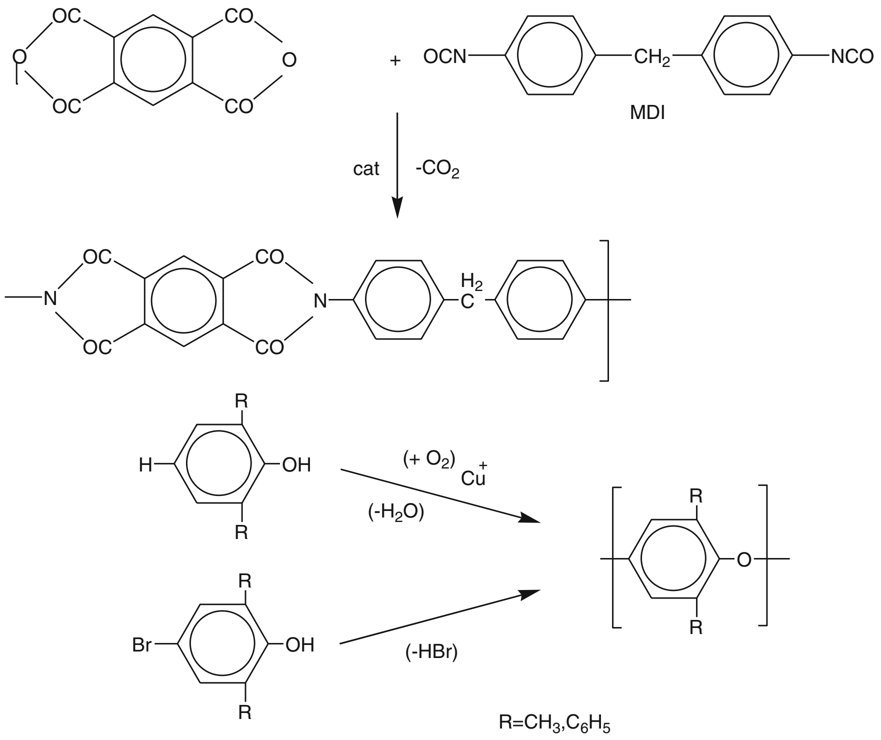
Four groups of aromatic polyethers are commercial: poly(phenylene oxide)s, poly(ether sulfone)s, poly(ether ketone)s, and poly(ether imide)s. Since poly(ether imide)s were presented in Sect. 6.3, this subchapter is focused on the first three groups of polyethers. Research on aromatic polyethers began in several chemical companies in the late 1950s or early 1960s. The first polyether, which was technically produced was poly(2,6-dimethyl-1,4-phenylene oxide) usually called poly(phenylene oxide) or PPO (commercialized in 1960). An unusual but technically feasible synthesis (for details see Chap. 8) was invented by Allan S. Hay in 1956, who was research chemist of G(eneral) E(lectric) in Schenectady (New York, USA) at that time [94]. Hay was born in July 1929 in Edmonton, Alberta (Canada). He studied chemistry at the University of Alberta up to the M.Sc. level, but gained the Ph.D. from the University of Illinois in 1955. Still in the same year he was hired by GE as research chemist and advanced to the position of manager of the Chemical Laboratories of the Research and Development Center. Since 1975, he was Adjunct Professor of the Polymer Science and Engineering Department of the University of Massachusetts in Amherst. After 1980, he left GE and took a professor position at the McGill University in Montreal. He contributed to the development of polyformals and poly(ether imide)s and received several honors and awards, for instance, the Carothers Award in 1985 [94, 95].

PPO is difficult to process due to its high melt viscosity, its methyl groups are sensitive to oxidation above 150 °C and its synthesis is relatively expensive. Therefore, the commercialization of neat PPO was not much successful, but PPO showed the unusual property to be miscible with polystyrene. Hence, PPO mainly serves as reinforcing component of polystyrene, and these blends were and are commercialized by GE under the Trademark “Noryl” [96].

Another polyether, which was commercialized by the Dutch ENKA NV under the name “Tenax” is poly(2,6-dipheyl-1,4-phenylene oxide) [97]. This polyether has a significantly higher crystallinity, thermostability, and oxidative stability than PPO. It is a niche product produced in the form of films or fibers. In addition to the oxidation of phenols with O_2 (catalyzed by Cu ions) several other methods were explored for the preparation of poly(phenylene oxide)s [98] (Formula 6.4, bottom).

6.6.2 Poly(ether solfone)s, PES’s

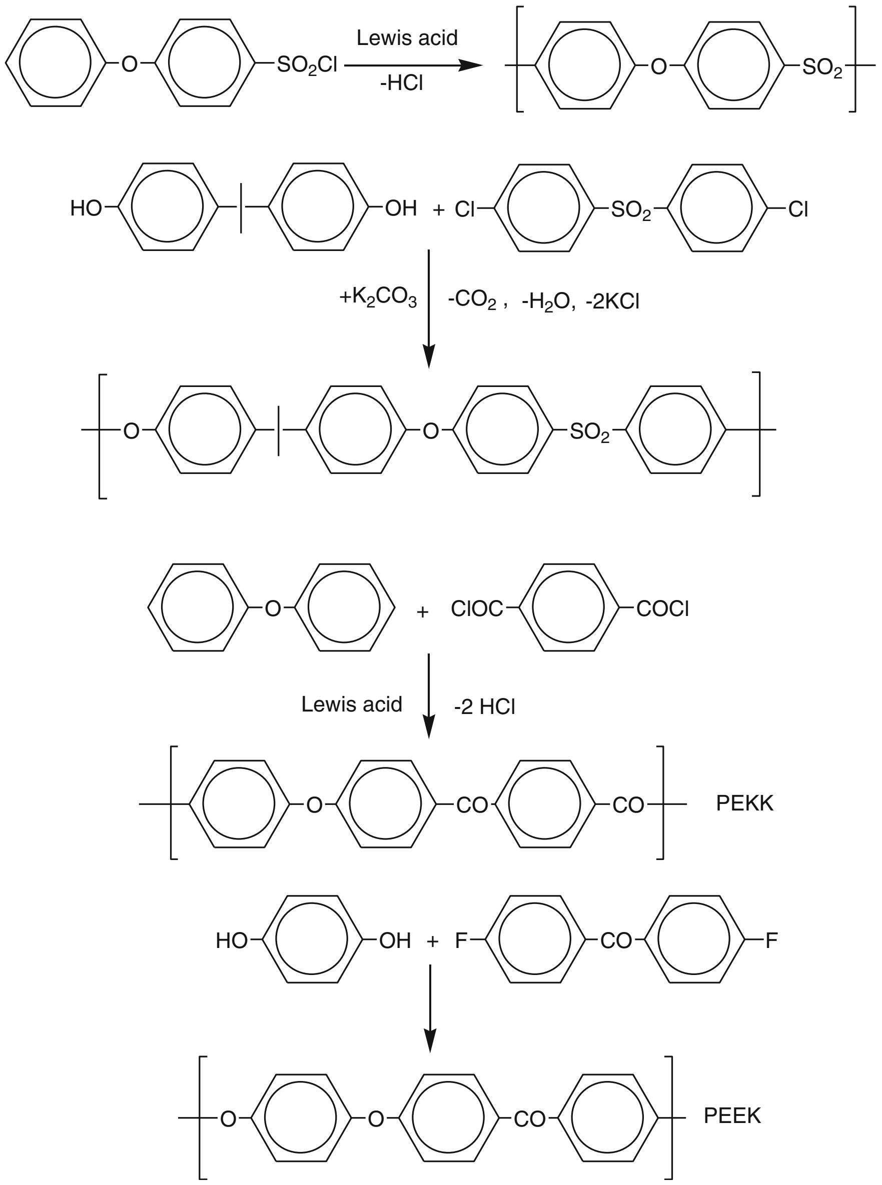
Syntheses and properties of PES’s were explored in the 1960 s by Union Carbide (USA), 3 M Corp (USA), and ICI plc (UK) [99–101]. Nearly at the same time. Two quite different synthetic strategies were elaborated, namely a Friedel–Crafts type polysulfonylation process (see Formula 6.5) and a nucleophilic substitution of 4,4′-



Formula 6.4

dichlorodiphenylsulfone by various diphenols (see Formula 6.5, “Udel”). The sulfonylation requires dry, polar, and expensive solvents (e.g., nitrobenzene) and may involve branching due to substitution of an ortho-position relative to the C–O bond. Therefore, all commercial PES’s were eventually produced by the nucleophilic substitution approach [98], which was first elaborated by Farnham and Johnson [98].

The most widely used PES seems to be “Udel”. This PES, based on bisphenol-A, was originally commercialized by Union Carbide around 1965. In 1977, Union Carbide also marketed a PES based on 4,4′-dihydroxybophenyl under the name “Radel”. Its production was taken over by AmocoCorp. in 1990. A similar PES was also commercialized by 3 M Corp. in 1967 under the trademark “Astrel”, but because of patent problems its production was abandoned in the late 1970 s, and the production rights were sold to Carborundum Corp. ICI had at first commercialized a PES named “Victrex 2000P” which had the structure outlined in the first line of Formula 6.5. Later a PES containing biphenyl units was commercialized under the name “Victrex 720 P” in competition to “Radel”. A patent war with Carborundum Corp. was solved in favor of ICI. Afterwards, Carborundum took a license of ICI and on the basis of the production rights purchased from 3 M continued the production of “Astrel” [102, 103].



Formulas 6.5

PES's are amorphous materials, because the bond angle of the SO_2 group is more than 10° smaller than that of the ether group (122–124°). Depending of the diphenol used as reaction partner of 4,4′-dichlorodiphenylsulfone the glass-transition may vary from 170 to 270 °C (see Table 6.5). PES's almost exclusively

Table 6.5 Influence of the diphenol (used as reaction partner of dichlorodiphenylsulfone) on the glass-transition[a]

Diphenol	Tg (°C)[b]
4,4′-Dihydroxydiphenyl oxide	170
4,4′-Dihydroxydiphenyl sulfide	175
4,4′-Dihydroxydiphenyl methane	180
Bis(4-hydroxyphenyl)propane	185
Hydroquinone	200
Bis(4-hydroxyphenyl)hexafluoropropane	205
4,4′-Dihydroxy benzophenone	205
4,4′-Dihydroxydiphenyl sulfone	220
4,4′-Dihydroxydiphenyl	220

[a] Data taken from Ref. [102]

[b] DSC onset values; the point of inflection is 5–10 °C higher

serve as engineering plastics and compete with aromatic polycarbonates and amorphous polyamides (see Sects. 6.1 and 6.5). The stability toward oxidation and the thermostability are higher, so that processing up to temperatures near 400 °C is feasible, and long-term service temperatures may be as high as 240 °C. The stability against alkaline or acidic water is again higher than that of the competitors, but the sensitivity to an attack of organic solvents is higher than that of polyamides. In other words, each group of engineering plastics has its characteristic advantages and applications.

6.6.3 Poly(ether ketone)s, PEK's

Although the first approach to syntheses of poly(ether ketone)s dates back to the years 1962–1964 [104, 105], it took more than 15 years until the first poly(ether ketone) labelled PEEK, was commercialized by ICI (1979). The first synthesis of a PEK was realized by a Friedel–Crafts type polyacylation either via 4-phenoxybenzoyl chloride or from diphenyl ether and terephthaloyl chloride (see Formula 6.5). Quite analogous to the Friedel–Crafts type synthesis of PES's this approach is unfavorable for a technical production, because expensive dry solvents (e.g., H_2F_2) are needed, and because branching may occur. The alternative approach, the nucleophilic substitution of aromatic difluoroketones by diphenols under basic conditions, was first elaborated by a research group of ICI [106]. The most widely used PEK, the poly(ether ether ketone) PEEK is produced by polycondensation of hydroquinone and 4,4′-difluorobenzophenone in the presence of K_2CO_3 (see Formula 6.5, bottom). Unfortunately, the expensive difluoroketone cannot be replaced by 4,4′-dichlorobenzophenone, because dichloroketone is not reactive enough.

In contrast to PES's, PEK's are crystalline engineering plastics having melting temperatures in the range of 320–420 °C. The tendency to crystallize is based on the fact that bond angles and steric demands of ether and keto group are quite similar.

Furthermore, unsubstituted para-linked benzene rings are required as building blocks. Whereas the chemical and thermal stabilities are quite similar to those of PES's, the crystallinity results in higher heat-deflection temperatures. However, PEK's are sensitive to UV light like all aromatic ketones. Carbon-fiber reinforced PEEK can rival with steel in terms of stiffness, toughness, and elastic modulus at a significantly lower weight. Further information on syntheses, modification, properties, and applications are available from review articles [98, 107–109].

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Part II
New Results

Chapter 7
The Role of Cyclization and a New Theory of Polycondensation

7.1 New Theoretical Concepts

Flory's original theory of step-growth polymerization as it was presented 1946 in Chem. Rev. [1] had two short-comings. First, it ignored any influence of intramolecular reactions, and second, in his mathematical equations he did not differentiate between KC and TC polycondensations, because in the absence of cyclization such a differentiation is not necessary. As discussed in Chap 5, the first revision was published in 1950 by Jacobson and Stockmayer [2, 3]. In his book "Principles of Polymer Chemistry" Flory accepted (and even enlarged) the J–S theory (see Sect. 5.3), and from this time on differentiation between KC and TC polycondensations as well as formation by cyclic oligomers via "back-biting" became established components of the theory of polycondensation. Nonetheless, Flory remained reluctant to accept a significant role of end-to-end cyclization (end-biting), he did not revise his calculation of polydispersity, and he did not extend the new insight into two-dimensional polycondensations to three-dimensional ones.

First experimental and theoretical studies dealing with a permanent competition of cyclization and chain growth in KC polycondensations were published by Stoll et al. [4–9]. Starting out from the synthesis of ambrettolide, a 17 membered unsaturated lactone (having an intensive odor), Stoll et al. launched a comprehensive research project on ring closure and polycondensation of ω-hydroxyalkane-α-carboxylic acids. Monomers having up to 23 carbon atoms in the chain were examined (see Sect. 7.2). Stoll et al. formulated for the first time a reaction scheme based on a permanent competition of intra- and intermolecular condensation steps (see Formula 7.1). Flory ignored this scheme, although he discussed the results of Stoll et al. in terms of cyclization constants versus ring size [10, pp. 96, 97]. Stoll et al. analyzed their results from a kinetic point of view. They expressed the total rate of esterification in Eq. (7.1), where L means the rate of cyclization of the monomer and ΣP means the sum of cyclization rates of all oligomers and polymers plus the reaction rates of chain growth steps. This second sum was termed αP and correlated with L according to Eq. (7.2). The ratio $L/\alpha P$ was called degree of cyclization and corresponds to the experimentally determined

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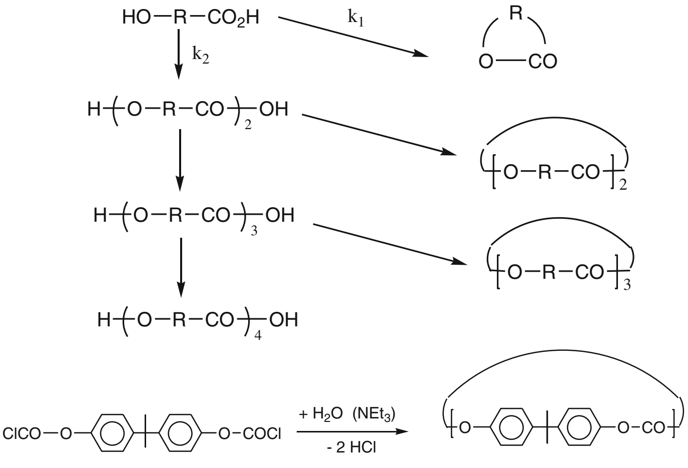
quotient: yield lactone/yield linear chains. Equation (7.2) indicates that the rate of cyclization (lactonization) L decreases with the monomer concentration c, in agreement with the Ruggli-Ziegler Dilution Principle (not cited by Stoll et al.). Those authors also defined a cyclization constant C as quotient of the monomolecular and bimolecular rate constants ($C = k_1/k_2$). The correlation of this cyclization constant with the yield of lactones is expressed in Eq. (7.3). The experimental results confirmed that the yields of lactones decreased with lower monomer concentrations, whereas C was independent of the concentration, but dependent on monomer structure, temperature, and reaction medium [5, 7, 9].

$$\mathrm{d}x/\mathrm{d}t = L + \sum P \tag{7.1}$$

$$\begin{gathered} L/\alpha P = K_1/K_2(1/c) \\ \text{with } \alpha P = k_2 C^2 \text{ and } c = \text{initial monomer concentration (IMC)} \end{gathered} \tag{7.2}$$

$$\%\mathrm{Lactone} = 100C/(C + c) \tag{7.3}$$

More than three decades later, Morawetz and Goodman [11] published a revision of the "Stoll-Rouve concept" saying: "The procedure of Stoll et al. is in error for two reasons. First, it disregards the fact that a single monomer disappears in the cyclization, while two monomers are consumed up in the intermolecular condensation. Second it neglects the disappearance of the monomer by reaction with the functional groups of the ends of the polymer chains". From their calculations they concluded: "It may be seen that the cyclization constants estimated by Stoll et al. from experimental *L/αP* values are too low by a factor which varies from 5 to 2.5 as *L/αP* increases from 0.01 to 2.0. However, the numerical correction does not devaluate the important concept of Stoll et al."



Formula 7.1

Morawetz et al. also presented another interesting contribution to the calculation of C. They started out from Kuhn's random flight theory of a coiled flexible chain which allows one to calculate the probability that one end group is directly neighboring the second end group of the same chain. This probability is, in turn, identical with C in Stoll's work. The largest ring studied by Stoll et al. (24 ring members) was considered, and the average end-to-end distance of an aliphatic chain of 24 atoms was taken from Flory's statistical calculations [12]. Using Eq. (7.4), where N_A is Avogadro's number and $<h^2>$ the mean square end-to-end distance, a C value of 0.1 was calculated, whereas $C = 0.007$ was calculated from the experimental data of Stoll et al. Among several arguments presented to explain this conspicuous difference, one argument is of general importance. Kuhn's model was designed for long flexible polymer chains under theta conditions, and thus, is not good model for oligomers and ignores the role of solvation.

$$C = (1000/N_A)\left(3/2\pi{<}h^2>\right)^{3/2} \tag{7.4}$$

$$<h^2> \; = K_{\mathrm{ch}} \times b'^2 = nl^2 \tag{7.5}$$

with n = number of skeletal bonds and l = bond length

$$\mathrm{d}[C_i]/\mathrm{d}t = [K_{\mathrm{intra}}][M_i] \quad \text{with } i = 1,\, 2,\, 3, \ldots, n \tag{7.6}$$

and with C_i and M_i = i-meric cyclic and linear oligomers

$$\mathrm{d}[M_i]/\mathrm{d}t = [K_{\mathrm{intra}}][M_i] - K_{\mathrm{inter}} \sum [M_j]\,[M_{i-j}] + 2K_{\mathrm{inter}}[M_j]S[M_j] \tag{7.7}$$

$$\mathrm{d}[C_i]/\mathrm{d}t' = \mathrm{EM}[M_i] \tag{7.8}$$

The weak point in the kinetic concept of Morawetz et al. was the assumption that cyclization of oligomers and polymers do not need to be considered. This short-coming was revised in the work of Mandolini et al. [13–15] who demonstrated that the cyclization factor C_1 of the monomer (M_1) depends on the cyclization factors of the oligomers and vice versa. However, the main purpose of their work was different and defined as follows: "We now describe a more refined approximation treatment, where the formation of both, linear and cyclic oligomers with DP's up to 12 is taken into account. The procedure involves the microcomputer-assisted numerical integration of the proper system of differential rate equations by the simple Euler method [16]".

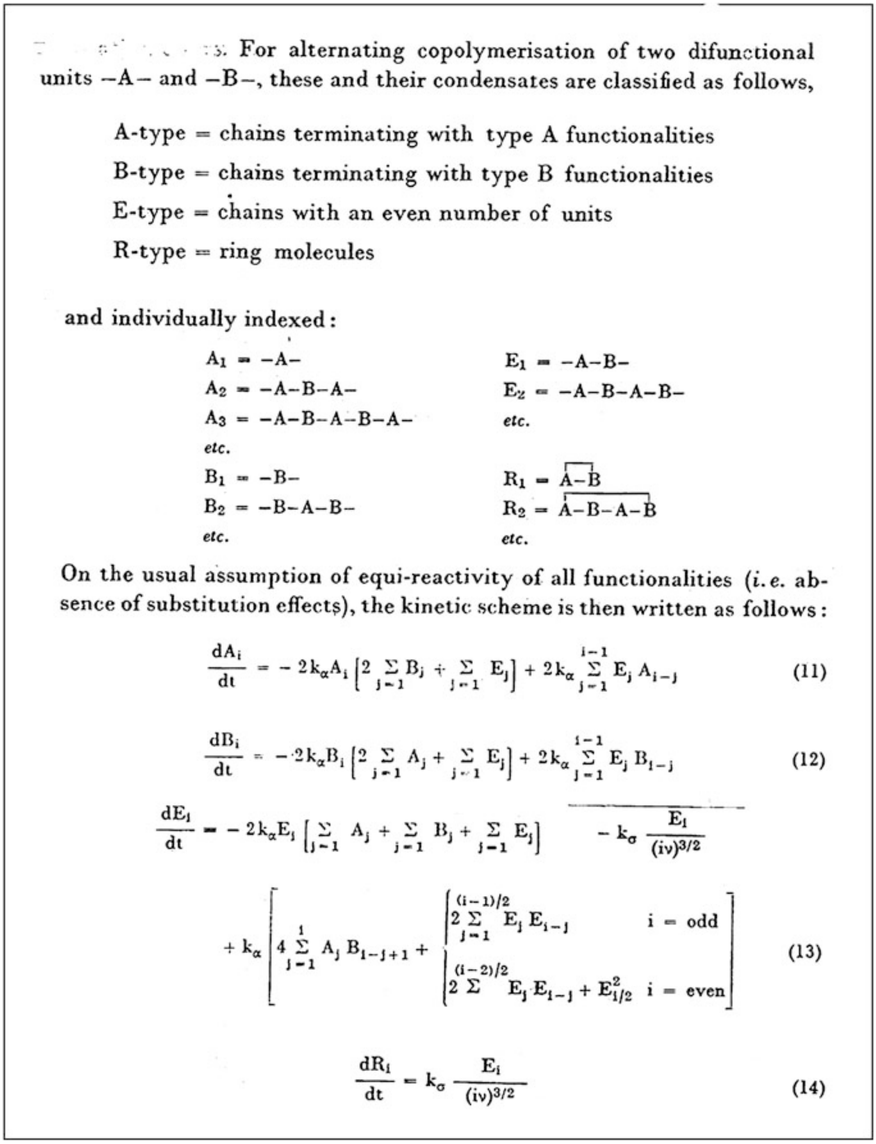
Mandolini et al. started out from the rate equations (7.6) and (7.7). These equations were simplified by a change of the time scale ($t' = ft$) so that the numerical values of the rate constants called EM (effective molarity), which in the case of the monomer EM_1 is identical with the cyclization constant C in Stoll's work. EM_1 was arbitrarily selected, and the consequences for the EMs of the higher oligomers were computed (and listed in tables). EM_2 was taken from the literature, and the higher EMs were calculated from Eqs. (7.4) and (7.5), where Kuhn's random flight model comes into the play. In Eq. (7.5) the mean square chain end distance is related to the number x and effective segment length b' (a measure of chain stiffness) via the so-called characteristic ratio K_{ch} [15]. With these data in hand Mandolini et al. were able to demonstrate how the yields of cyclic oligomers depend on EM_1, on the IMC and on the ring size. At this point it should be noted that calculations of EM values from Eqs. (7.4) and (7.5) were later also used by other research groups [17, 18] to find promising reaction conditions for the cyclization of preformed difunctional polymers, such as dianionic polystyrene.

Mathematical modeling of a complete KC step-growth polymerization involving permanent ring-chain competition was first started by Gordon et al. [19–25] and almost at the same time by Stepto et al. [26–28]. Both groups used different mathematical methods, but reached the same conclusions. Gordon et al. originally explored a method for calculating molecular parameters in irreversible step-growth polymerizations using the theory of stochastic branching processes [19]. This "cascade theory" is originally limited to systems where ring closure cannot occur. In such systems molecules may be pictured as "family trees". An arbitrarily selected monomer serves as the root and the units directly connected to this root represent the first generation and so on. Since roots are picked at random, the trees are absolutely statistical in nature, and meaning and usefulness of these trees were described as follows: "The chemical and physical properties of molecules consisting of atoms (or structural units) connected by freely rotating bonds can often be calculated with more than adequate accuracy by taking their structures as molecular graphs or more explicitly, as existing in their graph-like states" [20–22].

In order to take cyclization into account, the original cascade model was modified. Intermolecularly reacted functionalities were labeled α', unreacted functionalities ω', and ring closing functionalities σ'. The rings were incorporated into the graph-like tree structures by formal cleavage of the rings and treatment of the new chain end as dead functionalities (maintaining the σ label). The trees containing the randomly distributed s-functionalities were called "spanning trees" and the entire procedure was called "spanning tree model." This model was at first elaborated for three-dimensional polycondensations ($a_2 + b_n$) [22, 23] and later adopted to two-dimensional polycondensations [24]. Gordon and Temple formulated their model via probability generating functions, a mathematical tool, which is not inherent in the "spanning-tree model" and can be replaced by another mathematical approach (see papers of Valles et al. below). Those authors also elaborated an exact kinetic approach based on the formulas and equations summarized in Scheme 7.1. This approach is based on three premisses:

(1) The reactivities of the functional (end) groups are independent on the size of the molecules.
(2) Gaussian chain statistics as expressed by Eqs. (7.4) and (7.5) is valid.
(3) Excluded volume effects are neglected.

The accuracy of the kinetic approach depends on the truncation of the, in principle, endless series of condensation steps included in the computation of



[illegible] For alternating copolymerisation of two difunctional units –A– and –B–, these and their condensates are classified as follows,

A-type = chains terminating with type A functionalities
B-type = chains terminating with type B functionalities
E-type = chains with an even number of units
R-type = ring molecules

and individually indexed:

A_1 = –A–
A_2 = –A–B–A–
A_3 = –A–B–A–B–A–
etc.
B_1 = –B–
B_2 = –B–A–B–
etc.

E_1 = –A–B–
E_2 = –A–B–A–B–
etc.
$R_1 = \overline{A-B}$
$R_2 = \overline{A-B-A-B}$
etc.

On the usual assumption of equi-reactivity of all functionalities (*i.e.* absence of substitution effects), the kinetic scheme is then written as follows:

$$\frac{dA_i}{dt} = -2k_\alpha A_i\left[2\sum_{j=1} B_j + \sum_{j=1} E_j\right] + 2k_\alpha \sum_{j=1}^{i-1} E_j A_{i-j} \tag{11}$$

$$\frac{dB_i}{dt} = -2k_\alpha B_i\left[2\sum_{j=1} A_j + \sum_{j=1} E_j\right] + 2k_\alpha \sum_{j=1}^{i-1} E_j B_{i-j} \tag{12}$$

$$\begin{aligned}\frac{dE_i}{dt} = {} & -2k_\alpha E_i\left[\sum_{j=1} A_j + \sum_{j=1} B_j + \sum_{j=1} E_j\right] \qquad \overline{\qquad - k_\sigma \frac{E_i}{(iv)^{3/2}}} \\ & + k_\alpha\left[4\sum_{j=1}^{i} A_j B_{i-j+1} + \begin{cases} 2\sum\limits_{j=1}^{(i-1)/2} E_j E_{i-j} & i = \text{odd} \\ 2\sum\limits^{(i-2)/2} E_j E_{i-j} + E_{i/2}^2 & i = \text{even}\end{cases}\right]\end{aligned} \tag{13}$$

$$\frac{dR_i}{dt} = k_\sigma \frac{E_i}{(iv)^{3/2}} \tag{14}$$

Scheme 7.1 The exact kinetic approach of M. Gordon and W. B. Temple [24]

Eqs. (11), (12), and (13) in Scheme 7.1. Gordon et al. used about 400 equations despite the low computer capacity at that time. The good agreement of the results obtained by the spanning-tree and the kinetic approach is demonstrated in Fig. 7.1, which illustrates the dependence of the number of rings on the conversion plotted for three different IMCs. Both series of curves, solid lines and dots, also illustrate the RZDP, and more importantly, they suggest that the number of rings tends toward 100 % at 100 % conversion. Gordon and Temple also compared their results to those obtained with the method of Kilb [29],who had adapted the Jacobson–Stockmayer theory of TC polymerizations to KC polymerizations, but a considerably higher accuracy of the exact kinetic approach was found. Furthermore, Gordon and Temple compared their calculations with the experimental results of Stepto et al., who synthesized cyclic polyurethanes from oligo(ethylene glycol)s and 1,6-hexamethylene diisdocyanate [26] (see Fig. 7.2 and the next sections). An acceptable agreement between theoretical and experimental results was realized [25].

The work of Stepto et al. [26–28] included two aspects, namely, the aforementioned experimental work and the theoretical work based on the so-called “rate theory” [27, 28]. The rate theory involves a set of kinetic differential equations, which are based on the time dependence of the concentrations of monomers and reaction products. In Stepto’s approach the time dependence is converted into a dependence on the conversion. At first, the “rate theory” was elaborated for three-dimensional polycondensations excluding a significant influence of cyclization, and later, extended to two-dimensional polycondensations including cyclization. A detailed description of the complex equations is beyond the scope of this chapter, which is focused on the discussion of the consequences of Stepto’s work. Three results are particularly important:

(1) When the number of rings was plotted against the conversion, a satisfactory agreement of computed and experimental data (Fig. 7.2) was found.
(2) At a fixed conversion, the number of rings increases with decreasing IMC as predicted by the Ruggli-Ziegler Dilution Principle (RZDP).
(3) Regardless of the IMC, the number of rings approaches 100 %, when the conversion approaches 100 % (see Ref. [28, Figure 2]).

The latter result agreeing with Gordon and Temples calculations displayed in Fig. 7.1 is particular important, because it represents a revolution of Flory’s classical theory of step-growth polymerization. According to the theory of Gordon et al. and Stepto et al. the final aim of a any step-growth polymerization in the melt or in solution is the formation of cyclic polymers, and the linear chains are the reactive intermediates, whereas in Flory’s theory the linear chains are the sole reaction products, and one giant chain is the final reaction product at $p_{\max}$. Unfortunately, Gordon’s and Stepto’s work was not accepted by the international community of polymer chemists, and papers citing their work are hard to find. Two reasons account for this situation. First, further experimental results confirming their theory were missing for many years. Second, neither Gordon et al. [24, 25] nor Stepto et al. [28] developed a complete theory of step-growth polymerizations, because they did not elaborate new equations substituting Flory’s equations for DPn, number and mass distribution and dispersity.

This gap was partially closed by the work of Valles et al. [30, 31] and Fawcett et al. [32–34]. About the content of their first paper Valles et al. wrote [32]: “Mathematical models of kinetically controlled random copolymerizations with

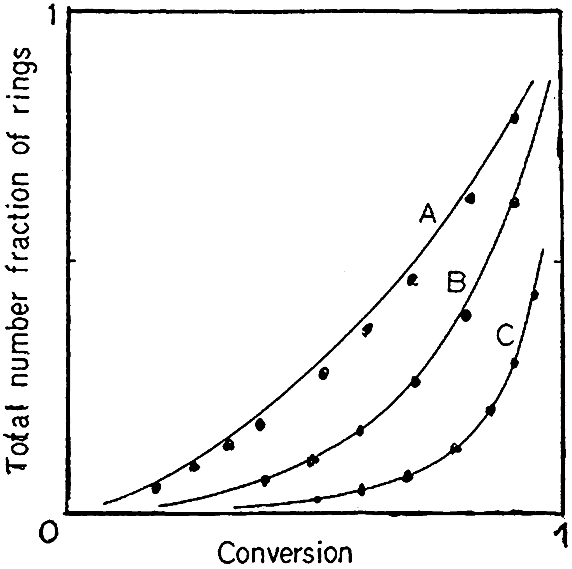


Fig. 7.1 Number fraction of rings versus conversion "*p*" calculated for three different IMCs. Comparison of the exact kinetic method (*solid lines*) and spanning tree method (*dots*). Reproduced from Ref. [24, Fig. 5] with permission (Copyright: Wiley–VCH Verlag GmbH&Co KGaA)

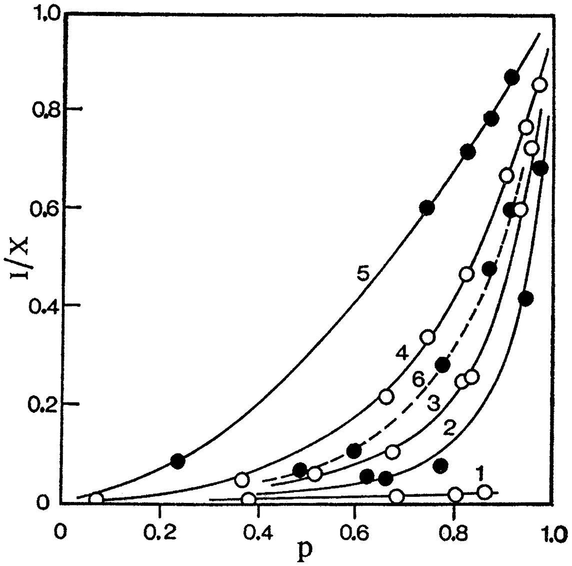


Fig. 7.2 Number fraction of rings versus conversion "*p*" determined from equimolar reactions of 1,6-hexamethylene diisocyanate and PEG-200 (*solid lines*) or PEG-400 (*dashed line*) with variation of the IMC. Reproduced from Ref. [26, Fig. 3] with permission (Copyright Wiley–VCH Verlag GmbH&Co KGaA)

intramolecular reactions have been developed for $a_2 + b_2$ and $a_2 + b_3$ type reactions, in which the b_2 monomer is long and flexible enough to have a Gaussian end-to-end distance. Concentrations of different molecular species are calculated as well as weight-average molecular weight, gel point, and various network parameters. The calculations show the influence and the concentration of reactants on the amount of intramolecular reaction. The results indicate had the main deviations from ideality are due to the smaller rings.

Whereas this first paper was dedicated to a special class of monomers, the second paper compares three models of KC step-growth polymerizations involving end-to-end cyclization. The first model called “reference model”, because the first version of this model which came closest to the reality, was used as reference for the other (simplified) versions and for other models. The reference model is, in principle a kinetic approach analogous to the kinetic model of Gordon and Temple (Scheme 7.1) [24, 25]. Valles et al. used a simplification for the mathematical evaluation called “kinetic-recursive method” which combines kinetic and Markovian analyses [35]. About the limitation of this reference model those authors wrote: “The main approximation of the method lies in the assumption that rings of order greater than N are not important. By taking a large enough N we can get a good approximation to the true answer. We calculated the weight distribution of species for all the arbitrary chemical systems in this paper using increasing values of N until no further change could be achieved. Depending on the system and the degree of dilution the required value of N ranged from 10 to 40”.

In a second version of the reference model the exactly calculated rings were limited to $N = 3$ and this version was termed “Limited Number of Rings” model (LNR): The third version called “hybride” model the first three or four rings were exactly calculated, and an approximation to calculate the larger rings was added. The most important aspect of the work of Valles et al. is the comparison of the “reference model” (first version) with the “spanning tree model” and with the “rate theory”. For this comparison the mathematical evaluation of those models was simplified by the recursive method, but the results were identical with those obtained by Gordon et al. [24, 25] or by Stepto et al. [28]. All comparisons were illustrated in two ways:

(A) by plotting the number of rings against the conversion,
(B) by plotting the weight fraction against DP.

The consequences of these comparisons were illustrated in numerous figures, but unfortunately, the equations used for most calculations of those diagrams were not given. Two important results were obtained by the “reference method” (first version). First, the weight distribution will be bimodal with a first maximum for the small rings. Second, in the low molar mass region, the number of odd-membered chains is slightly greater than that of even membered ones (Fig. 7.3). This effect was explained by considering that (in the case of $a_2 + b_2$ polycondensations) only the even-membered chains can cyclize. Cyclization of short chains is particularly efficient, and the concentration of the even-membered chains is not rapidly enough restored by intermolecular condensations of a- and b-terminated odd-membered chains. This argumentation sounds logic, but the experimental evidence is still lacking. In summary, Valles et al. concluded: “We have found that for this linear system (i.e., $a_2 + b_2$) some approximation never give good results, others may be used when ring formation is low, and the better ones may be applied

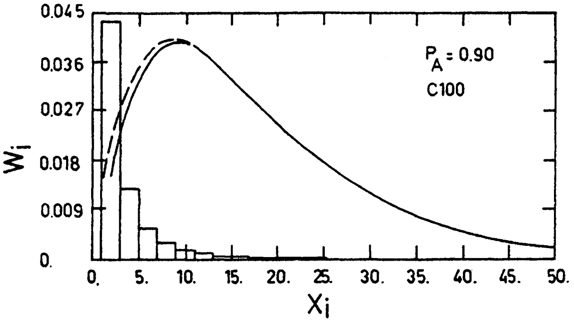


Fig. 7.3 Weight fraction against degree of polymerization (x_i) calculated via the reference model: even-numbered chains (*full lines*), odd-numbered chains (*dashed lines*) and rings (*bars*). Reprinted from Ref. [34, Fig. 12] with permission (Copyright 1990, American Chemical Society)

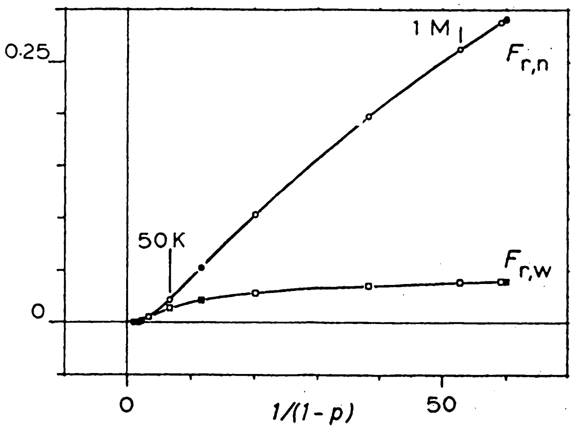


Fig. 7.4 Number (F_{rn}) and weight fraction (F_{rw}) of rings versus t the Carothers Equation as the polycondensation proceeds. Reprinted from Ref. [34, Fig. 2] with permission (Copyright 1995, American Chemical Society)

with low to moderate levels of intramolecular reactions. None of them is satisfactory when ring formation is very high".

In three publications Fawcett et al. [32–34] simulated the ring-chain competition in KC step-growth polymerizations by means of the Monte Carlo method. At first [32, 33], the molecules were arranged on a two-dimensional lattice, finally on a three-dimensional one [34]. The evolution of rings and chains with increasing reaction time was analyzed under the following restrictions: the size of the lattice was limited, any kind of conformational change was permitted, but the individual molecules were fixed To a certain site of the lattice, the maximum conversion at the end of the simulation was 98.3 % and solvent was not present. Despite these limitations the following interesting results were obtained. First, cyclization begins around 50 % conversion, because the concentration of oligomers is too low at lower conversions. However, this conclusion is not quite correct, because at 50 % conversion 25 % of the monomers have formed dimers and another 25 % has formed higher oligomers (in the absence of cyclization). If dimers cyclize rapidly, as usual, cyclization begins far below 50 % conversion. Second, as illustrated in Fig. 7.4, the number fraction of the rings increases more rapidly than the weight fraction, because their average molar mass is lower than that of the chain fraction (the numeric difference may reach a factor of 10). This aspect is of interest for the proper understanding of analytical measurements, because number fraction is reflected in MALDI-TOF mass spectra and the weight fraction on SEC measurements. For 98.3 % conversion a number fraction of 29.1 % along with a weight fraction of 5.7 % was calculated by Fawcett et al. These values seem to be too high, when compared to the calculations of Stepto et al. [28] for polycondensations in bulk. In agreement with the influence of self-dilution [36], the vast majority of the rings is formed above 98 % conversion (see Sect. 5.4 and discussion below). Third, Fawcett et al. [34] calculated a dispersity of 2.77 for the complete reaction product, and thus, postulated for the first time, that Flory's formula ($D = 1 + p$) is far from correct, when cyclization competes with chain growth. As will be noted in the next subchapter, the experimental D values are frequently even higher than 3. Fourth, for the number distribution of rings an exponent of −2.65 was found (Eq. (7.9)), quite similar to the exponent of −2.5 for higher cyclic oligomers in TC polycondensations (see Sect. 5.2).

$$Nr = A_o \mathrm{DP}^{-2.5} \tag{7.9}$$

$$W_{cn} = N_{c,0}(1 - p_c)2np_c^{n-1} \tag{7.10}$$

$$[La]_p = [La]_0(1 - p) \quad \text{with La = all linear species incl. monomers} \tag{7.11}$$

The Monte Carlo simulations also revealed new results concerning number and mass distribution of the linear chains. As illustrated in Fig. 7.5, the Monte Carlo data deviate slightly from the weight distribution calculated via Eq. (7.10). In this equation, proposed by Flory for the linear chains in TC polycondensations (see Sect. 5.3) p_c is the conversion of the linear chins alone. Even more conspicuous is the finding that the number of linear oligomers (X_n in Fig. 7.5) almost disappears at high conversions. Fawcett et al. explain this depletion of the short chains by a high probability of cyclization combined with molar concentration of the reaction partners due to their self-dilution (Eq. (7.11)) [35]. Experimental evidence and a mathematical formula exactly describing the number (and weight) distribution of linear chains in KC polycondensations were lacking until the end of 2012. However, it is obvious that when the "depletion effect" calculated by Fawcett et al. [34] is real, Flory's equations (e.g., Eq. (7.9)) doe not correctly describe KC step-growth polymerizations. Unfortunately, Fawcett et al. totally ignored the works of Gordon et al., Stepto et al. and Valles et al., so that no comparison with their theoretical or experimental results is available.

Irzhak et al. [36, 37] contributed two papers dealing with ring-chain competition in non-ideal KC polymerizations. The consequences for the number and mass distributions of the reaction products were discussed. Furthermore, six publications should be mentioned [38–43] reporting on the diffusion control of the rates of cyclization reactions. Yet, the course of KC polycondensations was not discussed. Furthermore, it should be mentioned that several authors have published

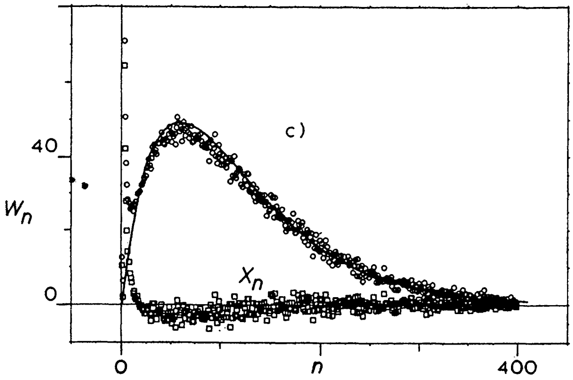


Fig. 7.5 Weight fraction and number fraction (X_n) of the linear chains versus degree of polymerization. Reprinted from Ref. [34, Fig. 6] with permission (Copyright 1995, American Chemical Society)

theoretical studies of the diffusion control of cyclization reactions, but consequences for the ring-chain competition and the distribution functions of the reaction products were not discussed [38–43].

Finally, it should be noted that in none of the aforementioned publications the consequences of the ring-chain competition for the Carothers equation was discussed, although it is evident that this equation in its original form is not applicable anymore, when significant amounts of cyclics are formed, regardless, if in KC or TC step-growth polymerizations.

At first, it should be recalled that the definition of conversion according Eq. (7.12) with $p = 1$ makes sense in KC polycondensation involving ring-chain competition without any restriction, because $p = 1$ now means that all reactions products have a cyclic architecture. As substitute for the Carother's equation Kricheldorf and Schwarz [44] have at first proposed Eq. (7.13), where X is a variable constant allowing for the adaption of this equation to individual step-growth polymerizations. The exponent α is the quotient of the rates of intra- and intermolecular condensation steps. A simpler version was later proposed by Wutz and Kricheldorf [45] in the form of Eq. (7.14). In this equation the cyclization factor β' is defined as the number of condensation steps effecting ring closure relative to all chain growth steps. A graphical representation of this equation is given in Fig. 7.6. It illustrates that competition of cyclization results in limited DPn's even at $p = 1$, and it illustrates that Eq. (7.14) (like Eq. (7.13)) covers any kind of monomers from the total absence of cyclization ($\beta' = 0$) to absence of any chain growth ($\beta' = 1$). These extremes are experimental reality and not sheer fictions. Syntheses of polyaramides from para-functional monomers (e.g., Kevlar/Twaron) are examples for $\beta' = 0$ as demonstrated by MALDI-TOF mass spectrometry [44]. The almost quantitative cyclizations of γ-amino- or of γ-hydroxybutyric acid are examples for $\beta' = 1$ [7].

However, both Eqs. (7.13) and (7.14) and the theoretical concepts of other authors presented above have in common that a variation of the cyclization tendency with increasing p was not taken into account. A decrease of β' may be expected for polycondensations of aliphatic monomers. Here the end-to-end

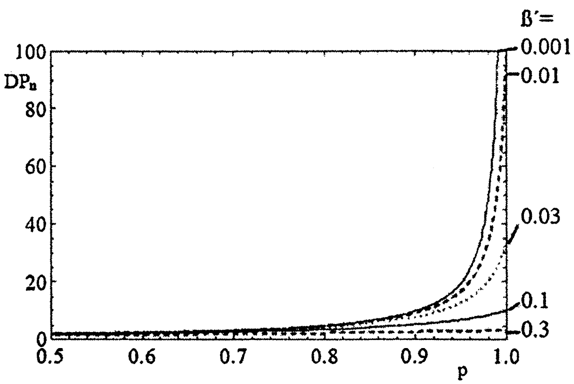


Fig. 7.6 Average number degree of polymerization of the reaction mixture versus conversion for different cyclization rates β' according to Eq. (7.14). Reproduced from Ref. [45, Fig. 3] with permission (Copyright: Wiley-VCH Verlag GmbH&Co, KGaA)

distance increases with $DP^{3/2}$ and the cyclization tendency decreases accordingly with $\mathrm{DP}^{-3/2}$, if the concentration is kept constant. Yet, in real polycondensations the molar concentration of all linear species decreases according to the Law of Self-Dilution (Eq. (7.11)) and the RZDP favours in turn, end-to-end cyclization. Therefore, β' will in fact decrease only with $\mathrm{DP}^{-1/2}$. When for polymers of different structure the end-to-end distance increase with $\mathrm{DP}^{2/2}$, β' is in fact independent on the conversion. Furthermore, it may happen that β' even increases with the conversion, a scenario which may be typical for polycondensations of ortho-functional aromatic monomers, such as derivatives of salicylic acid: For polycondensations of such monomers DPn's above 15 were never achieved despite optimization of the conversion [46]. Therefore, a constant β' is a simplification which is correct in special cases and which represents an average between all possibilities.

Unfortunately, mathematical equations describing exactly the dependence of DPn on both, conversion of the monomers and variation of the chemical structure are still lacking.

$$P = (N_{ao} - N_{at})/N_{a0} \tag{7.12}$$

$\mathrm{DPn} = 1/[1 - p(1 - X^{-\alpha})]$ with $\alpha = v_r/v_c$ (v_r, v_c : reaction rates of cyclization *and chaingrowth*)

$$\mathrm{DPn} = 1\Big/\Big[1 - p\Big(1 - \beta'\Big)\Big] \tag{7.14}$$

Finally, it should be emphasized that all the theoretical considerations presented above also apply to syntheses of hyper branched polymers as discussed in Chap. 11. Cyclization limits the chain growth according to Eqs. (7.13) or (7.14), it reduces the dispersity compared to Flory's calculations (see Sect. 4.3) and the law of self-dilution (Eq. (7.11)) is also valid together with the RZDP. Furthermore, the existence of a permanent competition of cyclization and chain growth in KC polycondensations is decisive for a proper understanding of non-stoichiometric polycondensations as discussed in Chap. 8.

7.2 Experimental Results

One of the first experimental studies formulating and examining the “ring-chain competition” in irreversible polycondensation reactions was the work of Salomon [47–49] published in 1933 and 1934. He studied the formation of cyclic alkylene imines by dehydrohalogenation of α-amino-ω-bromoalkanes. The influence of concentration, reaction medium, and length of the alkane chain were examined. Salomon tried to find the critical concentration, where the rate of chain growth was close to zero, so that the reaction rates measured by titration of H^+ or Br^- were exclusively due to ring closure. In this way the rate constants of the cyclizations were determined and compared to the lengths of the alkane chains. Monomolecular side reactions, if any, were separately analyzed.

Ring-chain competition almost free of side reactions were studied by Stoll et al. [4–9], who used ω-hydroxy carboxylic acids with up to 22 CH_2 groups as monomers. The esterification reactions were conducted using benzene sulfonic acid as catalyst in boiling benzene with azeotropic removal of water. After complete esterification the amount of monomeric lactone was quantified, and from model reactions it was concluded that these (poly)esterifications did not involve equilibration reactions and that they were almost bar of side reactions. From the yields of lactones and from the IMC cyclization constants were calculated as described above. In analogy to Salomon’s results high cyclization rates were found for small rings ($n < 7$), low cyclization rates for medium-sized rings, and somewhat higher rated for larger rings ($n < 13$). Quantification of cyclic oligomers was not feasible at that time due to the lack of chromatographic methods.

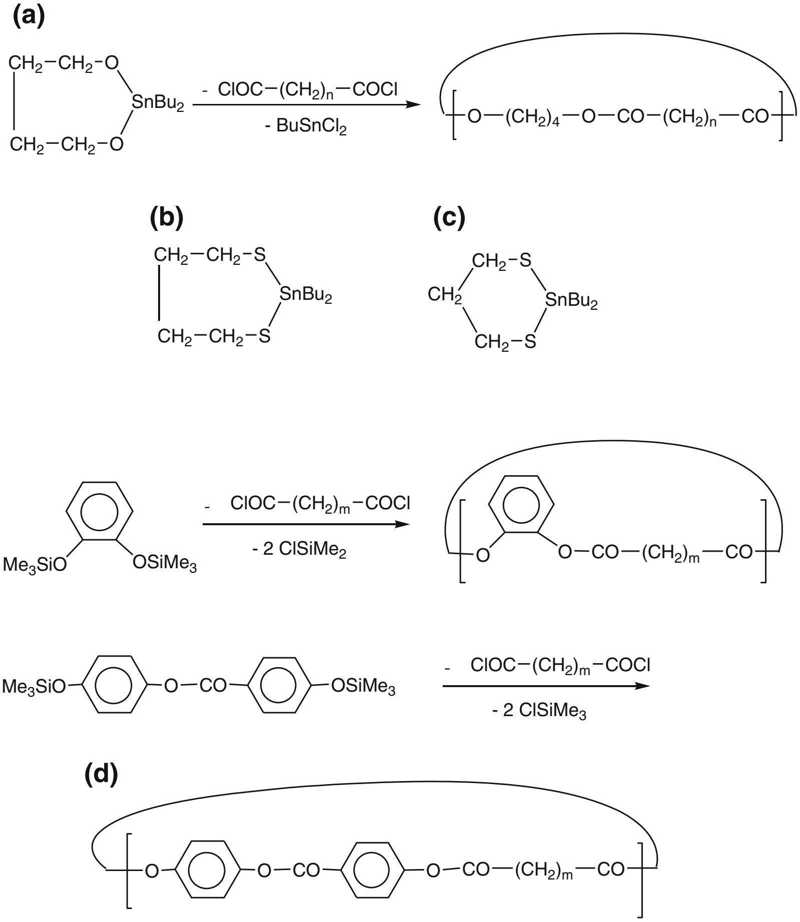
In 1972, Stepto and Waywell [26] analyzed catalyst-free polyadditions of oligo(ethylene glycol>)s (PEG 200 and 400) onto 1,6-hexamethylne diisocyanate, HMDI, in benzene at 70 °C. Several series of polyadditions were performed with variation of the IMC including a few experiments conducted in bulk. Since end-to-end cyclization contributes to the conversion but not to the chain growth, the extent of cyclization can in principle, be determined from accurate measurements of Mn’s from end groups and from absolute methods. The conversion was measured by titration of isocyanate groups (incorrectly assuming absence of side reactions), and absolute Mn’s was determined by cryoscopy. Large amounts of rings (yields >50 %) were found at high conversions for polyadditions in solution (see Fig. 7.2), proving that cyclization occurs at any stage of the polyaddition in agreement with the calculations presented in Ref. [28].

About 30 years later Kricheldorf and Schwarz [45] studied the addition of tetra(ethylene glycol), TEG, onto HMDI in benzene and in bulk at 60 °C. At that time MALDI-TOF mass spectrometry was available and the author observed that with 1/1 feed ratios a considerable fraction of linear chains having two TEG end groups existed in the reaction mixture indicating a consumption of HMDI by side reactions, such as the formation of allophanate groups. An excess of 4–7 mol % of HMDI was needed to transform all linear species into cycles. These results deviate from the comments of Stepto and Waywell, who concluded that a 1/1 feed ratio is optimum for the formation of rings, and that allophanate groups are only formed after consumption of all CH_2OH end groups. Furthermore, Kricheldorf and Schwarz [45] observed that part of the polyurethanes precipitated from the reaction mixture as colorless liquid covering the glass walls of the reactor. Since these polyurethanes and benzene possess nearly identical refractive indices the precipitation of small amounts of the polyurethane is difficult to detect. The polyurethanes of Stepto et al. [26] might have slightly higher solubilities, because PEG 200 and 400 are polydisperse in contrast to TEG. Stepto et al. themselves conceded that their polyurethanes aggregate via H-bonds in benzene. Therefore, the accuracy of their cryoscopic measurements is questionable, and it is surprising that their results fit in with their expectations and calculations. Yet, regardless of the accuracy, the work of Stepto et al. [26–28] has the historic merit that it confirmed for the first time the new theory of KC step-growth polymerization based on ring-chain competition.

In 1980, Horbach and other members of Bayer Ag reported [50, 51] on the formation of large fractions of cyclic oligo- and polycarbonates (incl. high molar mass cycles) in hydrolytic interfacial polycondensations of bisphneol-A bischloroformiate (see Formula 7.1). Their conclusion was based on Mn data derived from end-group analyses and with Mn values determined by SEC. Direct mass spectroscopic evidence was not available at that time, but was later contributed by Kricheldorf et al. (see below). After 1994, the first MALDI-TOF mass spectrometer became commercially available, and this new analytical tool improved the possibility to detect cycles in complex reaction mixtures dramatically. Unfortunately, this method did not and does not allow for a routine quantification of the ring molecules. Only a rough estimation can be obtained in combination with fractionation or when the observable mass range extends to Mn or beyond.

In 1999, Kricheldorf et al. [52]. reported that polyesters resulting from polycondensations of 2,2-dibutyl-2-stannepane ((a) in Formula 7.2) with dicarboxylic acid dichlorides (DADs) mainly consisted of rings in the observable mass range up to 5 kDa. Quite similar results were obtained from analogous polycondensations of the 2,2-dibutyl-2-stanna-1,3-dithacycloalkanes ((b) and (c) in Formula 7.2) [53, 54]. A broader study of polyester syntheses revealed [55–57] that the formation of a large number of rings below 10 kDa is not due to special interactions of cyclic tin compounds with DADs, but a normal consequence of the ring-chain competition in KC polycondensations. Remarkable are the polycondensations of silylated catechols with aliphatic DADs [55] (Formula 7.2), because these polycondensations were performed in bulk, and thus, demonstrate that the formation of cyclic polymers does not require dilution of the reaction mixture.

Polycondensations in bulk were also conducted with other silylated diphenols [58, 59], for instance, with hydroquinone 4-hydroxybenzoate ((d) in Formula 7.2). These experiments had the purpose to elucidate, if end-to-end cyclization occurs even in the nematic phase. Liquid-crystalline phases are based on a more or less parallel alignment of the polymer chains, which is the most unfavorable conformation for ring closure. Nonetheless, cyclic oligo-, and polyesters were detected, and interestingly the even-membered rings prevailed largely in contrast to



Formula 7.2

polycondensations of the same monomers in isotropic solutions. The predominance of the even-membered cycles indicates that the linear precursors existed in a folded conformation with a parallel alignment of the mesogenic moieties.

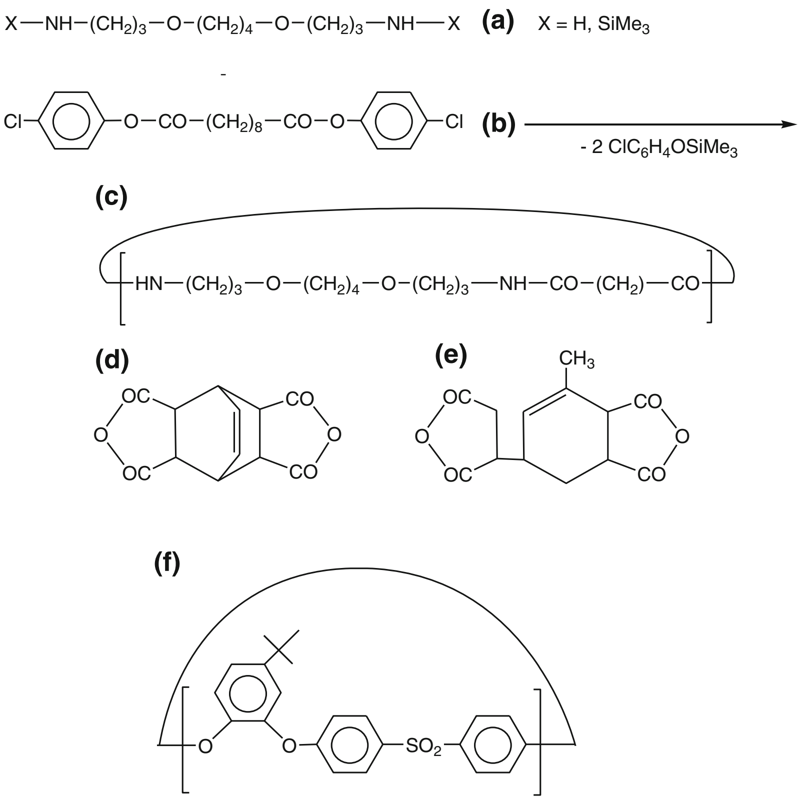
Further studies were devoted to syntheses of polyamides [60, 61] via KC polycondensations. The monomer combinations were selected so that polyamides having a moderate or good solubility in the reaction media were obtained, so that early precipitation of linear chains from the reaction mixture was prevented (e.g., (a) in Formula 7.3). From the best experiments spectra exclusively displaying mass peaks of cyclic polyamides up to 13 kDa were obtained. Similar results were found for soluble polyimides derived from the dianhydrides (b) and (c) (in Formula 7.3) and various aromatic diamines [62, 63].

Further interesting findings resulted from syntheses of aromatic poly(ether sulfone)s [64, 65]. The fraction of cycles increased at the expense of linear chains with increasing conversions. Due to the lower reactivity, 4,4′-dichlorodiphenyl sulfone yielded lower molar masses than 4,4′-difluorodiphenyl sulfone, with the consequence that the fraction of cycles was lower. Poly(ether sulfone)s derived from tert-butyl catechol ((d) in Formula 7.3) proved to be particularly well suited to MALDI-TOF mass spectrometry. The polyether with the highest molar mass gave a spectrum showing mass peaks of cycles up to 20 kDa. After fractionation mass peaks of cyclic polyethers up to 27 kDa were achieved and no signals of linear chains were detectable. However, the fraction above 27 kDa certainly contained linear chains, because in a real experiment 100 % conversion without any side reaction cannot be achieved. The formation of cyclic polyethers in syntheses of poly(benzonitrile ether)s (e.g. (a) in Formula 7.4), of poly(pyridine ether)s ((b) in Formula 7.4) and of poly(ether ketone)s was also screened by MALDI-TOF mass spectrometry [66–68].

Due to the aforementioned work of Horbach et al. [50, 51], Kricheldorf et al. [69–72] reinvestigated the hydrolytic interfacial polycondensation of bisphenol-A bischloroformiate and also the interfacial phosgenation of bisphenol-A and bisphenol-M. Tertiary amines and quarternary ammonium or phosphonium salts were used as catalysts, and the reaction conditions were optimized for high molecular weights (indicating high conversions). For reasons discussed in Chap. 8, extremely high conversions and molar masses were achieved (Mn's up to 400 kDa). As overriding trend, it was found that the fraction of cyclic polycarbonates increased with the molar mass of the entire reaction products. For the best samples the MALDI-TOF mass spectra exclusively displayed peaks of cycles observable up to 20 kDa. After fractionation mass spectra were obtained exhibiting peaks of cycles up to 50 kDa [69] or 55 kDa [71] (Fig. 7.7). This mass corresponds to a DP around 220 or to 2,600 ring forming atoms. This result allows three important conclusions:

(A) Flory's statement [1] that the end groups of long chains will not meet in the course of a normal KC polycondensation is definitely wrong. Cyclization can compete with chain growth at any chain length.
(B) The conclusions of Horbach et al. [50, 51] were justified.
(C) Since cyclic DNA in protozoa and other microorganisms frequently consist of approx. 400 base pairs corresponding to 2500 ring atoms, the gap between large cyclic biopolymers, and cyclic polymers formed in a normal KC polycondensation is closed.

Concerning point (C) Stasiak [73], who synthesized cyclic DNA in test tubes by means of the enzyme ligase stated: "Ligase which is frequently used for DNA circularization experiments waits until thermal motion brings together DNA ends in the correct polarity (3′ with 5′) and the connects these ends covalently". Certainly long DNA chains may form sequence-dependent loops and other conformations favoring ring closure more than the conformations of a freely rotating chain. Nonetheless, the formation of large DNA rings in living organism is not a

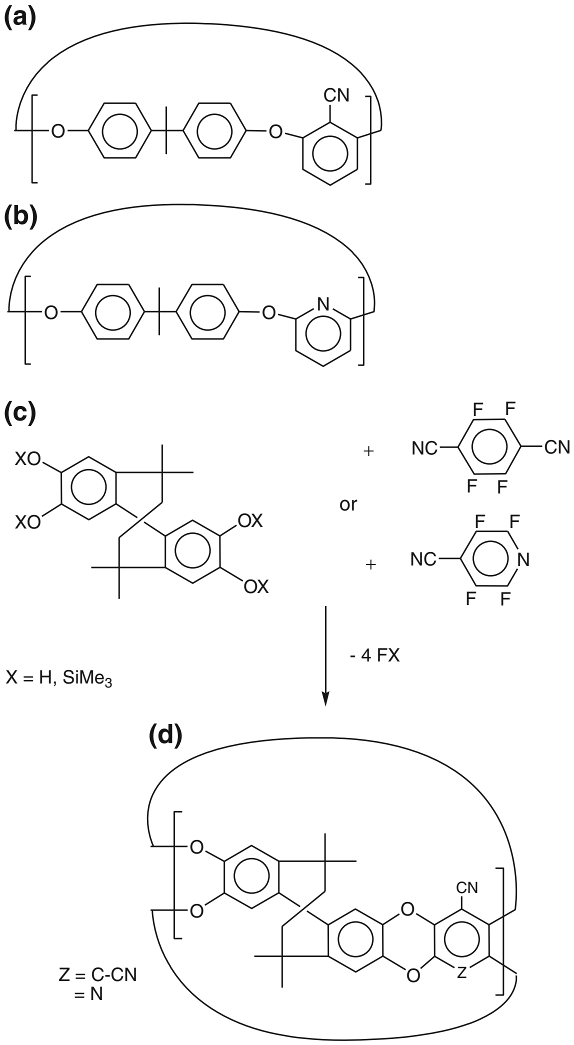


Formula 7.3

mystery anymore which differs largely from the formation of high molar mass cyclic polymers in a normal KC step-growth polymerization.

Kricheldorf et al. [74–76]. also found that not only polymers having single bonds in their backbone, but also ladder type polymers may cyclize easily in the course of a step-growth polymerization. From the polycondensations outlined in Formula 7.4(c) and (d) MALDI-TOF spectra were obtained exclusively displaying "ladder rings" having masses up to 13 kDa. At this point it should be mentioned that the frequently heard criticism that MALDI-TOF mass spectroscopy selectively favors detection of circular molecules is not justified for polymers as demonstrated for equimolar mixtures of various cyclic and linear polymers [65, 74, 77]. In summary, the experimental results presented above clearly prove that ring-chain competition occurs in all step-growth polymerizations conducted in bulk or in solution, where the polymer chains are mobile enough to adopt cyclic conformations. A particular conspicuous success of the concept of ring-chain competition is syntheses of multicyclic polymers (nanogels) via $a_2 + b_n$ polycondensations as discussed in Chap. 12.

Formula 7.4



7.3 Final Remarks

The calculations of Gordon et al. [24, 25], Stepto et al. [26–28] and other authors together with the experimental results of Kricheldorf et al. have unambiguously demonstrated that in KC polycondensations

(a) even very long polymer chains undergo end-to-end cyclization under normal experimental conditions,

(b) cyclization competes with chain growth at any stage of a polycondensation and at any IMC,

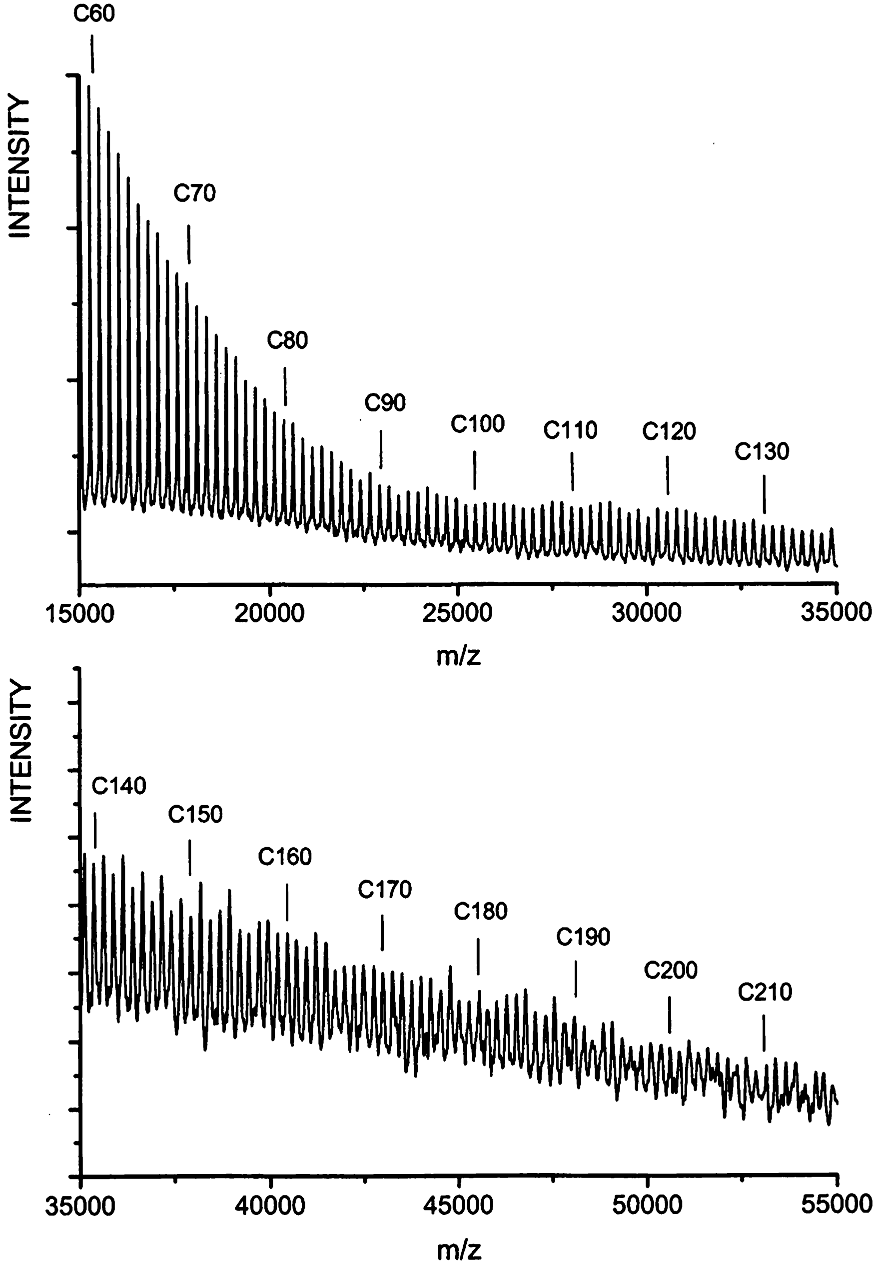


Fig. 7.7 MALDI-TOF mass spectrum of a fraction of polycarbonate prepared by triethylamine-catalyzed hydrolytic polycondensation of bisphenol-A bischloroformiate (C1000 means cycle with DP = 100). Reproduced from Ref. [44, Fig. 6] with permission (Copyright: Wiley–VCH Verlag GmbH&Co KGaA)

(c) the number and weight fractions of rings steadily increases with the conversion until all reaction products are cycles at 100 % conversion.

These results evidence that Flory's classical theory of step-growth polymerization is despite its immense historical merits only a half truth which needs to be combined and completed with the aforementioned results. At this point a comparison with TC polycondensations and the Jacobson–Stockmayer (J–S) theory (see Chap. 5) should be considered. When identical monomers are polymerized under KC and under TC conditions, and when both polymerizations are stopped at the same conversion, the reaction mixture of the TC polycondensation contains a higher fraction of rings, because the rings are formed by two different processes, back-biting and end-biting, whereas in the KC polycondensation only end-biting has occurred. Experimental evidence for this conclusion was presented by Kricheldorf et al. [78] for syntheses of PBT with variation of catalyst and reaction conditions. Furthermore, the distribution function and the DPn of the rings formed in a KC and in a TC polycondensation will be different. However, both kinds of polycondensation have one important aspect in common. The fraction of cycles increases with the conversion, and at 100 % conversion all reaction products are rings. The J–S theory predicts that above a so-called critical IMC quantitative cyclization, and thus, quantitative conversion are impossible. Yet, this mathematical result lacks experimental evidence, and for reasons discussed in Chap. 5 this aspect of the J–S theory seems to be incorrect. In summary, it is the theoretical and experimental evidence for the end-to-end cyclization which changes and completes the theories of Flory and J–S, and thus, justifies the title of this chapter.

Despite this enormous progress in the theory of step-growth polymerization, a noteworthy deficit is the lack of mathematical equations describing the dependence of dispersities on the conversion for both KC and TC polycondensations and taking into account that the cyclization tendencies of various polymers vary over abroad range. Fawcett et al. [34] calculated a maximum dispersity of 2.77 at 98 % conversion for aliphatic chains containing alkane moieties in the repeat unit, and for higher conversions even higher dispersities were expected. Using a different mathematical approach Szymanski [79] recently calculated again for aliphatic chains a maximum $D > 20$ for 100 % conversion. Experimental values reported by Kricheldorf et al. [44, 80–82] for KC polycondensations of aromatic monomers fell into the range of 3–15 (mainly 3–8). A range of 3–13 was reported by Niehaus and Jackson [83] for the TC syntheses of Nylon-6, Nylon-6,6 and PET. These high dipersities deviate largely from the dispersities around 2.0 reported in numerous publications. However, dispersities around 2.0 are only possible for linear polycondensates free of cycles (see Chap. 4). Since all polycondensations performed in the melt or in solution generate cyclic oligomers and polymers (with exception of Kevlar type polyaramides), the dispersities need to be higher than 2.0. The low dispersities reported in the literature are either a consequence of low conversions (<98 %), or a consequence of fractionation (e.g., by precipitation) or by Mn measurements which did not include all oligomers. In other words, systematic studies, how dispersities depend on the conversion on the one hand, and on the polymer structure on the other, are lacking with regard to both, experiments and mathematical treatment. Hopefully this comment will stimulate readers to close this gap.

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Chapter 8
Non-Stoichiometric Polycondensations

8.1 Introduction

Based on the definition of conversion given in Eq. (8.1), (or Eq. 4.1), and according to the correlation between DPn and conversion p (Eq. 8.2), a polycondensation should yield the highest molar mass, when:

(1) the conversion reaches 100 % ($p = 1$)
(2) the stoichiometry is perfect (1.0: 1.0 ratio of the functional groups)
(3) cyclization is absent ($ß' = 0$; s. definition in Chap. 7.1

$$p = (N_{a0} - N_{at})N_{a0} \tag{8.1}$$

$$\mathrm{DP_n} = 1/[1 - p(1 - \beta')] \tag{8.2}$$

In Flory′s classical theory of step-growth polymerization[1] only points (1) and (2) were considered, and thus, textbooks usually comment that polycondensations of a-b monomers offer the best chance for reaching high molar masses, because they possess a "built in" perfect stoichiometry. This apparently straightforward logic is supported by calculations of Flory (Eq. 4.3., Chap. 4), who found that stoichiometric imbalance in $a_2 + b_2$ polycondensations reduces the DPn. For instance, an excess of the a_2 monomer has the consequence that after complete conversion of the a_2 monomers telechelic a-terminated oligomers or low polymers are formed. The DP decreases, when then excess of a_2 increases.

On the other hand, it has been found over the past 20 years that the highest molar masses of polycondensates reported in the literature were obtained from non-stoichiometric $a_2 + b_2$ polycondensations. This discrepancy results from the fact in Flory's theory (and thus in all textbooks based on it) the role of end-biting cyclization is ignored. Polycondensations of a-b monomers exclusively yield oligomers and polymers terminated by one "a" and on "b" function, an optimum scenario for efficient cyclization, unless the growing chains are extremely stiff, but soluble or meltable. In the case of an $a_2 + b_2$ polycondensation only 50 % of all

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linear species possess on "*a*" and one "*b*" group and can cyclise. When, due to stoichiometric imbalance, the fraction of telechelic species having two "*a*" or two "*b*" end groups largely predominate, the influence of cyclization is considerable reduced. Why and when the stoichiometric imbalance results in low DPns according to Flory's theory or results in particularly high molar masses, as reported in several publications, is the object of the following discussion (the role of stoichiometric imbalance in $a_2 + b_\mathrm{n}$ polycondensations is discussed in the last subchapter).

Polycondensations of $a_2 + b_2$ monomer combinations may be subdivided into three categories according to their kinetic properties.

I Monomers, oligomers, and polymers possess nearly identical reactivities. In the case of a perfect 1:1 feed ratio linear chains having two "*a,*" two "*b,*" or one "*a*" and one"*b*" end group will be formed in a 1:1:2 ratio. This is the normal or standard case of an $a_2 + b_2$ polycondensation as discussed by Flory [1].

II The monomers react faster with each other than with oligomers or polymers. In this case, a relatively high concentration of dimers will be formed in the beginning of the polycondensation (e.g., < 60 % conversion), but the further course of the polycondensation will be similar to that of class I.

III The reaction of one monomer (e.g., a_2) with b_2 monomers or with "*b*" end groups is slower than the growing steps of "*a*" end groups. In other words, the "*a*" end groups are activated, when compared with the a_2 monomer. The rapid reaction of "*a*" end groups with b_2 has then the consequence that telechelic chains having two "*b*" end groups will prevail in the reaction mixture. This kinetic course is called non-stoichiometric polycondensation in a narrower sense. It is characteristic for these class III polycondensations that addition of an excess of a_2 accelerates the chain growth and yields higher molar masses.

8.2 Class I Polycondensations

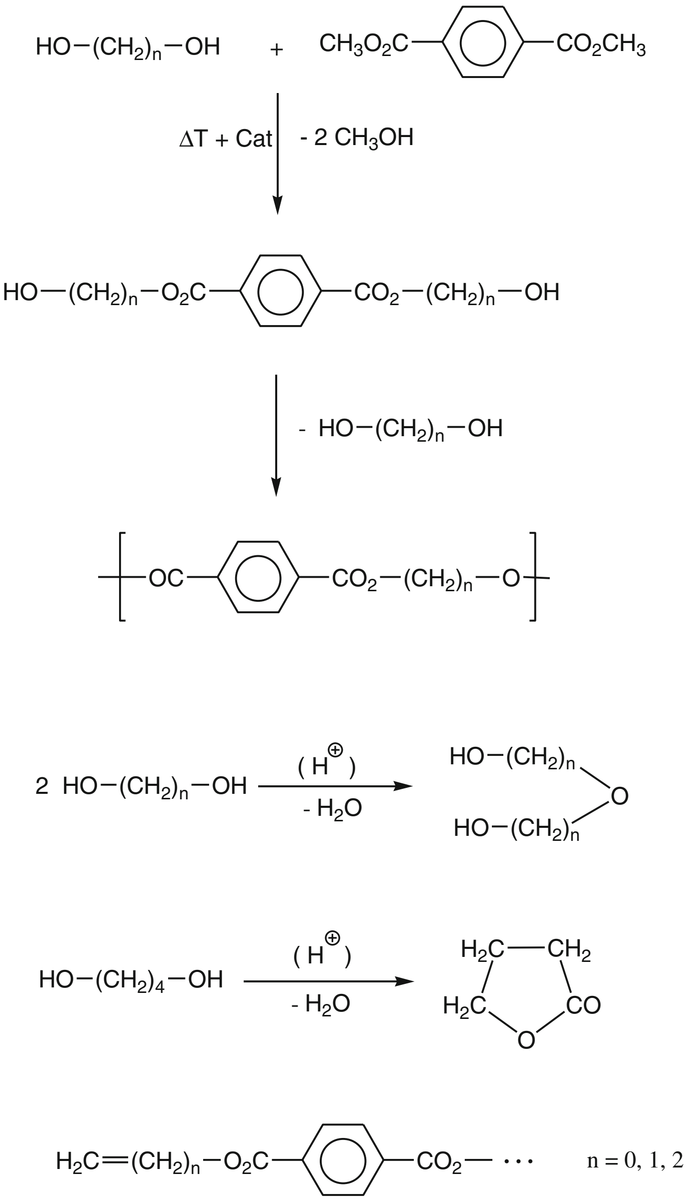
8.2.1 Polycondensations in the Melt

Syntheses of aliphatic polyesters and polyamides by $a_2 + b_2$ polycondensations in the melt were first studied by Carothers in the years 1930–1937 (see Chap. 3). Since that time Nylon-6,6 type aliphatic polyamides were and are prepared from equimolar monomer mixtures usually supplied in the form of diamine-dicarboxylic acid salts. In the case of aliphatic polyesters two different procedures are applicable, depending on the volatility of the reaction partners. Combinations of low boiling esters such as dimethyl succinate and low boiling dieols (e.g., ethanediol) are best polymerized in equimolar feed ratios Equimolar feed ratios are again advisable for combinations of long α,ω-alkanediols and dicarboxylic acids or their high boiling esters (e.g., dimethyl sebacate or terephthalate). Carothers indeed prepared his first "super polyesters" in this way. Equimolar monomer mixtures are also optimum for the preparation of aromatic polyesters from aromatic dicarboxylic acids and acetylated diphenols. Yet, the technical production of the most widely used polyesters, PET, PBT, and (more recently) PPT (see Chap. 6) is based on monomer mixtures containing a large excess of the relatively volatile diols[2–4]. The excess serves two purposes. First, it should compensate for the loss of diol by evaporization. Second, it should compensate for a loss of CH_2OH groups by side reactions. Typical side reactions are formation of linear ethers, such as di(ethylene glycol), formation of cyclic ethers, such as tetrahydrofuran or dioxane, and formation of vinyl groups via ß-cis-elimination (see Formula 8.1).

The technical production of the aforementioned polyesters is conducted in two steps. A first transesterification step involves dimethyl terephthalate and a large excess of a diol at temperatures up to 180–190°C. The following polycondensation step is performed in vacuo at temperatures up to 240 °C for PBT or 280 °C for PET. The first step exactly obeys the theory of Flory. The large excess of the diol generates telechelic oligomers having two diol end groups (see Formula 8.1)[5–7]. Polycondensation of these oligomers at high temperatures in vacuo eliminates more or less the excess diol, so that at long reaction times these polycondensations change from non-stoichiometric to stoichiometric ones. Nonetheless, for three reasons very high molar masses ($M_n > 15$ kDa) are difficult to obtain. First, it is difficult to remove small amounts of diols from the viscous melt of the polyesters. Second, side reactions (e.g., decarboxylation of terephthalic acid end groups) destroy functional groups. Third,, large numbers of cyclics are formed.

The predominance of diol terminated linear chains reduces the influence of "end-biting", but the formation of cyclics by "back-biting" cannot be suppressed. The role of ring-chain equilibria and the extraction and characterization of cyclic oligoesters is discussed in Chap. 5. However, it was also demonstrated by means of MALDI-TOF mass spectrometry that high molar mass PBT contains cyclic polymers with masses at least up to 12 kDa and not only cyclic oligomers [8].

Another technical polycondensation, which resembles that of PET, PBT, and PPT, is the production of poly(bisphenol-A carbonate) by transesterification of bisphenol-A with diphenyl carbonate in the melt. An excess of diphenyl carbonate has the consequence that initially oligomers having one or (mainly) two phenyl carbonate end groups are formed. With increasing reaction time and conversion the excess of diphenyl carbonate is gradually removed in vacuo together with the liberated phenol, and the non-stoichiometric polycondensation shifts to a stoichiometric one. Cyclic carbonates are formed by "back-biting" and their fraction increases with the conversion. The only significant side reaction is branching resulting from Fries-Rearrangement, which is typical for all polyester of diphenols at temperatures > 280 °C. In summary, these non-stoichiometric polycondensations obey the theories of Flory and Stockmayer (see Chaps. 4 and 5), and the excess of one monomer has the purpose to control the DPn and to compensate for side reactions.


HO−(CH2)n−OH
+
CH3O2C
CO2CH3
ΔT + Cat
- 2 CH3OH
HO—(CH2)n−O2C
CO2−(CH2)n—OH
- HO−(CH2)n−OH
OC
CO2−(CH2)n—O
2 HO−(CH2)n−OH
(H⊕)
- H2O
HO−(CH2)n
O
HO−(CH2)n
HO−(CH2)4−OH
(H⊕)
- H2O
H2C
CH2
H2C
CO
O
H2C═(CH2)n−O2C
CO2— · · ·
n = 0, 1, 2

Formula 8.1

8.2.2 Polycondensations in Solution

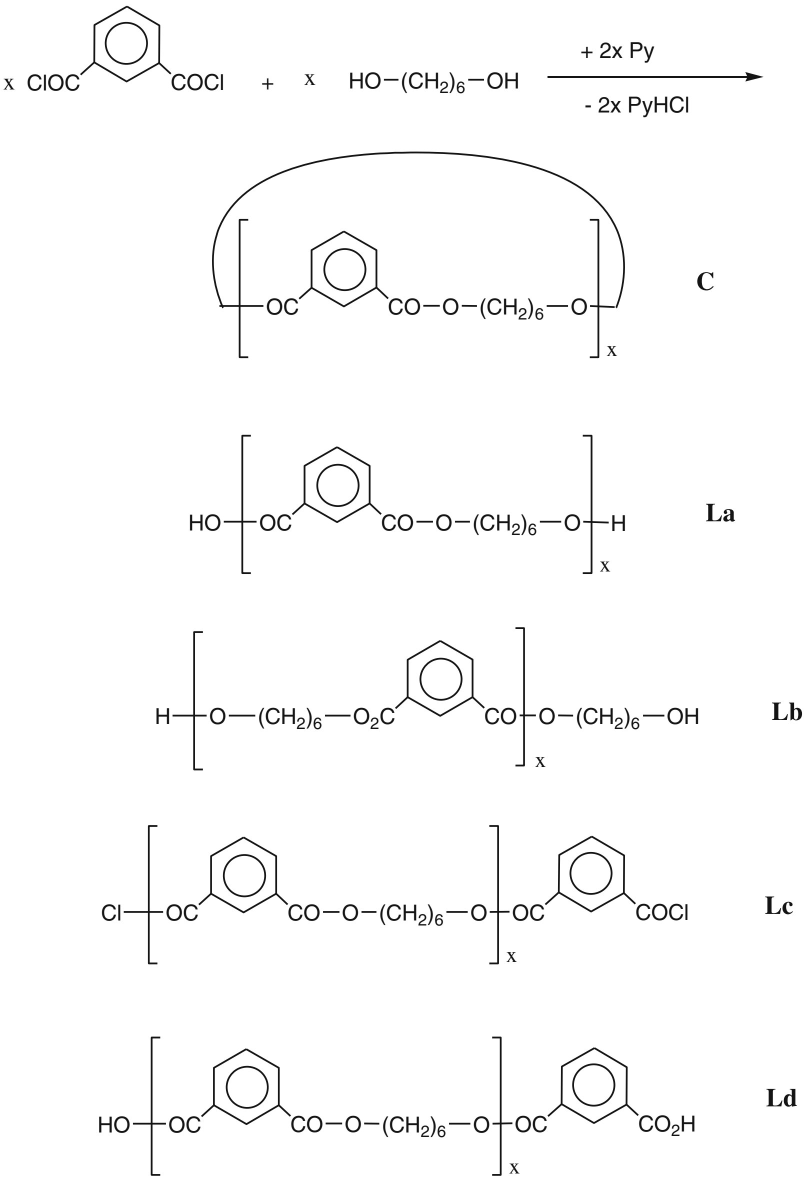
Various commercial polycondensates are prepared in solution, for instance, polyaramids, polyimides, poly(ether sulfone)s, and pol(ether ketone)s (see Chap. 6). Their syntheses are usually conducted with equimolar monomer mixtures and the molar masses are controlled addition of chain terminators or by limitation of the reaction time (conversion).

However, non-stoichiometric polycondensations are of interest for the preparation of telechelic oligomers and polymers. For example, OH-terminated oligo(ether sulfone)s were prepared by several research groups [9–11], because their high Tgs and good solubilities render them useful building blocks for (multi)block-copolymers. Numerous other telechelic oligoethers were reported in the literature [9, 10], but a complete listing and discussion were not intended in this book.

When $a_2 + b_2$ polycondensations have the purpose to prepare high molar mass polymers, three experimental procedures may be considered (in contrast to a-b monomers). These three procedures should here be discussed for pyridine-promoted polycondensations of 1,6-hexanediol and isophthaloyl chloride (IPCl) [12], because these polycondensations are the only systematic study known to the author.

(A) 1,6-hexanediol and IPCl are mixed in solution and pyridine is (slowly) added.
(B) 1,6-hexanediol and pyridine are mixed in solution and IPCl is slowly added
(C) A solution of 1,6-hexanediol and pyridine is slowly added to a solution of IPCl.

When a polycondensation according to procedure (A) takes an ideal course, the linear species La, Lb, and Lc (see Formula 8.2) are formed in a molar ratio of 2:1:1 regardless of the conversion. Cyclic polymers result from “end-biting” of the La chains, and their formation limits the chain growth. In the case of procedure (B), the Lb chains are the prevailing species up to high conversions, and the influence of cyclization is reduced. Yet, when the addition of IPCl goes to completion, cyclization gains in efficiency, and at 100 % conversion all reaction products are cyclic quite analogous to (A). However, the Mn is higher than in the case of (A). Procedure (C) is so-to-say the mirror image of procedure (B), and the molar masses should again be higher than those obtained by (A). It is decisive for the success of procedures (B) and (C) that the chain growth is faster than the addition of the second monomer. The results obtained with 1,6-hexanediol and IPCl are not conspicuous, but support the above concept. The kinetic scenario of interfacial polycondensations is particularly well suited to prepare high molar mass polymers, when side reactions are negligible.



Formula 8.2

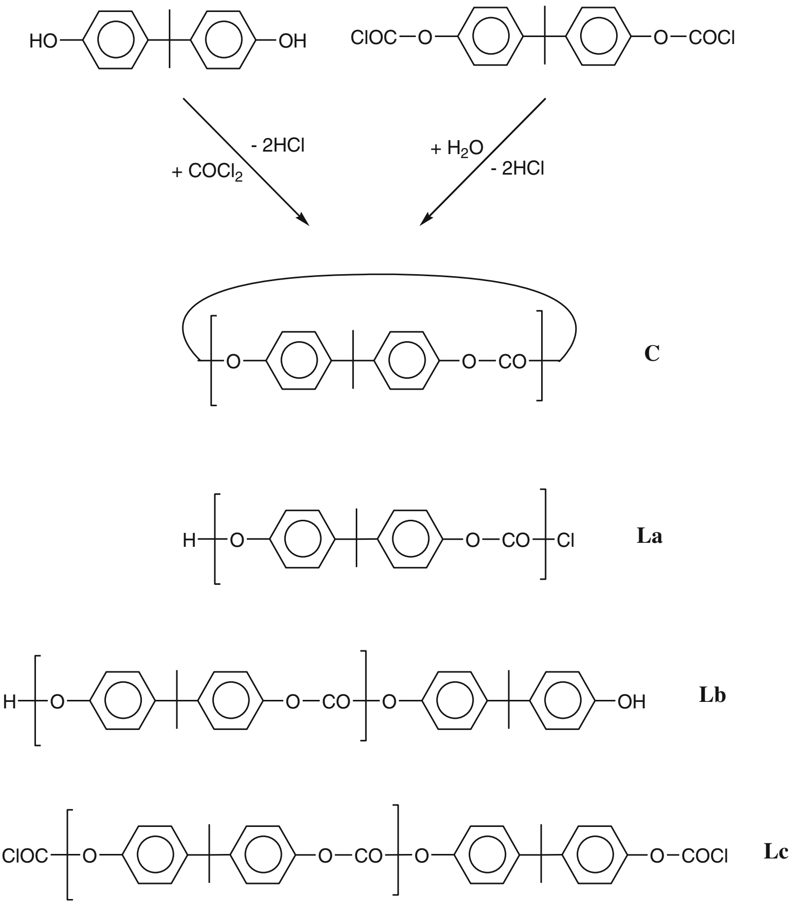
8.2.3 Interfacial Polycondensations

The concept of interfacial polycondensations was first described by Magat and Strachan in a patent for syntheses of aliphatic polyamides [13]. In the years 1959–1965, Morgan and other members of E.I. DuPont elaborated a comprehensive study of interfacial polycondensations for various polymers [14–16]· This synthetic strategy has found broad application for research purposes, because relatively high molar masses can be achieved without perfect stoichiometry. However, for the technical production of polymers it has two disadvantages. First, dry organic solvents are needed, when reactive monomers, such as dicarboxylic acid chlorides, should be used. Second, large amounts of salt solutions are formed as byproducts. Nonetheless, the production of polycarbonates has proven to be a viable technical process for more than 50 years [17, 18].

Commercial polycarbonates are mainly or exclusively prepared from bisphenol-A and possess usually Mn's $<$ 30 kDa. For the extrusion (e.g., for the production of “safety glass”) relatively high are used, but extremely high Mns, and thus, extremely high melt viscosities are not desired. Yet, for injection molding low melt viscosities are advantageous, and the Mns of polycarbonates used for compact disks fall normally into the range of 11–13 kDa. Therefore, chemical companies did not have much interest to study reaction conditions yielding maximum molar masses. Almost 50 years after the invention of polycarbonates (see Chap. 6) Kricheldorf et al. [19–23]. launched a detailed study of phosgenation of bisphenol-A and bisphenol-M. In analogy to the technical process dichloromethane and aqueous sodium hydroxide served as reaction media and triethylamine or quaternary ammonium and phosphonium salts were used as phase-transfer catalysts (see Chap. 12). From triethylamine, the technical catalyst, it is known for a long time that it plays a dual role in the phosgenation. First, it forms a salt with the phenolic OH groups and facilitates the phase transfer. Second, it forms a complex with phosgene and chloroformiate groups (Formula 8.3). This complexation activates the CO–Cl group and accelerates chain growth and cyclization, but it also favors hydrolysis. The onium type catalysts exclusively act as efficient phase-transfer catalysts. This difference needs to be noticed, because both types of catalysts show opposite trends in otherwise identical experiments. Triethylamine gave the highest molar masses at low catalyst concentration, whereas tetrabutyl ammonium chloride was most effective at high concentration (see Chap. 12). The best experiments gave Mns in the range of 300–400 kDa with Mw's above 1,000 kDa (determined by SEC with triple detection). These values seem to be the highest reliably measured molar masses of polycondensates.

The MALDI-TOF mass spectra exclusively revealed peaks of cyclic polycarbonates detectable up to masses around 55 kDa after fractionations (Figs. 7.7 and 7.8). Similar results were obtained, when the hydrolytic polycondensation of bisphenol-A bischloroformiate was optimized [23]. The large fraction of cyclic polycarbonates including high molar masses indicates that the reaction conditions of the best experiments were close to the optimum.

Furthermore, polycondensations of bisphenol-A and diphosgene were performed in a homogeneous phase with pyridine as catalyst and HCL acceptor. The excess of diphosgene was varied to compensate for the loss due to side reactions. After optimization of the reaction conditions the MALDI-TOF mass spectra displays again an almost exclusive formation of cyclic polycarbonates, but the highest Mn amounted only to 15 kDa. In other words, the interfacial polycondensations



Formula 8.3

yielded Mns which were at least by a factor of 20 higher than those obtained in a one-phasic system. This conspicuous discrepancy can be rationalized in the following way. The migration of bisphenol anions into the organic phase is slower than the chain growth. In the organic phase, the bisphenol anions are confronted with a large excess of (di)phosgene and oligomers having chloroformiate end groups. Therefore, the intermediately formed La chains are short, and the Lc chains are prevailing for most of the reaction time. In contrast, the La chains are the predominant species in the homogeneous phosgenation, so that cyclization is far more efficient in the one-phasic system. However, even in the interfacial polycondensation the Lc chains will finally be converted to La chains and cyclize, but the Mn will be higher, because the competition of cyclization with chain growth was largely suppressed for most of the reaction time.

When bisphenol-C was polycondensed with IPCl either in homogeneous solution or in a biphasic system, the same trends were observed. The maximum molar masses and the difference between homogeneous and interfacial polycondensations were smaller [12] The lower Mn values compared to a phosgenation are a consequence of the fact that hydrolysis of a carboxylic acid chloride group is a irreversible termination step, whereas a loss of phosgene or chloroformiate groups may be compensated for by an excess of phosgene.

Another group of polycondensations which allows for comparison of one-phasic and biphasic systems are polycondensation of bisphenols or bisthiophenols with α,ω-dibromoalkanes or bis(chloromethyl)aromatics. However, syntheses of polyamides from primary diamines are not suited for such studies, because association and precipitation of polyamide chains (via H–bonds) interferes with chain growth and cyclization.

A significant influence of a biphasic reaction mixture on the competition between chain growth and cyclization is not limited to interfacial polycondensation involving two liquid phases. Reactions between a dissolved monomer and a solid reaction partner may also obey the trends discussed above. A typical example is the polycondensation of dichloro methyl phenyl silane mediated by metallic sodium in toluene under ultrasonic irradiation [24]. Since the resulting oligo and polysilanes can delocalize radicals and electric charges along their conjugated backbone, the Si–Cl end groups are more reactive toward sodium than the Si–Cl groups of the monomers. At first a radical anion is formed which after elimination of a Cl anion yields a sodium silicide end group. The silicide anion reacts fast with Si–Cl groups of monomers, because which due to the lack of conjugation are more electrophilic than the Si–Cl groups of oligomers and polymers. Hence, in early stages of the polycondensation the reaction mixture mainly contains polysilane chains having two Si–Cl end groups, which cannot cyclize but continue the chains growth. Consequently, long polysilane chains are formed at low conversions, but more and more cycles are formed at higher conversions.

8.3 Class II Polycondensations

To the best knowledge of the author, non-stoichiometric polycondensations of this class have not been studied yet, A recently published speculative discussion[12] of suitable monomer combinations should not be repeated in this book.

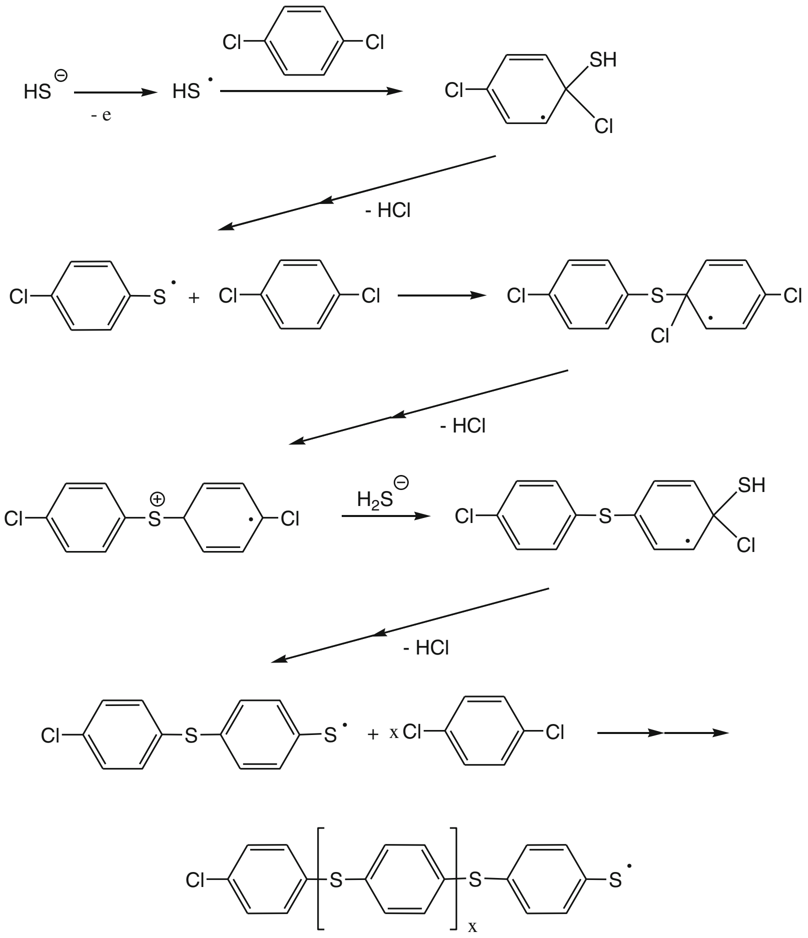
8.4 Class III Polycondensations

Presumably, the oldest non-stoichiometric polycondensation of class III is a synthesis poly(phenylene sulfide), PPS, which was patented in 1967 by Edmonds and Hill [25]. The first(nonintended) synthesis of low molar mass PPs was found by

Friedel [26] in 1888 by heating benzene and elemental sulfur in the presence of $AlCl_3$. A few years later Genvress published a more detailed study of this reaction [27]. Fifty years after Friedels publication McCallum described a more convenient laboratory method [28], namely, a polymerization of 1,4-dichlorobenzene with elemental sulfur and potassium carbonate. Lenz and other members of Dow Chem [29–31] tried to the problems of the McCallum method (branching and cross-linking), but a satisfactory procedure, suitable for a technical production of PPS was not found. However, heating of 1,4-dichlorobenzene with sodium sulfide in NMP as described by Edmonds and Hill yielded linear PPS. With addition of certain metal carboxylates as catalysts molar masses around 35 kDa were achieved [32]. Further variations of this approach were reported by other authors [33]. Based on this method Phillips Petroleum elaborated a technical production and commercialized PPS under the trade mark “Ryton”.

It is characteristic for the Edmonds-Hill method that an excess of Na_2S accelerates the polymerization and enhances the molar mass. Both trends were also observed for all other class III polycondensations, but in the case of PPS the excess of Na_2S has the additional effect that more than the stoichiometric amount of sulfur is incorporated into the main chain forming disulfide groups. Sergev et al. [34, 35] formulated a mechanism based on a normal nucleophilic substitution in analogy to the mechanism proposed by Lenz [31] for the polycondensation of 4-chlorothiophenol, but such a mechanism cannot explain the formation of disulfide groups. In a detailed mechanistic study Koch and Heitz also found [36, 37] that the reactivity of the C-X group increases in the order $Cl < Br < I$ which is exactly opposite to the reactivity pattern known from the normal nucleophilic substitution at aromatic C-X groups. Yet, the reactivities observed by Koch and Heitz agree well with those reported by Bunett [38] for nucleophilic radical substitutions (S_{NR}). Furthermore, it was found that a relatively large fraction of high oligomers is formed below 50 % conversion in contrast to the Carothers equation (Eq. (8.2), $ß' = 0$). The second-order kinetic typical for the first 50 % conversion was followed by a 40 times faster chain growth of the oligomers. The radical-cationic mechanism outlined in Formulas 8.4 was called “reactive intermediate mechanism”. It was assumed that the monomers react preferentially with the oligomers and polymers, because the positive charge and the lone electron are better stabilized in longer chains than in dimers. Rajan et al [39, 40] described a mathematical treatment of this PPS synthesis and calculated a two-step kinetic with a chain growth 45 times faster than the formation of dimers. However, a potential influence of cyclization was not discussed and the Koch-Heitz mechanism does not explain all results of the Edmonds-Hill method.

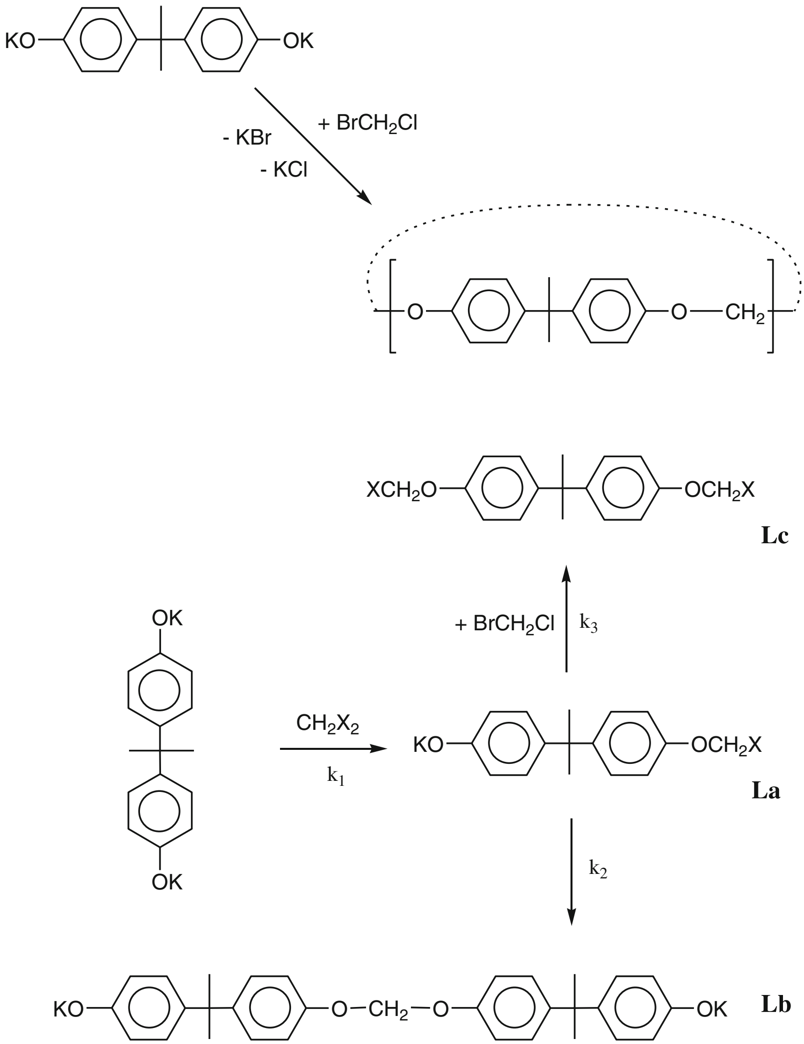
Around 1983 Hay and other members of General Electric [41–43] began to explore the preparation of high molar mass polyformals by polycondensation of diphenols with dibromo or dichloromethane (see Formula 8.5) using tetraalkylammonium chlorides as catalysts. Under optimized reaction conditions polymers free of cyclic oligomers having Mn’s up to 250 kDa and Mw’s up to 333 kDa were obtained. From their own results and from model reactions of other research groups [44–46] Hay et al. derived the following mechanistic concept. When only



Formula 8.4

small amounts of bisphenol-A salts slowly dissolve in polar reaction media, the slowly formed La chains will have higher concentrations than Lb or Lc chains. Nonetheless, their absolute concentration is low, so that cyclization can effectively compete with chain growth, and the DP remains relatively low. Yet, all parameters favoring rapid dissolution of bisphenol salts accelerate the transformation of La into Lb chains (and thus high DPs), because the reactivity of the OCH_2-X groups is higher than that of CH_2X_2 ($k_2 \gg k_1$ in Formula 8.5). In other words, those authors attributed for the first time the successful synthesis of high molar mass polycondensates to the suppression of cyclization.

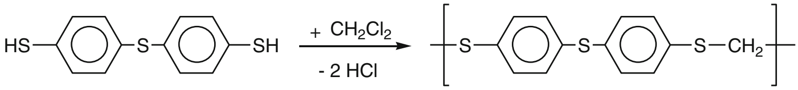
From the preparative point of view it should be noted that Hay et al. prepared polyformals for more than 15 bisphenols. Fluorine substituted polyformals were later contributed by a Japanese research group [47]. Those authors observed the

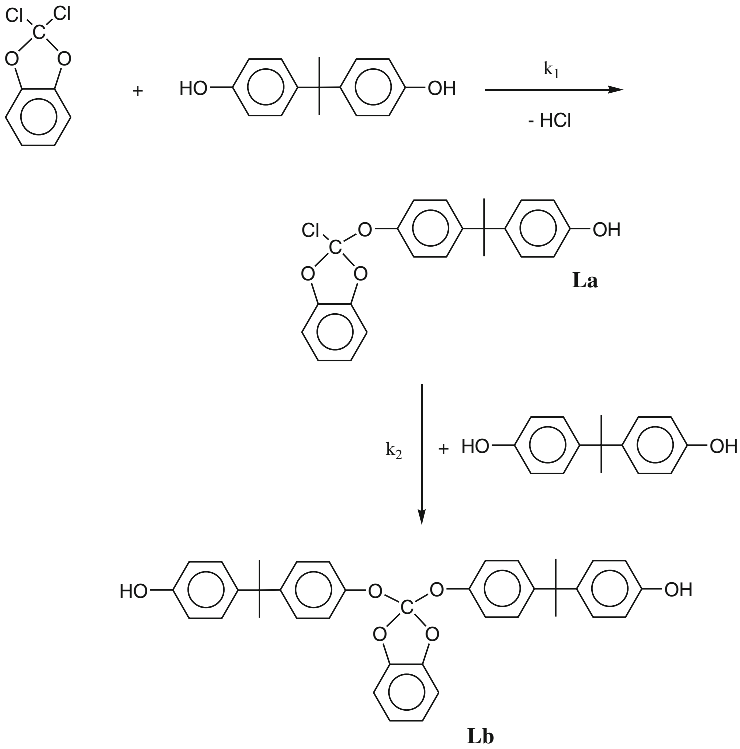


Formula 8.5

same kinetic phenomena reported by Hay et al. but molecular weight measurements were not performed. Ueda and coworkers, [48] studied a similar non-stoichiometric polycondensation using bis(4-mercaptodiphenyl)sulfide as reaction partner of CH_2Br_2 and obtained an aromatic polythioformal (Formula 8.6 top). They found again a two-step kinetic with $k_2 = 61 \times k_1$, and observed that an excess of CH_2Br_2 enhances both, the rate and the degree of polymerization. Molecular weight data were not reported.

In 1999 Endo et al. [49] reported on the polycondensation of bisphenol-A with 2,2-dichloro-1,3-benzobisoxazole (see. Formulas 8.6). Again a two-step kinetic

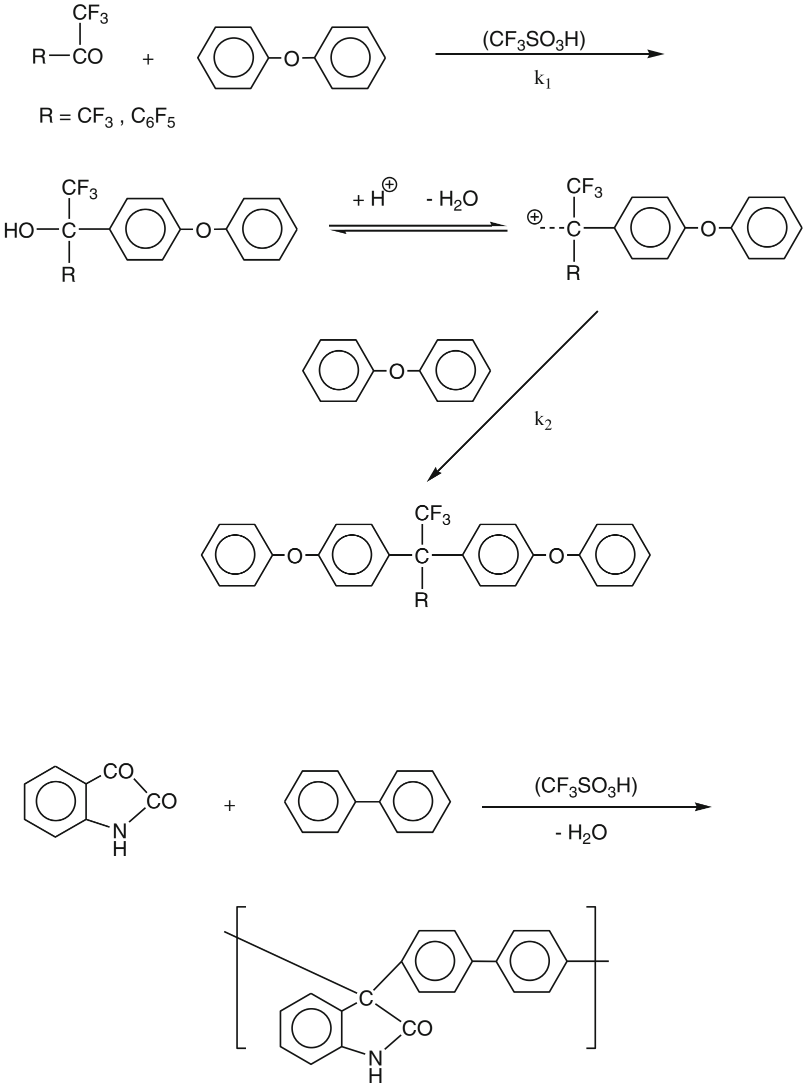




Formula 8.6

was found, and from model reactions a k_2/k_1 ratio of 27 was deduced. Both, polymerization rate and DP increased, when an excess of the dichloromonomer was added. Optimization of the reaction conditions yielded poly(ortho-carbonate)s having Mn’s up to120 kDa (polystyrene-calibrated SEC measurements). Endo et al. did not cite the work of Hay and they did not discuss reaction pathway and kinetic on the basis of the intermediates La, Lb, and Lc. However, it is obvious that the influence of the excess dichloromonomer is analogous to that of CH_2X_2 in the work of Hay et al.

Finally, proton-catalyzed polymerizations of nucleophilic aromatics with fluorinated ketones need discussion. Polycondensations of phenols with aldehydes or their substitutes (e.g., hexamethylene tetramine) are known since 1870 and culminated in the technical production of Bakelite (see Chap. 2). During the past 10 years Zolotukhin et al. [50–56]. studied polycondensations of fluorinated ketones (or isatin) with monomers such as biphenyl, diphenyl ether and other phenyl ethers (see Formula 8.7). Trifluoromethane sulfonic acid served as catalyst, and it was found that an excess of the ketone dramatically enhanced the molar masses of the reaction products. For the polymer derived from trifluoroacetone and 4,4-diphenoxybenzophenone a maximum Mn around 250 kDa was obtained, and the inherent viscosities of other polymers suggest that in most cases Mn′s > 100 kDa were achieved [56]. Kinetic measurements were not performed, but calculations of activation energies suggested that growing steps (k_2 in Formula 8.7) were faster



Formula 8.7

than the condensation of two monomers (k_1). MALDI-TOF mass spectra indicated that cyclization was not completely suppressed even when an excess of ketone was used, but a clearcut correlation between reaction conditions and extent of cyclization was not elaborated.

In summary, two conclusions may be drawn. First, non-stoichiometric polycondensations of class III may give much higher molar masses than polycondensations of a-b monomers. Second, the kinetic course of the polymerizations deviate largely from that of a normal step-growth polymerization, and the term non-stoichiometric polycondensation is rather a formal label than a correct terminology. In the extreme case, when cyclization is totally suppressed, class III polymerization exactly obeys the definition of an $a_2 + b_2$ "condensative chain polymerizaion". This term was proposed by IUPAC, and numerous "condensative chain polymerizations" are known from a-b monomers as discussed in Chap. 16.

8.5 $a_2 + b_n$ Polycondensations

Whereas for $a_2 + b_2$ polycondensations the equimolar and equifunctional feed ratio is necessarily identical, both feed ratios are quite different in $a_2 + b_n$ polycondensations and yield different architectures. Therefore, three different regimes of non-stoichiometric polycondensations may be defined:

(1) $[a_2]/[b_n] <$ equimolar (1.0/1.0)
(2) Equimolar $< [a_2]/[b_n] <$ equifunctional (1.5/1.0 for b_3 or 2.0/1.0 for b_4)
(3) $[a_2]/[b_n] >$ equifunctional

Furthermore, it must be taken into account that the IMC plays a greater role for the course of $a_2 + b_n$ polycondensations. Even without considering kinetic details, the four parameters mentioned above allow for the definition of eight scenarios yielding different architectures.

(A) $[a_2]/[b_n] < 1/1 +$ moderate or high IMC's (e.g., $>$ 0.2 mol/L) yield more or less branched oligomers and low molar mass polymers almost free of cyclic elements and exclusively "decorated" with "b" groups.
(B) Equimolar stoichiometry + high IMC (e.g., $>$ 0. 6 mol/L) yield (hyper)-branched polymers mostly containing a cyclic core and only "b" groups at 100 % conversion.
(C) $[a_2]/[b_n] >$ 1.0/1.0 and $<$ 1.5/1.0 (b_3) or $<$ 2.0/1.0 (b_4) + high IMC's yield gels.
(D) $[a_2]/[b_n] >$ 1.0/1.0 and $<$ 1.5/1.0 (b_3) or $<$ 2.0/1.0 (b_4) + moderate IMC's (e.g., 0.01-0.2 mol/L) may yield soluble multicyclic polymers rich in "b" groups Equifunctional feed ratios + high IMC′s yield gels.
(E) Equifunctional feed ratios + moderate IMC′s (e.g., 0.01-0.1 mol/L) yield multicyclic polymers free of functional groups at 100 % conversion (see Chap. 12).

(F) Equifunctional feed ratios + low IMC’s (e.g., 10-5 mol/L) yield bicyclic or tricyclic oligomers.

(G) $[a_2]/[b_n]$ > equifunctional + high IMC’s yield gels and multicyclic polymers having “*a*” groups at molar ratios close to equifunctional or yield branched oligomers at very high $[a_2]/[b_n]$ ratios

Non-stoichiometric polycondensations according to the scenarios (1) were not systematically studied. $[a_2]/[b_2]$ feed ratios < 1.0/1.0 yield hyperbranched oligomers, which after complete conversion of the “*a*” functions possess numerous “*b*” end groups. Syntheses of Novolac from formaldehyde with excess of phenol are example of such a polycondensation (see Chap. 2). Numerous examples are mentioned in the literature dealing with equimolar polycondensations (see Chap. 10). To the best knowledge of the author, non-stoichiometric polycondensations according to scenario (3) were never systematically studied. Several examples of non-stoichiometric polycondensations according to (2) were published in connection with syntheses of multicyclic polymers from equifunctional polycondensations (see Chap. 12).

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Chapter 9
Ring-Opening Polycondensation

9.1 Introduction

Since the days of Carothers polycondensations and other step-growth polymerizations were described in the review articles and textbooks on the basis of linear monomers. Having reactive “a” and/or “b” groups, on the other hand, cyclic monomers were usually presented in combination with Ring-Opening Polymerizations (ROPs) which obey the kinetic scheme of a chain-growth polymerization. This means that chain growth exclusively proceeds by reactions of monomers with the active end groups of the growing chains. However, heterocycles having at least to identical reactive bonds in the ring may serve as a_2 monomer in step-growth polymerizations. Since polycondensations of cyclic monomers automatically involve a ring-opening step, this kind of polymerizations may be called ring-opening polycondensation, which in this text will be abbreviated RO-PC to avoid confusion with standard ring-opening polymerization, which is usually (also in this book) abbreviated a ROP. Since the kinetic course of a RO-PC obeys the definition of a normal polycondensation (see Chap. 1), one might ask, why RO-PCs need separated discussion. Yet, apart from preparative aspects it should be kept in mind that all polymerizations have a thermodynamic aspect, and the thermodynamic properties of RO-PCs are different from that of a normal polycondensation.

The polycondensation of linear monomers is characterized by elimination of one small molecule (e.g., H_2O, HCl, or CH_3OH) in each growing step. The liberation of the byproduct compensates for the loss of entropy resulting from the loss of three-dimensional translational motion of the monomers. Hence, the reaction entropy is close to zero (the exact value depends on the extent of rotational motion in monomer and repeating unit). A typical RO-PC is based on two different growing steps. The first one is an addition reaction and elimination of a byproduct only occurs in the second step which is a condensation reaction as illustrated for the polycondensation of an α,ω-alkanediol with maleic anhydride (see Formula 9.1). Therefore, RO-PCs have a negative reaction entropy which needs to be overcompensated by a negative reaction enthalpy (i.e., by an exothermic

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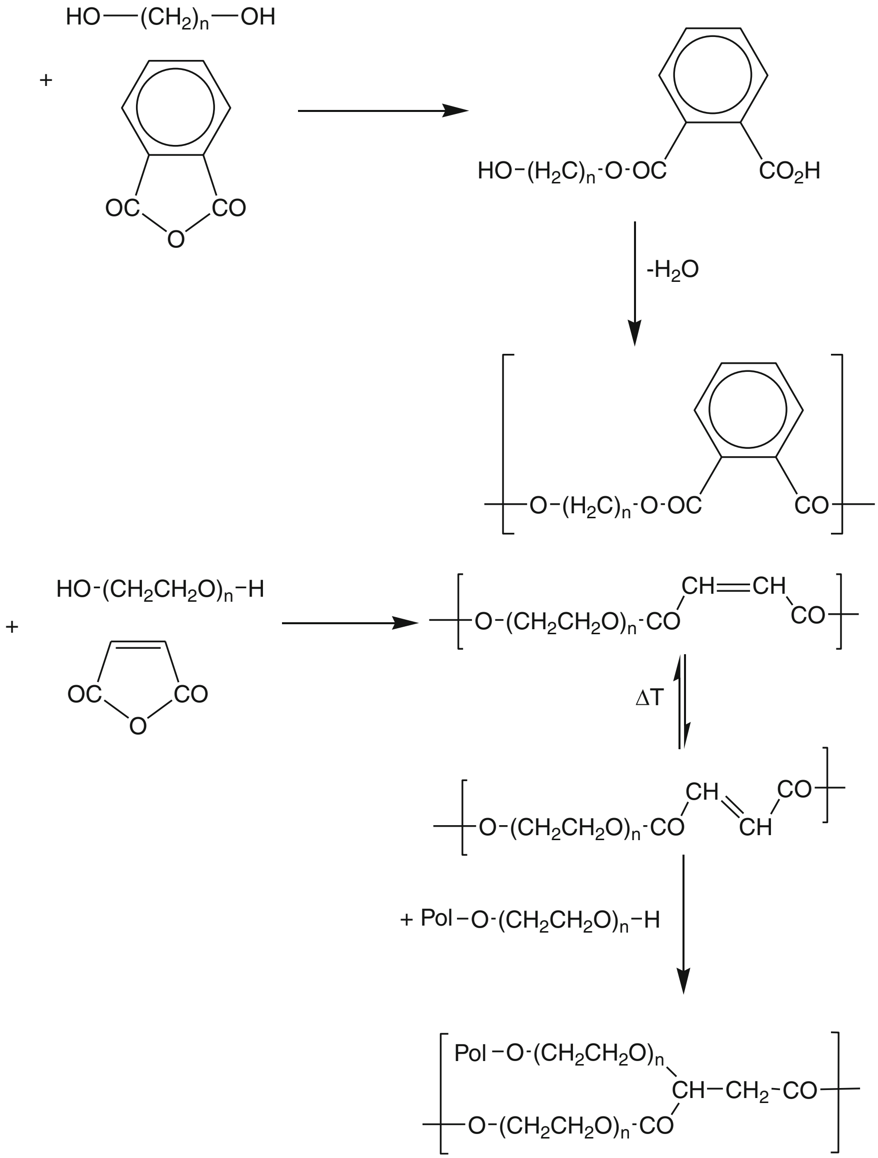
reaction). The amount of ΔS depends on the ring size, because ring-opening may free rotational motions. With regard to rotational motions and their consequences for ΔS cyclic monomers may be subdivided into three categories.



Formula 9.1

(i) Small cycles with severely hindered internal motion. These cycles generate a modest gain of entropy upon ring-opening which slightly reduces the negative ΔS resulting from the loss of translational motion.

(ii) Cycles having 8–10 ring members with hindered rotational motion. The unfreezing of the full rotation may then compensate for 50 % of the negative ΔS.

(iii) Large cycles with almost free rotational motions. The ring-opening of large cycles does not make any significant contribution to the reaction entropy.

A handful of RO-PCs is known which is based on two cyclic monomers, a cyclic "a_2" monomer and a cyclic "b_2" monomer so to say. The classification of cyclic monomers given above is valid again, but the gain in rotational freedom may now be higher by a factor of two. This means, that the reaction entropy is close to zero, when two monomers of class II react with each other.

RO-PCs involving cyclic anhydrides have a tradition of almost 100 years, and thus polycondensations of cyclic anhydrides will be discussed first.

9.2 RO-PCs of Cyclic Anhydrides

Apparently, the first polycondensation of a cyclic anhydride is described in a patent of 1916 which deals with the reaction of phthalic anhydride and glycerol. This reaction and other polycondensations of glycerol represent examples of "a_2" + "b_3" polycondensations, which are discussed in Chap. 10. RO-PCs of phthalic anhydride with α,ω-alkanediols were mentioned in papers and patents of Carothers, but a detailed description of individual examples was never provided. Homopolyesters of phthalic acid have never found any application, but phthalic anhydride plays a role as comonomer in unsaturated copolyesters based on maleic and/or fumaric acid.

The concept of unsaturated polyesters (international abbreviation: UP) which can be cured and hardened by heating with sources of radicals was developed by C. Ellis in the 1930s [1–3], and the first patent application was submitted in 1936 Ellis also discovered that dilution of the unsaturated polyesters with vinyl monomers, such as styrene (most widely used) or vinyl acetate is favorable for most applications. The dilution reduces the viscosity. Eases the dissolution of additives and catalysts and lowers the costs. The most frequently used catalysts for the curing process are peroxides. The variation of their structure allows for optimization of the cure. The most important application of UPs are:

(1) as thermosetting resins for reinforced composites
(2) as coatings
(3) as insulating lacquers

These quite different applications require a broad variation of the properties. For instance, stiffness and harness can be enhanced by incorporation of rigid monomers such as phthalic anhydride and by a higher crosslinking density. Softer, more flexible, and elastomeric materials result from incorporation of oligo(ethylene oxide)s (see Formula 9.1), and from a lower crosslinking density usually combined with longer blocks of polystyrene or other vinyl polymers. Furthermore, maleic anhydride may partially be replaced by the more bulky tetrahydrophthalic anhydride, and trimellitic anhydride may be incorporated, when branching is desired. The numerous applications and variants of UPs were described and discussed in many book chapters and review articles, a selection of which is given in Refs. [4–12].

The preparation of UPs from maleic anhydride is usually performed at temperatures from 140–180 °C The liberated water is removed in vacuo until the desired viscosity is achieved. A more precise control of molecular weights and viscosity may be achieved by addition off monofunctional reagent, such as saturated or unsaturated fatty acids. These polycondensations involve two (mostly) undesired side reactions. The most frequent side reaction is isomerization of maleic acid units to fumaric acid moieties (see Formula 9.1). The fumarate units are thermodynamically more stable, and isomerisation is favored by longer times and higher temperatures Technical products typically contain 40–70 % fumarate units. Addition of a catalyst, such as morpholin, may raise the extent of isomerization up to 99 %. High contents of fumarate groups are desired because they react about 20 times faster with styrene than th maleate units, and they are less reactive toward the addition of alcohols. The addition of OH end groups of diols or oligomers onto maleate groups is the second side reaction (see Formula 9.1). This addition reaction transforms double bonds into saturated groups and is called after its discoverer the “Ordelt Saturation” [13, 14].

Quite recently, the author and coworkers demonstrated [15, 16] that polycondensation of alkanediols with maleic anhydride or substituted maleic anhydrides proceeds without isomerisation or other side reactions, when the temperature is limited to 100 °C Such low temperatures require metal triflates as catalysts, and the highest molar masses (Mns up to 12 kDa) were obtained with Sn triflate in the case of maleic anhydride or with Bi triflate in the case of citraconic anhydride. Unfortunately, this approach is not suited for technical production of UPs, because relatively large amounts of expensive catalysts are required.

In various areas of step-growth polymerization, the past 20 years have seen increasing interest in monomers from renewable resources. An early example, namely a patent of 1962 [17] describes syntheses of UPs from maleic anhydride and mixtures of isosorbide and other diols. Isosorbide is synthesized from glucose and can technically be produced at relatively low costs, when quantities of 50,000 tons or more are needed.

Another monomer which can be produced from renewable resources is succinic acid or its anhydride. Aliphatic polyesters of succinic acid are crystalline and biodegradable. Particularly interesting and commercial is poly(1,4-butanediol succinate), because its melting temperature ($T_m = 120$ °C) is higher than that of all other polyesters from α,ω-alkanediols. For most syntheses of poly(alkane succinate)s described in the literature succinic acid was used as monomer, but recently two papers of the author et al. [18, 19]. reported on RO-PCs of succinic anhydride. The reaction of the anhydride with a diol is faster and reduces the risk that in small scale experiments monomers distil out of the reaction mixture. Not only polyesters but also polyamides were prepared from succinic anhydride, methylsuccinic anhydride, and glutaric anhydride [20]. Secondary diamines such as 1,6-bis(methylamino)hexane and 4,4-trimethylene dipiperidine, were used as reaction partners, because primary diamines preferentially yield imide end groups.

Finally, RO-PCs of two different cyclic monomers are worth mentioning. Only two monomer combinations have been reported so far (see Formula 9.2).

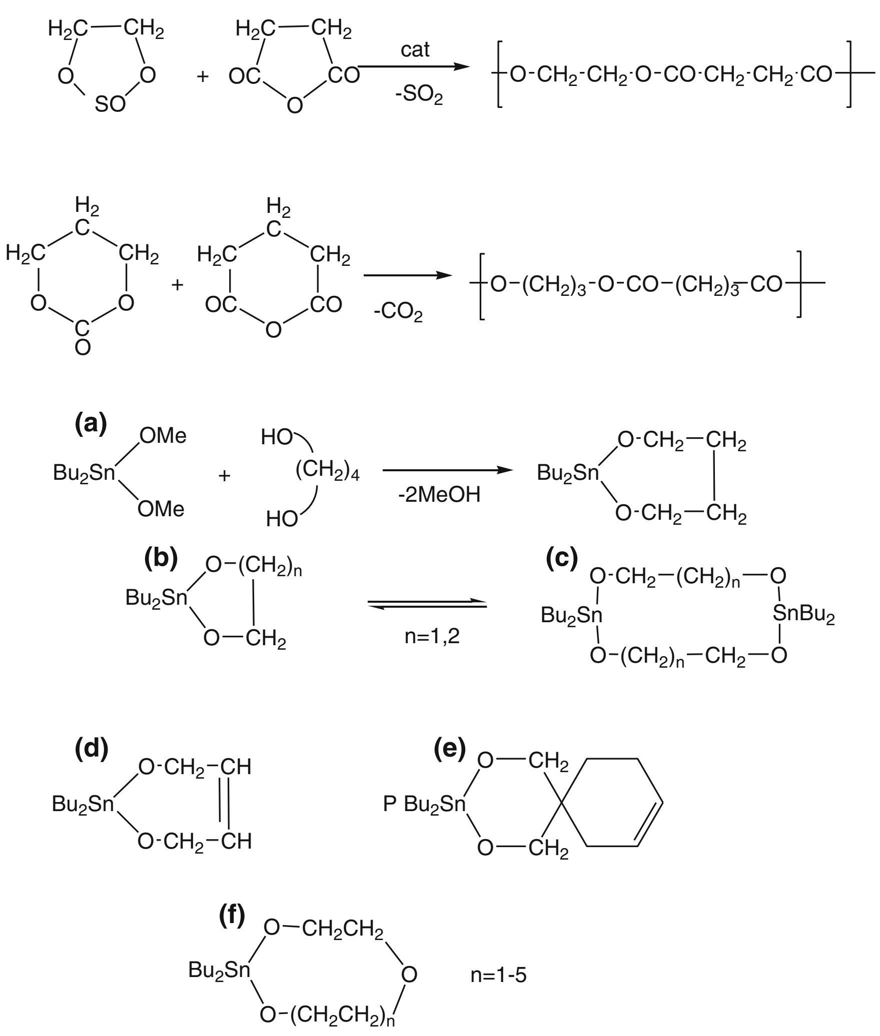
(a) Cyclic sulfites + cyclic aliphatic anhydrides [21],
(b) Cyclic carbonates + cyclic aliphatic anhydrides [22].

N,N-Dimethyl-4-aminopyridine proved to be the best catalyst, and Mns up to 10 kDa with Mws up to 21 kDa (Ps calibrated SEC measurements) were obtained.

9.3 Tin and Silicon Containing Monomers

(Poly)Condensations of dibutyltin dimethoxide with various diols give 2-stanna, 1,3-dioxaheterocycles in high yields (see Formula 9.2 a–f) [23, 24]. The tin atom enhances the nucleophilicity of the adjacent oxygen, and tin alkoxides react rapidly and exothermically with a variety of electrophilic reaction partners [25]. As reported by the author [25], mixing of 2,2-dibutyl-2-stanna-1,3-dioxepane with aliphatic dicarboxylic acid dichlorides results in a highly exothermic reaction, which raises the temperature by 120–130 °C (see Formula 9.3, top). Therefore, rather high molar masses were obtained even without catalyst and without removal of the high-boiling byproduct Bu_2SnCl_2. Mns in the range of 15–30 kDa were achieved based on polystyrene calibrated SEC measurements (which overestimate the real Mns of aliphatic polyesters by 50–60 % [25–30]). The MALDI-TOF mass spectra evidenced a high number fraction of cycles which indicated that cyclization made a significant contribution to the limitation of the chain growth. Analogous polycondensations of other stanna-heterocycles (b–f in Formula 9.2) have not been reported yet. Since, tin alkoxides also react easily with ester groups, the 2-stanna-1,3-dioxaheterocycles may be used as initiators for the ring-expansion polymerization of lactones [31]. The Sn-O bonds of the resulting cyclic polyesters react with dicarboxylic acid dichlorides like the small “stannacycles” and yield chain extended polylactides (see Formula 9.3). This synthetic approach slows for a broad variation of all components, and a more detailed discussion of this working field is presented in Chap. 14.

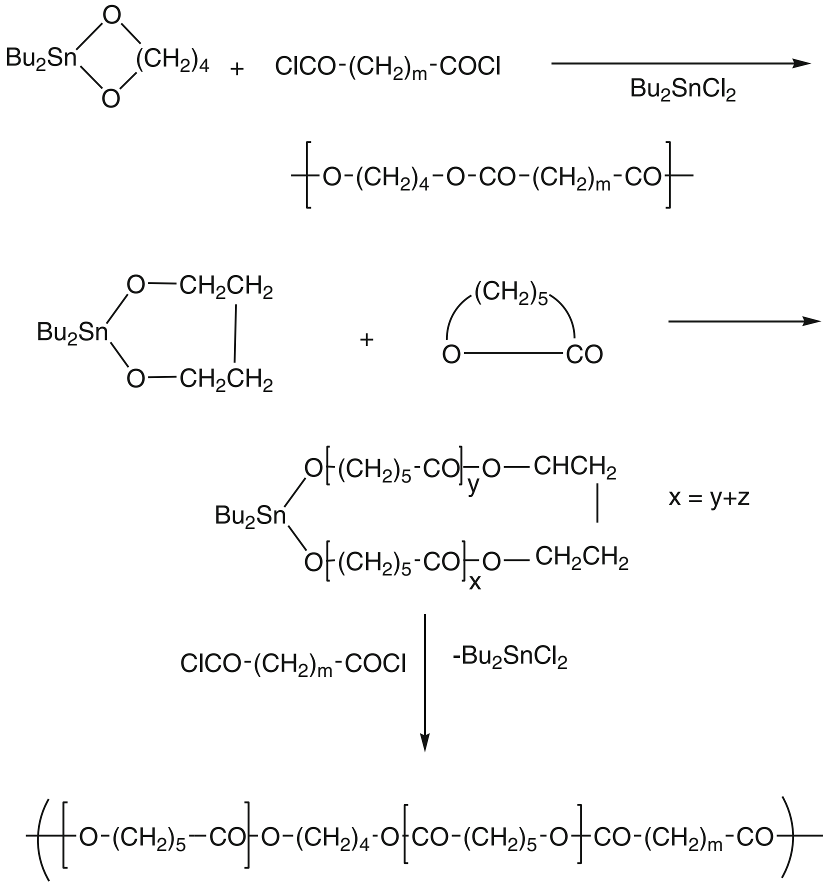
When 2,2-dibutyl-2-stanna-1,3-dioxepane ((a) in Formula 9.2) was mixed with bisphenol-A bis-chloroformiate, again an exothermic reaction took place, and polycarbonates having corrected Mns up to 30 kDa with PDs around 1.5 were obtained [32] (see Formula 9.4). Due to the fact that the Sn-S bond is



Formula 9.2

thermodynamically more stable than the Sn-O bond (better overlapping of the free d-orbitals of Sn with the electrons of the p-orbitals of S), 2,2-dibutyl-2-stanna-1,3-dioxepane also reacts with the bis(thiophenyl)esters of dicarboxylic acids (see Formula 9.4). Yet this RO-PC is less exothermic, and the resulting Mns are lower than those obtained from RO-PCs of dicarboxylic acid dichlorides (Mns up to 10 kDa) [33].

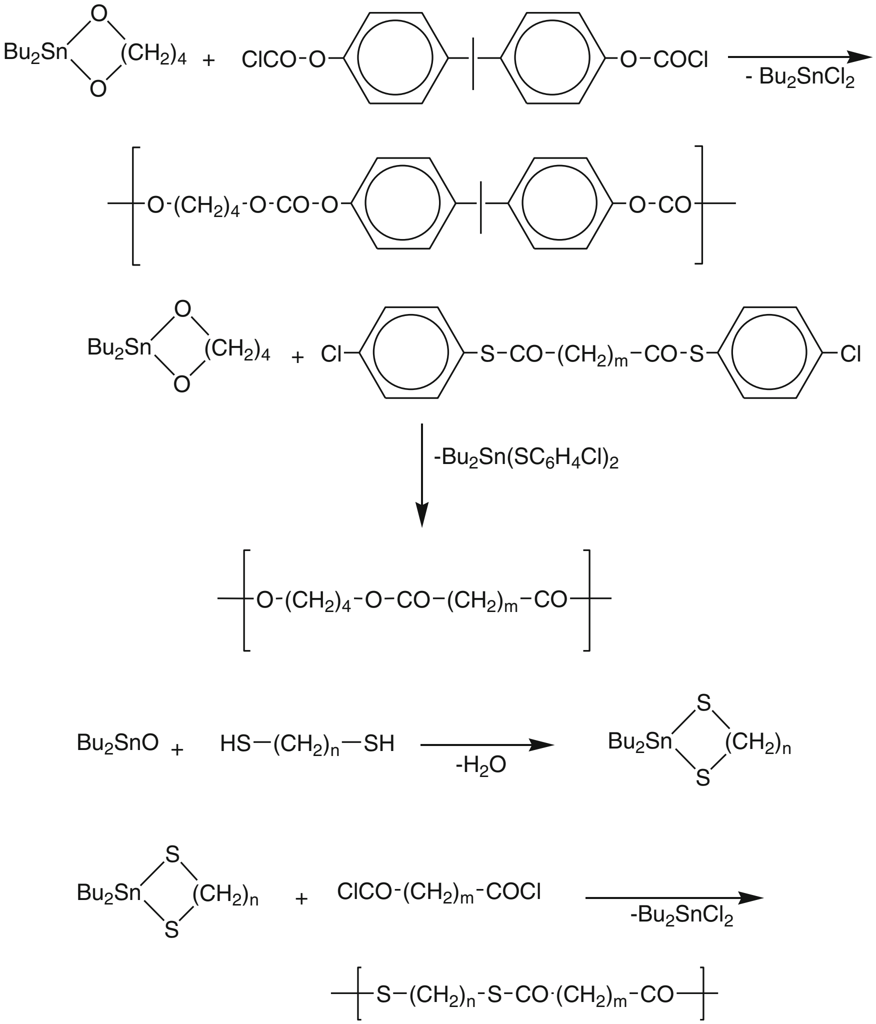
Since the formation of Sn-S bonds is kinetically and thermodynamically favorable 2-stanna-1,3-dithiolanes or—dithianes are easy to prepare, for instance from dibutyltin dimethoxide or from dibutyltin oxide (see Formula 9.4, bottom).



Formula 9.3

These heterocycles are crystalline and stable on storage, and thus represent easy to handle active derivatives of dimercaptanes. They react exothermically with dicarboxylic acid dichlorides. In dilute solution cyclic oligoesters were obtained [34, 35], whereas RO-PCs in bulk yielded poly(thioester)s (see Formula 9.4) [36, 37] having Mns in the range of 20–25 kDa with polydispersities around 2.0. These crystalline poly(thioester)s showed the unexpected property that two exotherms were detectable in the DSC heating curves. The exotherm (and the endotherm observed upon cooling) represent a reversible change of the crystal modification, a property which is unknown from analogous polyesters of α,ω-alkanediols.

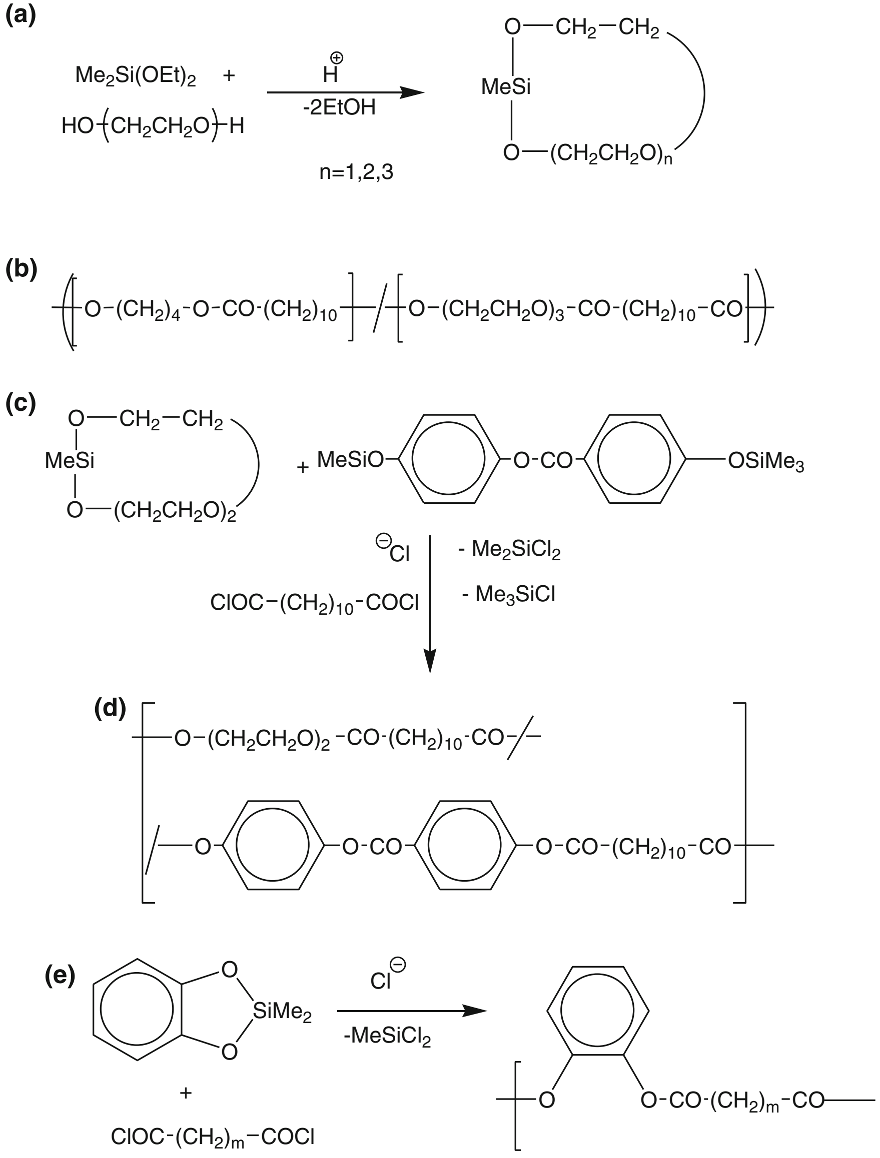
Further studies of RO-PCs were based on the Si-containing heterocycles (a) in Formula 9.5. Surprisingly, these heterocycles can be obtained in good yields by polycondensation of diethoxydimethylsilane and oligo(ethylene glycol)s in bulk



Formula 9.4

(see Formula 9.5), whereas analogous polycondensations of a,ω-alkanediols mainly yield linear oligomers and polymers [38].

RO-PC with decane-1,10-dicarbonyl chloride were not significantly exothermic. They required chloride ions as catalysts, temperatures up to 240 °C and removal of the volatile byproduct Me_2SiCl_2 [39]. In this way polyesters were obtained, the Mns of which fell into the range of 12–30 kDa or 18–48 kDa depending on the calibration of the SEC elution curves. Further homopolyesters were prepared by RO-PCs with terephthaloyl chloride, naphthalene-2,-dicarbonyl



Formula 9.5

chloride, or with an imide monomer. It was expected that crystalline or liquid-crystalline polyesters were formed, but all reaction products were amorphous.

Two different kinds of copolycondensations should be mentioned First, it was demonstrated by the author that a mixture of 2,2-dibutyl-2-stanna-1,3-dioxepane and "silacycle" (o), n = 2, (see Formula 9.5) is suitable for RO-PC with decabne-1,10-dicarbonyl chloride despite their different reactivities. When the RO-PC is started at room temperature, the exothermic reaction of the “stannacycle” comes first and the polycondensation of the “silacycle” follows at high temperatures. In the absence of transesterification, block-copolymers should be formed, and the reaction product was indeed crystalline ((b) in Formula 9.5). Unfortunately, neither ^{1}H NMR nor ^{13}C NMR spectra provide sequence information in this case. A second approach was realized by cocondensation of the silacacle” (a), n = 2, and silylated hydroquinone 4-hydroxybenzoate ((c) in Formula 9.5) [39]. Since this diphenol is a mesogenic building block, it was hoped that the resulting copolyester ((f) in Formula 9.5) might be liquid-crystalline, but this hope was in vain.

Finally, RO-PCs of the aromatic “silacycle” (e) (Formual 9.5) with various dicarboxylic acid dichlorides were studied [39]. These polycondensations were again performed in bulk using chloride ions as catalysts. The ^{1}H NMR spectra indicated almost complete conversion, but the solution viscosities were so low that the Mns certainly did not exceed 2 kDa. The Fast-Atom-Bombardment mass spectra exclusively displayed peaks of cyclic oligoesters, suggesting that the chain growth was mainly limited by cyclization.

“Silacycles containing Si-S or Si-N bonds should be far more reactive than the “silacycles” discussed above, but RO-PCs of such reactive “silacycles” have not been reported yet.

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Chapter 10
Hyperbranched Polymers by $a_2 + b_n$ Polycondensation

10.1 Introduction

The term “hyperbranched (hb) polymers,” meaning a tree-like type of architecture, was coined by Kim and Webster [1] in a paper describing the synthesis of branched polyphenylenes from 3,5-dibromobenzene boronic acid (see Chap. 11). Although this working field has a long tradition (see below) its systematic and intensive exploration began only after 1980. Its rapid growth is illustrated by the fact that only a handful of pertinent papers appeared in 1989, whereas more than 500 papers per year appeared 20 years later. This flood of publications has entailed numerous review articles the vast majority of which is presented in the References. [2–26].

With regard to both, synthetic strategies and architecture hb polymers may be subdivided into two large groups: polymers prepared from $a_2 + b_n$ monomer combinations and polymers derived from ab_n monomers. The most conspicuous and characteristic differences between both groups are:

(1) The $a_2 + b_n$ polycondensations allow for a variation of the stoichiometry, and thus, a variation of end groups in contrast to ab_n monomers. Further consequences of such a variation are discussed in Chaps. 8 and 12.
(2) HB polymers prepared from $a_2 + b_n$ monomers may possess two or more “a” functionalities, when the conversion is not complete. In the case of ab_n monomers the maximum number of “a” functionalities is unity regardless of the conversion.
(3) HB polymers derived from ab_n monomers can only form one cyclic element, so that the architecture changes from tree-shaped to sun-shaped with increasing conversion. Yet, hb polymers based on $a_2 + b_n$ monomers may contain two or more cyclic moieties at high conversions. Such polymers may be considered as multicyclic polymers having hb side chains (see Chap. 12).
(4) As already mentioned by Flory [27], polycondensations of ab_n monomers do never result in crosslinking, when side reactions are absent, whereas $a_2 + b_n$ monomers will yield gels at a_2/b_n ratios > 0.9, and at high monomer concentrations and conversions.

H. Kricheldorf, *Polycondensation*, DOI: 10.1007/978-3-642-39429-4_10,

(5) ab_n monomers are not commercial in contrast to several b_n and numerous a_2 monomers, so that $a_2 + b_n$ monomer combinations are better suited for large-scale production of hb polymers.

When compared to linear polymers hb polymers require an additional parameter for the characterization of their architecture, namely the degree of branching (DB). A first definition was presented by Hawkwer and Frechet [28] on the basis of NMR spectroscopic results. If terminal groups (T), branching units (B) and linear repeat units (L) may be identified and quantified, the DB may be defined and calculated according to Eqs. (10.1) or (10.2). Another definition, taking into account that the DB depends on the conversion (p), is given in Eq. (10.3) [29, 30]. The influence of chemical structure, architecture and DB on various physical and mechanical properties is discussed in most recent reviews.

$$\mathrm{DB} = (\mathrm{B} + \mathrm{T})/(\mathrm{B} + \mathrm{T} + \mathrm{L}) \tag{10.1}$$

$$\mathrm{DB} = 1/(1 + \mathrm{L}/2\mathrm{B}) \tag{10.2}$$

$$\mathrm{DB} = 2\mathrm{p}/(5 - \mathrm{p}) \tag{10.3}$$

Since polycondensations of $a_2 + b_n$ monomers have a much longer history, their description and discussion will be presented first. Syntheses of hb polymers from ab_n monomers will be discussed in Chap. 11. To avoid misunderstandings, it should be emphasized that the text of both Chaps. 10 and 11, is limited to true polycondensation processes. Synthses of hb polymers based on addition-polymerizations, ring-opening polymerizations, or stepwise construction of dendrimers are not considered.

10.2 Symmetrical b_n Monomers

The consequences for the architecture of the reaction products resulting from variation of the feed ratio are discussed in Chaps. 8 and 11. Therefore, this subchapter focuses essentially on equimolar polycondensations, which had the purpose to yield soluble hb polymers having numerous functional end groups. It is mentioned in a paper of Kienle and Horvey [31] that J. J. Berzelius (1779–1848), one of the great pioneers of modern chemistry, who performed the first $a_2 + b_3$ polycondensation by heating tartaric acid and glycerol (the author was not able to find a precise reference). About four decades later studies of $a_2 + b_3$ polycondensations were resumed by those chemists who were interested in reactions of phenol with aldehydes. As discussed in Chap. 2, these research activities ended successfully with the commercialization of Novolac (used for coating and insulating purposes) and with technical production of Bakelite.

Systematic studies of $a_2 + b_3$ polycondensations began with the work of W. Smith [32], who reported in 1901 on polycondensations of glycerol and phthalic anhydride. In the following four decades numerous patents and publications were contributed by chemists of General Electric [33–40].These polycondensations were mainly based on glycerol with aliphatic dicarboxylic acids or cyclic anhydrides as reaction partners, and the role of time and temperature was examined. At relatively short times and lower temperatures soluble resins recommended as varnishes were obtained, which upon heating were transformed into crosslinked coatings and solid articles (typically commercialized as insulating materials). The group of Kienle [37–40] tried to analyze the kinetic course of these complex reactions by titration of CO_2H end groups. Further experimental and theoretical studies were contributed by Flory [27] and later by Argyropoulos [41]. Because for the final application crosslinking was desired, all these studies and technical productions were conducted with feed rations $> 1{:}1$, usually with equifunctional feed ratios. Only one patent [42] was focused on equimolar ratios of glycerol and its reaction partners, with the purpose to reduce the risk of gelation during production and storage of the resins.

A new stimulus came into the field of $a_2 + b_3$ polycondensations after 1980 by Aharoni and other members of Allied Corp. This research group published a dozen of papers on syntheses and characterization of polyaramide networks, but reported in a few papers also on the extraction of soluble highly branched polyamides [43–47]. However, it should be mentioned at this point that Aharoni coined the term “fractal polymers” for the soluble branched polymers to make clear that their architecture is different from that resulting from ab_2 monomers. Unfortunately, this useful terminology was not accepted by other researchers. Jikei et al. [48]. were the first groups reporting on hb polyaramides prepared from equimolar feed ratios of the reactants. Those authors purposely selected the equimolar feed ratio to reduce the risk of crosslinking and they optimized the reaction conditions by lowering the monomer concentration to 0.1 mol/L of each monomer. Trimesic acid (TMA) and 1.4-diaminobenzene or 4,4′-diphenyl ether were polymerized by means of triphenylphosphite + pyridine (Yamazaki method) in analogy to Aharonis experiments. Similar equimolar polycondensations of trimesic acid and 1,4-diaminobenzene were also studied by Russo et al. [49, 50]. The question to what extent cyclization favored by the low monomer concentration reduced the risk of gelation was not discussed.

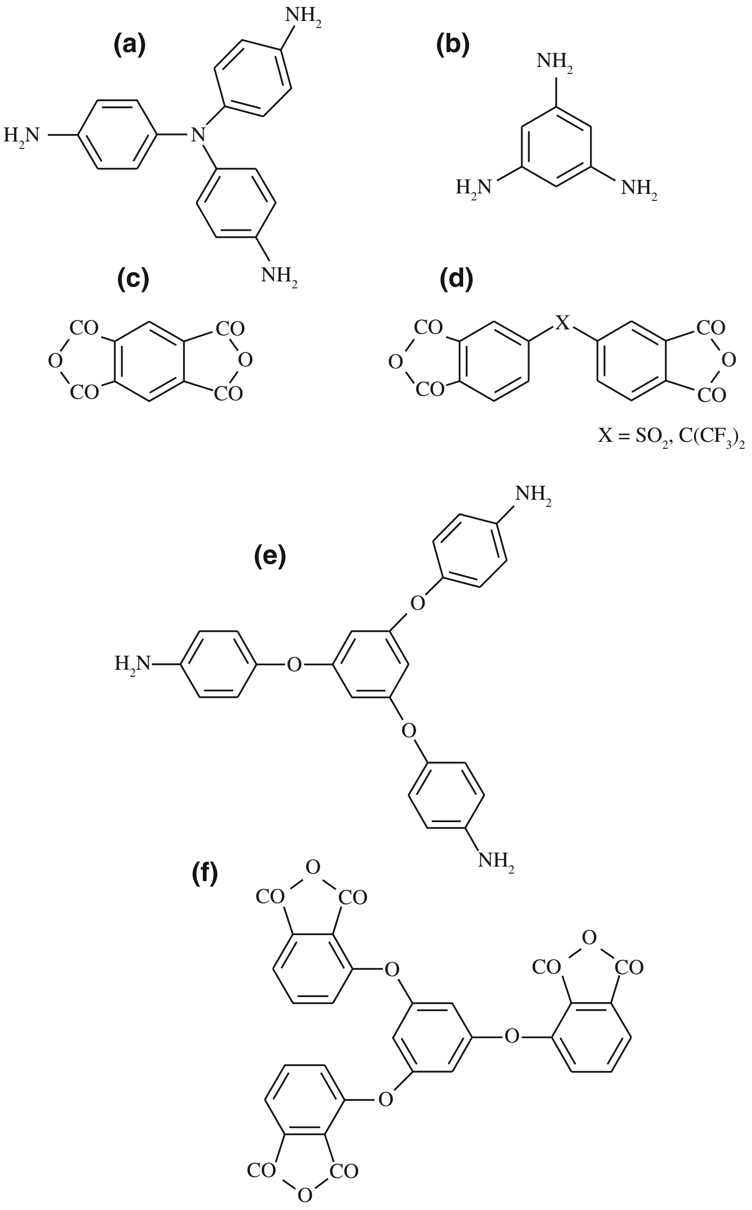
Several research groups reported on syntheses and characterization of hb polyimides [51–58].The first contribution came from Okamoto et al. [52], who used the triamine (a) (Formula 10.1) in combination with commercial tetracarboxylic anhydrides ((c) and (d)) as monomers in a_2/b_3 ratios of 1:1 and 2:1 at low concentrations (0.025 mol/L). These feed ratios had the purpose to generate either hb polyimides rich in “b” end groups or rich in “a” groups and to reduce the risk of cross-linking. The same feed ratios and anhydride (d), but triaminopyrimidine (b) were used by Liu et al. [52]. A third triamine ((e) in Formula 10.1) served as b_3 monomer in the work of Chen and Yin [53–55]. The alternative concept, namely the polycondensation of a trifunctional anhydride ((f) in Formula 10.1) with commercial diamines was explored by the research group of Kakimoto and Jikei [56–58]. Again, equimolar feed ratios and low monomer concentrations

(0.025 mol/L) were used. The authors also compared $a_2 + b_3$ with ab_2 polycondensations, so that hb polyimides having identical repeat units but different branching architecture were formed. Most authors dehydrated the initially formed polyamic acids by means of acetic anhydride, and only in one paper [52] azeotropic distillation at 180 °C was applied.

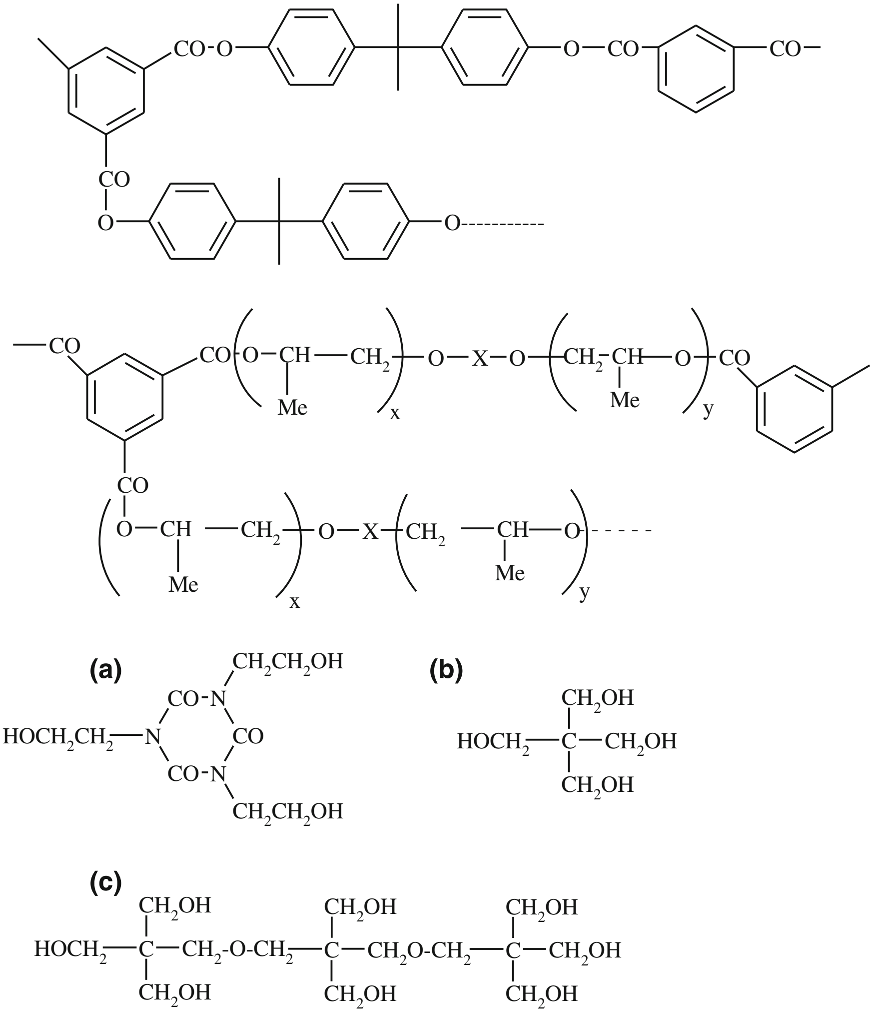
The preparation of hb polyesters by equimolar $a_2 + b_3$ polycondensation, first described in a patent of Downs [42], was recently resumed by Fossum et al. [59]. and Long et al. [60–62]. In a short communication Fossum et al. reported on polycondensations of 1,1,1-tris(methylol)propane with fumaric acid or its diethyl ester in the melt. The risk of cross-linking was reduced by moderate conversions and a_2/b_3 ratios $< 1{:}1$. Aromatic hb polyesters were prepared by Long et al. [60]. via polycondensation of bisphenol-A and trimesoyl chloride in dilute solution (0.025 mol/L) to avoid gelation. The excess of COCl groups were converted to CO_2Me groups by addition of methanol. In further studies Long et al. attempted to vary and control the distance between the branching points by using oligo(ethylene glycol)s or oligo(propylene glycol)s of low PD as a_2 monomers (see Formula 10.2). When these polycondensations were performed in dilute solution with trimesoylchloride as b_3 monomer, completely soluble poly(ether ester)s were obtained. Yet, transesterification with trimethyl trimesate in the melt resulted in gelation, unless the conversion (monitored by ^{1}H NMR spectroscopy) was stopped at 90 %. Similar results were found by Kricheldorf et al. [63]. from polycondensations of dimethyl sebacate and pentaerythritol, the only equimolar $a_2 + b_4$ polycondensation reported so far. Regardless of catalyst and reaction conditions, transesterification in the melt yielded gels above 91 % conversion.

Another approach to polyesters having only few branching points consist of the copolycondensation of $a_2 + b_2$ monomers with small amounts of a_3 or b_3 monomers. In addition to trimesic acid or its trimethylester, the multifunctional alcohols outlined in Formula 10.2 served as "branching monomers." This approach was intensively studied by several research groups to modify the physical and mechanical properties of commercial polyesters such as PET, PBT, or poly (butylene succinate). A detailed discussion of syntheses, properties, and applications presented in the excellent review of Long et. al [64].

HB polyarylenes were synthesized by two research groups via different C–C coupling methods. Smet et. al [65]. studied the condensation of isatins with a trifunctional phenyl ether (see Formula 10.3). Trifluoromethane sulfonic acid served as catalyst and the low monomer concentration prevented gelation. This approach is, in principle, a variant of the acid catalyzed aldehyde-phenol polycondensation developed more than 100 years before for the production of Novolac and Bakelite (see Chap. 2). Fossum et al. [66]. studied Pd-catalyzed polycondensations of 1,4-benzene diboronic acid with tri(4-bromophenyl)phosphioxide (see Formula 10.3).



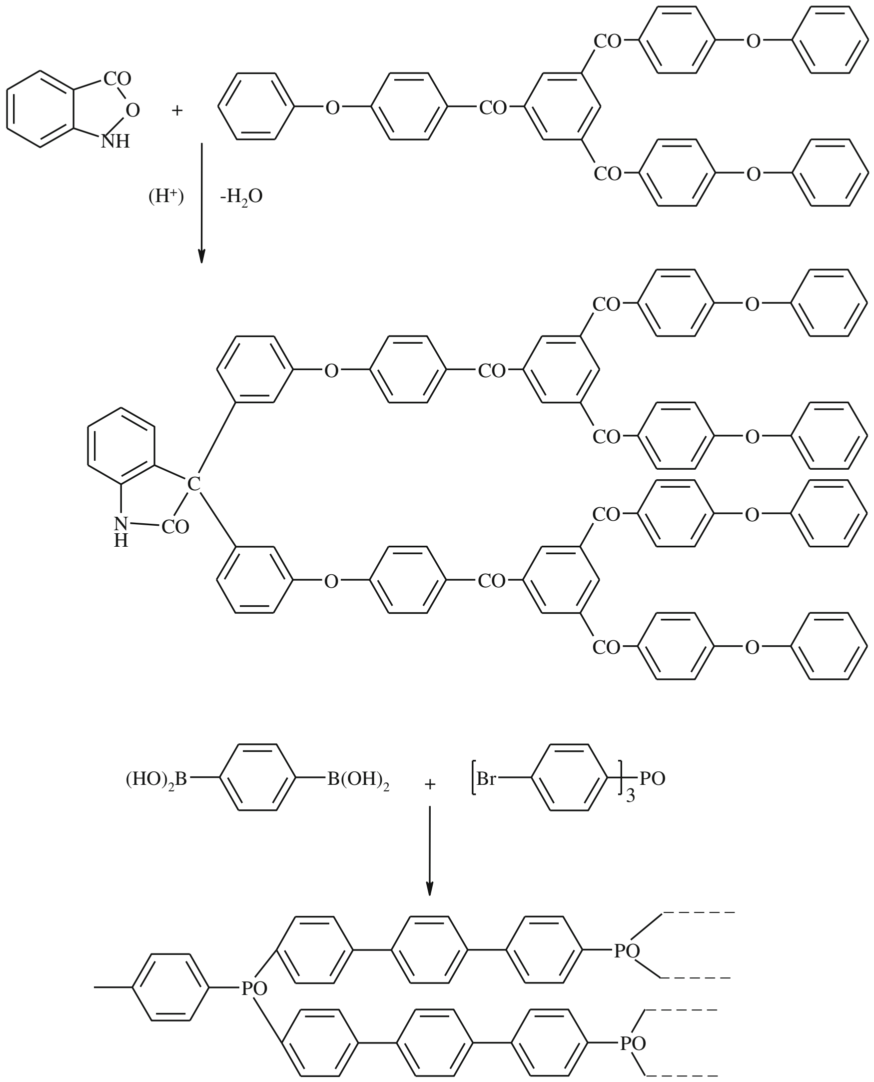
Formula 10.1



Formula 10.2

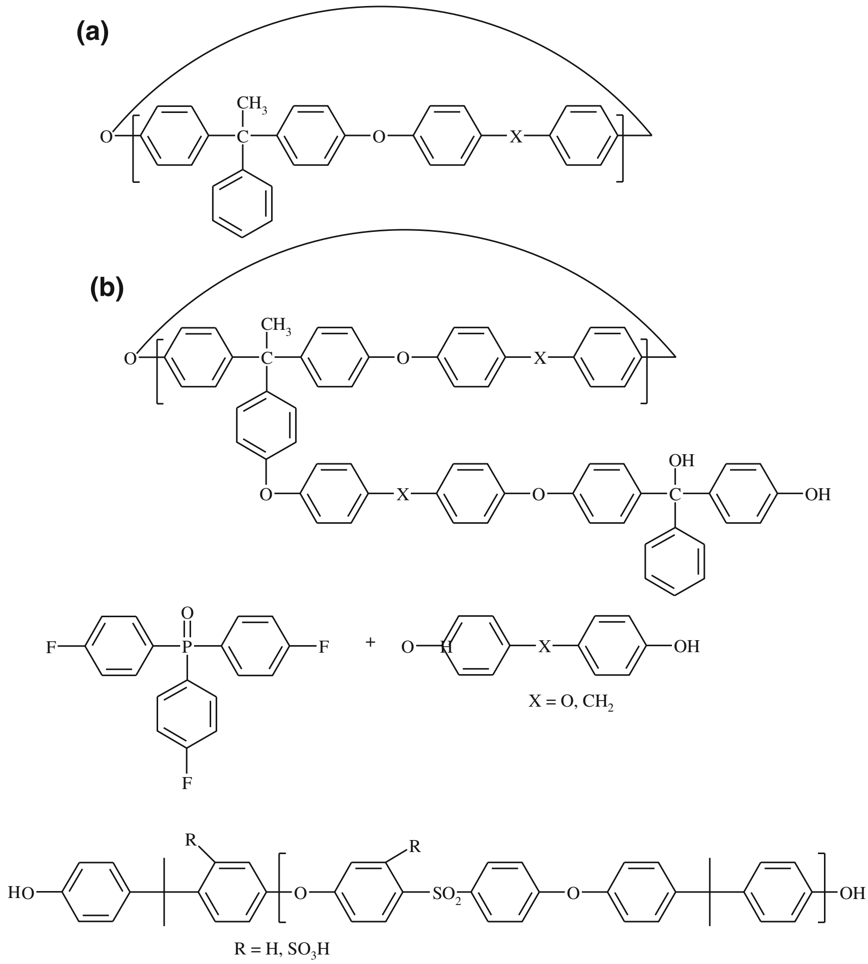
10.3 Polyethers and the Role of Cyclization

Aromatic hb polyethers were prepared from equimolar $a_2 + b_3$ polycondensations by Kricheldorf et al. [67–69], Fossum et al. [70], and Long et al. [71, 72]. The Kricheldorf group studied polycondensations 1,1,1-tris(4.hydroxyphenyl)ethane or its trimethylsilylderivative with 4,4′-bis(4-fluorophenyl sulfone) and with 1,4-bis(4-fluorobenzoyl)benzene [68] in moderately concentrated solutions. The MALDI-TOF mass spectra revealed a high fraction of cyclic species, and even polyethers containing two cyclic elements were detectable in the mass range above



Formula 10.3

2,000 Da. A slight increase in the a_2/b_3 feed ratio from 1.0/1.0 to 1.1/1.0 entailed a conspicuous change of the architectures. Openly branched polyethers almost disappeared, and the fraction of multicyclic polyethers dramatically increased (see Formula 10.1). The formulas BnCX used in these mass spectra are defined and illustrated in Chap. 11. A species like B_3C12 that this polymer consist of four cyclic elements and 12 repeat units. It should be noticed that the mass spectra do not allow for a differentiation between plain cycles ((a) in Formula 10.4) and



Formula 10.4

branched cycles (b), when the side chain is terminated by the b_3 monomer, because these cycles are isomers.

For the proper understanding of the influence of cyclization it should be emphasized that $a_2 + b_2$ (two-dimensional) and $a_2 + b_n$ polycondensations obey opposite trends. In two-dimensional polycondensations the cyclization tendency decreases at higher molar masses, because the distance between "a" and "b" end groups increases proportional to the molar mass. Hence, the presence of cycles in the low molar mass range of a mass spectrum does not say the high molar mass fraction contains as significant percentage of cyclic polymers. However, the high molar mass fraction of an $a_2 + b_3$ polycondensate contains initially numerous "a" and "b" groups, which enhance the probability of cyclization and enable the formation of more than one cyclic element in one polymer "chain".

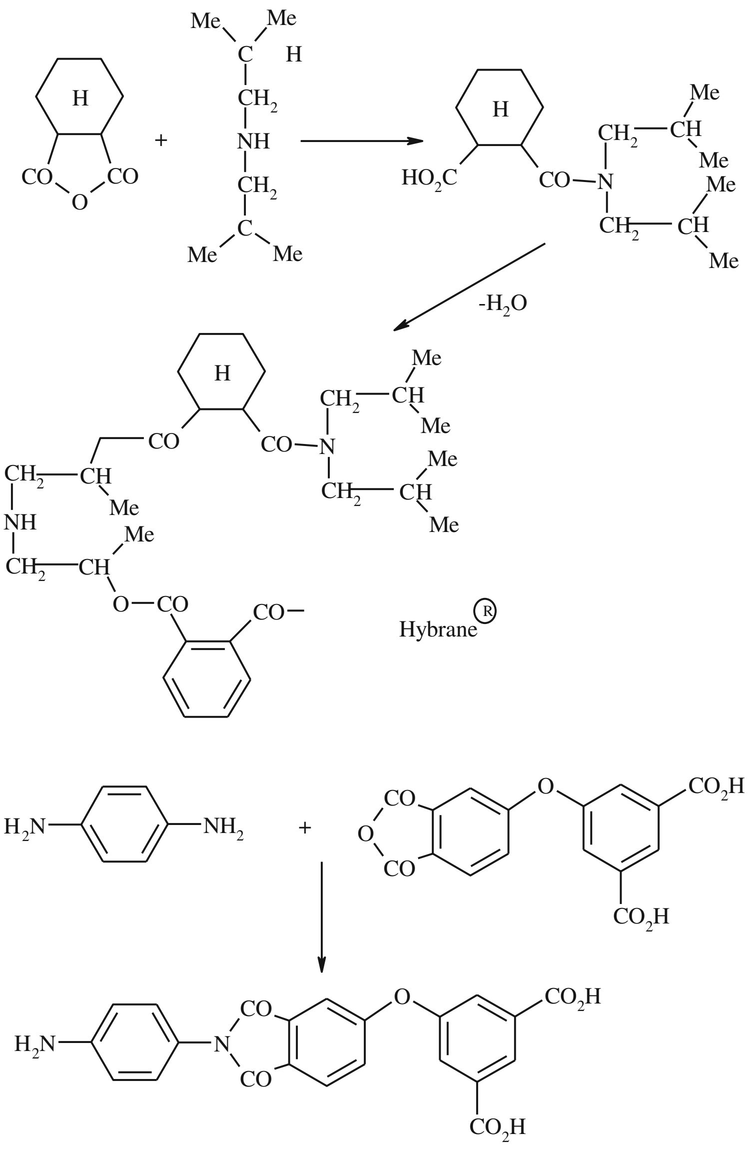
None of the authors cited above has characterized their hb polymers by mass spectroscopy. Considering Chap. 7 and the results of Kricheldorf et al. [67–69] it is absolutely unlikely that the hb polymers prepared by other authors were free of cyclics. The avoidance of gelation at low monomer concentration is a reliable indicator that the cyclization played an important role in the polymerization process. In other words, syntheses of openly branched polymers by equimolar $a_2 + b_n$ polymerization is rather fiction than reality.

When Fossum et al. studied equimolar polycondensations of tris(4-fluorophenyl)phosphinoxide with commercial diphenols [70] (see Formula 10.4), they observed that lowering the monomer concentration from 0.17 to 0.05 mol/L prevents gelation. They attributed this effect to the influence of cyclization, but they did not present mass spectra. Those authors also performed a careful examination of the "slow addition procedure." This procedure means that one monomer is slowly added to a solution of the other monomer, so that chain growth is faster than monomer addition. This procedure was also used by Jikei [56], Okamoto [51] and Long [60], but without detailed study of its effect. Furthermore, the slow addition was studied before by other authors for two-dimensional and a_2b_n polycondensations (see below), and a significant lowering of the PD was observed together with a control of the average DP, when an initiator (or chain stopper) molecule was added. This effect was also found by the Fossum group, and they could confirm that the avoidance of cyclization is due to the low monomer concentration and not due to the slow monomer addition. At this point it should be emphasized that a successful "slow addition polymerization" is not a polycondensation anymore (see Chap. 1) but obeys the definition of a condensative chain polymerization as discussed in Chap. 15.

Long et al. [71, 72]. used the same b_3 monomer as Fossum et al., but telechelic oligo(ether sulfone)s were used as a_2 monomers to increase the distance between the branching points (see Formula 10.4, bottom). Monomer concentrations in the range of 0.05–0.17 mol/L were applied and the absence of gelation was ascribed to cyclization reactions with reference to the work of Kricheldorf et al..Oligo(ether sulfone)s having pendant SO_3H groups were included in those studies [72] with the purpose to prepare proton-transporting membranes for electronic applications. In this connection computer simulations of $a_2 + b_3$ polycondensations including the influence of cyclization reactions [73, 74] are worth noting.

10.4 Non-symmetrical b_n Monomers (b_2b')

Polycondensations of symmetrical b_n monomers generate in early stages reaction mixtures containing unreacted monomers and various classes of oligomers, such as ab_{n-1}, a_2b_{n-2}, a_3b_{n-3}, b_{n-1}-b_{n-1} etc. Yet, the composition of the reaction mixture changes dramatically, when non-symmetrical monomers, so-called b_2b'monomers, are used. If the "b'"group is far more active than both "b" groups, the first reaction step is a fast reaction with a_2 yielding an ab_2 monomer. If "b'" is much



Formula 10.5

less reactive, the rapid reaction with two a_2 monomers yields an a_2b'oligomer. In both cases the further course of the polycondensation and the resulting architecture corresponds to those of a normal ab_2 polymerization (see Chap. 11).

A monomer such as glycerol represents borderline case, because the primary and secondary OH groups do not differ much in reactivity. Hence, cross-linking occurs at conversions predicted for symmetrical b_3 monomers, when glycerol is heated with a highly reactive a_2 monomer, such as cyclic anhydrides [31–40]. In contrast, enzymatic polycondensations with the far less reactive adipic acid yield under mild conditions a nearly linear polyester having numerous free secondary OH groups [75]. Heating of glycerol with adipic acid in the melt represents an intermediate scenario [76] yielding moderately branched oligomers for equimolar feed ratios. Higher feed ratios resulted in gelation, when the conversion was not stopped below 80 %. Syntheses of polyimides from 2,4,4′-triaminodiphenyl ether took a similar course, because the amino groups in para position possess similar reactivities which are 40–50 times higher than that of the ortho-NH_2 group [77]. Therefore, the risk of branching was reduced and the DB was considerably lower than 0.5, the characteristic value for symmetrical b_3 monomers.

A perfect transformation of an $a_2 + b_2b'$ into an ab_2 polycondensation was first reported by a team of DSM NV [78, 79]. Bis(2hydroxypropyl)amine reacts rapidly and almost quantitatively with the amino group, so that a bis(hydroxyalkyl) carboxylic acid is formed (see Formula 10.5). The polyesterification at higher temperatures yields a poly(ester amide), which was commercialized under the trademark “Hybrane.” Another example of an “in situ” formation of an ab_2 monomer was described by Shu et al. [80]. The reaction of 1,4-diaminobenzene with the monoanhydride of a diphenyl ether tetracarboxylic acid (see Formula 10.5) produces an amino dicarboxylic acid which upon further polycondensation yields a hb poly(amide imide). Polycondensations of 4,3′,5′-trifluorodiphenylsulfone with commercial diphenols were studied by the Fossum group [81, 82]. The para C–F bond id particular reactive and substitution of one meta-position lowers the reactivity of the last C–F group. Therefore, variation of the reactions conditions allows for systematic variation of the DB.

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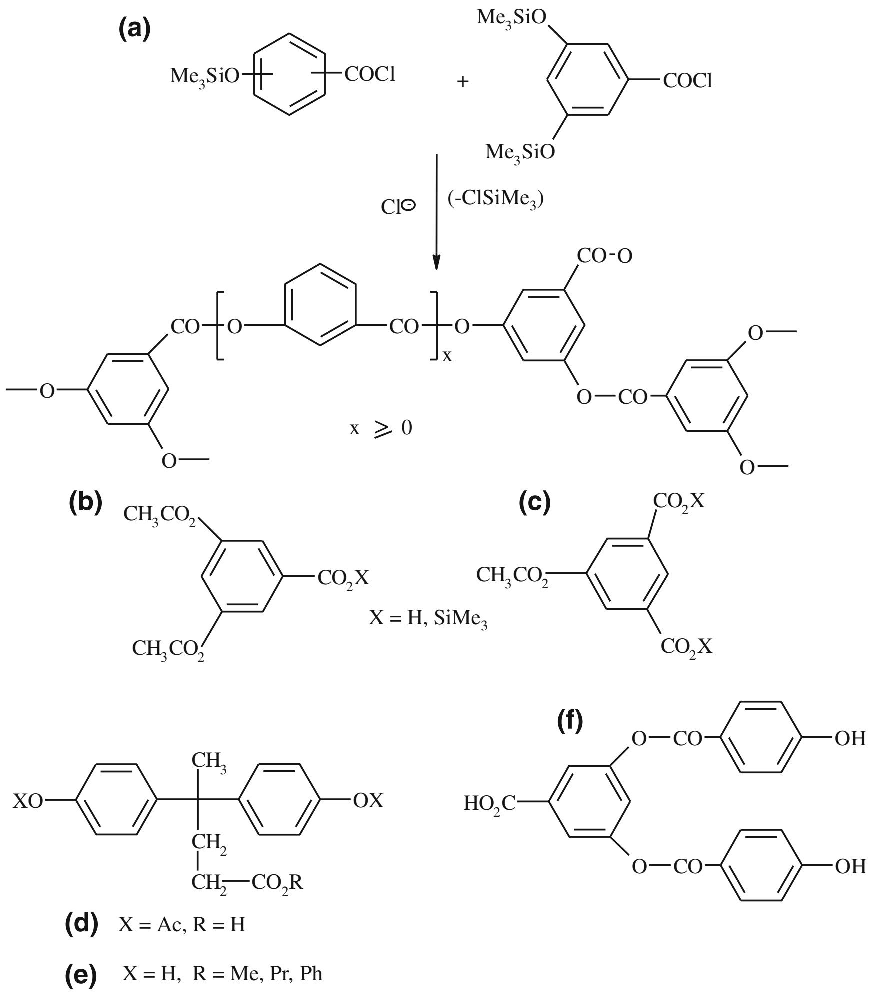
Chapter 11
Hyperbranched Polymers by ab_n Polycondensations

11.1 Terminology

Hyperbranched (hb), a term coined by Kim and Webster [1], means a tree-like type of branching. This type of branching is an invention of the evolution, which is present in many plants and animals in the form of amylopectin and glycogen, respectively. A tree-like architecture, where the "a" end group is a formal analogy to the root end of the tree, is not the only kind of architecture. Cyclization involving the only "a" group which exists in a hb polymer converts the tree-shaped into a sun-shaped architecture. Polycondensation with a_n monomers yield star-like architectures with "n" hb star arms. When "a_n" is a telechelic oligomer, the resulting A-B-A triblock copolymer has a Manacle architecture. Copolymerizations of ab_n monomers with ab monomers yield hb copolymers with larger distances between the branching points. Examples of all these different architectures were prepared in the field of polyesters, and this is one reason, why the text below, which is subdivided according to classes of polymers (in analogy to Chap. 10) begins with polyesters.

The history of synthetic hb polymers derived from ab_n monomers begins with Flory's cascade theory (see Chap. 4) [2]. Flory was the first, who recognized that a clean (co)polycondensation of ab_n monomers may yield hb polymers without any risk of crosslinking. However, Flory incorrectly attributed the experimental origin of ab_n polycondensations to a paper of Hunter et al. [3], describing the dehydrohalogenation of 2,4,6-triphenols and to a paper of Jacobson [4] dealing with reactions of benzyl halides. Yet, those authors neither intended to synthesize branched polymers nor did they isolate and characterize branched polymers, but this misleading citations were later repeated by other authors [5]. The first synthetic approach which allowed for the preparation of hb homo and copolyesters was reported by Kricheldorf et al. [6, 7], who described syntheses and polycondensation of trimethylsiloxybenhzoyl chlorides (Formula 11.1). This historic aspect is the second reason, why the following presentation of hb polymers and synthetic strategies begins with polyesters.

H. Kricheldorf, *Polycondensation*, DOI: 10.1007/978-3-642-39429-4_11,



Formula 11.1

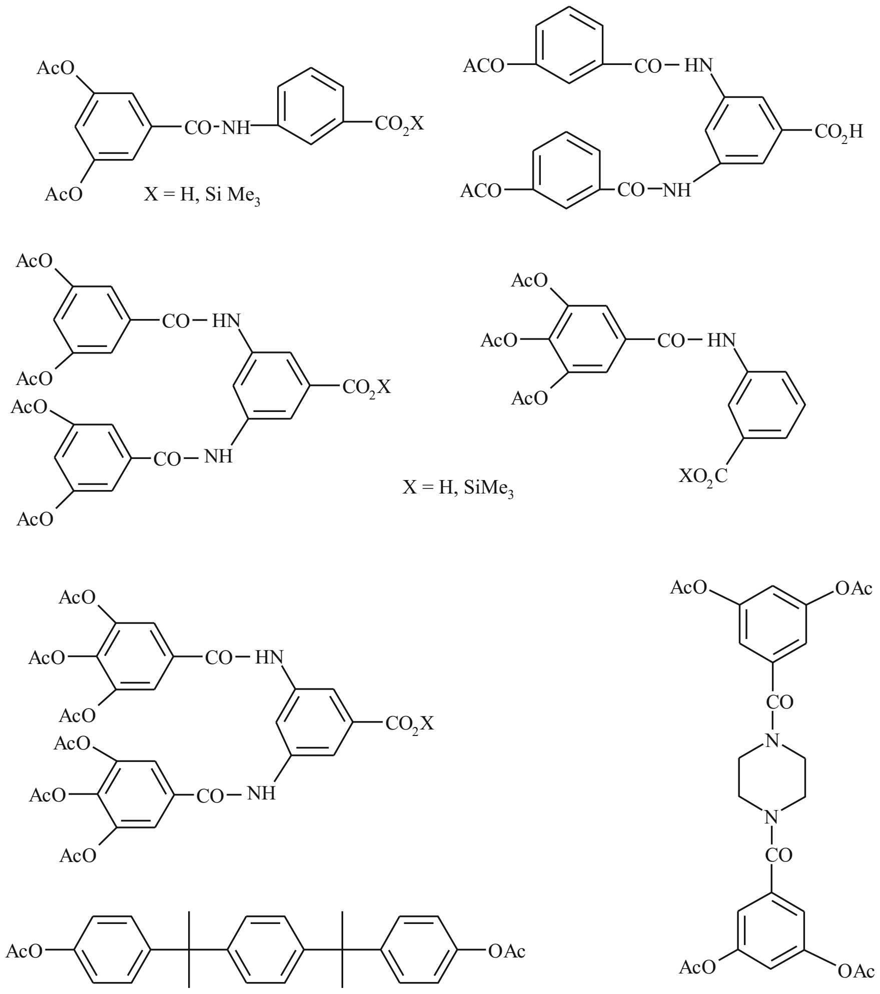
11.2 HB Polyesters

Whereas, Kricheldorf et al. [7] synthesized a first hb copolyesters to mimic the architecture of amylopectin or glycogen, the same authors and other research groups focused later their studies ob homopolycondensations of 3,5-bistrimethylsiloxy benzoyl chloride [5, 8–10]. In this connection Hawker and Frechet [7] defined for the first time, the DB as an important characteristic for the description of hb polymers (see Chap. 10). Furthermore, Mws up to 80 kDa were determined by light scattering. This “silyl method” has two advantages. The siloxy end groups allow for an almost quantitative in situ modification by acylation with acyl chlorides, so that various functional groups can be introduced and the Tgs varied over a wide range [10]. Furthermore, the OH end groups can be liberated by slightly acidic water without hydrolysis of ester groups.

However, the alternative approach, polycondensation of multifunctional acetylated hydroxyl acids (acetate method) is more versatile, the monomers are easy to synthesize and to purify, and thus, more studies were devoted to that approach [7, 8, 11–23]. The first systematic study in this direction was presented by Turner and Voit [8, 11, 12] using 3,5-bisacetoxy benzoic acid or 5-acetoxy isophthalic acid as ab_2 monomers ((b), (c), Formula 11.1). Quite analogous to the results of the "silyl method" [5] DBs around 0.5 and Mws up to 100 kDa were found (the question to what extent PS-calibrated SEC measurements are accurate and reliable should not be discussed here). Since acidic protons may cause Fries-Rearrangement and crosslinking at the high reaction temperatures (230–250 °C) Kricheldorf et al. preferentially used the trimethylsilyl esters of the monomers, which eliminate the volatile trimethylsilyl acetate above 250 °C. The risk of side reactions is reduced even at 280 °C [13, 14]. In addition to homopolyesters, various copolyesters were prepared [15, 16], and acetylated tetraphenols were used as a_4 monomers to obtain a star-shaped architecture [13]. With telechelic oligo(ether ketone)s as a_2 "core monomers" in combination with monomer (b), $X = SiMe_3$, a manacle-type A-B-A triblock architecture was realized [17]. Kricheldorf et al. [18, 19] also introduced acetylated gallic acid (3,4,5-trisacetoxy benzoic acid) as ab_3 monomer, and prepared the homopolyester and liquid-crystalline (LC) copolyesters using mesogenic ab comonomers. Incorporation of coumarin groups into hb polyesters via the "acetate method" was described by Fomine et al. [20].

The "acetate method" in combination with silylated carboxylic groups also proved to be a versatile approach to the preparation of hb copoly(ester amide)s [21–25]. As illustrated in Formula 11.2, ab_2, ab_3, ab_4 and ab_6 monomers came into play. Several polycondensations were performed in the presence of acetylated a_2 or a_4 "core monomers" (see Formula 11.2). However, the "acetate method" is not restricted to fully aromatic monomers and polymers, and several semi-aromatic monomers were polymerized by this approach [26]. The polycondensation of monomer (e), Formula 11.2, is remarkable, because large amounts of cyclics were detected (see Sect. 11.7). Furthermore, several LC copolyesters were prepared from monomers (a)–(c), Formula 11.3 [27, 28].

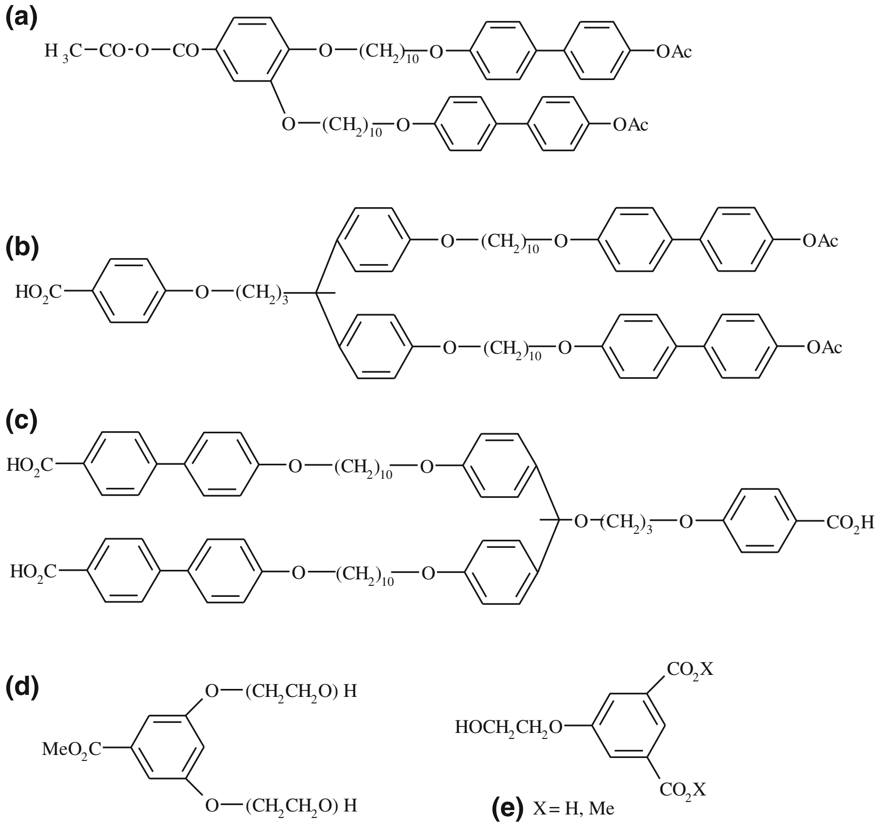
Acidolytic transesterification is a satisfactory method for the (poly)condensation of phenols, but it does not work well with aliphatic OH groups Alcoholytic transesterification involving carboxylic acid esters and direct esterification of OH and CO_2H groups are the alternatives. Only a handful of papers described syntheses of hb polyesters via alcoholytic transesterification [29–32]. Hawker et al. [29, 30] studied polycondensations of monomer (e), Formula 11.1, with variation of the ester group. As expected, only low conversions and molar masses were obtained from the alkyl esters, but a high molar mass polyester from the phenyl ester (Mw up to 130 kDa by SEC-MALLS). The normal DB of 0.5 did not depend on the ester group. HB poly(ether ester)s dissolving Li-salts were prepared by the same authors from monomers of structure (d), Formula 11.3 [31]. Park and Feast



Formula 11.2

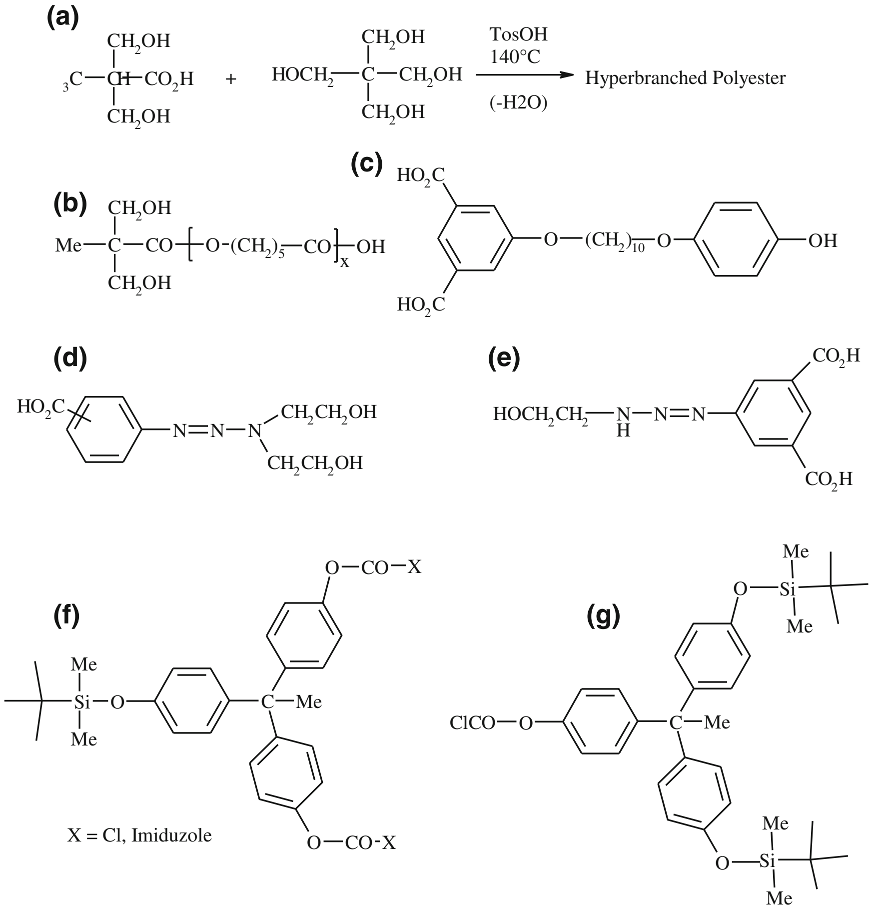
[32] studied the transesterification of monomer (e), Formula 11.3 (X = Me) in the melt and used dimethyl isophthalate as a_2 “core monomer”.

Polycondensations of free hydroxyl acids involving direct esterification were realized with various different coupling methods. The classical proton-catalyzed esterification of alcohol and carboxylic groups was used by Hult et al. [33, 34] for the preparation of hb polyesters from commercial 2,2-bis(hydroxymethyl)propionic acid. This work is remarkable for two reasons. First, those authors described for the first time (simultaneously with the Kricheldorf group [21, 22]) aq polycondensation of an ab_2 monomer in the presence of a core molecule (see Formula 11.4, top). Second, the resulting polyester was the first commercialized hb polymer.



Formula 11.3

However, side reactions, such as formation of ether groups or cyclization, were not investigated. Turner et al. [11] reported on the $Bu_2Sn(OAc)_2$-catalyzed polycondensation of 5-(2′-hydroxyethoxy) isophthalic acid in bulk at 190 °C. Dimethyl isophthalate served as “core monomer” in several experiments. Polycondensation promoted by bis(cyclohexyl)carbodiimide (DCC) were reported for the aromatic monomer (f), Formula 11.1 [35]. The mild reaction conditions prevented transesterification, but only low molar mass polyesters (Mw < 17 kDa) were obtained. Similar molar masses were achieved by Voit et al. [36] for carbodiimide promoted polycondensations of the triazene monomers (b) and (c), Formula 11.4. Somewhat more successful were DCC-activated polycondensations of trifunctional oligo(e-caprolactone)s such as (d), Formula 11.4, reported by Hedrick et al. [37, 38]. Syntheses of LC polyesters from monomers (e), Formula 11.4, and isomers were achieved by means of thionyl chloride and pyridine [39].

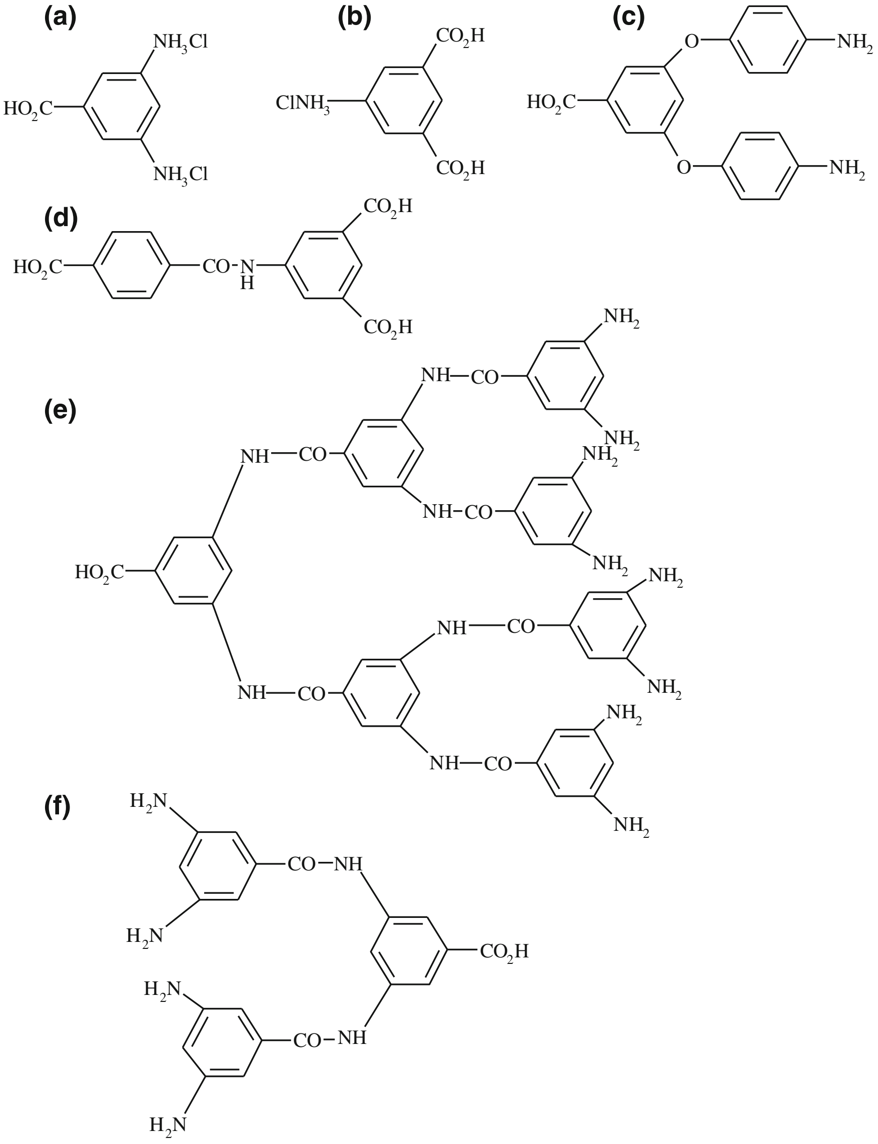


Formula 11.4

Finally, syntheses of hb polycarbonates from monomers such as (f) and (g), Formula 11.4, catalyzed by AgF should be noted [40, 41]. After hydrolysis of the end groups OH-terminated polymers having DBs around 0.53 and Tgs around 200 °C were obtained.

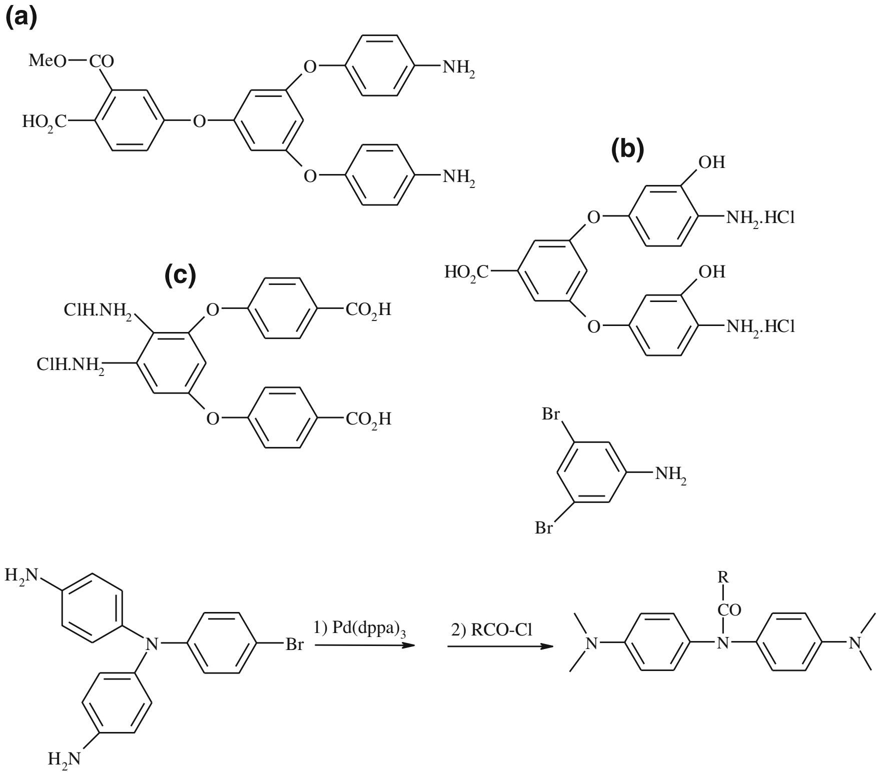
11.3 Polyamides and Polyamines

The present section deals with syntheses of polyamides via formation of amide bonds. Other synthetic strategies are discussed in the preceding and in the following sections. The first approach described by Kim in 1992 [42], was based on $SOCl_2$ as activation/condensing agent. 3,5-Diaminobenzoic acid and 5-amino



Formula 11.5

isophthalic acid were transformed into the acid chloride hydrochlorides ((a), (b) in Formula 11.5), which were polymerized at 0 °C in NMP containing $CaCl_2$ quite analogous to the preparation of linear polyaramides (see Chap. 6). The resulting hb polyamides were soluble in amide solvents and allowed for SEC measurements,



Formula 11.6

whereby Mw values in the range of 24–46 kDa were found. The hydrochloride of the amine-terminated polyamides was even soluble in water.

With one exception, all the ab$_n$-type amino acids outlined in Formulas 11.5 and 11.6 were polymerized by in situ activation with phosphorous reagents. Either triphenylphosphite (TPP) + pyridine were used in NMP at 100 °C (Yamazaki method) or diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate (DBOP) + triethylamine. This approach has the important advantage that monomers which are stable on storage and insensitive to moisture may be used. The contributions came from Russo et al. [43, 44], Ueda et al. [45] and mainly from the research group of Jikei and Kakimoto [46–54]. For the hb polyamide derived from monomer c, Formula 11.5, a Mw of 98 kDa was determined by SEC-MALLS along with a DB of 0.48 [45]. From other synthese only viscosity data were reported. Kakimoto et al. [46] studied the influence of the monomer structure on the DB. For the polycondensations of 3,5-diamino benzoic acid an unexpectedly low DB of 0.32 was found and ascribed to steric hindrance. The high DBs of 0–72 were measured for the polycondensate of monomer (f) and 0.844 for (e), Formula 11.5, these extraordinarily high values result from the 100 % branching in the dendritic monomers themselves.

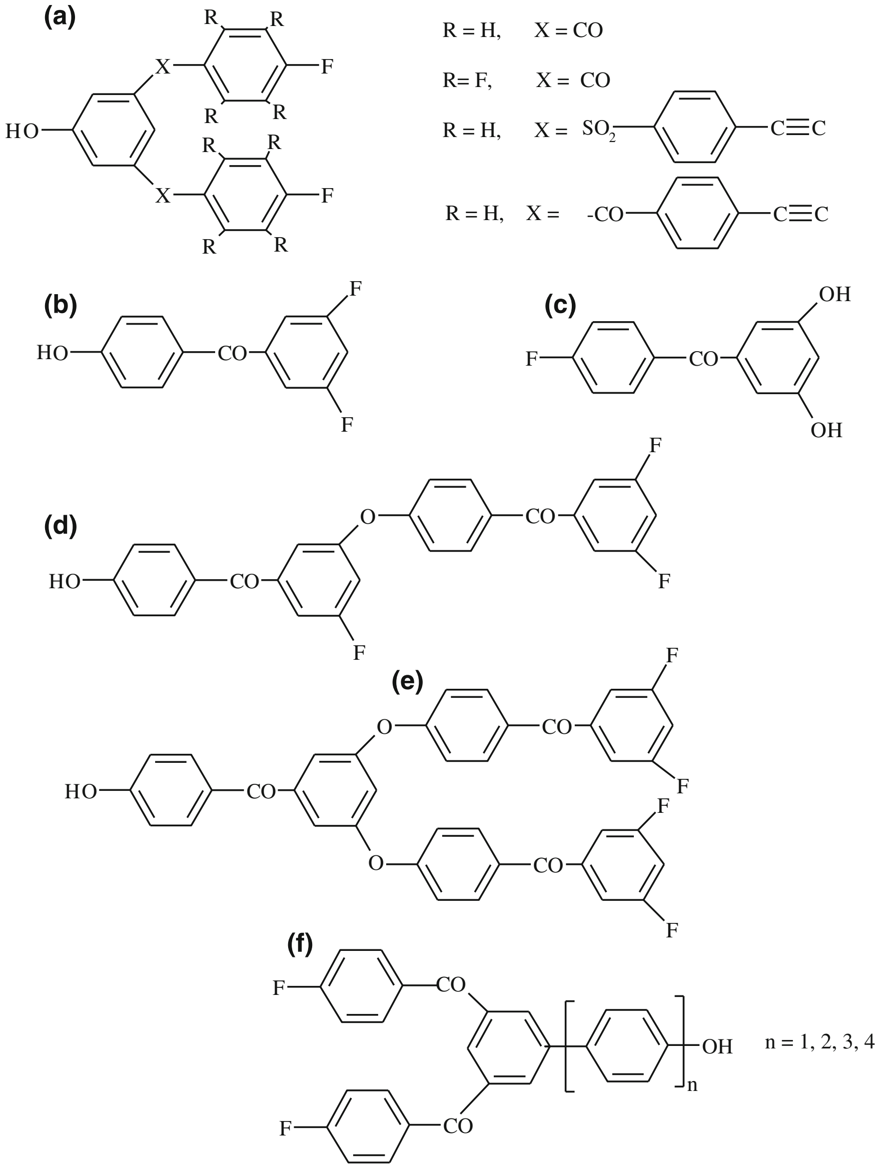
Polycondensations by means od DBOP or TPP also proved useful for the preparation of hb polymides which served as precursors of polyimides [47–49] ((a) Formula 11.6) or polybnezoxazole)s (from (b) or (c) in Formula 11.6 [50–54]. For the best polyimide a DB of 0.48 and a Mw of 188 kDa were determined (by SEC-MALLS). Polycondensations of di or multifunctional aromatic amines and carboxylic acids in the melt are usually not successful, because the high temperatures (>300 °C) are needed to keep the reaction products in the molten state to cause partial decarboxylation. However, in the case of monomer (c), Formula 11.5, polycondensation at 235 °C proved successful, and a Mw of 74 kDa with a PD of 2.6 was achieved [54].

Finally, two syntheses of aromatic polyamines via Pd-catalyzed formation of C–N bonds should be noted [55, 56]. In the first report, 3,5-dibromoaniline served as monomer and a bromo-diaminotriphenylamine in the second study (see Formula 11.6, bottom). However, the molar masses were rather low, and alternative syntheses based on C–C coupling are discussed below.

11.4 Polyethers

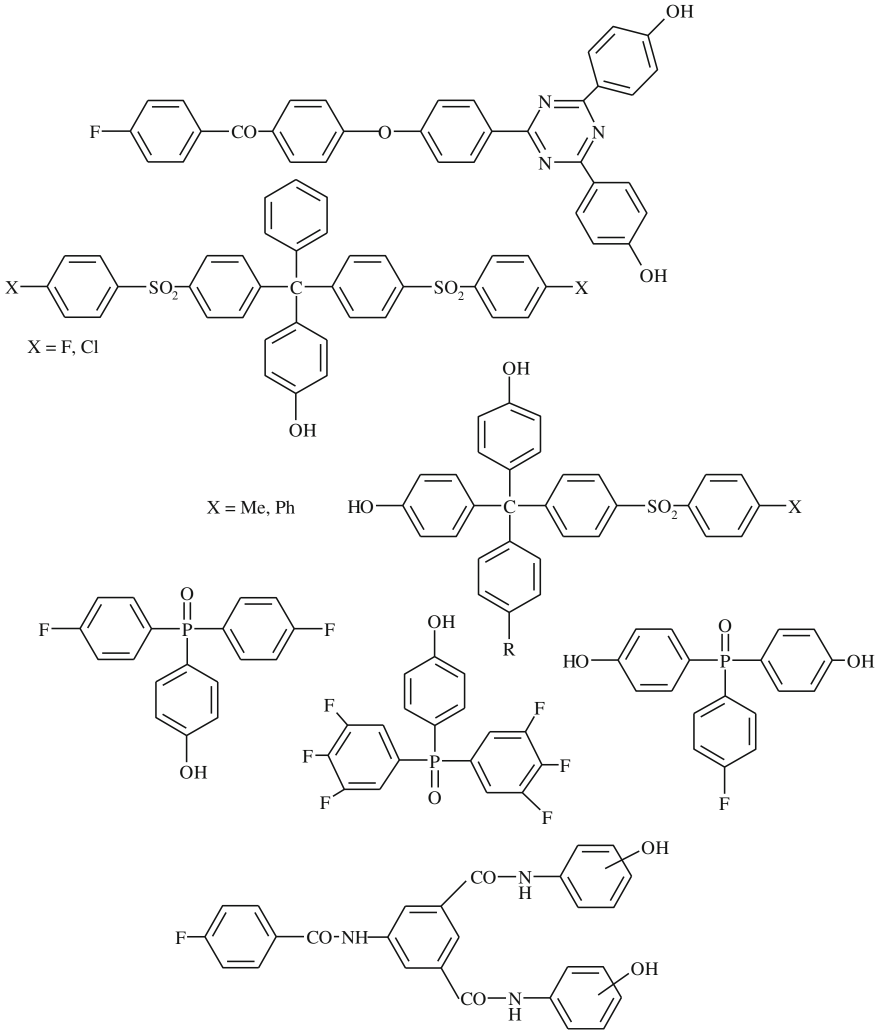
All hb polyethers prepared by polycondensation before 2010 were aromatic or semi-aromatic polymers, and almost all of them were prepared by nucleophilic substitution involving phenoxide ions. In most cases, these phenoxide anions were generated in situ by addition of K_2CO_3 to the reaction mixture. In few cases NaH served as deprotonating agent [57]. A third method is based on the transformation of silylated phenols into phenoxide ions by means of CsF. The Si–F bond is the strongest of all Si-bonds, and thus, the fluoride ion is capable of liberating phenoxide ions from the silylated precursor. This method was first elaborated by Kricheldorf and Bier [58] for syntheses of linear polyethers, but also proved useful for the polycondensations of silylated ab_n monomers. The electrophilic reaction partners are aromatic C–F (rarely C–Cl) bonds or CH_2Br groups. Typical reaction media were DMAc, NMP, DMSO, or diphenylsulfone, and when K_2CO_3 was used as base, toluene was added for the azeotropic removal of water.

The first syntheses of hb polyethers were conducted by Miller et al. [57] using the monomers of structure (a), Formula 11.7. The C–F bonds of these monomers are activated by neighboring F-atoms or by electron-withdrawing groups in para-position. Activation of the C–F bonds by CO, SO_2 or PO groups is the characteristic structure–property relationship of all other monomers outlined in Formulas 11.7 and 11.8 [59–72]. Miller et al. found by SEC measurements Mw values in the range of 11–134 kDa, depending on the reactivity of the C–F bond. In favorable cases short-term thermostabilities up to 500 °C were observed and Tgs in the range of 135–231 °C. Hawker et al. [59, 60], who studied polycondensations of the monomers (b)–(c), Formula 11.7, obtained similar results. Both, Tg and thermostability, depended mainly on the nature of the end groups and not so much on the structure of the main chain.



Formula 11.7

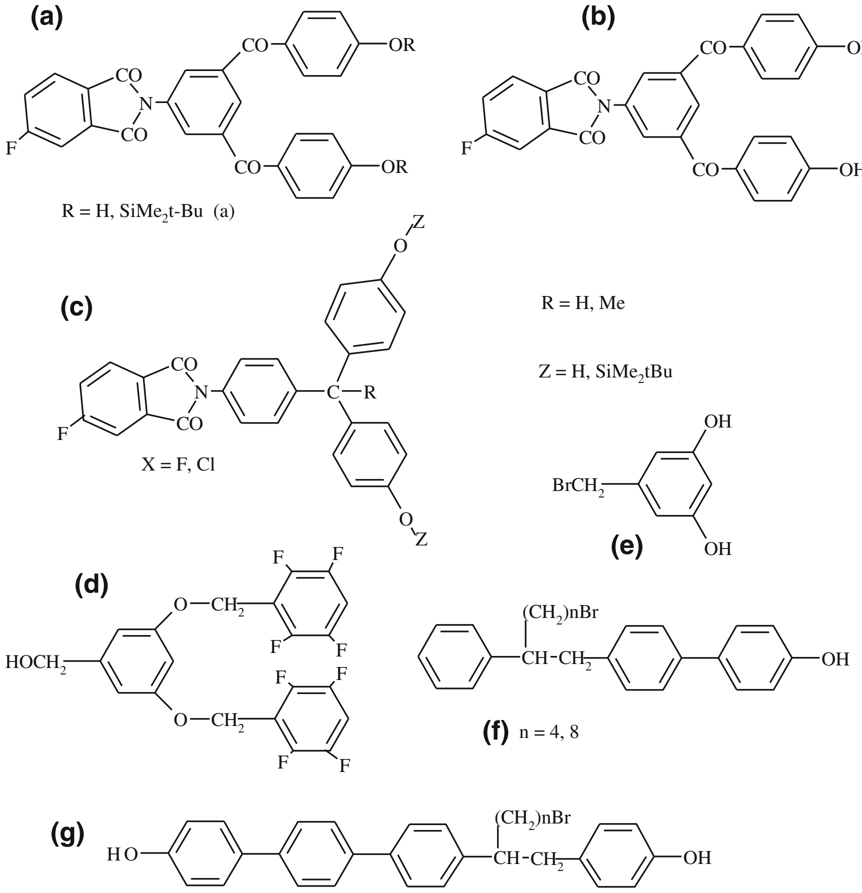
Sufficient activation was also observed, when the C–F bonds were attached to benzene rings fused with electron-withdrawing heterocycles, such as imide rings [73–78], oxazole rings [79], or quinoxalines [80–82]. Monomers used for the preparation of hb poly(ether imide)s are formulated as (a)–(c) in Formula 11.9.



Formula 11.8

The tert-butyldimethylsilyl groups are less sensitive to hydrolysis than trimethylsilyl groups and allow crystallization of the monomers, but they react easily with the fluoride anions of the catalyst.

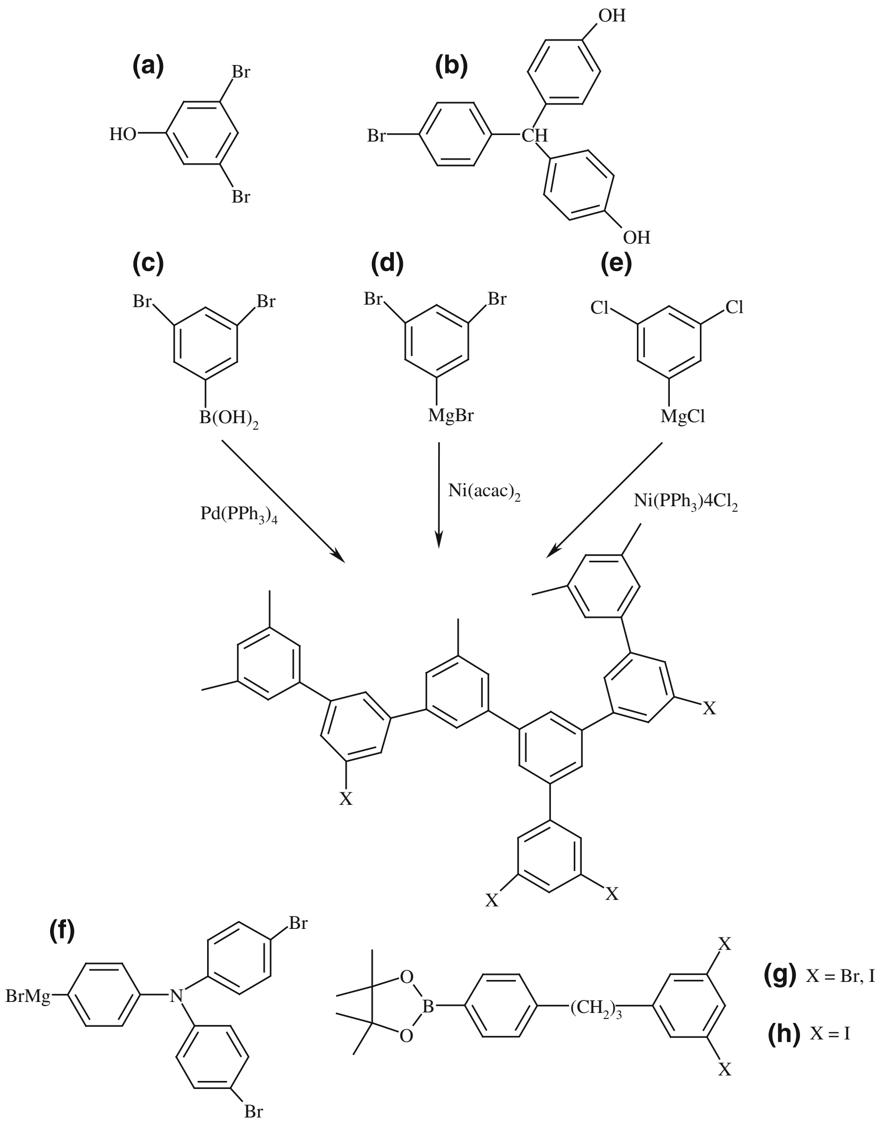
Aromatic–aliphatic hb polyethers were first prepared by Turner et al. [83] from 3.5-dibromobenzyl bromide by means of K_2CO_3 and 18-crown-6. Despite side reactions soluble polyethers were obtained, and the Mw values determined by LALLS (Mw > 180 kDa) were 3–5 times higher than those calculate from PS-calibrated SEC measurements These data confirm a general trend The small



Formula 11.9

hydrodynamic volume of hb polymers results in a systematic underestimation of the molar masses in PS-calibrated SEC. The highly fluorinated hb polyethers prepared from monomer (d), Formula 11.9 [84, 85], will be discussed in the Sect. 11.7. Finally, the work of Percec et al. [86, 87] should be noted, which deals with syntheses of LC polyethers from the monomers (f), (g) and isomers, Formula 11.9.

While all the hb polyethers mentioned above were the products of ionic nucleophilic substitutions, a couple of hb polyethers were prepared via the "Ullmann reaction" from the dibromophenols (a) and (b), Formula 11.10 [88, 89]. Quite analogous to inefficient syntheses of linear polyethers only low molar mass hb polyethers were isolated from those trifunctional monomers.



Formula 11.10

11.5 HB Polymers via C–C Coupling

The C–C coupling methods used for the syntheses of hb polymers may be subdivided into four categories:

1. Ni- or Pd-catalyzed coupling of aromatic monomers having C–B(OR)$_2$, C–Cl, C–Br, or C–J groups.
2. Pd-catalyzed polycondensations of aromatic C-X bonds with aromatic vinyl or ethynyl groups (Heck reaction).
3. Nucleophilic substitution of C–Cl groups by carbanions.
4. Proton-catalyzed electrophilic substitution of phenyl ethers by keto groups (acting as b_2 function).

After patenting in 1987 Kim and Webster reported in the open literature [1, 90] on the preparation of hb polyphenylenes from 3,5-dibromophenyl boronic acid/c), Formula 11.10. These polyphenylenes were the first hb homopolymers, and their publication (and oral presentation on conferences) greatly stimulated further research on polycondensation of ab_n monomers. Alternative synthetic methods involving the reactive intermediates (d) and (e), Formula 11.10, were also studied. Based on PS-calibrated SEC, Mws n the range of 3–35 kDa were obtained, along with low dispersities ($D < 1.5$), which, when correctly measured, disagree with a normal polycondensation kinetic. All hb polyphenylenes were soluble in organic solvents such as 1,2-dichlorobenzene, tetrachloroethane, or THF. Chemical modification of the C-X end groups was intensively studied. The same synthetic approach was used for syntheses of hb polymers derived from triphenylamine [91]. Such polymers are of interest, because of their electrical conductivity and electroluminescence properties.

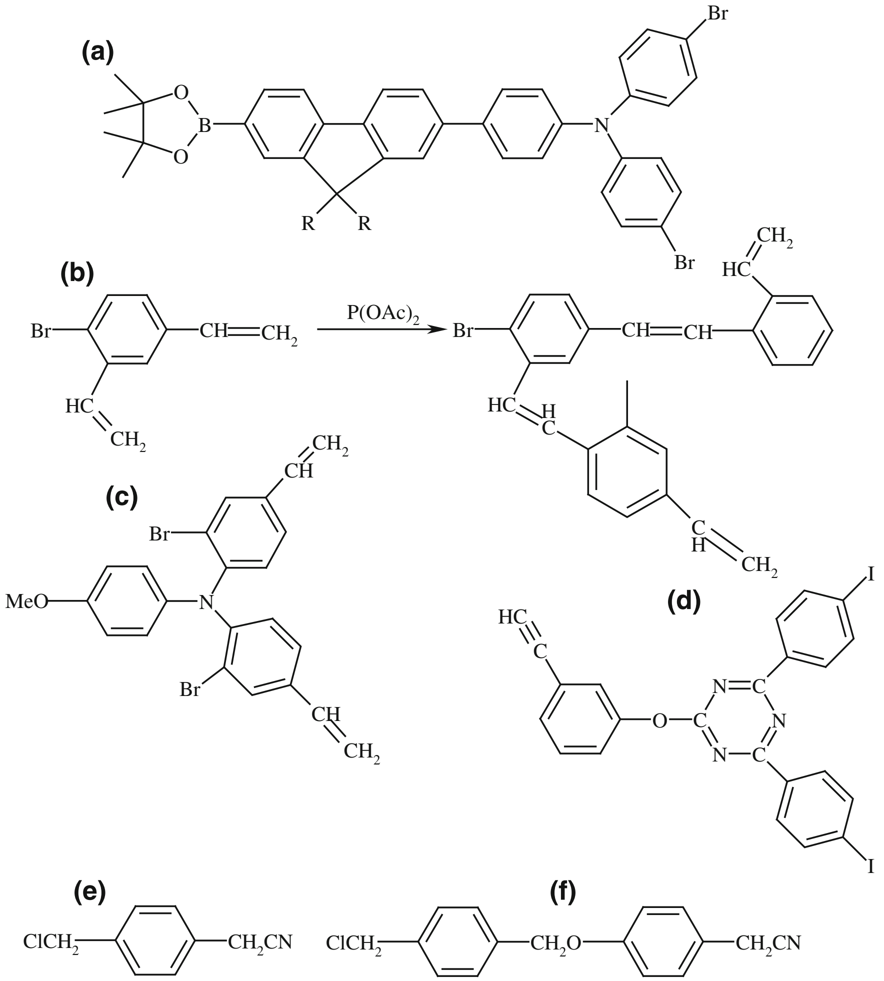
Whereas, the Ni(acac)$_2$-catalyzed polycondensation of monomer (f), Formula 11.10, gave only low molar mass products; high molar masses (Mw up to 169 kDa) were reported fro hb polymers prepared from monomer (a), Formula 11.10, by means of Pd(Ph$_3$)$_4$ [92].

Bo et al. [93] found a PD of 1.16, which is in sharp contrast to a step-growth mechanism, but this discrepancy was not discussed. Finally, the stepwise cocondensation of monomer (g) with the more reactive monomer (h), Formula 11.10, should be mentioned [94].

Two research groups [95, 96] worked on syntheses of poly(phenylene-vinylene) via the Heck reaction. In addition to 5-bromo-1,3-divinylbenzene (b), Formula 11.11, the triphenylamine derivative (c) was polymerized. Both classes of conjugated hb polymers were characterized with regard to UV-spectroscopic and electrical properties. The Pd-catalyzed polycondensation of the acetylene (d), Formula 11.11, yielded Mws between 6 and 10 kDa based on SEC along with PDs in the range of 1.6–3.0. In addition to the desired phenylene-ethynylene moieties, diacetylene groups were found resulting from oxidative coupling [97].

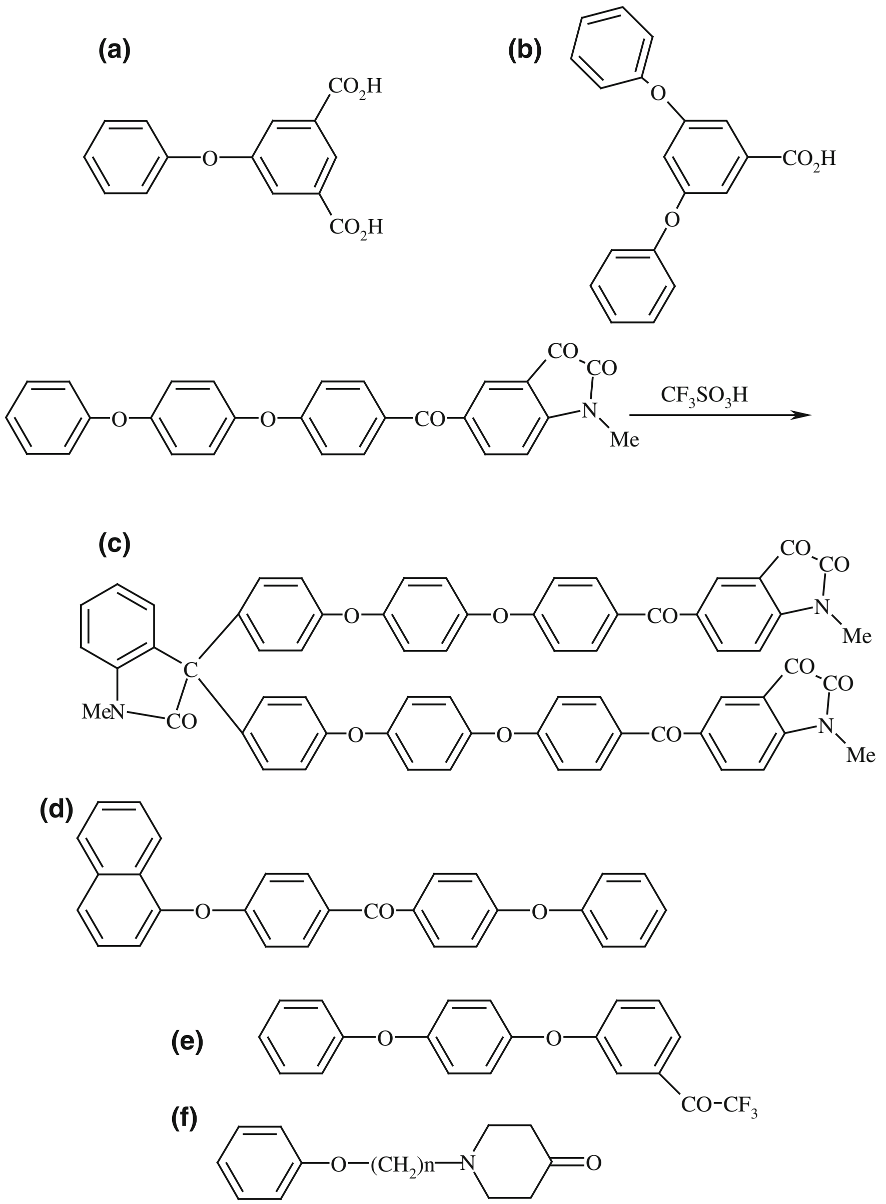
The usefulness of monomers (e) and (f), Formula 11.11, for C–C coupling by nucleophilic substitution was investigated by Jin et al. [98, 99]. With NaOH as base in DMSO only low molar mass polymers were obtained from (e), but hb polymers having Mns up to 9 kDa from monomer (f). Unfortunately, broad ^1H NMR signals prevented determination of DBs.

Electrophilic substitution of phenoxy groups was described by three research groups. Shu et al. [100, 101] studied polycondensations of the phenoxy carboxylic



Formula 11.11

acids (a) and (b), Formula 11.12, with P_4O_{10} in methane sulfonic acid. Protonated carboxylic groups are most likely the reactive intermediates. Smet et al. [102–104] used isatin ((c) in Formula 11.12) or acenaphthene groups ((d) in Formula 11.12) as electrophilic reaction partners. The CO group was activated by protonation with trifluoromethanesulfonic acid and reacted with two phenoxy groups. The second arylation step is as fast as or faster than the first (chain growth) step, so that a polymer with a DB of 1.0 (i.e., 100 % branching) as obtained. The same strategy was explored by Ueda et al. [105–107]. But the electrophilic reaction sides were a trifluoroacetophenone ((d) in Formula 11.12) or a piperidinone group (e). Again hb polymers having DBs around 1.0 were obtained.



Formula 11.12

11.6 Various HB Polymers

Three methods were described for syntheses of hb polymers via formation of Si–O bonds. Kakimoto et al. [108, 109] transformed the stable precursor (a), Formula 11.13, into the reactive intermediate (b), which yielded a hb polysiloxane under elimination of diethylamine. Two research groups prepared hb poly(ethoxysilane)s from commercial tetraethoxysilane via unstable ab_3 intermediates [110, 111]. HB Si-polyesters were also prepared, namely by oxidative polycondensation of monomer (c), Formula 11.13.

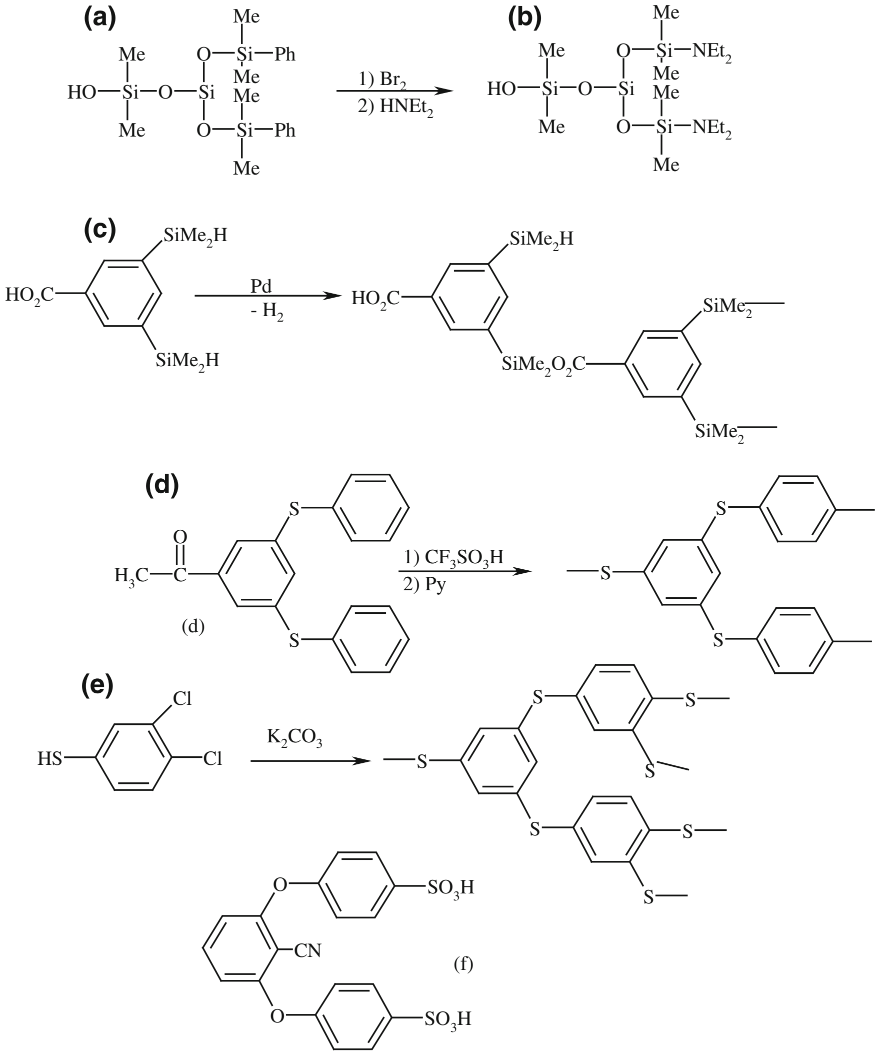
In three publications [112–114], syntheses of hb polymers via formation of C–S bonds were reported. HB poly(phenylene sulfide) was first prepared by proton-catalyzed polycondensation of the sulfoxide (d), Formula 11.13, followed by a treatment with boiling pyridine. This approach (which was known from syntheses of linear PPS) gave Mw values around 26 kDa with a D of 1.46, which disagrees with a step-growth kinetic (see Chap. 8). The second approach to hb poly(phenylene sulfide), the dehydrohalogenation of monomer (e) was also known from linear PPS [114]. A Mw around 17 kDa with a PD of 2.0 was found by SEC-LS measurements. Finally, the preparation of a hb polysulfone by polycondensation of monomer (f) in P_4O_{10}/methane sulfonic acid should be noted [115]. Due to the numerous SO_3H end groups this polymer was soluble in water.

11.7 Cyclization Reactions

Immediately after the commercialization of MALDI-TOF mass spectrometers, several research groups reported on the detection of cyclic oligomers and polymers in their reaction products [26, 32, 61, 79, 85, 116–121]. The first systematic study of the role of cyclization reactions in ab_n polycondensations was performed by Feast et al. [32, 116, 117] and by Dusek et al. [118]. The Feast group studied polycondensations of monomer (e), Formula 11.13, at 240 °C in the melt using Sb_2O_3 as transesterification catalyst. It was found the fraction of cycles increased with the conversion, and at long reaction times (40 h) only peaks of cycles were detectable in the mass spectra (up to the technical limit of the mass spectra at 5 kDa).

Consequently, the limitation of the chain growth (plateau of Mn) was attributed to the influence of ring formation consuming the “a” functions. Those authors also performed polycondensations in the presence of b_2 or b_3 core monomers and observed that these core monomers did not prevent cyclization.

Interestingly, Frey et al. [119] reached exactly the same conclusions, although their polycondensations were kinetically controlled, whereas Feast et al. had worked on a thermodynamically controlled system involving cyclization by “back-biting”. Frey et al. reinvestigated the proton-catalyzed polycondensation of 2,2-bishydroxymethyl propionic acid ((a) in Formula 11.4). It was found that Hult′s polyesters (incl. the commercial Perstorf products) possess extremely low



Formula 11.13

molar masses (Mn < 1.2 kDa) limited by cyclization, and for high a_2b_3/b_3 ratios the fraction of cyclics amounted to 48 %. Already 3 years earlier Dusek et al. [118] had reinvestigated Hults work using "Electron Spray Mass Spectrometry" (ESI/FT MS) as analytical tool. Within the observable mass range of 2 kDa the fraction of cyclics increased with the conversion. Unfortunately, that paper, which was focused on the elaboration of a kinetic scheme, does not contain an experimental part, and it is not clear, how the fraction of cyclic and tree-shaped species were determined. Furthermore, the only mass spectrum presented in that paper exhibits a maximum of the peak intensities at DPs around 8 and 9, what is in contradiction to the typical frequency (number) distribution of a polycondensate. Nonetheless, the publication of Dusek et al. is important, because it criticized on the basis of experimental and theoretical results for the first time Flory's cascade theory for ignoring the role of cyclization.

When studying polycondensations of monomer (d), Formula 11.1, in the melt, Kricheldorf et al. [26] also found increasing fractions of cycles with higher conversions, and the mass peaks of cyclic hb polyesters were observable up to 11 kDa. Kricheldorf et al. [120] also reinvestigated polycondensations of monomer (a), R = H, X = CO in Formula 11.7, first described ba Miller et al. [57]. The trimethylsilyl derivative of this monomer was included in this study and the reaction conditions were varied to achieve high conversions without side reactions. High fractions of cycles were found in all reaction products, and the best experiment yielded a mass spectrum exclusively displaying peaks of cyclic hb polyethers up to 14 kDa. By comparison with the relatively low Mn (4–8 kDa) it was concluded that more than 95 mol % of the reaction products had a cyclic core. These results definitely prove that cyclization in a_2b_n polycondensations is not limited to oligomers, regardless if under kinetic or thermodynamic control.

All results together allow two important conclusions.

1. In polycondensations of a_2b_n monomers cyclization competes with chain growth yielding more and more cycles with increasing conversion, and at 100 % conversion all hb polymers necessarily possess a cyclic core. A tree-shaped architecture presented in almost all publications and review articles is a fiction, when the hb polymers are prepared with high conversions.
2. Cyclization limits the chain growth (see Chap. 7) and reduces the dispersity, when compared with Flory's calculation. For the dispersity cyclization plays an opposite role in two- and three-dimensional polycondensations, because it yields higher dispersities in two-dimensional polycondensations than calculated by Flory (e.g., Ds 3–15 [121, 122]). In fact, the experimentally observed range of dispersities is the same for both, two- and three-dimensional polycondensations.

Quite recently (2011), a review of publications dealing with theoretical aspects of a_2b_n polycondensations has appeared [123], but amazingly, the role of cyclization and the results discussed above were completely ignored. Finally, it should be mentioned that other review articles dealing with syntheses, properties, and applications of hb polymers were cited in Chap. 10 under the Refs. [2–26].

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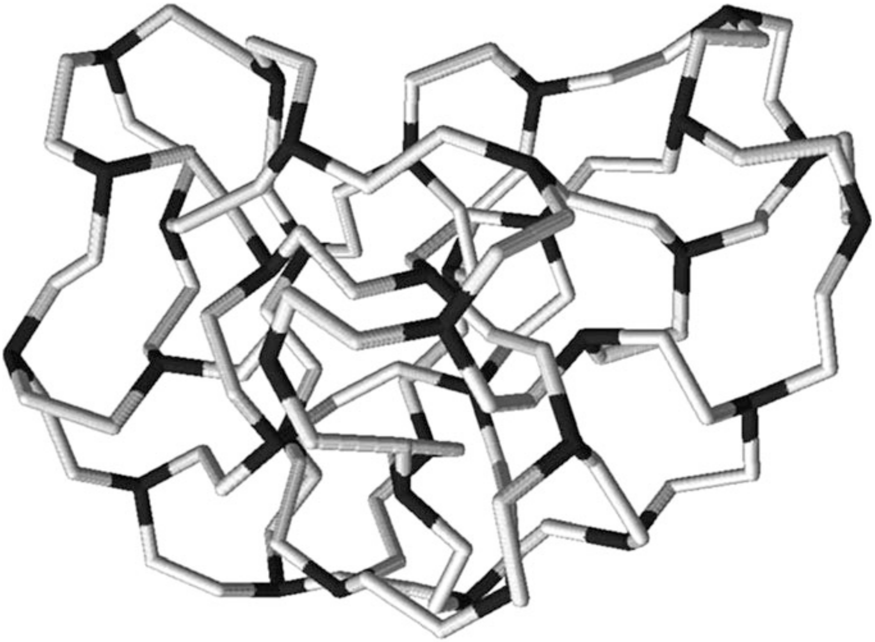
Chapter 12
Multicyclic Polymers

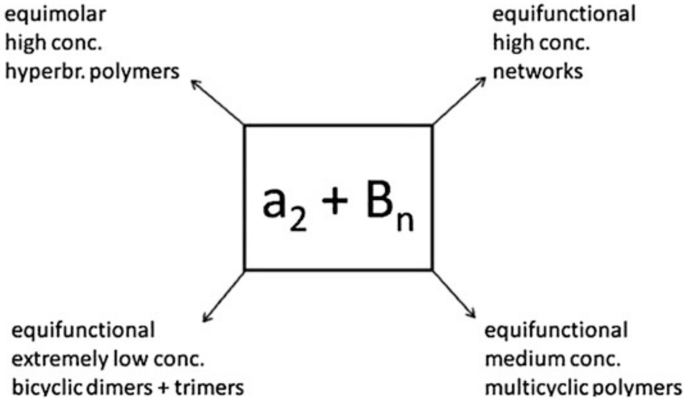
12.1 Introduction

When $a_2 + b_3$ or $a_2 + b_4$ polycondensations are conducted with high conversion and with a_2/b_n ratios $> 1.0/1.0$ the reaction products will contain more than one cyclic element. Therefore the author has coined the term "multicyclic" oligomers and polymers for this new architecture. Formula 12.1 provide a 3-dimensional illustration of a higher multicyclic oligomer resulting from an $a_2 + b_3$ polycondensation performed with eqifunctional stoichiometry. The scheme in the bottom of Formula 12.1 demonstrates what kind of reaction products may be expected from an $a_2 + b_n$ polycondnsation, when equimolar (feed ratio 1.0/1.0) or equifunctional (feed ratio 1.5/1.0 for b_3 or 2.0/1.0 for b_4) are conducted with variation of the initial monomer concentration. Syntheses of (hyper)branched polymers by equimolar $a_2 + b_n$ polycondensations are discussed in Chap. 11. This chapter is focused on equifunctional polycondensations including variation of the stoichiometry between equimolar and equifunctional. As indicated by the Scheme of Fig. 12.1 the outcome of equifunctional polycondensations varies between two extremes. For very low initial monomer concentrations (IMC $< 10^{-5}$ mol/L) the formation of dicyclic- or tricyclic oligomers is favored over the formation of multicyclic or crosslinked polymers as consequence of the Ruggli-Ziegler Dilution Principle. Only a couple of papers deals with such syntheses [1, 2]. However, such condensations belong to the field of organic chemistry and will not be discussed here in detail.

The other extreme is the formation of networks (gels) by polycondensations conducted in bulk or at IMCs > 1.0 mol/L. Flory [3] has calculated two simple Eqs. (12.1) and (12.2), which correlate the critical conversion (p_{cr}) at which gelation becomes detectable with the functionality "n" (or "f" in Flory's work) of the b_n monomers. He found that equifunctional polycondensatzions of $a_2 + b_3$ monomers will form gels at a p_{cr} 71.5 % in theory and 76–77 % in real experiments [4–6]. He attributed the difference to the occurrence of a few cyclization reactions. For $a_2 + b_4$ monomer combinations a p_{cr} of 58 % was calculated as theoretical value, and a p_{cr} of 63 % was found by Stockmayer et al. [7] for

H. Kricheldorf, *Polycondensation*, DOI: 10.1007/978-3-642-39429-4_12,





Formula 12.1

polycondensations of pentaerythritols and aliphatic dicarboxylic acids [5]. The finding that the risk of crosslinking increases with a higher functionality of the b_n monomers was one reason (few commercial b_4 monomers were the second one) why after Flory's publication equifunctional polycondensations of $a_2 + b_4$ monomers have not attracted much interest.

$$\alpha = 1/(n-1) \tag{12.1}$$

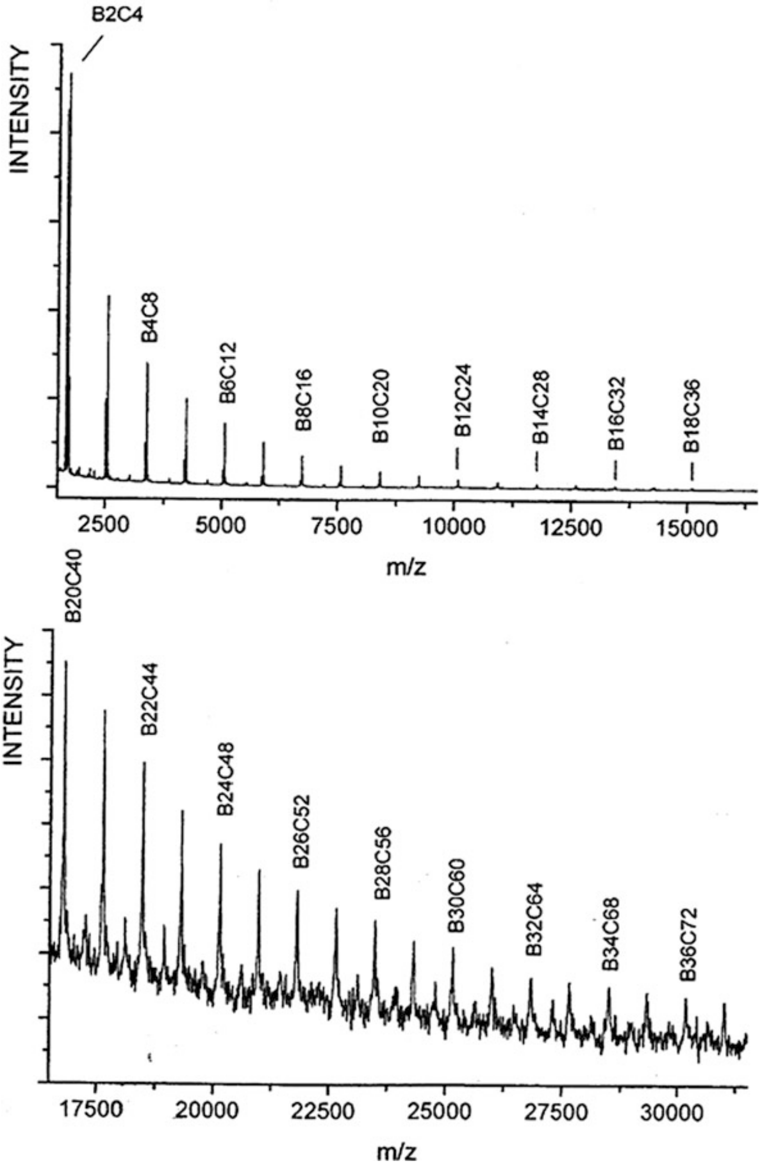


Fig. 12.1 MALDI-TOF mass spectrum of a multicyclic polyether prepared from THPE and 2,6-difluoropyridine with a feed ratio of 1.0/1.52. Figure 4 reproduced from Ref. [13] with permission (Copyright 2004, Wiley Periodicals)

$$\alpha = rp_a^2 = p_b^2/r \tag{12.2}$$

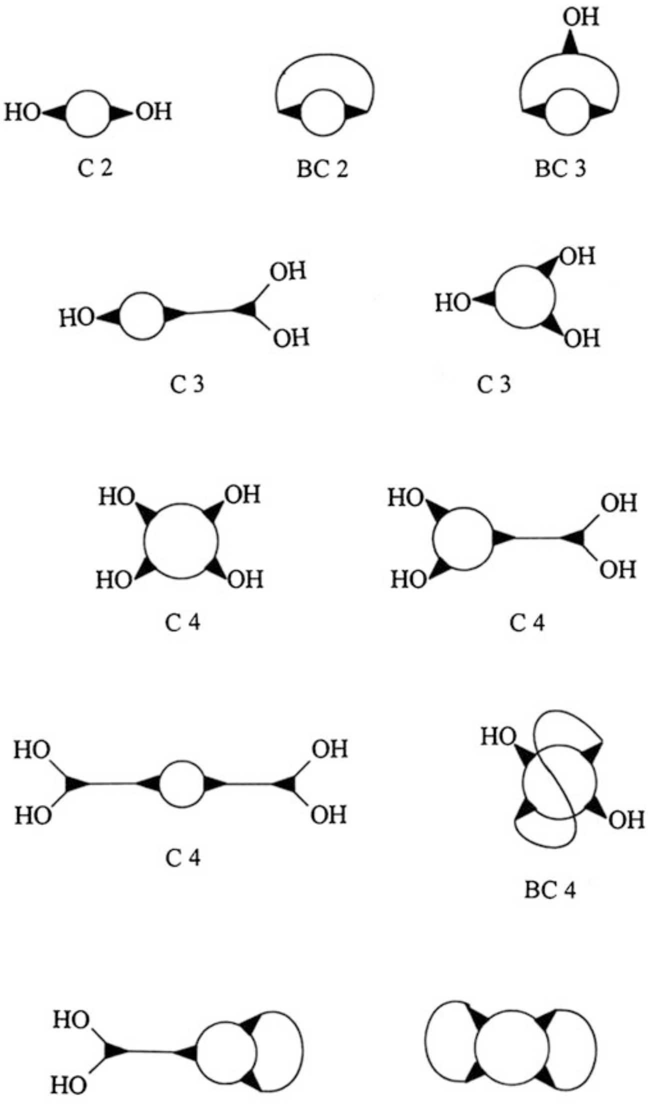
with $r =$ “a”/“b” and p_a, $p_b =$ conversions of “a” or “b” groups

About ten years ago the author speculated that between the extremes mentioned above a third set of reaction conditions and a third group of reaction products might exist, namely reaction conditions yielding soluble multicyclic polymers. Such polycondensations yield a complex mixture of reaction products which cannot satisfactorily be characterized by classical spectroscopic methods such as IR-, ^{1}H NMR and ^{13}C NMR spectroscopy. Mass spectrometric methods such as Fast-Atom-Bombardment, and above all, MALDI-TOF mass spectrometry are required, and even these methods do not answer all questions concerning the structure of the reaction products. Hence, a systematic exploration of this new working field was not feasible before the year 2000, i. e. before powerful MALDI-TOF mass spectrometer became commercially available.

12.2 "$a_2 + b_3$" Polycondensations

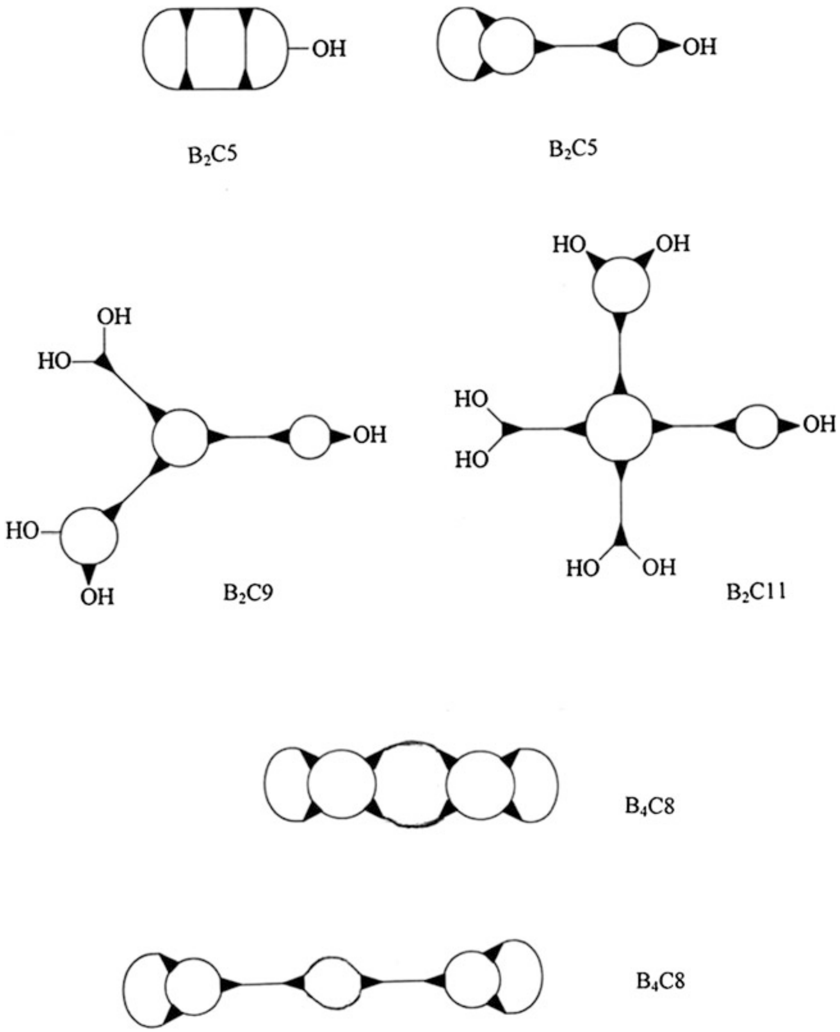
The efficient description of multicyclic reaction products and their mass spectra requires a new formula language. For the reaction products of $a_2 + b_3$ polycondensations simplified structural formulas allowing for an identification of the numerous isomers was obtained in such a way that the units of the b_3 monomers were symbolized by filled triangles and the "*a*-units" by solid lines. Examples are presented in Formulas 12.2 and 12.3. An appropriate "sum formula" for the text, for the labelling of mass peaks and for the denomination of the structural formulas is the term "BnCN". In this term C stands for cyclic, N represents the degree of polymerization, DP (based on one "a_2" plus one "b_3" unit), and B stands for bridge unit meaning additional "a_2" units bridging or connecting two rings. Formulas 12.2 and 12.3 illustrate the correlation between structural formulas and sum formulas. In a two-dimensional drawing a multicyclic polymer prepared by equifunctional polycondensation consists of $B_n + 1$ (or BnC) cycles.The multicyclic polymers resulting from $a_2 + b_3$ polycondensations may be subdivided into five classes.

1. Perfect multicycles free of functional end groups. They can only exist for even-numberd DPs. They are the result of anequifunctional polycondensation under (nearly) ideal conditions with almost quantitative conversion (e.g. B_4C8 in Formula 12.3, bottom).
2. Multicyclic polymers bearing one functional "*b*" group (Formulas 12.2 and 12.3, top). Such multicycles are typical for odd-membered DPs and almost quantitative conversion.
3. Multicyclic polymers having two or more "*b*" functions. These multicycles result from polycondensations with molar a_2/b_3 ratios $< 1.5/1.0$ and quantitative conversion of "*a*" (see Formulas 12.2 and 12.3).
4. Multicycles having free "*a*" groups (Scheme in Formula 12.2) are the consequence of molar feed ratios $> 1.5/1.0$ and quantitative conversion of "*b*".
5. Multicyclic polymers having both "*a*" and "*b*" functions. Such multicycles indicate incomplete conversion regardless of the feed ratio.



Formula 12.2

MALDI-TOF mass spectroscopy allows for a detection and identification of all these different classes of multicycles in contrast to all other analytical methods, and thus, is an absolutely unavoidable analytical tool for studies of $a_2 + b_n$ polycondensations. However, FAB and MALDI-TOF mass spectrometry do not allow for the distinction and identification of the isomers which are necessarily



Formula 12.3

formed in the course of $a_2 + b_n$ polycondensations. Formulas 12.2 and 12.3 contain examples of isomeric species. It is trivial to say that the number of isomers increases exponentially with DP.

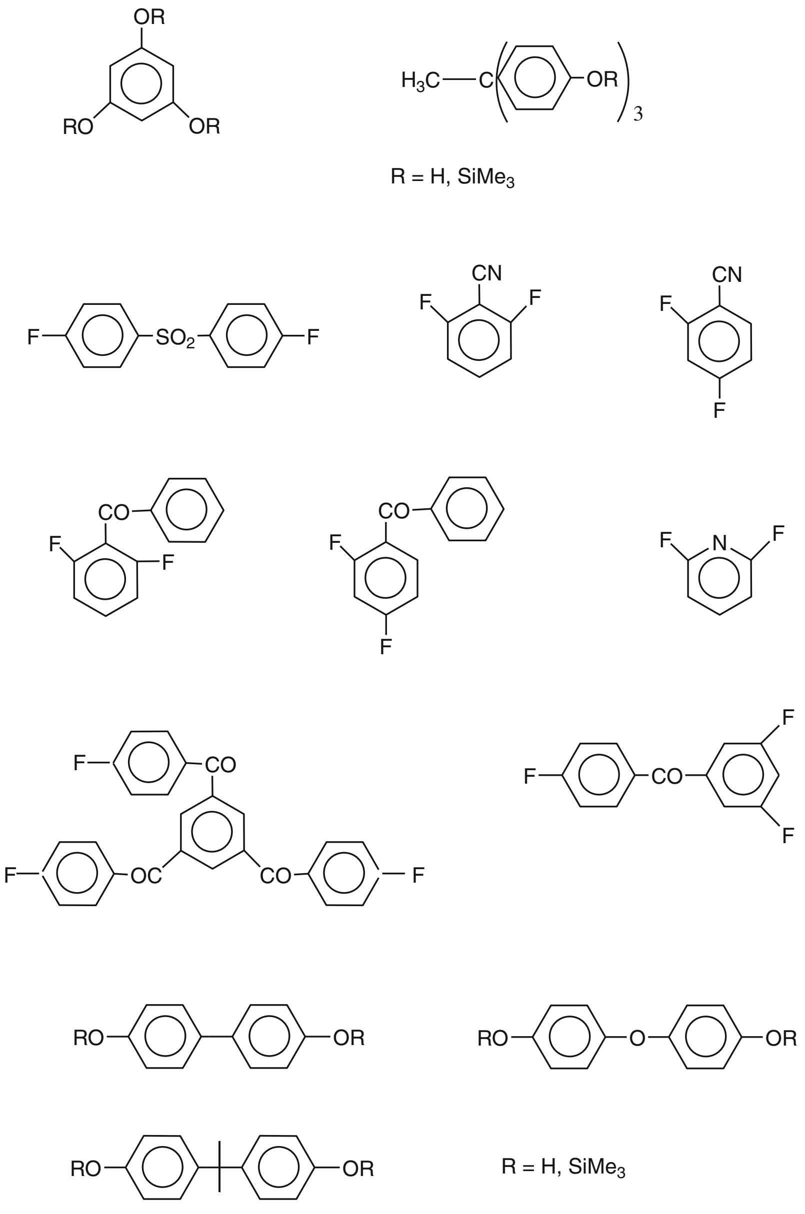
When a series of $a_2 + b_3$ polycondensations is performed with variation of the feed ratio from 1.0/1.0 to 1.5/1.0, the following changes in the composition of the reaction mixture are detectable. At the 1.0/1.0 ratio mainly linear chains, simple cycles and a few bicyclic molecules are detectable. At a 1.1/1.0 ratio the fraction of cycles increases and the a few tricyclic oligomers appear. At higher feed ratios the simple cycles vanish and a broad variety of multicycles having "*b*"-functional groups is formed. At a ratio of 1.5/1.0 (equifunctional) a simple mass spectrum appears axclusively displaying peaks of perfect multicycles when the conversion is close to 100 %. This trend was exemplarily illustrated for polycondensations of 1,1,1-trishydroxyphenyl ethane, THPE, and 4,4′-difluorodipheyl sulfone [8, 9] or difluorocyanaobenzenes [10].

For the success of $a_2 + b_3$ polycondensations high conversions and suitable IMCs are required. High concentrations entail gelation, whereas lower concentrations favour the formation of soluble multicycles. Therefore, each monomer combination requires optimization of the IMC. Most multicyclic polymers prepared from $a_2 + b_3$ monomers, thus far, are aromatic polyethers. The first studies in this direction were undertaken with silylate phloroglucinol [11] orTHPE [8, 9] as nucleophilic b_3 monomers. The trimethylsilyl derivatives were preferred to the free phenols, because they are less sensitive in alkaline reaction media to oxidation and allow for cleaner polycondensations. This effect is particularly conspicuous in the case of phloroglucinol, because this triphenol is extremely sensitive to oxidation under alkaline conditions. When polycondensations of silylated phloroglucinol with 4,4′-difluorodiphenyl sulfone (DFDPS) were conducted at an IMC beginning at a 1.0/1.0 feed ratio, it was found that gelation began at a feed ratio of 1.3/1.0 whereas the reaction products remained soluble at lower feed ratios. This result demonstrates that increasing a_2/b_3 ratios not only favour the formation of multicyclic species, but also enhance the risk of crosslinking. When silylated THPE was polycondensed with DFDPS the IMC had to be lowered to 0.05 mol/L to avoid gelation for all feed ratios (up to 1.5/1.0). Soluble perfect multicyclic poly(ether sulfone)s were achieved in this way, and he molar mass measurements gave Mn values upto 6 kDa and Mw upto 27 kDa, but the calibration of the SEC measurements with polystyrene is certainly not an highly accurate approach.

Since THPE is far less sensitive to oxidation than phloroglucinol silylated THPE was polycondensed with various activated difluoroaromats (see Formula 12.4). Particularily interesting results were obtained with 2,4- and 2,6-difluorobnezonitriles as a_2 monomers [10].

At an IMC of 0.12 mol/L the 2,6-isomer caused gelation,when a feed ratio $>$ 1.1/1.0 was used Yet, at the same concentration the 2,4-isomer yielded completely soluble products up to feed ratios of 1.5/1.0. In other words soluble, perfect multicycles were obtained. This conspicuous difference between the polyethers of both isomers was explained by different conformations of the intermediates. A computer simulation of the energy profiles of different conformations supported this interpretation. Analogous results were obtained, when silylated THPE was reacted with the isomeric difluorobenzophenones listed in Formula 12.4 [12]. At an IMC of 0.12 mol/L complete soluble products up to perfect multiycles were only obtained from the 2,4-isomer.

Polycondensations of silylated THPE with 2,6-difluoropyridine [13] were of interest for two reasons. Fist,it should be found out, if the cyclization tendency of 2,6-difluoropyridine resembles that of 2,6-difluorobenzonitrile or that of the 2,4-isomer. Second, incorporation of a tertiary amine into each repeat unit should enable quarternization with strong alkylation agents, such as methyl



Formula 12.4

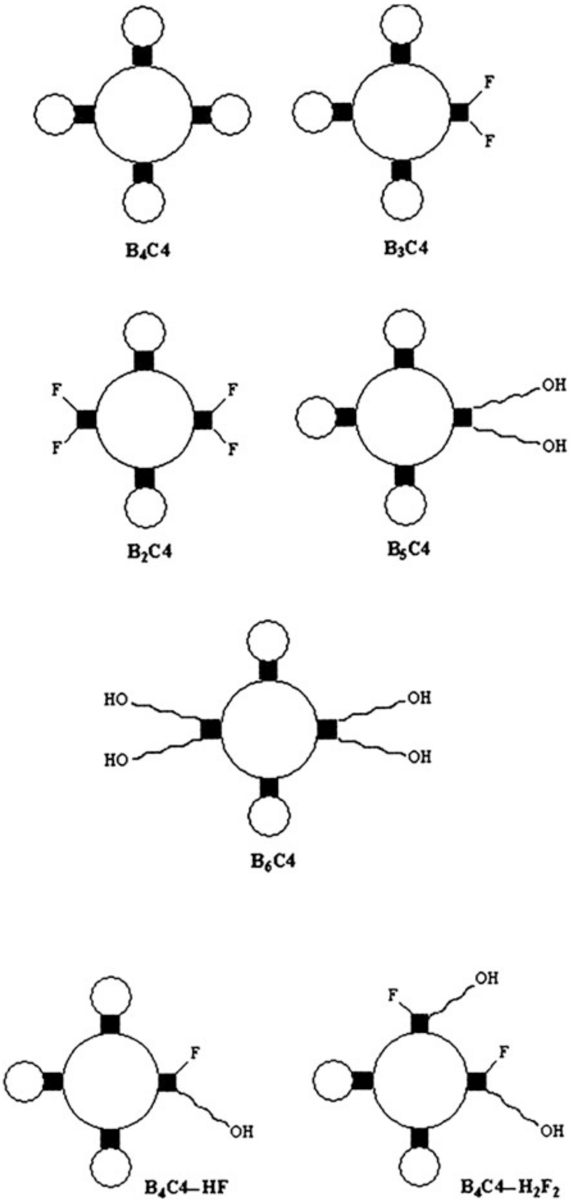
trifluoromethane sulfonate. In this way it should be feasible to prepare multicyclic polyelectrolytes. Previous polycondensations with silylated bisphenol-A had revealed that the cyclization tendency of aromatic poly(pyridine ether)s may be extraordinarily high [14]. This tendency was confirmed by the polycondensations with silylated THPE which yielded at an IMC of 012 mol/L soluble multicycles regardless of the feed ratio. A noteworthy result of that study was a mass spectrum of the reaction product obtained from an 1.52/1.0 feed ratio which displayed the mass peaks of perfect multicycles up to 32,000 Da corresponding to a DP of 78 (see Fig. 12.1). This mass spectrum proved that the formation of the multicyclic architecture is not limited to oligomers.

Further attempts to prepare multicyclic polyethers were performed in such a way that electrophilic b_3 monomers were polycondensed with three silylated diphenols (see Formulas 12.4) [15, 16]. Regardless, if 2,6,4′-trifluorobenzophenone or 1,3,5-tri(4-fluorobenzoyl)benzene served as b_3 monomers, the results varied largely with flexibility an bond angle of the diphenol. The highest tendency of crosslinking was observed for the stiff 4,4′-dihydroxybiphenyl and the lowest for bisphenol-A, whose bond angle (110°) is smaller than that of the diphenyl ether (123°). In the soluble products prepared with an 1.5/1.0 ratio the perfect multicycles were the prevailing species, but complete conversion was never achieved.

Finally, polyesters prepared from trimesoyl chloride and various aliphatic diols should be mentioned [17]. Equifunctinal polycondensations of a,ω-alkanediols ($n = 4$, 6, 8) resulted in gelation even at IMCs as low as 0.04 mol/L. However, soluble, perfect multicycles were obtained from tri- and tetra(ethylene glycol) even at he high IMC of 0.4 mol/L: These results demonstrate the high cyclization tendency inherent in oligoether chains based on the high fraction of gauche conformations, a correlation which is well known from the easy synthesis of crown ethers. The multicyclic poly(ether-ester)s also reacted like crown ethers and solubilized all kinds of alkali metal benzoates in dioxane by complexation of the metal ion.

12.3 “$a_2 + b_4$” Polycondensations

For the description of multicyclic polymers prepared by $a_2 + b_4$ polycondensation, in principle, the same type of structural formulas and sum formulas can be used designed for $a_2 + b_3$ polycondensates (Formulas 12.5). However, two characteristic differences should be emphasized. First, depending on the stereochemical properties of the b_4 monomers even the bridged bicyclic monomers may yield isomers. As illustrated by scheme (a) in Formulas 12.6 (top), b_4 monomers based on a tetravalent carbon such as pentaerythritol and its derivatives [e.g. (b) and (c) in Formulas 12.6] cannot form isomers. Yet, for the bicyclic monomers of tetrafunctional benzene derivatives two or three isomers may exist. The condensation of a non-symmetrical b_4 monomer, such as tetrahydroxy spirobisindane (TTSBI) with flexible a_2 monomers may yield 8 isomeric dimers [18]. In other words, the exponential increase of the number of isomers with higher DPs is steeper than in the case of $a_2 + b_3$ polycondensates. The second characteristic difference is the fact, that in $a_2 + b_4$ polycondensations monofuctional multicycles (analogous to those in Formulas 11.2 and 12.3, top) cannot be formed. Hence, only four not five different classes of multicycles exist:



B_4C4 B_3C4

B_2C4 B_5C4

B_6C4

$B_4C4–HF$ $B_4C4–H_2F_2$

Formula 12.5

1. Perfect multicycles free of end groups having the sum formula BnCN with $n = N$ (see Formula 12.5).
2. Multicycles exclusively having "*b*" end groups resulting from a_2/b_4 ratios $< 2.0/1.0$ with high conversion.

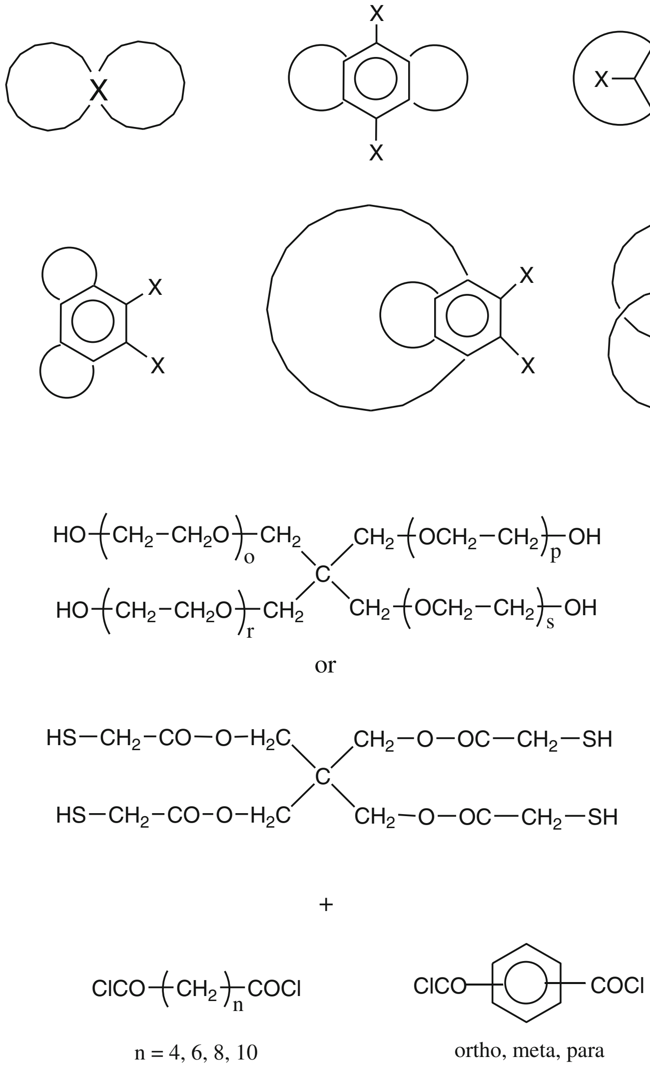
3. Multicycles exclusively having "*a*" end groups result from a_2/b_4 feed ratios $>$ 2.0/1.0.
4. Multicycles having "*a*" and "*b*" end groups indicating incomplete conversions.

Examples illustrating the correlation of sum formulas and simplified structural formulas are presented in Formulas 12.4 and 12.5.

The experimental work reported so far may be subdivided into two groups: firstly, polycondensations based on nucleophilic b_4 monomers (which will be discussed first), and secondly, polycondensations involving electrophilic b_4 monomers. In principle, pentaerythritol, threitol or the methyl glycoside of glucose may be considered to be useful and relatively inexpensive b_4 monomers. However, all these tetraols are poorly soluble in inert reaction media. Therefore, ethoxylated pentaerythritols ore the mercaptoacetate and mercaptopropionate were used (see Formula 12.6). Two versions of ethoxylated pentaerythritols (EPEs) are commercial and served as reaction partners of dicarboxylic acid dichlorides (DADs). The monomer called EPE-3 contains on the average three ethylene oxide units, whereas 15 ethylene oxide units are typical for EPE-15.

Sebacoyl chloride, and the three isomeric benzene dicrboxylic acids were reacted with both EPEs in a mixture of dry dioxane and pyridine [19]. In th case of EPE-3 gelation occurred even at the low ICM of 0.04 mol/L regardless which DAD was used. Eqifunctional poylcondensations of EPE-15 yielded yielded soluble perfect multicycles at an ICM of 0.08 mol/L with phthaloyl and isophthaloyl chloride. Te polycondensations of sebacoyl and terephthaloyl chloride reqired ICMs of 0.04 mol/to be successful. SEC measurements revealed the expected high polydispersities and Mn values in the range of 6,000–22,000 Da were found. When the tetramercaptoacetate of pentaerythritol was reacted with the aliphatic DADs presented in Formula 12.6 [20], soluble perfect multicycles were only obtained with suberoyl and sebacoyl chloride. All these experiments together proved again that ethylene oxide units favour cyclization due to the high percentage of gauche conformations, whereas alkane chains are unfavourable due to the preference of the trans conformation.

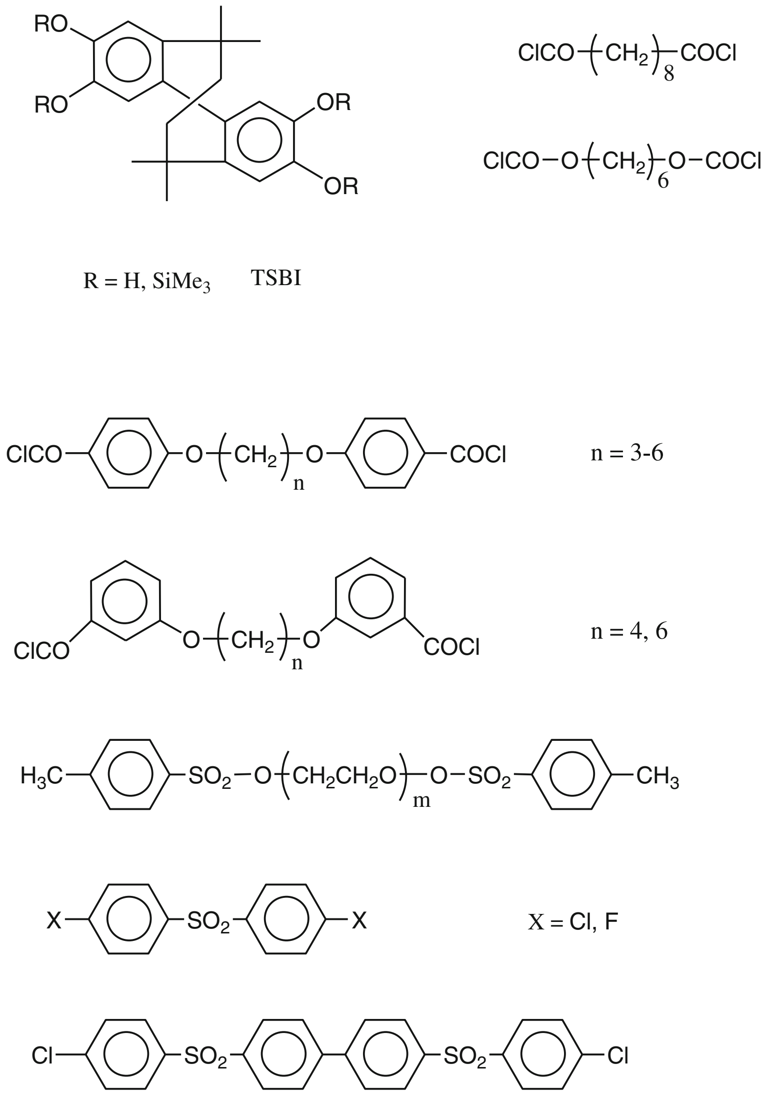
TTSBI which is soluble in various polar solvents was used as nucleophilic monomer for several syntheses of multicyclic polyesters [21] and polyethers [22]. With sebacoyl chloride or 1,6-hexanediol bischloroformiate (see Formula 12.7) gelation occurred even the ICM was lowered to 0.02 mol/L. At this ICM asoluble multicycles were obtained, when the aliphatic–aromatic DADs outlined in Formula 12.7 were used as reaction partners and with the m-isomers an ICM of 0.04 was sufficient. Soluble, multicyclic polyethers were isolated from polycondensations of TTSBI and tosylated di- and tri(ethylene glycol) at an ICM of 0.02 mol/L [19]. These materials possess the expected properties of multicyclic crown ethers (or cryptants) and form complexes with all alkali metal ions. Attempts to prepare multicyclic aromatic polyethers were less successful [23]. Despite optimization of the reaction conditions nearly quantitative conversions were never achieved regardless, if 4,4-dichlor- or 4,4-diffluorodiphenyl sulfone



Formula 12.6

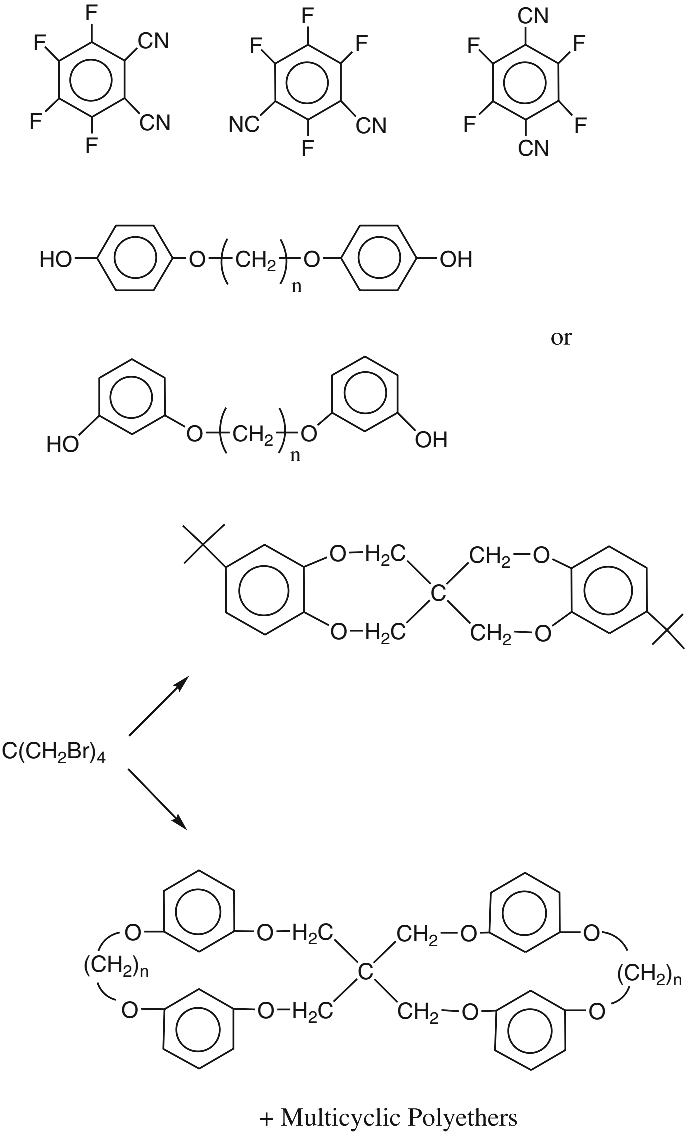
and 4,4-bis(4-chlorophenylsulfonyl)biphenyl (Formula 12.7) were used. The best results were achieved with the long a_2 monomer although DFDS is more reactive Hence, it may be concluded that with the short diphenyl sulfones cyclization of several isomers is sterically hindered.

The second group of $a_2 + b_4$ polycondensations was conducted with electrophilic b_4 monomers When pentaerythritol tetrabromide was reacted with tert.-



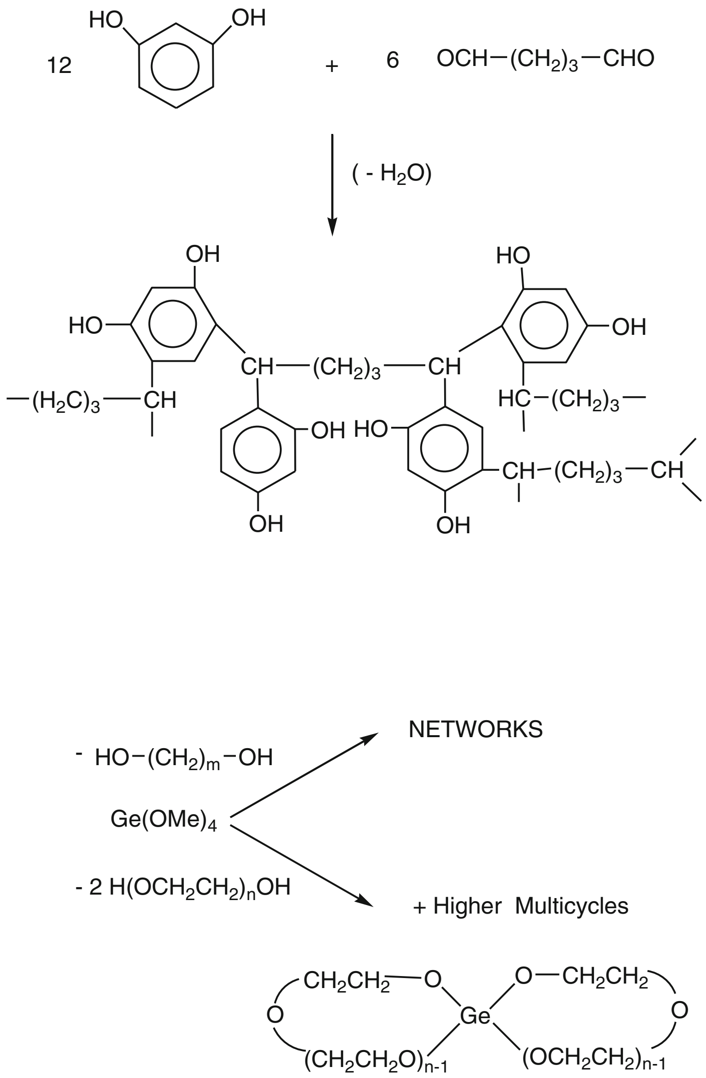
Formula 12.7

butylcatechol or 2,2′-dihydroxybiphenyl at an IMC of 0.05 mol/L the spirocyclic monomers were the main products [24]. All other diphenols yielded soluble multicycles, but perfect multicycles were only obtained by equifunctional polycondensation bis(m-hydroxyphenoxy)alkanes (see Formula 11.8). Furthermore, the three isomeric dicyanotetrafluorobenzenes were reacted with bis(hydroxyphenoxy)alkanes (Formula 12.8) [25, 26]. Two trends were detectable. First, the 1,3-dicyano isomer mainly reacted as a b_3 monomer in agreement with the



Formula 12.8

substitution rules of organic chemistry. Second, the a, ω-bis (m-hydroxyphenoxy) alkanes evidenced again a higher cyclization tendency than the analogous p-isomers, and yielded soluble, perfect multicyclic polethers of 1,2- and 1,4-dicyanotetrafluorobenzenes.



Formula 12.9

Finally, a study of Nishikubo et al. [27, 28] should be mentioned in which resorcinol was used as a_2 monomer and glutaraldehyde (pentanedial) as b_4 monomer (see Formula 12.9). Under optimum reaction conditions a craystalline monodisperse multicyclic oligomer was isolated and after modification of the free OH groups characterized by X-ray crystal structure anlysis. Its unique structure was nick-named “noria”, the latin word for water-wheel.

12.4 Thermodynamically Controlled Polycondensations

All afore-mentioned polycondensations belong to the category of kinetically controlled polycondensations, what means that all reaction steps were irreversible (see Chap. 5). A few thermodynamically controlled (TC) $a_2 + b_4$ polycondensations were also reported from trialkyltin alkoxides it is known that a spontaneous exchange of alkoxide groups occurs via O–Sn donor acceptor interaction. Such interactions also exist for alkoxides of other metals having energetically favotable free d-orbitals. Equifunctional polycondensations of EPE-3 or EPE-15 with dibutyltin dimethoxide yield sirupy materials which certainly contain multicylic oligomers which depending on the temperature equilibrate with each other [29, 30]. The moderate melt viscosities of these multicyclic tin alkoxides suggest that high molar mass components are absent and that the bicyclic (spirocyclic) monomers are the predominant reaction products.

When germanium tetraethoxide was condensed with various diols (Formula 12.9) insoluble networks were obtained [31] from a,ω-alkanediols (with exception of 1,3-propanediol), whereas soluble viscous products resulted from polycondensation with oligo(ethylene glycol)s [32, 33]. These findings suggest that the predominance of trans conformations in the alkanedils favors the formation of gels at the expense of multicycles, whereas the gauche conformations of the oligo(ethylene glycol)s favour the formation of soluble multicycles. Unfortunately the hydrolytic sensitivity of metal alkoxide bonds prevented reliable SEC measurements.

12.5 Multicyclic Polymers by ROP

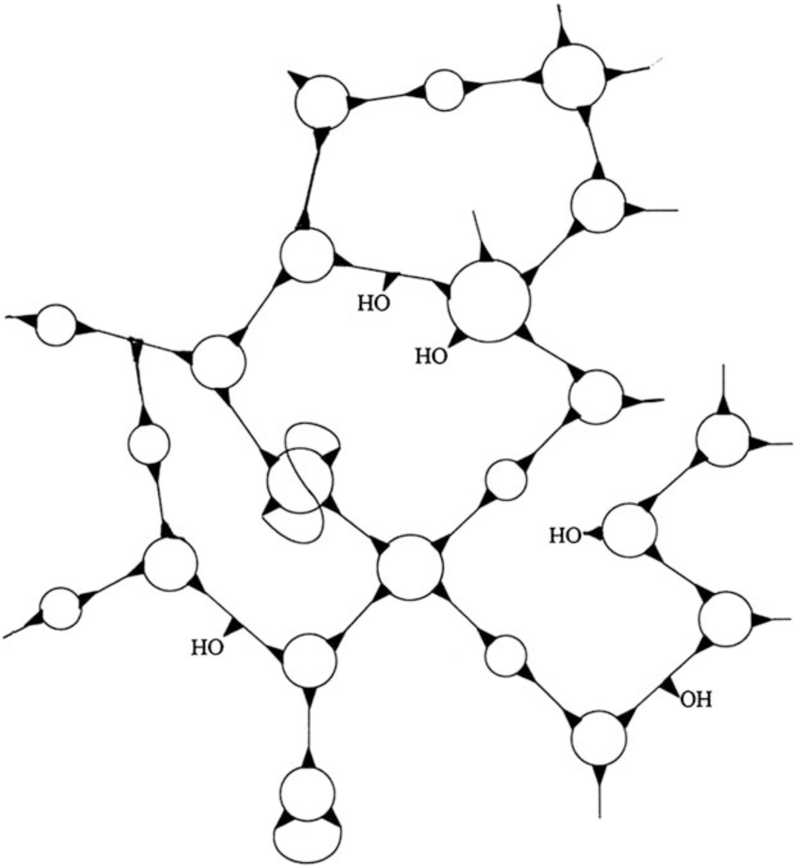
Quite recently Chojnowski et al. [34] published the first example for the preparation of a multicyclic polymer by combined ROP and polycondensation. Cyclo(tetramethyl siloxane), ($[\text{–SiHMe–O–}]_4$) was polymerized by means of $B(C_6F_5)_3$, a Lewis acid, which is capable to abstract hydride ions from Si–H groups. The ROP was followed condensation steps resulting in elimination of gaseous $MeSiH_3$ and formation of branching points. After prolonged heating multicyclic poly(methyl siloxane)s were obtained

12.6 Properties and Potential Applications

Studies of syntheses and properties of multicyclic polymers are still in their infancy. The following properties are known or predictable and allow for speculations about certain applications. Due to the compact structure and the lack of long linear chain ends both melt and solution viscosities are particularly low. Yet, due to the lack of entanglements film forming properties are poor. Multicyclic polymers may play the role of host molecules for ions and small organic molecules such as drugs or dyes. The ring and pore size may be varied and fine-tuned by the length of the a_2 monomers. Multicycles are more stable than linear or branched polymers against thermal degradation of the molar mass, because one, two or three chain scissions do not automatically reduce the molar mass. Multicyclic polymers are particularly well suited as thermosets and high temperature adhesives. These properties are inherent in their architecture, whereas the chemical structure is only relevant for the minimum (or optimum) temperature of such an application. These applications result from the fact that the thermal cleavage of a bond (regardless which one) generates two radicals which may attack a neighbouring molecule and thus, induce a three-dimensional chain growth and crosslinking process. The thermally generated radicals may also attack surfaces of other materials, thereby generating stable covalent bonds with a neighbouring material. Certainly research for more than one decade will be necessary to explore these and other applications in detail.

12.7 Multicyclic Polymers and the Theory of Gelation

The classical network theory is based on the experimental and theoretical studies of Flory [3, 35, 36] (see Chap. 4) and Stockmayer [36, 37]. Their theory is characterized by the relationship of between gel point and conversion according to Eq. (12.3) which is a more general version of the combined Eqs. (12.2) and (12.3). The Flory–Stockmayer theory is based on two assumptions. First, the reactivities of the functional groups is independent of the conversion and independent of the extent of branching and crosslinking. Steric hindrance and reduced mobility of functional groups in the neighbourhood of branching points is not considered. Second, cyclization plays a negligible role (see Sect. 12.1) and only occurs close to the gel point in large hyperbranched molecules containing numerous "*a*" and "*b*" functionalities. This second assumption was revised by Stepto [38, 39], who, together with Gordon and Temple [40, 41], developed a new theory of KC step-growth polymerizations [42] (see Chap. 7). This new theory is characterized by a permanent competition of cyclization and chain growth, so that cyclization begins at the first percent conversion (i.e. formation and cyclization of dimers) and ends up at 100 % conversion with the consequence that all reaction products are cycles. Stepto computed [38, 39] that in the case of three-dimensional polycondensations. The fraction of cyclic structures increases more rapidly than in the case of analogous two-dimensional polycondensations. However, Stepto did not say anything about the exact structure of the cyclic species, and thus the formation of bicyclic and multicyclic oligomers and polymers was not mentioned or discussed. Yet, the structure of the low molar mass reaction products is decisive for the structure of the networks and for the composition of the sol–gel phase.



Formula 12.10

$$(n_a - 1)p_a(n_b - 1)p_b = 1 \tag{12.3}$$

with

na, *nb* number of "*a*" or "*b*" functionalities

p_a, p_b conversions of a_n or b_n monomers

The MALDI-TOF mass spectrometry has evidenced that any kind of cyclic and multicyclic oligomers and polymers can be formed (see Formulas 12.2, 12.3 and 12.5), whereby their molar fraction depends, of course, on the a_2/b_n ratio and on the conversion. Those cyclic and multicyclic species having functional groups serve as building blocks for larger hyperbranched or crosslinked molecules, so that networks contain small cyclic structures in combination with large loops which are typically formed immediately before and after the gel point. Formula 12.10 presents a segment of such a network. Since lower IMCs favour the formation of small cycles, the fraction of small cyclic elements in the final networks increases with dilution. A typical consequence for the macroscopic properties of the gels is a lower elasticity.

The perfect bicycles and multicyclic oligomers and polymers represent an inert species in KC step-growth polymerizations. In the Flory–Stockmayer theory the sol phase consists of openly branched oligomers and polymers which can react with each other and with the network molecules [3, 43]. Therefore, the sol phase disappears at $p_{\max}$, and one giant network molecule is formed comprising all monomers ($p = 1$ is impossible in the F–S theory). In contrast, the formation of perfect bicyclic and multicyclic species yields a chemically stable sol phase, which does not disappear even at the highest conversion. Hence the mass fraction of the gels depends on the cyclization tendency inherent in the chemical structure of the monomers and it depends on the IMC due to the RZDP. In other words, $p_{\max}$ is the sum of p_N, the conversion responsible for the network molecules, and p_m, the conversion yielding the perfect multicycles. The ratio p_N/p_m is highest, when the polycondensation is conducted in bulk and it decreases with lower IMCs until p_N vanishes at the critical concentration. In summary, the syntheses of multicyclic polymers have shed more light on the course of $a_2 + b_n$ polycondensations, but further experimental studies and improvements of the theory of gelation is still needed to achieve a full understanding of three-dimensional step-growth polymerizations.

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Chapter 13
Polycondensation Via Electrostatic Self-Assembly

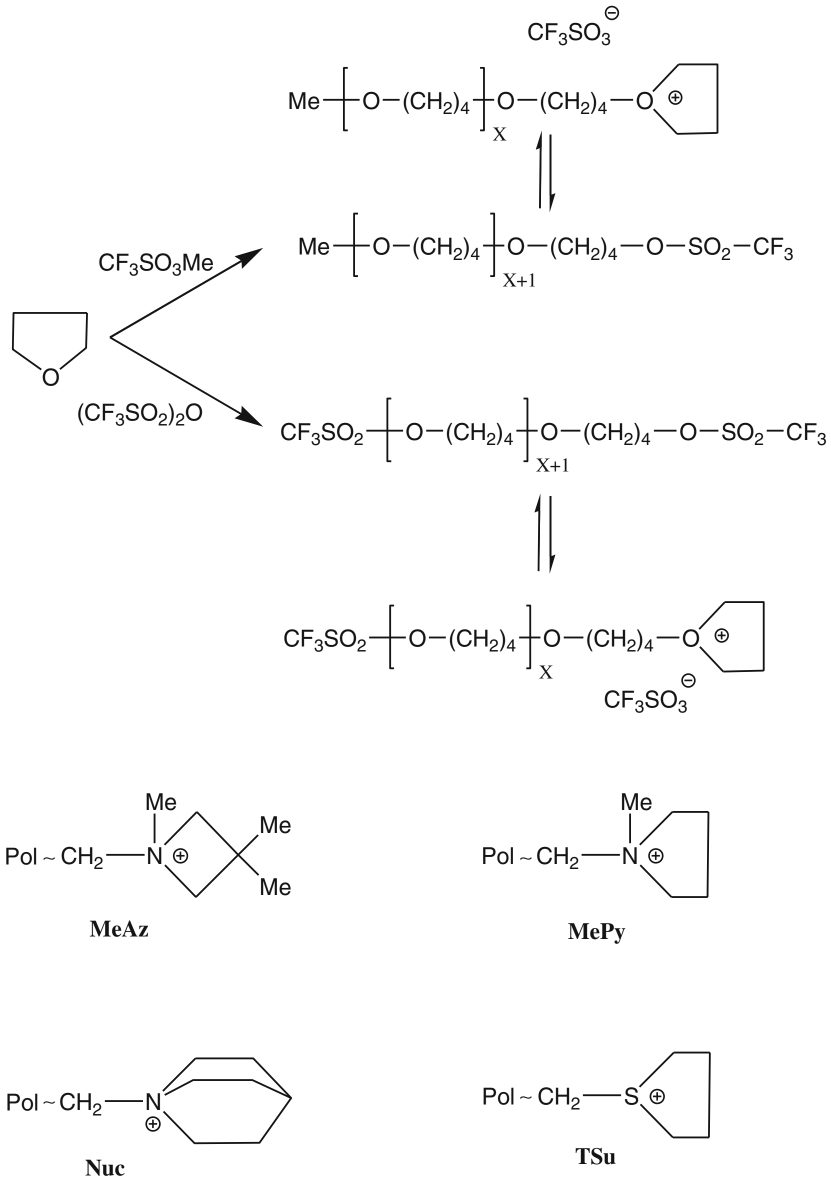
13.1 Introduction

A polycondensation via electrostatic self-assembly (PvSA) is a two-step process involving two ionic (end) groups. The first step consists of the formation of an ionic bond based on an exchange of ions which is a reversible process resulting in the self-assembly of the organic reaction partners. The second step which may occur almost simultaneously or at a later time and at higher temperatures consist of an irreversible formation of a covalent bond, the so-called covalent fixation. Of course, only both steps together yield a new stable product and only both steps together may be understood as polycondensation. In the present chapter which is based on the work of Goethals, Tezuka and coworkers, all examples include metal salts of carboxylic acids as one kind of reactants, so that the covalent bond formed in the second step are ester groups. In other words these polycondensations may be understood as syntheses of polyesters via alkylation of carboxylate ions. The term self-assembly is justified by the fact that the electrostatic interaction between the ionic (end) groups brings the reaction partners in close contact even when the ionic groups were initially randomly dispersed in the more or less polar polymer matrices.

13.2 Open Systems

Syntheses of polymers having carboxylic end groups or pendant carboxylic groups were well-known at the beginning of Goethals's and Tezuka's studies, and thus the key to the success was the preparation of telechelic polymers bearing cyclic tetraalkyl ammonium or cyclic sulfonium end groups [1]. The first class of telechelic oligomers and polymers having one or two onium end groups were prepared by the cationic ring-opening polymerization (ROP) of tetrahydrofuran by means of methyl triflate or triflic anhydride. Such polyethers contain covalent triflate end groups in equilibrium with cyclic oxonium groups [1] (Formula 13.1). These end

H. Kricheldorf, *Polycondensation*, DOI: 10.1007/978-3-642-39429-4_13,



MeAz

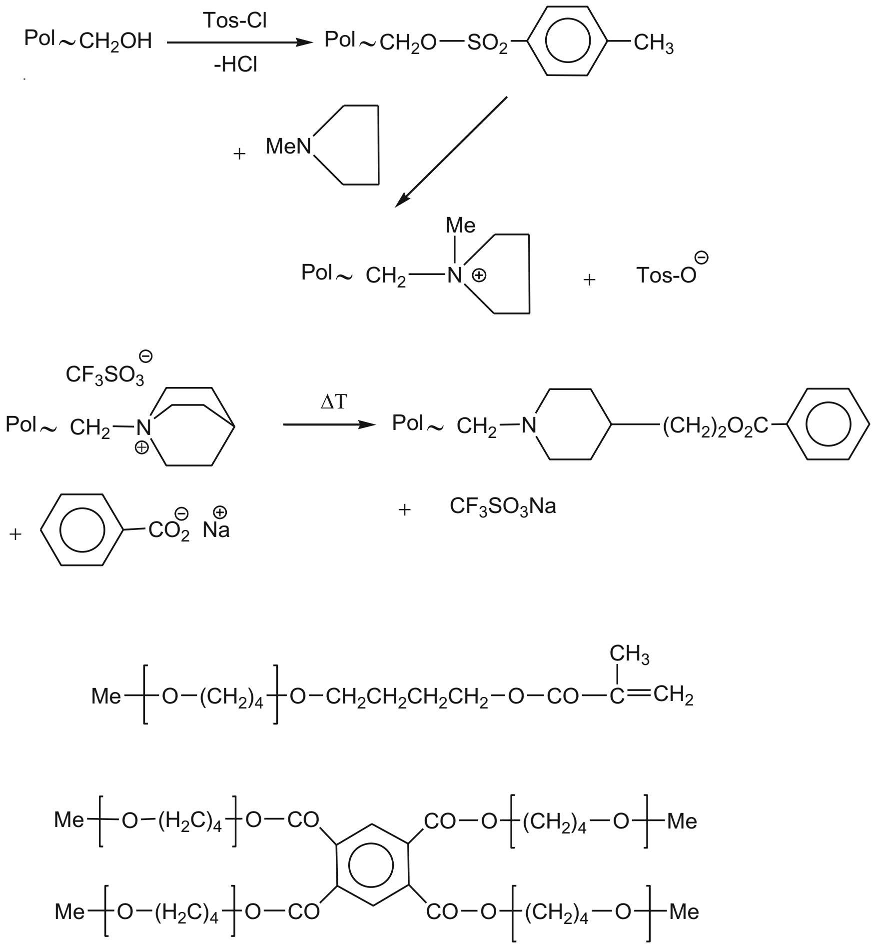
MePy

Nuc

TSu

Formula 13.1

groups are powerful alkylating agents, which allow for a quantitative formation of stable ammonium triflate end groups by reaction with cyclic tertiary amines [2–6] (see Formula 13.1). Yet, when tert-butyl aziridine was used as reaction partner, the excess of tert-amine underwent cationic polymerization [7]. A similar dependence of the reactivity on the ring size was observed for the cyclic sulfonium ions



Formula 13.2

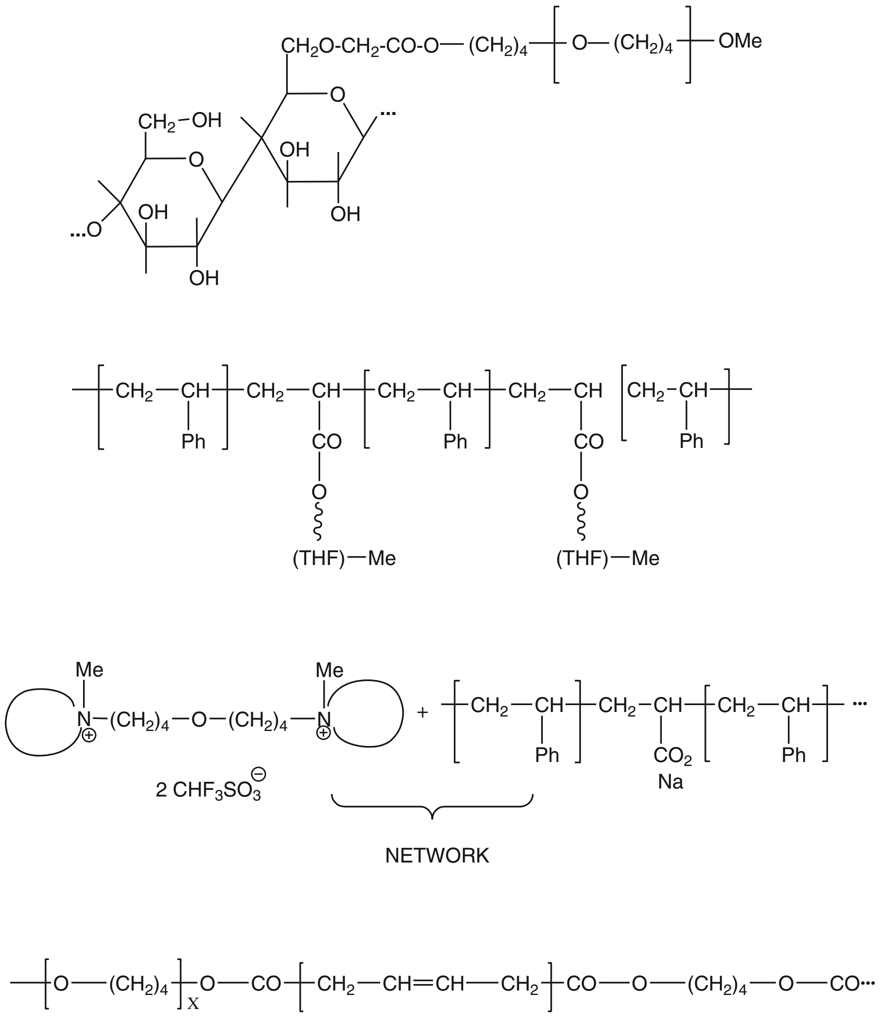
resulting from the alkylation of cyclic thioethers. The alkylation of the four-membered thietane was accompanied by spontaneous cationic polymerization of thiethane, so that a two-component network was obtained consisting of polyTHF and poyl (propylene sulfide) segments [8]. In contrast, tetrahydrothiophene yielded a stable but highly reactive five-membered cyclic sulfonium end group [9].

An alternative approach was elaborated by the functionalization of poly (dimethylsiloxane) [10–12], polystyrene [13, 14], and poly (ethylene oxide) [15]. The first two polymers were prepared in such a way that two CH_2OH end groups were introduced, whereas commercial poly (ethylene glycol) has two CH_2OH end groups anyway. These end groups were quantitatively tosylated by means of tosyl chloride and 4-dimethylamino pyridine. The resulting tosylates were, in turn, reacted with *N*-methyl pyrrolidine (Formula 13.2).

The exchange of the triflate ions against other anions revealed that carboxylate ions had a sufficient, but not too high reactivity for the purpose of PvSA. With azetidinium ions and tetrahydrothiophene groups a rapid reaction took place even at 20 °C, so that a controlled self-assembly process was not feasible. Yet, the reaction of benzoate ions with *N*-methyl pyrrolidinium groups occurred at 100 °C and with quinuclidine groups at 130 °C (Formula 13.2), so that the latter two groups proved to be particularly useful for PvSA [4, 6]. Nonetheless, the high reactivity of the azetidinium and sulfonium end groups were useful for rapid and quantitative reactions with low molar mass carboxylate anions in aqueous solutions. A first interesting application of these highly reactive onium end groups was the synthesis of a polymeric azoinitiator for radical polymerizations by alkylation of 4,4′-dicyano-4,4′-azodivalerate with monofunctional polTHF [16]. The preparation of a macromer from pyrrolidinium functionalized polyTHF [9] and methacrylate anions, and the preparation of star-shaped polymers from the reaction with benzene-1,2,4,5-tetracarboxylic acid are illustrated in Formula 13.2. In the latter case, an excess of the telechelic polyTHF was used to ensure a quantitative alkylation of all four carboxylate groups. The pure star polymer was obtained by repeated precipitation.

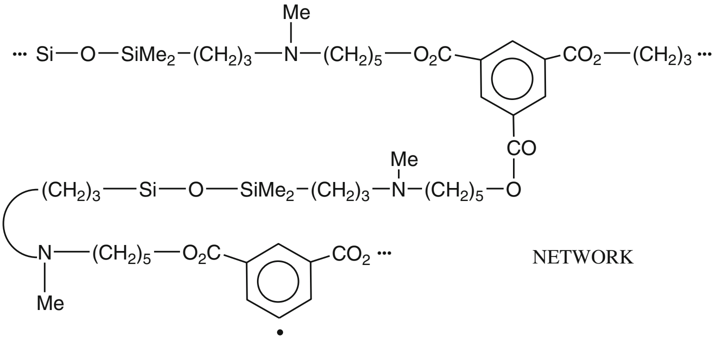
These syntheses were facilitated by the fact that the low molar mass carboxylic acid salts were soluble in water and reacted easily with the THF solution of the monofunctional polyTHF. The usefulness of a water soluble polymeric reaction partner was tested with the sodium salt of carboxymethyl cellulose [6]. Grafting of monofunctional polyTHF ammonium salts was indeed achieved (Formula 13.3). The PvSA concept was then extended to the coupling of a water insoluble and incompatible polymers. The procedure was modified in such a way that the THF solution of the ammonium or sulfonium functionalized polyTHF and the THF solution of the reaction partner were coprecipitated into water. The ionic end groups found each other at the water-polymer interphase. In this way graft copolymers were prepared from styrene-acrylate copolymers (containing approximately 5 % of acrylate units) and monofunctional polyTHF [17]. With difunctional polyTHF a two-component network was formed [17] (Formula 13.3) Grafting of monofunctional polyTHF onto sodium polyacrylate was reported in another paper [18]. Polycondensation of difunctional polyTHF with the sodium salt of poly (butadiene) endcapped with two carboxylic groups yielded a multiblock copolymer [19] (Formula 13.3). For this polycondensation, the four different onium groups depicted in Formula 13.2 were compared. It was found that the coprecipitation of the polymeric reaction partners was immediately followed by a slow formation of ester groups, when azetidinium or sulfonium groups were involved. With the pyrrolidinium and quinuclidine groups solid aggregates were isolated which underwent covalent fixation at 100 or 130 °C quite analogous to the model reaction with benzoate ions.

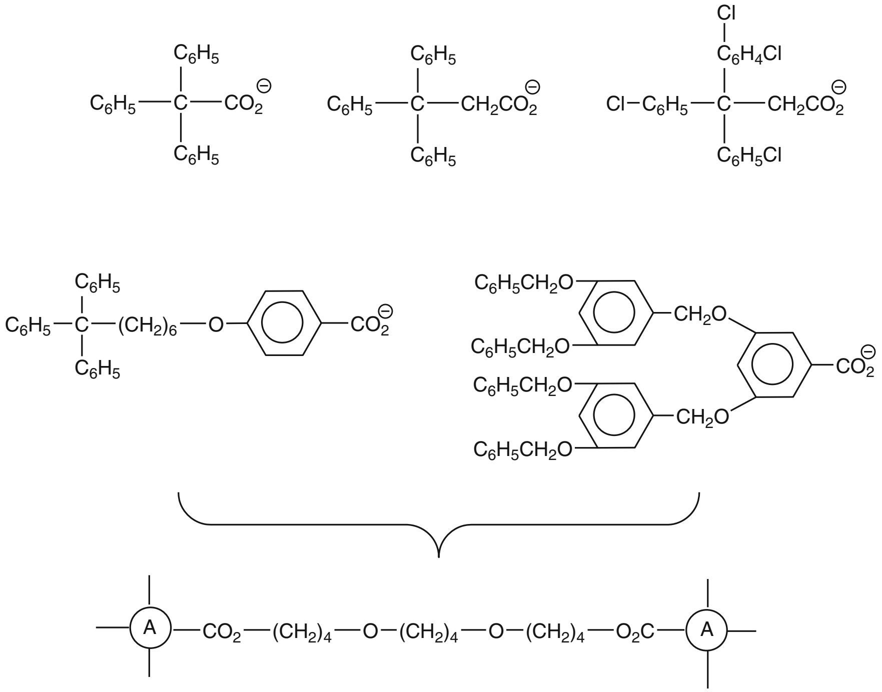
Further studies of networks included syntheses of networks containing poly (dimethylsiloxane) segments. One-component (homopolymer) networks were prepared by the reaction of poly (dimethylsiloxane) having two pyrrolidonium end groups with aqueous salt solutions of trimesic acid (Formula 13.4) or of



Formula 13.3

pyromellitic acid [20]. Star-shaped polymers were synthesized from the same tri or tetrafunctional carboxylic acids and monofunctional poly(dimethylsiloxane)s [20]. Furthermore, two-component networks were obtained from difunctional poly (dimethylsiloxane)s and polystyrene containing a small percentage of acrylate anions [21] (compare Formula 13.3 bottom which is based on polyTHF). In this case, the swelling behavior was in the focus of the study. Three different types of binary solvent mixtures were examined. The swelling behavior was also studied for two-component networks prepared from polyTHF and copoly (styrene-acrylate). Such networks had already been prepared before (Formula 13.3 and Ref.





Formula 13.4

[17]), but for the new study the chain lengths were systematically varied and the swelling behavior was investigated [22].

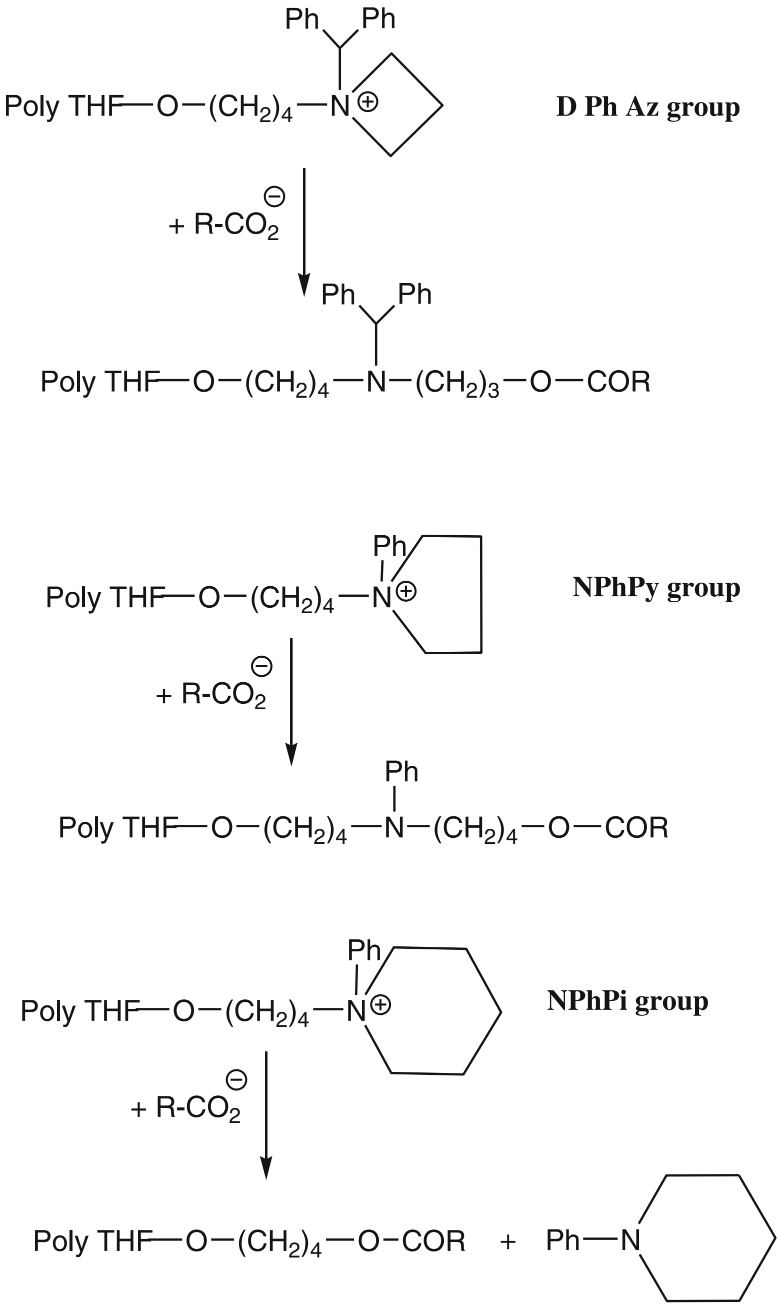
Using bifunctional oligoTHFs endcapped with pyrrolidinium or sulfonium groups several attempts were made to synthesize rotaxanes [23]. The bulky carboxylic acids (in the form of sodium salts) depicted in Formula 13.4 were used as anionic reaction partners The condensation reactions were conducted in the presence of 30-crown-10 or cyclodextrines [24].

Whereas a nearly quantitative introduction of bulky end groups was achieved, a trapping of macrocycles, and thus, syntheses of rotaxanes were unsuccessful.

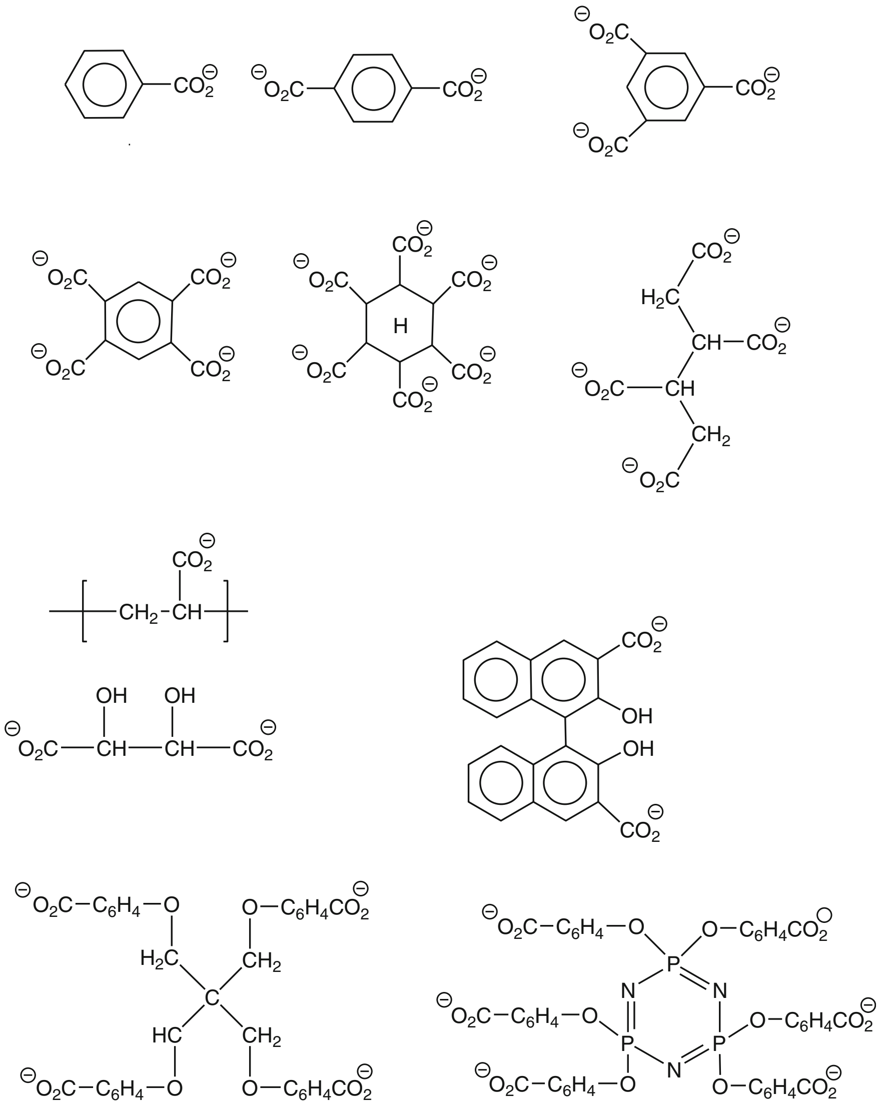
In the years 1999–2001, the Tezuka group began to explore two new aspects of their working field:

(1) The onium groups used in their previous work (Formula 13.1) were replaced by cyclic *N*-phenyl ammonium groups (Formula 13.5).
(2) The PvSA strategy was developed in direction of cyclic polymers and architectural (topological) isomers.

The introduction of new cyclic ammonium end groups was stimulated by the observation that in the case of the most widely used MePy group the nucleophilic attack of the crboxylate anions resulted to an extent of 5–20 % in demethylation. Instead of ring-opening, formation of methyl ester and pyrrolidine end groups took place. In contrast, a nucleophilic cleavage of the *N*-phenyl bond does not occur under the given reaction conditions. The reactivity of the oxonium and triflate end groups of polyTHF (Formula 13.1) enables quantitative quaternization of cyclic *N*-phenylamines. Yet, the relatively low reactivity of *N*-phenyl amines does not allow for a clean and quantitative reaction with tosylate groups. Therefore, the cationic functionalization of telechelic poly (dimethylsiloxane)s, polystyrenes, or poly (ethylene oxide)s with cyclic *N*-phenyl amines was unsuccessful. Furthermore, it was observed that the reactivity of the *N*-phenyl ammonium end groups depended largely on the ring size or, in other words, on the ring strain. Whereas, the desired ring-opening alkylation was the only reaction observed for the four- and five-membered rings, the Ph-piperidinium (PhPi) group reacted by elimination of *N*-phenyl piperidine [25] (Formula 13.5). Because the Ph-pyrrolidinium group (PhPy) combined low costs, easy preparation, and formation of stable aggregates (at 20 °C) with sufficient reactivity above 90 °C the PhPy group was preferentially used for syntheses of topological isomers. At first the reactivity of the Ph-azetidinium (PhAz) groups was explored using the anions listed in Formula 13.6 as reaction partners. In all cases, nearly quantitative alkylation was achieved [24]. With PhPy functionalized polyTHF four- and six-armed stars were prepared using the multifunctional carboxylic acids depicted in Formula 13.6 [26]. For the quantitative alkylation of these multifunctional carboxylic acids, an excess of activated polyTHF was needed which was finally removed by washing and reprecipitation. Quite analogous to previous syntheses of star-shaped polymers, the conversions were monitored by ^{1}H NMR spectroscopy and SEC measurements. Furthermore, a variety of comb-like branched polymers was prepared from low molar mass polyacrylates having a narrow MWD. Branched copolymers combining polyTHF side chains of different chain length or having different ether end groups in the same polymer were prepared from mixtures of monofunctional polTHF [27, 28].


Ph
Ph
Poly THF—O—(CH2)4—N⊕
D Ph Az group
+ R-CO2⊖
Ph
Ph
Poly THF—O—(CH2)4—N—(CH2)3—O—COR
Ph
Poly THF—O—(CH2)4—N⊕
NPhPy group
+ R-CO2⊖
Ph
Poly THF—O—(CH2)4—N—(CH2)4—O—COR
Ph
Poly THF—O—(CH2)4—N⊕
NPhPi group
+ R-CO2⊖
Poly THF—O—(CH2)4—O—COR
+
Ph—N

Formula 13.5



Formula 13.6

13.3 Cyclic Systems

Before presenting the contribution of the Tezuka group to the field of cyclic polymers and topological isomers, the term topological isomer needs discussion and definition. Topological isomers mean isomers possessing different architectures. In order to comply with the definition of isomers, long existing in organic chemistry and to avoid misunderstandings, it is advisable to subdivide the numerous topological isomers which exist in polymer science into three categories:

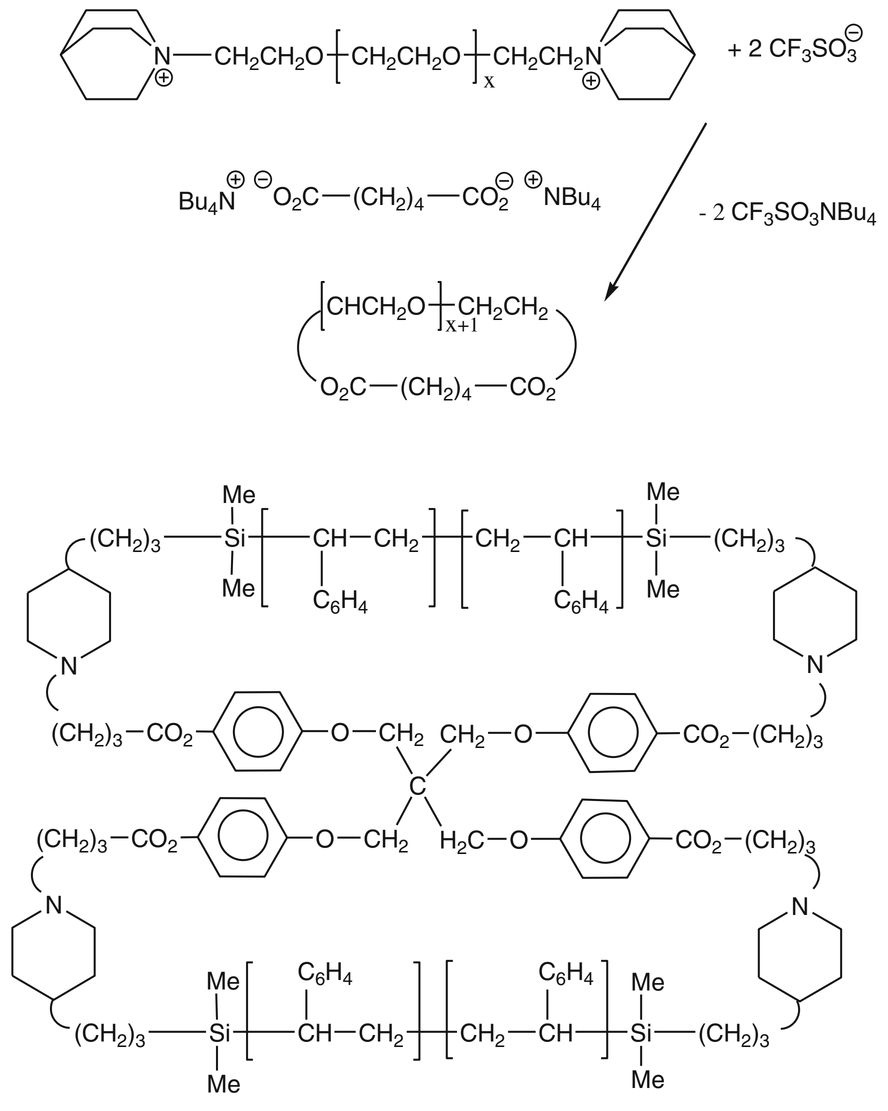
(I) Monodisperse isomers having identical sum formulas and masses according to the definition in organic chemistry may be called ideal isomers. Such isomers are formed as multicyclic oligomers and polymers in equifunctional $a_2 + b_n$ polycondensations as discussed in Chap. 12.

(II) Polydisperse isomers are characterized by identical MWDs. Example are monocyclic polymers and catenanes prepared from the same linear precursor polymers. In this case, the term polydisperse topological isomers are a long but correct lable.

(III) The term pseudoisomers is adequate for the third category. When, for instance, linear and cyclic polymers of the same MWD are called topological isomers (as it is done by Tezuka and other authors), it is ignored that the end groups of the linear chains do not exist in the cycles A similar difference in the sum formula and in the masses exists when monocyclic and multicyclic polymers are compared. This problem is even more severe, when star-shaped polymers and linear chains or cycles are called topological isomers. Therefore, the author proposes to use the term topological pseudoisomers. The term isomer per se is definitely wrong.

As discussed by the author in a previous review article [29], syntheses of (multi)cyclic polymers should be classified according to the synthetic strategy and according to the coupling method. As synthetic strategy Tezuka and coworkers exclusively used polycondensation under (pseudo)high dilution exploiting the Ruggli-Ziegler-Dilution-Principle [30, 31]. The coupling method is the combination of self-assembly and covalent fixation as discussed above. Cyclic poly (ethylene oxide), PEO, was obtained via PvSA from linear PEO having two quinuclidine end groups [32]. The precipitated aggregate was isolated and converted into the cyclic polyester by heating in dilute solution (Formula 13.7). Analogously a linear pseudoisomer having propionate end groups was synthesized. In a similar fashion cyclic polystyrene was prepared [33]. The 3-hydroxypropylsilyl end groups were again transformed in quinuclidine groups. The ion exchange was performed with sodium benzoate (yielding linear chains) or with sodium terephthalate in aqueous methanol. The covalent fixation occurred in refluxing toluene. Using a tetra carboxylic acid, the spirocyclic polymer depicted in Formula 13.7 was obtained. For all the cyclic PEOs [32] and polystyrenes [33], linear pseudoisomers were prepared and compared by SEC and in several cases also by MALDI-TOF mass spectrometry. For the bicyclic polystyrene (Formula 13.7), an analogous star-shaped polymer having OCH_3 end groups served as pseudoisomer.

Numerous cyclic species were also prepared from polyTHF activated by PhPy end groups [34–46]. In addition to mono and bifunctional polyTHFs the trifunctional monomer (a), Formula 13.8, was synthesized and included in these studies [34]. Monocyclic polymers with (see below) and without [34, 35] functional

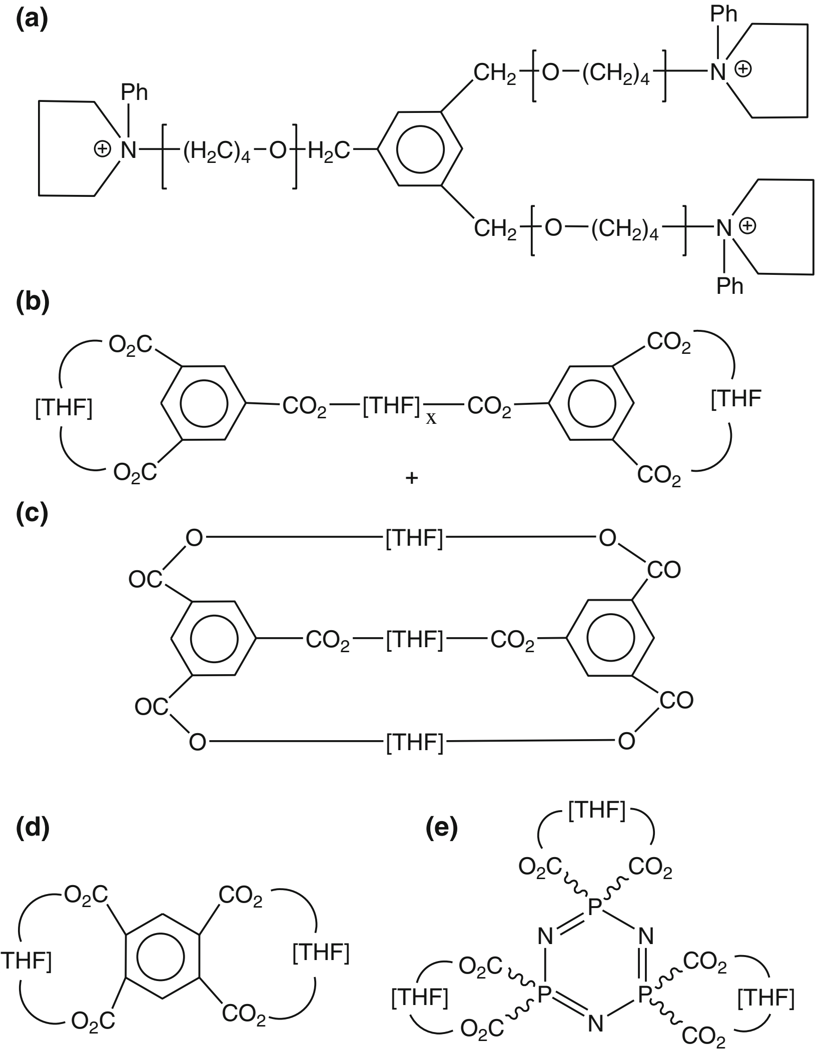


Formula 13.7

groups and various bicyclic polymers ((a), (b), (c) in Formula 13.8) were prepared [34, 36], and even tricyclic polyTHFs ((e)) were isolated [34].

Furthermore, syntheses of cyclic polyTHFs having one or two linear branches (e.g., (a) in Formula 13.9) were described [37, 38]. However, attempts to synthesize rotaxanes proved to be unsuccessful [39].

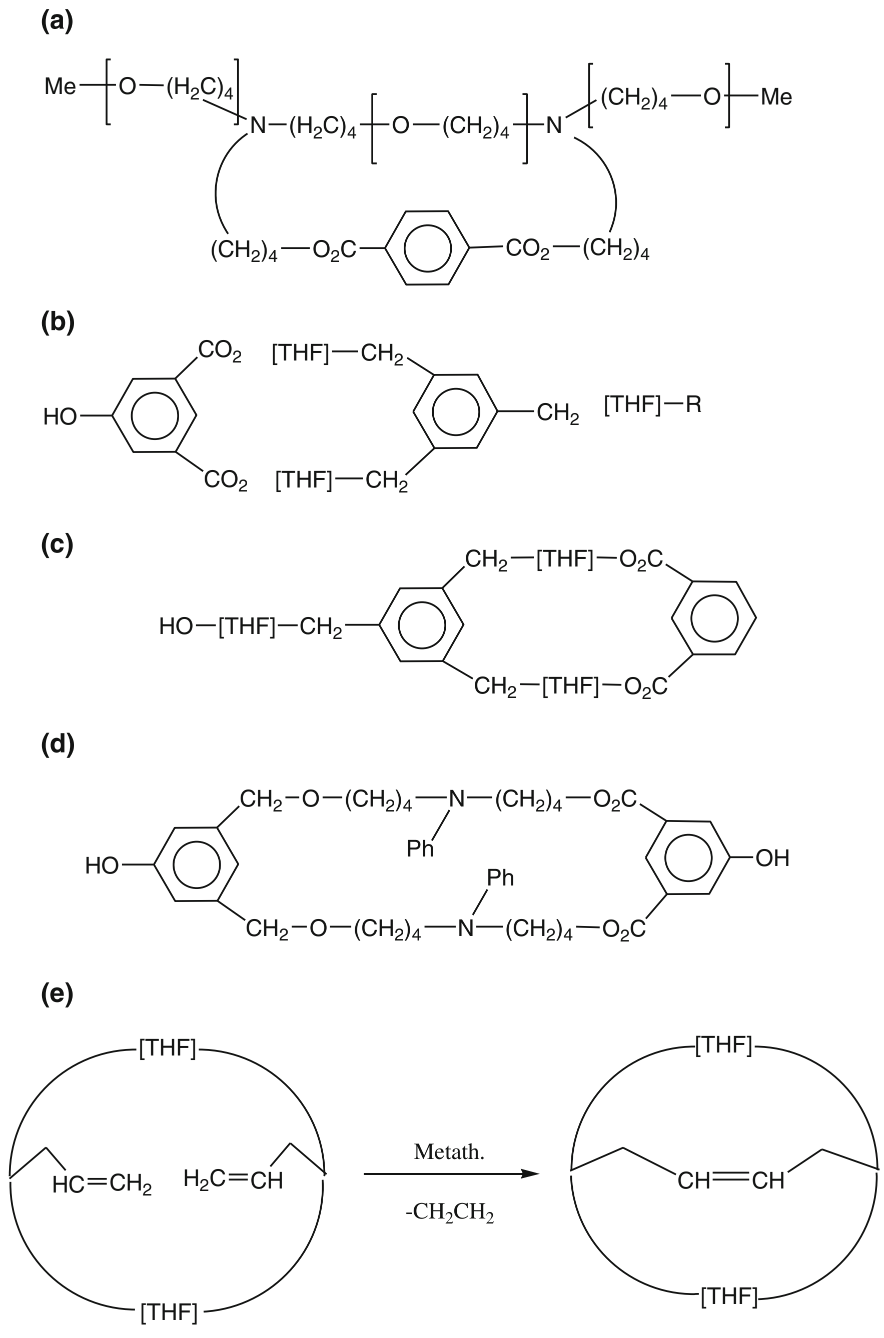
Among the various experiments designed to yield rings having functional groups, the syntheses of the pseudoisomeric tadpole molecules, (b) and (c) in



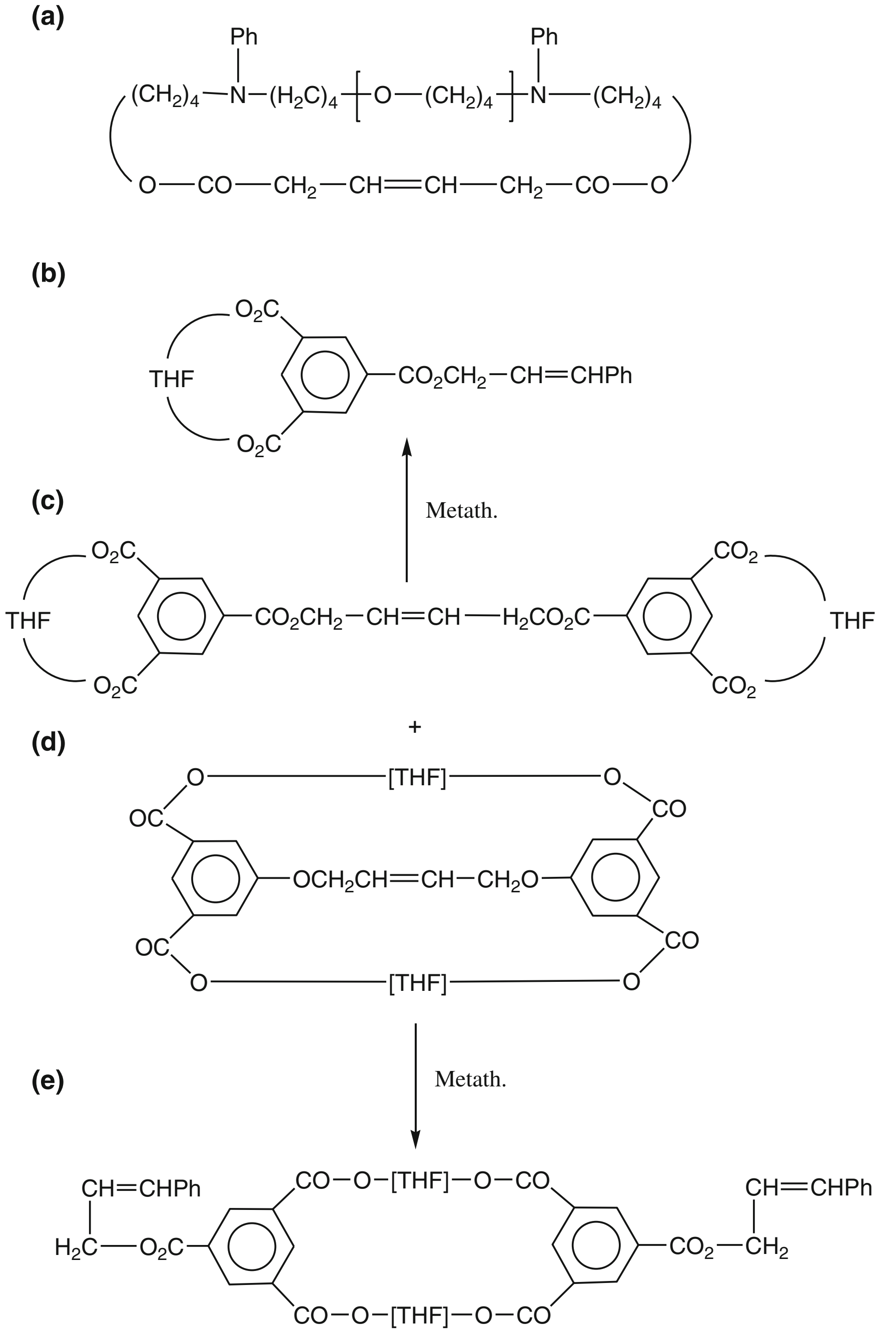
Formula 13.8

Formula 13.9, are noteworthy [40]. A new class of bifunctional cyclic oligomers was created having two OH groups in opposite positions of the ring ((d) in Formula 13.9) [41]. These so-called "kyklotelechelics" may serve as building blocks in addition or condensation type step-growth polymerizations.

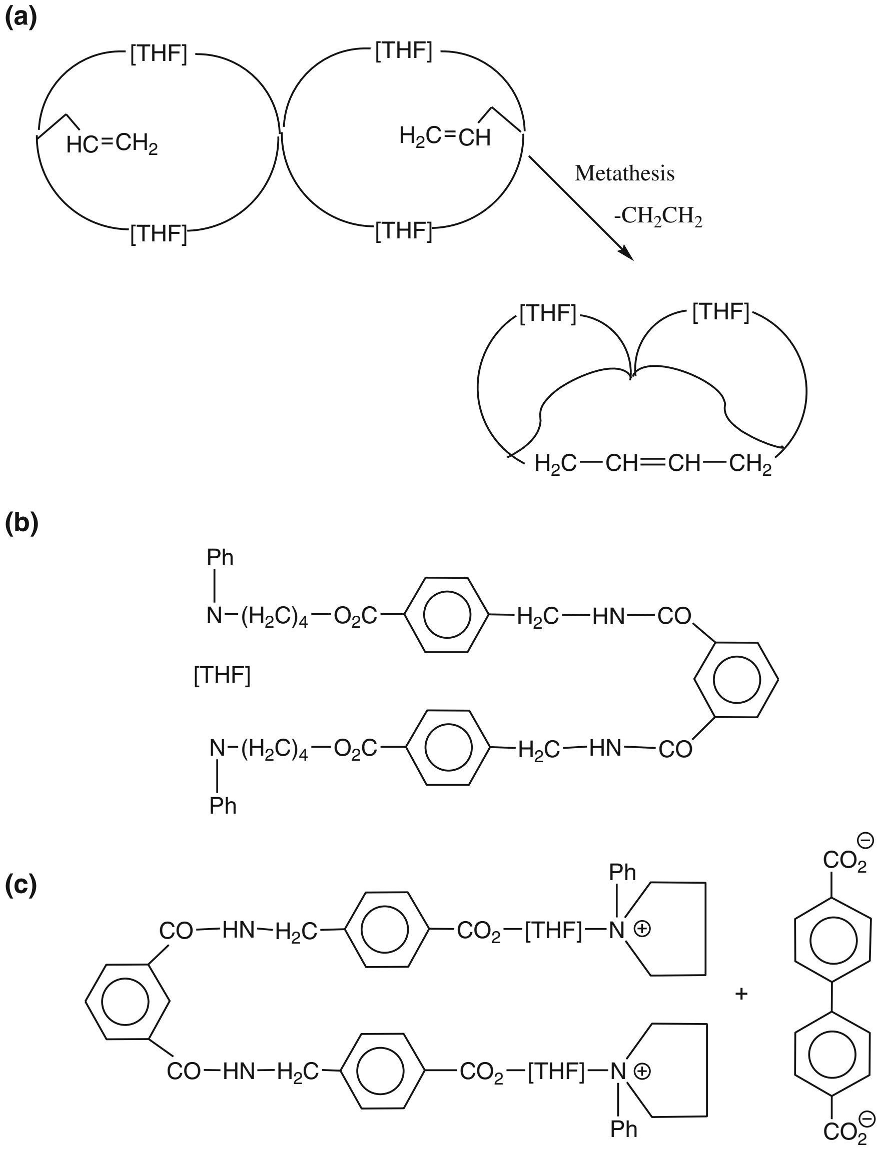
Several publications were focused on syntheses and reactions of cyclic or bicyclic polyTHFs containing one or two olefinic groups suited for metathetic condensation reactions [35, 42–45]. A monocycle derived from a PhPy-activated polyTHF and an unsaturated "adipic acid" is outlined in (a), Formula 13.10 [35].



Formula 13.9



Formula 13.10



Formula 13.11

The metathesis reactions studied by the Tezuka group served two purposes, either they were used to analyze complex reaction mixtures, or they served as ring closing step. An example for an analytical application is illustrated in Formula 13.10. The reaction mixture consisting of two isomers (c) and (d) was subjected to metathesis with a ruthenium-based Grubbs catalyst [45]. Whereas, (c) yielded two tadpole molecules of structure (b), one ring of structure (e) resulted from the bicyclic species (d). The reaction products (b) and (c) were easy to identify and to quantify. Efficient ring closing condensations exclusively yielding fused bicyclic or tricyclic polymers were outlined in Formula 13.9 ((e), bottom) and in Formula 13.11 (top) [42, 43]. An attempt to prepare a dicatenane by a combination of PvSA and metathesis condensation failed [45]. However, another approach avoiding metathesis proved finally successful [46]. A cyclic polyTHF containing one isophthalamide group ((b) in Formula 13.11) was prepared first, and a linear PhPy-activated was synthesized as "reaction partner" ((c) in Formula 13.11). The linear chain threaded through the preformed ring due to the formation of H-bonds between the isophthalamide groups, and ring closure by means of 4,4′-biphenyl dicarboxylic acid yielded the catenane.

Finally, a publication discussing structure and nomenclature of topological isomers [47] and two recent review articles [48, 49] should be mentioned.

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Chapter 14
Solid State Polycondensation

The term solid state polycondensation (SSP) simply says that chain growth by condensation steps occur under conditions, where at least one reaction partner exists in the solid state. As discussed below, SSP encompasses a broad variety of condensation reactions and substrates. Seemingly, the first example of a SSP (but not recognized as such) was the synthesis of poly(4-hydroxybenzoic acid), poly(4-oxybenzoate) by “dry distillation” of 4-hydroxybenzoic acid (see Chap. 2, Refs. [64–66]). A more detailed discussion of syntheses of poly(4-hydroxybenzoic acid) will we presented in Sect. 14.3. The first section is dedicated to SSPs of peptide esters which were also described for the first time before World War I.

14.1 Polypeptides

Curtius observed in 1883 the spontaneous polycondensation of glycine ethyl ester at room temperature, whereby the cyclic dimer and the ethyl ester of tetraglycine were formed as main products [1]. Since the ethyl ester of diglycine is crystalline, its further condensation steps represent the first example of a SSP of an oligopeptide. A well-defined SSP was then reported by Fischer in 1906 [2, 3]. He found that the methyl esters of triglycine $(Gly)_3$, of AlaGlyGly and of LeuGlyGly yield the corresponding hexapeptides (as methyl esters) upon heating at 110 °C in the solid state. No polycondensation occurred when the methyl ester of tetraglycine (Gly_4OMe) was heated to 100 °C for several hours [3]. These findings prompted several research groups after WWI to study SSPs of oligopeptide in more detail. The first systematic studies were presented by Pacsu and Wilson in 1939 [4–6] and almost at the same time by Frankel and Katchalski [7–9]. The former authors prepared several oligopeptide esters, but focused their work on SSP of oligoglycines. They confirmed that condensations of dipeptide esters yield cyclic dimers (2,5-diketopiperazines) as main products, and thus, were not much attractive for the preparation of polypeptides. They also confirmed that Gly_4OMe is stable at 110 °C. However, Gly_3OMe proved active, even at temperatures below 100 °C, and its polycondensation was studied at 102 and 130 °C over a long period of time.

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Furthermore, Gly_6OMe was isolated in high yields under certain reaction conditions and shown to polymerize above 100 °C. From quantification of NH_2 and OMe end groups it was concluded:

(1) that significant amounts of cyclic oligopeptides were not formed, and
(2) that polypeptides up to a DP of 96 can be obtained.

These results were perhaps a little too optimistic, because it was later shown by Rees et al. [7] that tripeptide esters have a certain tendency to form cyclic hexamers upon heating. Yet the presence of smaller amounts of cyclic oligopeptides cannot be detected or excluded by end group analyses.

Frankel and Katchalski [8–10] performed polycondensations of GlyOMe, GlyOEt, and D,L-AlaOMe at 100 °C. They purified the higher oligopeptides, thus obtained, from low molar mass byproducts and heated the higher oligopeptides to 130–150 °C. They concluded from end group analyses that further polycondensation steps in the solid state had taken place. PolyGly having a DP of 42 was isolated from the SSP of oligoGlyOEt, a DP of 110 from SSP of oligoGlyOMe and polyalanine with a DP of 23 from oligoAlaOMe.

Sluyterman et al. [11, 12] studied the reactivity of Gly_4OMe in the solid state at 100 °C for 700 h or for a short time at 185 °C. They found a small fraction of higher oligopeptides, but they also detected numerous side reactions, above all the formation of sarcosyl units. Rydon and Smith [13] studied the SSP of various olgioGlyOEts at 100 °C and obtained results which largely agreed with those mentioned above for oligoGlyOMes. Bockmann and Musso [14] reported in a short communication without exp. part that addition of Na or K trityl to a solution or suspension of amino acid or di- and tripeptide ethyl esters catalyzes their polycondensations, so that oligopeptides with DPs up to 13 could be obtained at 20 °C. Nonetheless, it was clear around 1955 that SSPs of oligopeptide alkyl esters was not a successful approach to the preparation of long polypeptide chains [15].

A new stimulus came from progress in the field of stepwise peptide syntheses. The usefulness of various activated ester groups for racemization-free and nearly quantitative formation of peptide bonds was explored. The results were, in turn, used for poylcondensations of activated esters of di-, tri- and tetrapeptides. Ester groups derived from *N*-hydroxysuccinimide, catechol, 4-nitrophenol, 2,4,6-trichlorophenol and pentachlorophenol (PCP) were examined. PCP esters proved to be particularly attractive due to a high crystallization tendency which eased the purification of the oligopeptide esters. Most polycondensations were conducted in DMF solution, and even, when the resulting polypeptides formed gels, these polycondensations cannot be defined as SSPs. However, it was found by several research groups [16–18] that suspensions of oligopeptide esters in benzene may give higher molecular weights than polycondensations in DMF solutions. In the "benzene system" a small fraction of activated oligopeptides may be soluble and growing steps may occur in three ways:

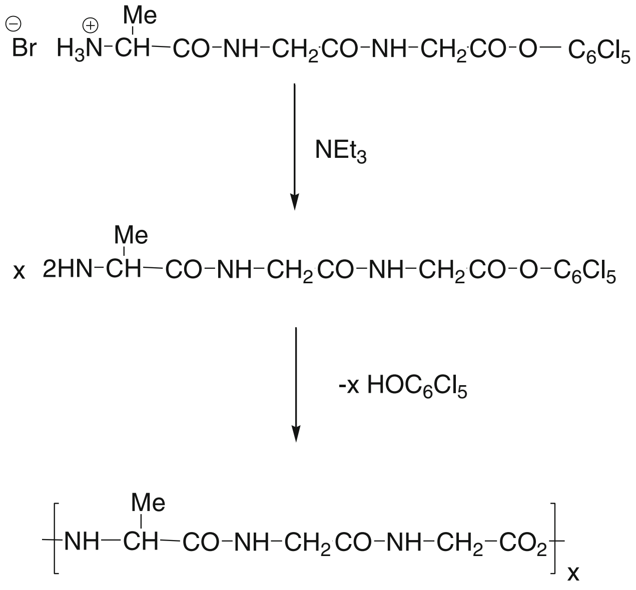
(a) by reaction between two dissolved monomers,
(b) by reaction of a dissolved monomer and functional end groups on the surface of insoluble particle (crystals),
(c) by reaction between neighboring functional groups on the surface of the peptide particles/crystals.

Reaction pathway "c" is an option, because the oligopeptidesstudied in Refs. [16–20] form β-sheet lamellae which usually possess an antiparallel arrangement of peptide chains, so that amino end groups have activated ester groups as neighbors and vice versa. For polycondensations in suspension typically molecular weights (Mn) in the range of 10–15 kDa were reported, but Mn's up to 30 kDa were also found. At this point a review article summarizing all polycondensations of oligopeptide esters known before 1974 should be mentioned [21]. A new approach to the SSP of activated oligopeptide esters was elaborated by Goodman and coworkers after 1970 [22–24]. Those authors prepared PCP esters of tri- or tetrapeptides stabilized as trifluoroacetates (see Formula 14.1). Dilute solutions or suspensions were mixed with dry Celite (silica gel) and the solvent was evaporated, so that the oligopeptides were deposited on a large inert surface. The "monomer-Celite" powder was then heated in vacuum to temperatures around 125 °C for several days. Neither triethylamine nor any other base was added, so that the risk of racemisation was minimized. For the purified polypeptides average molecular weights (MW's) in the range of 40–80 kDa were estimated from viscosity measurements. The usefulness of this approach was underlined by successful syntheses of polydepsipeptides containing lactic acid [24] (see Formula 14.1). Furthermore polycondensations of the same monomers in solution gave considerably lower molecular weights. The only short-coming of this approach is its limitation to small quantities of monomers. Finally, it should be mentioned that the molecular weights of reaction products of activated oligopeptide esters were determined for intensively purified and dialyzed polypeptides isolated in moderate yields.

14.2 Polyamides and Polyesters

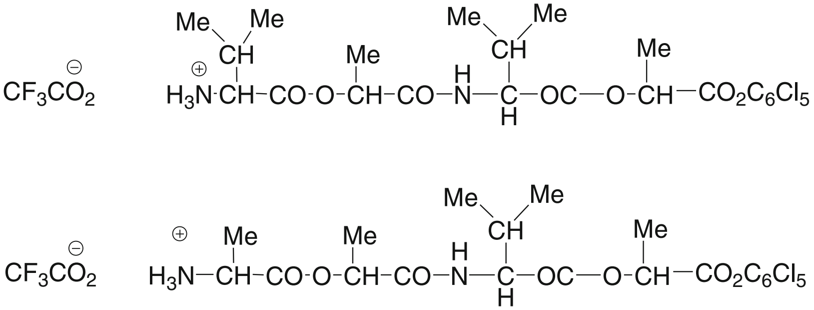
SSP of commercial polyamides and polyesters is nowadays a standard procedure used by all chemical companies producing such polymers [25, 26]. SSP is mainly used as postcondensation after the production of oligomeric or polymeric precursors in solution or in the melt. The molecular weights should be enhanced according to the needs of customers. The procedure is relatively simple from the technical point of view, but heating to temperatures above 200 or even above 250 °C is a costly process and not well suited for very large quantities.

Information about SSP of aliphatic polyamides was for the first time disclosed in a patent of DuPont [27] concerning Nylon-6,6. In this patent, polycondensation of hexamethylene diammonium adipate (AH-salt) was initially conducted in the



$$\overset{\ominus}{Br}\ H_3\overset{\oplus}{N}\text{-}\overset{Me}{CH}\text{-}CO\text{-}NH\text{-}CH_2CO\text{-}NH\text{-}CH_2CO\text{-}O\text{-}C_6Cl_5 \xrightarrow{NEt_3} x\ 2HN\text{-}\overset{Me}{CH}\text{-}CO\text{-}NH\text{-}CH_2CO\text{-}NH\text{-}CH_2CO\text{-}O\text{-}C_6Cl_5 \xrightarrow{-x\ HOC_6Cl_5} \left[NH\text{-}\overset{Me}{CH}\text{-}CO\text{-}NH\text{-}CH_2CO\text{-}NH\text{-}CH_2\text{-}CO_2\right]_x$$

Example for a polycondensation in suspension



$$\overset{\ominus}{CF_3CO_2}\quad H_3\overset{\oplus}{N}\text{-}\overset{(Me)_2CH}{CH}\text{-}CO\text{-}O\text{-}\overset{Me}{CH}\text{-}CO\text{-}\overset{H}{N}\text{-}\underset{H}{\overset{(Me)_2CH}{C}}\text{-}OC\text{-}O\text{-}\overset{Me}{CH}\text{-}CO_2C_6Cl_5$$

$$\overset{\ominus}{CF_3CO_2}\quad H_3\overset{\oplus}{N}\text{-}\overset{Me}{CH}\text{-}CO\text{-}O\text{-}\overset{Me}{CH}\text{-}CO\text{-}\overset{H}{N}\text{-}\underset{H}{\overset{(Me)_2CH}{C}}\text{-}OC\text{-}O\text{-}\overset{Me}{CH}\text{-}CO_2C_6Cl_5$$

Monomers used for the matrix assisted synthesis
of polydepsipeptides (in vaccum at 90 or 110°C)

Formula 14.1

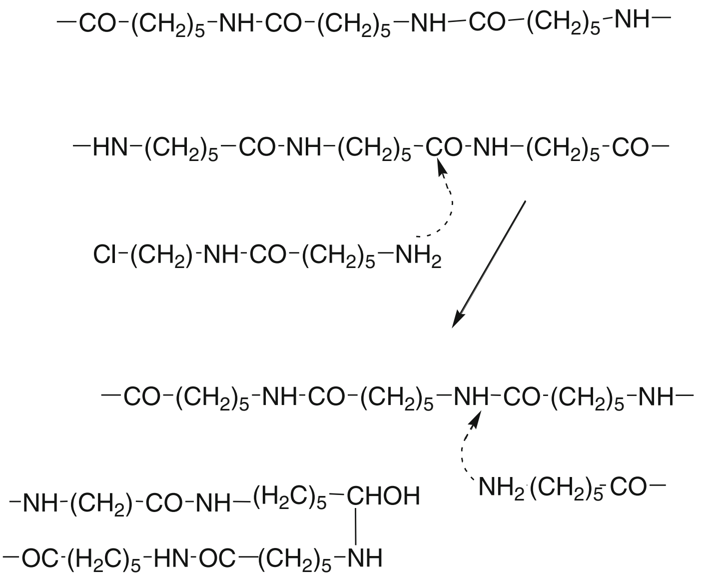
melt, but the temperature was then kept below the Tm's of the solidifying oligo- and polyamides, so that the further chain growth proceeded in the solid state. A first detailed study of SSP of the AH-salt was published by Chambert [28]. Since the AH-salt melts at 183–185 °C, the SSP was started at 179–180 °C, and the temperature was then raised in a stepwise manner up to 255 °C. It was found that a temperature only 10–150 °C below the optimum temperature may stop or significantly reduce the rate of chain growth. Yet, even at the optimum temperature application of vacuum was absolutely necessary to maintain chain growth. Another chapter described SSP of 11-amino undecanoic acid [29]. SSP at 185 °C was compared with polycondensation at 210 °C in the melt. As expected, SSP was far slower, but it yielded the polyamide (Rilsan) in the form of a wide powder which may be useful as a "melt adhesive". For SSP of Nylon-6 Fakirov and Avramova [30] not only found higher molecular weights, but also narrowing of the molecular weight distribution along with better mechanical properties. Kinetic studies of Gaymans [31] suggest that the mobility of end groups in the amorphous phase is decisive for the rate of chain growth. For annealing of Nylon-6,6 fibers above 220 °C Srinivasan et al. concluded that the SSP follows "step-growth bulk polymerization kinetics" [32]. In a later publication [33], a broader mathematical treatment of SSP of polyamides and polyesters was presented. In this work like in all previous papers the role of cyclics was ignored.

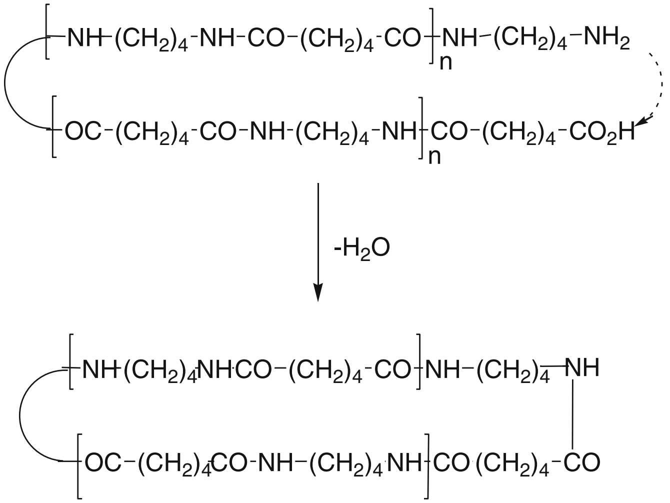
Assuming that the cyclics which are usually present in a flexible polycondensate (see Chaps. 5 and 7) are enriched in the amorphous phase, because they do not fit well in the crystal lattice of the linear chains, four kinds of chain growth reactions may be defined:

(I) Condensation steps of two end groups inside the crystallites.
(II) Condensations of end groups located on the surface of crystallites with end groups of mobile chains in the amorphous phase.
(III) Reactions of end groups inside the crystallites with cyclic oligomers or polymers embedded in the crystal lattice.
(IV) Reactions of end groups on the surface of crystallites with cycles in the amorphous phase.

Furthermore, it should be taken into account that functional groups may indirectly migrate in the crystal lattice by a series of trans reactions with neighboring chains as illustrated in Formula 14.2 for the aminolytic cleavage of polyamide chains.

It may be expected that the growing steps I an III are relatively rare, so that a SSP is dominated by reactions of type II and IV, but to the best of our knowledge, a detailed study elucidating existence and extent of these four growing steps has not been published until 2012. It maybe assumed that due to the growing steps III and IV the content of cyclics will decrease in the course of a SSP. A paper of Semlyen and coworkers [34] seemingly confirms this expectation. Four samples of Nylon-6 equilibrated in the melt were subjected to SSP 46 °C below its Tm, and the content of cyclic oligomers was determined. Sample (i) had the original composition of the equilibrate, whereas all cycles having DPs < 7 were extracted from sample (ii). After annealing for 32 days cyclic oligomers were formed again in sample (ii), but the total content of cyclic oligomers in both samples was lower than in the equilibrated Nylon-6. Another interesting result was reported by





Formula 14.2

Rulkens and Peters in 2011 for the SSP of Nylon-4,6 [35]. Those authors found that due to a special steric situation in the oligoamide crystals, the cyclic decamer and dodecamer were formed in relatively large quantities (see Formula 14.2).

Owing to a hairpin conformation both end groups were directly neighboring each other on the surface of the crystalline lamellae. When heated to the molten state, equilibration reduced their concentration, and the cyclic tetramer formed the top of the frequency distribution.

Closely related to SSP is the so-called chemical healing. This term includes all chemical reactions which go on at the interphase when two pieces of a polymer are pressed together. Both, condensation steps and trans reactions are usually involved [36]. When pieces of identical polymers or miscible polymers brought together migration of polymer chains from one particle to another one may also take place, a process called physical healing. However, chemical healing may also occur between two immiscible polymer such as a polyamide and a polyester and then may called heterochemical healing [37]. A broader discussion of healing processes is presented in Ref. [38].

In the case of high melting polyesters such as PET and PBT SS-postcondensation is again a standard method to enhance the molecular weights [24, 25]. Most studies of polyesters concern SSP of PET [24, 25, 39–48]. Most PET samples used for these studies had a relatively high molecular weight, meaning an inherent viscosity in the range of 0.5–0.7 dL/g. This is the maximum usually achieved in melt polycondensations of dimethyl terephthalate and ethanediol [45]. Such inherent viscosities are sufficient for many applications, but for bottle-blowing viscosities >1.0 are desirable, and such high viscosities can easily be achieved by SSP as demonstrated in the early work of Ravens and Ward [39] or by Karayanidis et al. [45].

A comprehensive and detailed study of kinetic and property parameters was published by Jabarin and Loffgren in 1986 [43]. They developed equations describing relationships of time, temperature, and final molecular weight for specific catalyst and precursor systems. Moisture concentration, oxygen exposure, and nitrogen flow were also taken into account. Measurements of inherent viscosities carboxyl end group concentration and residual acetaldehyde and Tm were conducted. In another paper [46] the influence of Sb_2O_3, a particularly useful catalyst for the production of PET, was investigated. Furthermore, the influence of microwave irradiation was studied [47]. Measurements of the diffusion of small molecules in the amorphous phase were performed by Chang as early as 1960 [40]. A mathematical modeling of all relevant processes (but ignoring the role of cyclics) was later reported by Kwon [48].

Further studies of the SSP of PET were performed with oligoesters as precursors [41, 42, 49, 50]. Miyagi and Wundrlich [41] obtained linear oligomers free of cyclics by etching the chain folds from the surface of lamellar crystals. Droescher and Wegner [42] prepared their oligoesters by polycondensation of bis(2-hydroxyethyl)terephthalate, BEHT, with terephthaloyl chloride in solution, a method certainly involving cyclization. Nonetheless, both research groups agreed in that the SSP of oligoesters may enhance the molecular weights of oligoesters by a factor of 10. Changes in the crystal lattice during SSP of PET or PEN oligoesters were analyzed by Sivaram and coworkers [49].

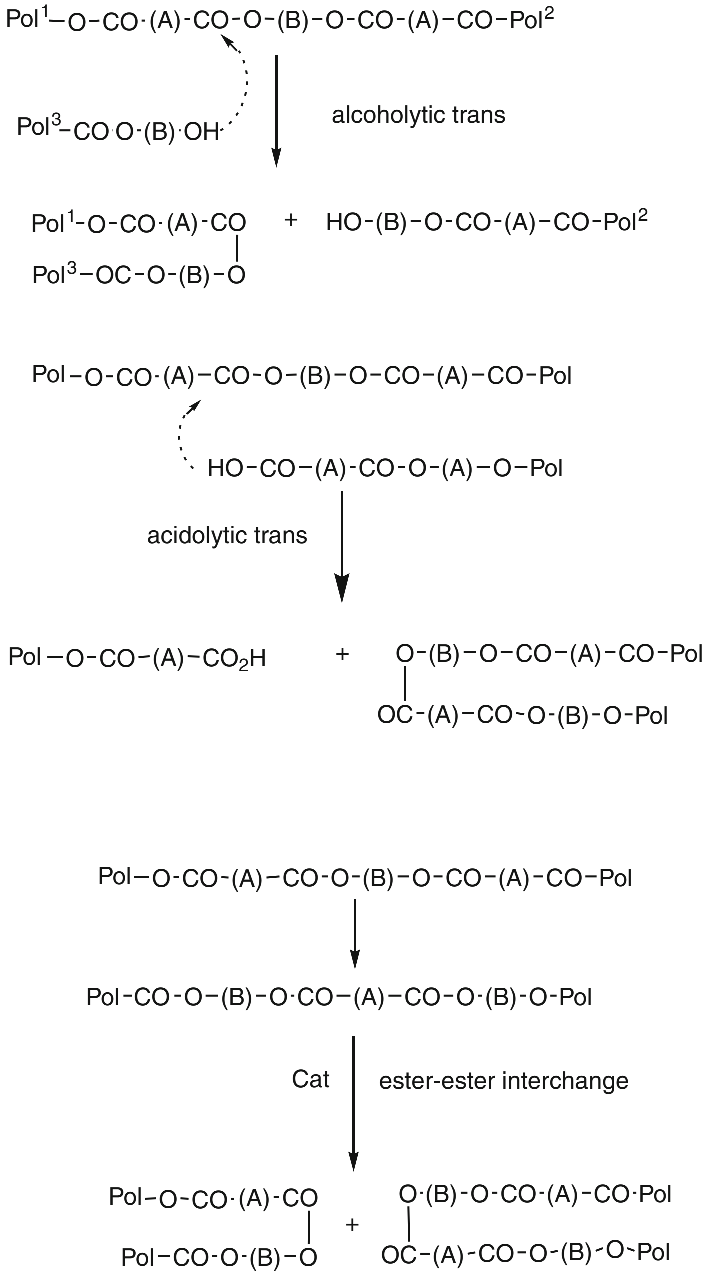
Solid state reactions of PET and related polyesters were (and are) not only of interest for enhancing the molecular weight, but also as an approach to modify the chemical structure. In other words, transformation of homopolyesters into copolyesters having blocky sequences was the object of such studies [51–58]. The preparation of copolyesters by transesterification of homopolyesters can easily be achieved in the melt, when problems of the immiscibility can be overcome. Transesterification in the melt may be quite rapid (depending on the catalyst) and nearly random sequences may be obtained in a short time. However, random sequences have usually the consequence that crystallinity and good mechanical properties get lost. Therefore, polyesters having longer crystallizable blocks are of interest, and controlled syntheses via solid state transesterification is an attractive approach to this goal.

The preparation of copolyesters from two homopolyesters or from a homopolyester and a diol may involve condensation steps, and three different kinds of transesterification reactions (see Formula 14.3): (a) alcoholytic transesterification, (b) acidolytic transesterification, and (c) ester–ester interchange, EET. A model reaction of EET was performed in such a way that a PET film was doped with an oligoester containing a diethylene glycol unit with blocked end groups [51]. It was concluded that an acidolytic transesterification involving the CO_2H end groups of PET played a predominant role. Transesterification between PET and PEN was studied by three research groups [52–55]. It was found that both, condensation and transesterification steps took place, but all reactions occurred in the amorphous phase, so that the blocks forming the crystallites were not affected.

Another approach, namely incorporation of non-volatile diols into the amorphous phase of PBT as extensively studied by Koning et al. [56–59]. Kinetics, sequences, and properties of the resulting copolyesters were characterized by various analytical methods, including ^{1}H- and ^{13}C-NMR spectroscopy, DSC- and SEC-measurements. An initial decrease of the molecular weight due to alcoholytic transesterification was followed by chain growth via SSP. The partial exchange of 1,4-butanediol against less mobile diols had the desired consequence that the Tg increased without sacrificing the crystallinity. BEHT and bis(2-hydroxyethoxy)diphenyl propane (dianol) were used in that work.

14.3 Simultaneous Chain Growth and Crystal Growth Polymerization

Simultaneous chain growth and crystal growth (SCCG) are characteristic for crystalline, high melting aromatic polymers which are insoluble in most, if not in all, reaction media. Such polymers include polyesters, polyamides, polyimides, and other polymers based on heterocyclic monomers. The Tm's are above 400 °C and in most cases above 500 °C, so that even trimers or tetramers may have Tm's above 300 °C. Polycondensations in bulk may be feasible, when the monomers


Pol¹–O–CO·(A)-CO-O–(B)–O–CO–(A)–CO–Pol²
Pol³–CO O·(B)·OH
alcoholytic trans
Pol¹-O-CO·(A)-CO
Pol³–OC–O-(B)–O
+
HO-(B)–O–CO–(A)–CO-Pol²
Pol–O-CO·(A)–CO-O-(B)–O–CO–(A)–CO–Pol
HO–CO–(A)·CO-O-(A)–O–Pol
acidolytic trans
Pol –O–CO–(A)–CO₂H
+
O–(B)–O–CO–(A)–CO–Pol
OC-(A)–CO-O-(B)-O-Pol
Pol–O-CO-(A)–CO-O-(B)–O–CO–(A)–CO–Pol
Pol-CO-O–(B)-O·CO–(A)–CO–O·(B)-O-Pol
Cat
ester-ester interchange
Pol–O-CO·(A)-CO
Pol–CO-O-(B)–O
+
O·(B)-O-CO·(A)-CO·Pol
OC–(A)-CO-O-(B)-O-Pol

Formula 14.3

melt below 250 ± 100 °C (at higher temperatures side reactions, such as decarboxylation, may become intensive). However, the rapid solidification of the reaction mixture hinders further chain growth and evaporation of byproducts. Hence, cleaner polymers, higher molecular weights, and more perfect crystals may be achieved when the polycondensation is performed in an inert, thermostable liquid reaction medium.

The most widely studied example is the SCCG of poly(4-oxybenoate), POB, also called poly(4-hydroxybenzoic acid).PHB. Since the abbreviation PHB is also used for poly(β-hydroxybutyric acid), this abbreviation is avoided in this text. Early attempts to polymerize 4-hydroxybenzoic acid, 4-HBA; are discussed in Chap. 2. In the twentieth century several derivatives of 4-HBA were successfully used as monomers (see Formula 13.4), but polymerization of 4-HBA itself was also conducted in solution by means of dehydration agents, such as trifluoroacetic acid [60], thionyl chloride [61], poly(ethyl phosphate) plus imidazole [62], and various other phosphorous reagents [63]. However, these polycondensations were typically conducted at temperatures <150 °C and yielded oligomers. More than 90 % of all publications dealing with synthesis and characterization of POB are based on polycondensations of 4-acetoxybenzoic acid, 4-ABA, at temperatures around or above 300 °C. A first attempt to polymerize 4-ABA in bulk at temperatures up to 300 °C was published in 1959 [64]. The resulting polyester was described as intractable and thermally unstable above 350 °C.

A first systematic study was performed by Economy et al. around 1970 [65, 66]. Those authors used both, 4-ABA and the phenyl ester of 4-HBA as monomers, and performed the polycondensations in a high-boiling thermostable liquid called “Therminol” at 200, 280, 300, or 320 °C. 4-ABA proved to be the more reactive monomer and yielded high molecular weight POB as estimated from IR spectroscopic end group analyses. Depending on the reaction conditions various morphologies were formed. Above 300 °C and at high conversions 4-ABA mainly yielded lamellar crystals also called “slab-like” crystals which formed stacks at high monomer concentration [66]. Single crystals and needle-like crystals were also observed after long reaction times [65]. Single crystals of oligomers and polymers, the DPs of which were determined by ^{1}H NMR end group analyses, were also studied by Lieser using transmission electron microscopy [67, 68]. In agreement with the Economy group it was found that for experiments at 320 °C that oligomers having DPs in the range of 6–8 precipitate from the reaction mixture forming slabs with the oligomer chains perpendicular to the flat surface. Two different growth mechanisms were postulated for the SSP. First, individual oligoesters grown in solution react with the end groups on the surface of the slabs [66]. Second, inside the stacks of slabs end groups of neighboring slabs react with each other in the interphase (see Formula 15.1, Scheme A), so that long chains grow across several slabs [69].

The group of Kimura and Yamashita [70–72] focused on preparation and characterization of needle-like crystals (called whiskers) by polycondensation of 4-ABA in paraffin at 320 °C using a low monomer concentration. Based on EM pictures displaying “shish-kebap”-like crystals they postulated that oligoesters deposit from solution on the flat surface of the slabs, so that a spiral crystal growth proceeds (Formula 14.1, Scheme B). However, another interpretation of "shish-kebap" crystals was forwarded by Petermann et al. [69]. Whisker-like crystals were also obtained from the trimethylsilyl ester of 4-ABA [73]. This monomer avoids the acidic protons which can catalyze side reactions such as the "Fries-Rearrangement". This aspect is of interest, because impurities having functional groups may hinder the crystal growth of whiskers, even when they do not stop the SSP [74].

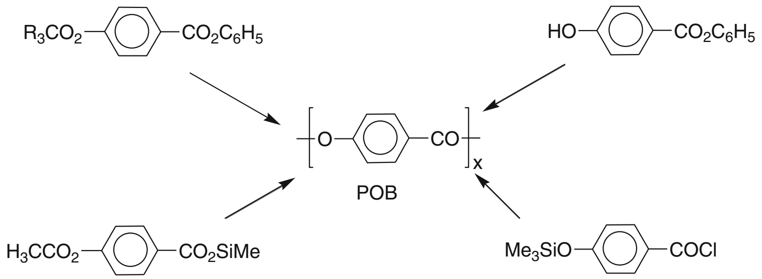
The X-ray and TEM studies of Economy et al. [64], Lieser [67, 68] and Hanna and Windle [75] revealed that POB can adopt two different orthorhombic crystal modifications (I and II) mainly influenced by the DP. It turned out that whiskers prepared >320 °C consist of long chains exclusively adopting modification I. Such whiskers are the most perfect single crystals of POB, and are thus, best suited to study the properties of POB at high temperatures. Based on DSC measurements up to 600 °C and X-ray measurements up to 500 °C the author found 4 phase transitions labeled α, β, γ, δ (with increasing temperature). Slab-like crystals show a reversible transition at 330–337 °C, whereas the same transition of whiskers occurs at 354–365 °C [74, 75]. The weak β-transition occurs at 427–438 °C, the γ-transition at 510–517 °C, and the final melting at 554–565 °C immediately followed by rapid decomposition [76]. The α-transition is decisive for efficient SSP of 4-ABA (and other monomers), because above a smectic-E phase with columnar, hexagonal chain packing is formed [77] This phase is characterized by lateral expansion do to a higher mobility of phenyl rings and end groups, and thus, enables efficient transesterification. The γ- and δ-transition indicate a further increase of the segmental mobility.

High molecular weight POB was prepared from 4-ABA also in such a way that 4-HBA and acetic anhydride were heated in a suitable reaction medium (e.g., "Marlotherm") up to 320 or 350 °C whereby 4-ABA is formed in situ [63]. The only disadvantage is a discoloration of the reaction mixture resulting from side reactions of acetic anhydride. This problem can be avoided by using the anhydrides of higher carboxylic acids, but the bulkier acyl groups reduce the rate of SSP and thus the DP. However, this synthetic approach has the important advantage that it allows for convenient syntheses of polyesters from various aromatic hydroxyl acids including substituted 4-HBAs. 3-Methoxy-, 3-chloro-, 3,5-dimethyl-, 3,5-dichloro-, and 3,5-dibromo-4-HBA were polymerized in this way. Although all polyesters were crystalline, none of them showed an α-transition in the DSC trace. Nonetheless, it was found that polycondensations at 320 °C gave far higher DPs than those performed at 220 or 260 °C.

In contrast to polyesters of substituted 4-HBAs polyesters of other unsubstituted aromatic hydroxyl carboxylic acids showed physical properties quit analogous to those of POB;. for instance, the polyester of 2-hydroxy-6-naphthoic acid (see Formula 14.4). This polyester was first prepared by Calundan [78] and later characterized by several research groups [70, 79–83]. Whisker-like crystals were prepared by the Kimura–Yamashita group [66, 79] and by the author [82] under different reaction conditions. DSC and WAXS measurements of single crystals revealed an α-transition around 330 °C, a β-transition around 455–460 °C, and melting with rapid degradation above 540 °C [83]. Again the α-transition yielded a mobile smectic-E phase favoring efficient SSP. The polyester of 4-hydroxybiphenyl-4′-carboxylic acid (see Formula 14.4) was first prepared by the authors [84, 85]. Its crystal modifications were also studied by Liu et al. [86]. Phase transitions at 305 and 409 °C were difficult to detect in the DSC trace and depended very much on the reaction conditions. Due to the high thermostability of this polyester the Tm was as high as 585 °C, and successful polycondensations were performed at temperatures up to 400 °C, but unfortunately no information about DPs was reported. The polyester of 4-mercaptobenzoic acid was also first prepared by the author [87]. The dimensions of the crystal lattice below and above the α-transition at 365 °C were quite similar to those of POB. Successful SSPs yielded DPs up to 200 [87] and, surprisingly, whiskers were prepared below the α-transition [88]. Due to the low thermostability transformation into a crosslinked resin began shortly above the α-transition [88]. Oligoesters of 4-hydroxycinnamic acid were prepared by Elias using thionyl chloride [89] and whiskers were later prepared by the Kimura group [90, 91]. The same group also reported on SCCG of an acetylated hydroxyl carboxylic acid containing an azomethin group (see Formula 13.4) [92], but neither information on DPs nor on phase transitions was disclosed [90–92].

Further studies of SCCG concerned hydroxyl carboxylic acids containing heterocycles (see Formula 14.4 and 14.5) [93–97]. The acetylated carboxylic acids and their trimethylsilyl esters were used as monomers. Due to the high thermostabilities of these polyesters most polycondensations were conducted at 350 or 400 °C. Whisker-like crystals were obtained in most cases suggesting that efficient SCCG took place, but no information on DPs or molar masses was disclosed. Furthermore, SCCG of poly(ester amide)s from *N*-(4′-hydroxybenzoyl)-4-aminobenzoic acid or its trimethylsilyl ester (see Formula 14.5) were reported [98]. Various crystalline morphologies were found including “shavings”, but detailed information the chain growth in the solid state was not provided. From the analogous vanillic monomer only copolyesters containing 4-HBA were prepared [99].

All these polyesters presented above have in common that the syntheses are based on hydroxycarboxylic acids. Little attention has been paid to SSP of diphenols and aromatic dicarboxylic acids [100–105]. Whiskers of poly(hydroquinone terephthalate) were prepared by Yamashita et al. [100]., but a phase transition below Tm was only observed for copolyesters rich in 4-HBA units [101]. In one paper of the author [102] acetylated hydroquinone or 4,4′-dihydroxybiphenyl were polycondensed with terephthalic acid or 4,4′-biphenyl dicarboxylic acid and their trimethylsilyl esters. In this way four homopolyesters were prepared at 350 or 400 °C. No phase transitions were detected blow 500 °C. No information on the extent of the chain growth was given. Unfortunately, end group analyses do not yield reliable information about DPs for $a_2 + b_2$ polycondensations. Yet, the relatively high concentrations of CO_2H end groups suggest that oligomers having two CO_2H end groups preferentially precipitated from the reaction mixture, but an excess of such oligomers in the solid state hinders efficient chain growth.

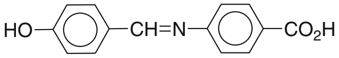


6-Hydroxy-Z-naphthaoic acid

4-Hyroxybiphonyl-4-carboxylic acid

4-Mercaptrobenzoic acid

4-Hyroxycinnumic acid



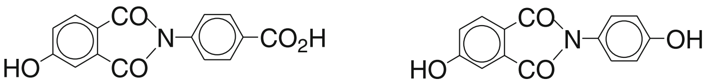
N-(4'-hydroxybenzyidene)-4-amino-benzoic acid

Formula 14.4

In addition to homopolyesters, a large number of copolyesters of 4-HBA were prepared by numerous research groups. These copolycondensations may be subdivided into three categories:

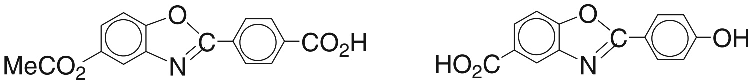
(I) Cocondensations yielding liquid crystalline (LC) copolyesters, which may be processed from the nematic phase below 400 °C.
(II) Copolycondensations yielding crystalline copolyesters which decompose upon melting.
(III) Copolycondensations yielding almost neat POB

LC copolyesters were usually prepared by cocondensation of 4-HBA and comonomers in bulk, in the molten state, and thus, do not deserve further discussion in this chapter. Yet, it should be mentioned that several nematic copolyesters were commercialized under various trademarks. Numerous crystalline



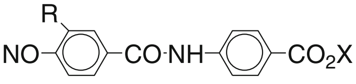
N-(4-Hydroxylphenyl)-5-acetophthalimide

N-(4-Hydroxylphenyl)-5-carboxyphthalimide



5-Hydroxy-Z-(4'-carboxy) benzoxazole

2-(4'Hydroxyphenol)benzoxazole -5-carboxylic acid



R = OCH_3
X = $SiMe_3$

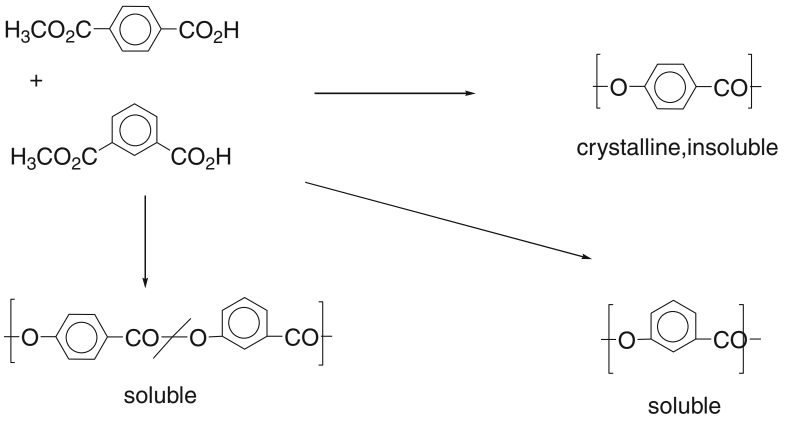
N-(4'-Hydroxylbenzoyl)-4-aminobenzoic acid

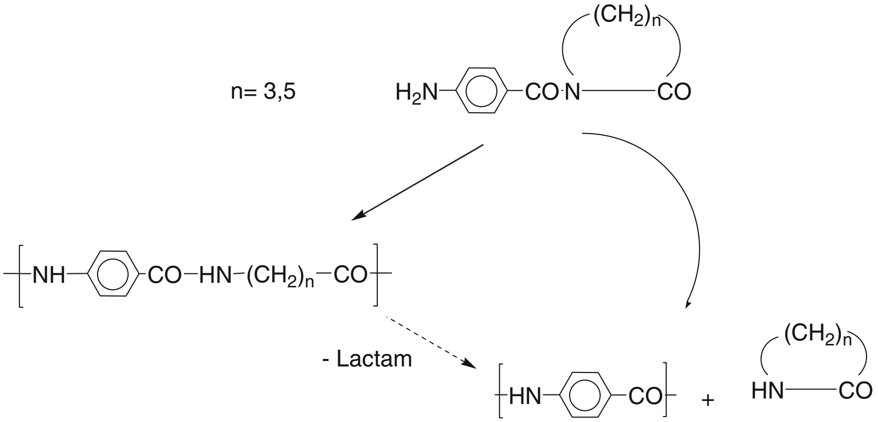
N-(4'-Hydroxyl-3'-methoxybenzoyl)-4-aminobenzoic acid

Formula 14.5

copolyesters (point II) were prepared by the author[106–111] from 4-HBA (or its trimethylsilyl ester) and various comonomers. Compatibility of the counits with one of the crystal lattices of POB was a prerequiremenmt for the success of these cocondensations. Characteristic for most copolyesters is the appearance of an α-transition when the molar fraction of 4-HBA exceeds 50 %. In these cases, SCCG proceeds certainly quite analogously to that of POB, and DPs above 50 can easily be reached. Random copolyesters prepared from mixtures of 4-HBA and acetylated 4-mercaptobenzoic acid did not show unusual morphologies [87, 112–114]. Yet when a mixed dimer such as S-(4′-acetoxybenzoyl)-4-mercaptobenzoic acid was polymerized, whiskers were obtained which seemingly consisted of an alternating copolyester [112–114]. An example for category III is the cocondensation of 4-HBA with 3-HBA. Repeat units of 3-HBA do not fit into the crystal lattice of POB, and oligoesters almost exclusively consisting of 4-HBA units crystallized from solution [115–117] (see Formula 14.6). The same result was obtained from polycondensations of mixed dimers indicating that rapid transesterification reactions took place in the reaction mixture generating 4-ABA.

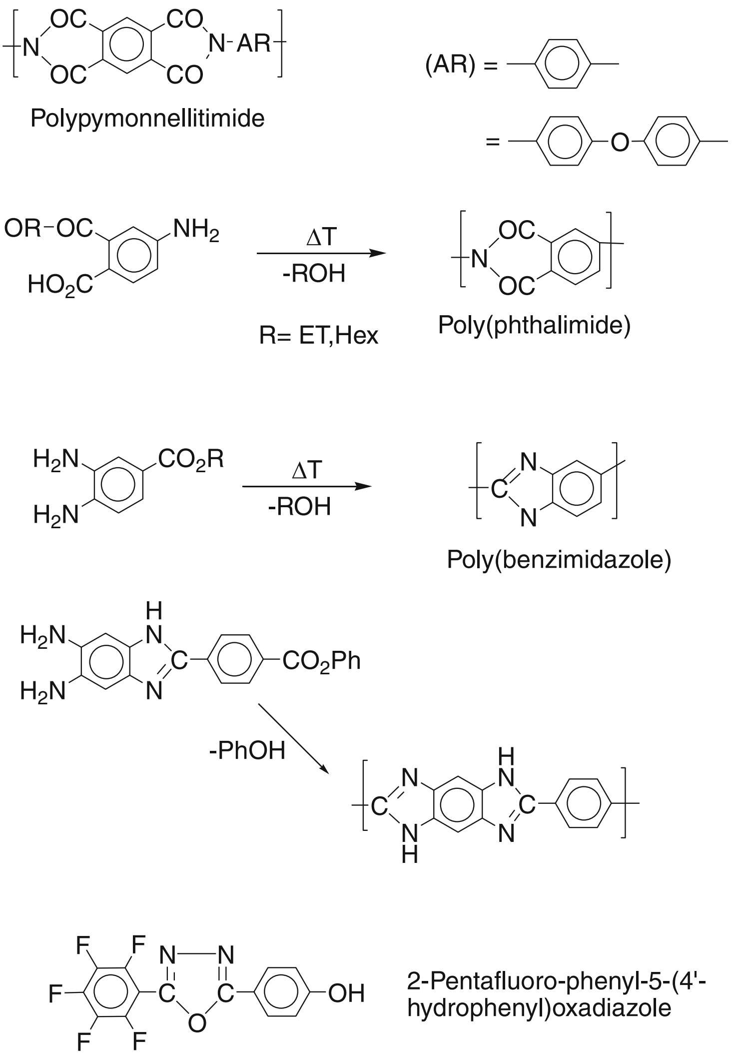
A new dimension in the field of SCCG is polycondensations yielding polymers bare of ester groups. A first example was published by the author in 1996 [118]. *N*-4-Aminobenzoyl lactams were polymerized in Marlotherm-S at temperatures in





Formula 14.6

the range of 180–400 °C (Formula 14.6). In this process, polyaddition yielding alternating copolyamides and polycondensation yielding poly(4-benzamide) compete with each other. However, elimination of lactam from an alternating copolyamide can not be ruled out at temperatures >350 °C. The highest molecular weights were achieved at 350 °C. The resulting crystalline polyamides contained 95 mol % of 4-aminobenzoyl units. More recently, the Kimura group contributed further examples [118–130] including polyimides, polybenzimidazoles, and poly(oxadiazole)s (see Formula 14.7) All these studies were focused on the morphology of the crystalline reaction products and only low to moderate solution viscosities were achieved.



Formula 14.7

Finally, it should be noted that whiskers of POB or of poly(ester imide)s proved to be useful reinforcing components in nanocomposites based on polyamide matrices [131, 132]. Unfortunately, the preparation of polyester whiskers is too expensive for technical production.

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Chapter 15
Combined Ring-Opening Polymerization (ROP) and Polycondensation

15.1 Definitions

The combination of ring-opening polymerization (ROP) and polycondensation in a "one-pot procedure" is a relatively new aspect in the field of polycondensation, and two quite different scenarios may be defined.

(I) ROP and (poly) condensation occur simultaneously and their separation is not possible. Most polymerizations belonging to this scenario are kinetically controlled (KC), but a few thermodynamically controlled polymerizations (TCPs) are also known.
(II) ROP is performed as a first step and yielding oligomers or polymers having two (or more) reactive end groups, which allow for continuing the polymerization via polycondensation as a second step.

Regardless of the scenario it must be kept in mind that a ROP plus polycondensation process needs two different definitions of conversion for its proper description. For the ROP part the conversion is defined by the consumption of monomers as usual for a chain-growth polymerization. Yet, for polycondensations the conversion is defined by the consumption of functional (end) groups regardless, if inter- or intramolecular condensation steps take place.

15.2 Simultaneous ROP and Polycondensation

15.2.1 Kinetically Controlled Polymerizations of Cyclic Monomers

Characteristic for this group of polymerizations is a ROP yielding linear chains having two end groups which can react with each other under the conditions of the ROP. The linear chains have three options.

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(A) They react with monomers continuing the ROP.
(B) They undergo an intermolecular condensation step, which in this chapter will be called chain extension and not chain growth to distinguish it from the propagation step of the ROP.
(C) They undergo an intramolecular condensation step meaning cyclization by "end-biting".

In a KCP, cyclics cannot be formed by "back-biting", and thus the formation of cyclic oligomers and polymers is indicative for the intermediate formation of linear chains having two reactive end groups. In other words, the formation of cyclics is indicative for simultaneous ROP and (poly)condensation steps. If side reactions are absent, and if the linear chains are mobile enough for cyclization, cyclics will be the only reaction products, and combined ROP and polycondensation is an efficient strategy for the preparation of cyclic polymers in high yields.

The average molecular weight of the cyclic polymers depends on the kinetic scenario. For a short discussion of the correlation between ring size and kinetic course of the entire polymerization process, the four reaction rates defined in Eqs. (15.1)–(15.4) will be helpful.

$$\mathrm{v_{in}} = \mathrm{k_{in}}[\mathrm{I}]\,[\mathrm{M}] \tag{15.1}$$

initiationrate of the ROP

$$\mathrm{v_{pr}} = \mathrm{k_{pr}}\left[\mathrm{a} - (\mathrm{M})_{\mathrm{x}} - \mathrm{b}\right][\mathrm{M}] \tag{15.2}$$

propagation rate of the ROP

$$\mathrm{v_{ce}} = \mathrm{k_{ce}}\left[\mathrm{a} - (\mathrm{M})_{\mathrm{x}} - \mathrm{b}\right]^2 \tag{15.3}$$

rate of chain extension by intermolecular condensation

$$\mathrm{v_{cy}} = \mathrm{k_{cy}}[\mathrm{a}(\mathrm{M})\mathrm{x} - \mathrm{b}] \tag{15.4}$$

rate of cyclization by "end-biting".

Two extreme cases should be discussed to illustrate the relationship between average ring size and these four reaction rates: (a) formation of high molar mass cyclic polymers, and (b) formation of low molar mass cyclics. Favorable for (a) is high initial monomer concentration and $\mathrm{v_{in}} > \mathrm{v_{pr}}$, so that all chains are initiated almost simultaneously. A high concentration of difunctional linear chains favors, in turn, a high $\mathrm{y_{ce}/v_{cy}}$ ratio according to the Ruggli-Ziegler Dilution Principle. Furthermore, a relatively high ratio of $\mathrm{v_{pr}/vc_{y}}$ is helpful, so that in the optimum case almost all monomers were consumed by the ROP yielding long chains before cyclization begins. Favorable for (b) is a low initial monomer concentration and $\mathrm{v_{pr}} > \mathrm{v_{in}}$. This kinetic situation has the consequence that only few chains are initiated per time unit, their molar concentration will be low thus favoring relatively high $\mathrm{v_{cy}/v_{pr}}$ and $\mathrm{v_{cy}/v_{ce}}$ ratios.

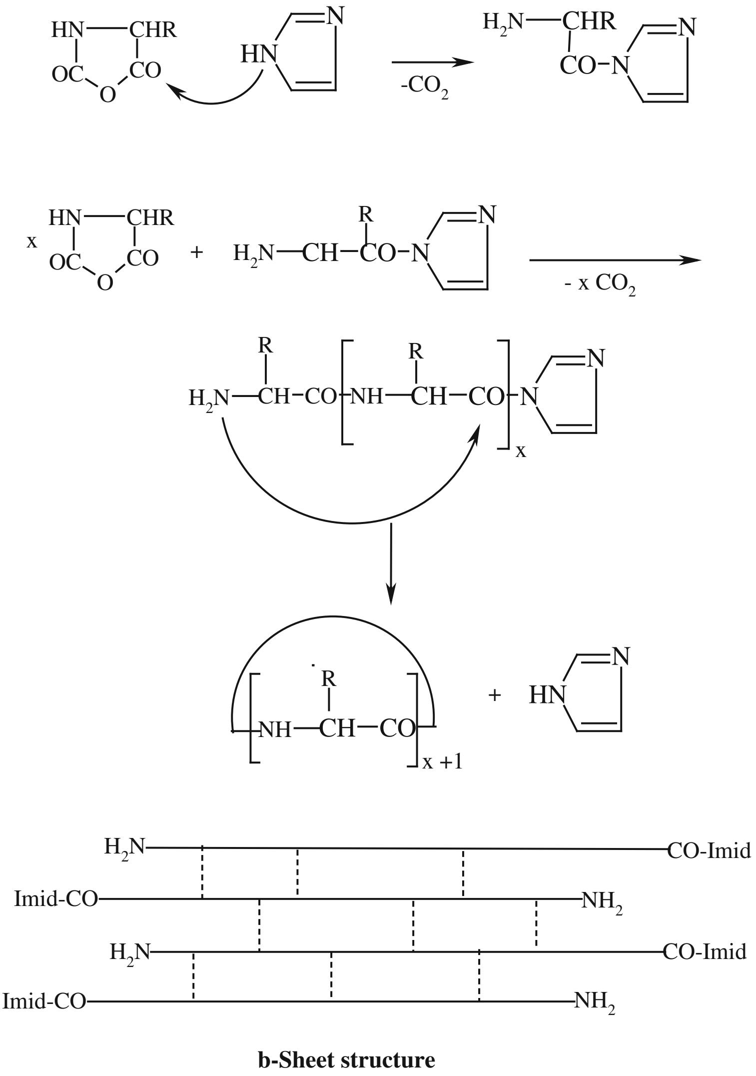
A high v_{cy}/v_{ce} ratio does not only depend on the molar concentration of the linear chains, it also depends on their chemical structure the influence of which may be described by three parameters: chain stiffness, preferred conformation, and solvation (i.e., end-to-end distance).

For instance, ortho-functional aromatic rings favor cyclization more than meta- or para functional ones. Furthermore, the gauche conformations of poly(ethylene glycol) chains favor cyclization more than the all-trans conformation preferred by alkane chains. Moreover, poor solvents enhance the coil density, and thus reduce the distance between the chain ends.

The oldest example of KCPs combinig ROP and simultaneous polycondensation is polymerizations of α-amino acid N-carboxyanhydrides (NCAs). As formulated and discussed in Chap. 16, polymerizations of NCAs initiated by protic nucleophiles, such as primary amines sterically nonhindered secondary amines, alcohols and water, proceed via a normal condensative chain polymerization exclusively yielding linear chains. Neither inter- nor intramolecular condensation steps can occur, because the initiation step generates stable (dead) end groups. However, initiation with imidazole changes the situation, because the imidazolide end group can react with amino groups even at room temperature [1, 2] (see Formula 15.1). The NH_2-terminated oligopeptides have the three options mentioned above, they can react with NCAs continuing the ROP, they can react with imidazolide end groups of another oligo- or polypeptide, and they can undergo an intramolecular condensation yielding cyclic peptides. Poly(D,L-amino acid)s which possess a relatively high solubility in polar organic solvents yielded reaction products mainly or exclusively consisting of cyclics [2]. However,

L-alanine-NCA yielded a mixture of cyclic and linear oligopeptides, which had CO_2H end groups when the reaction mixture was worked up with water, or CO_2CH_3 end groups, when it was worked up with methanol. Obviously, the virgin reaction product contained a high fraction of chains having imidazolide end groups, which reacted with water or methanol. This result was explained by the well-known fact that oligomers of L-amino acids have a high tendency to precipitate from solution in the form of lamellar crystals which are stacks of ß-sheets (see Formula 15.1, bottom). The formation of ß-sheets is based on intermolecular H-bonds between antiparallel peptide chains, and this immobilization prevents cyclization.

Primary amine-catalyzed polymerization of NCAs in various solvents revealed that certain polar solvents themselves act as catalysts [3]. Characteristic for the catalytically active solvents is a relatively high nucleophilicity [4] (see left column in Table 15.1). This observation and the formation of cyclic polypeptides from the N-substituted sarcosine-NCA evidenced that a zwitterionic polymerization mechanism was catalyzed, which involves ROP and condensation steps (see Formula 15.2). Pyridine is known for many decades to activate carboxylic anhydrdies by charge separation, i. e., formation of carboxylate anions plus N-acyl pyridinium ions Therefore, it is obvious that pyridine catalyzes the same zwitterionic mechanism as the nucleophilic polar solvents [5]. In the case of N-unsubstitued NCAs the initiation step will be again a charge separation, but instead of



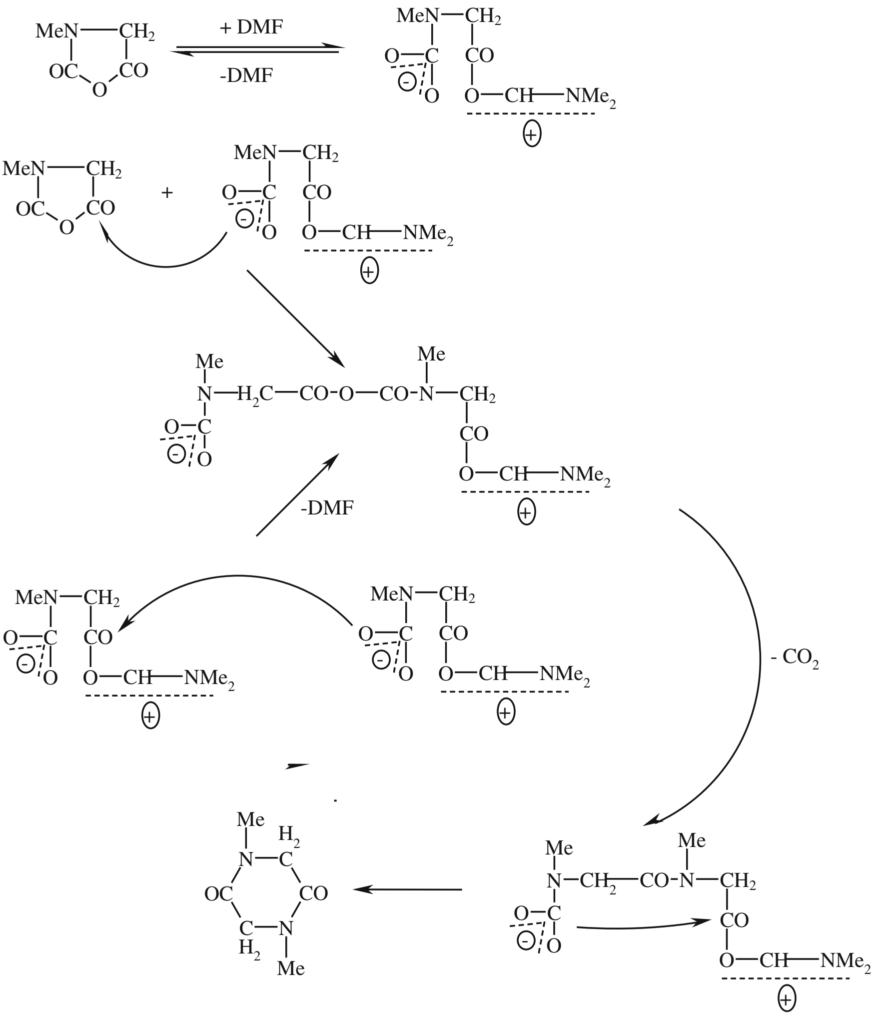
Formula 15.1

a zwitterionic polymerization analogous to that of Sar-NCa an energetically more favorable, nonionic polymerization is the more likely alternative. As outlined in Formula 15.3, reaction of the zwitterion with a NCA may involve a rapid proton transfer and decarboxylation of the resulting carbamic acid, so that a N-aminoacyl NCA is formed as reactive intermediate. This intermediate has the three options to continue the ROP or to undergo inter- and intramolecular condensation steps (see Formula 15.3).

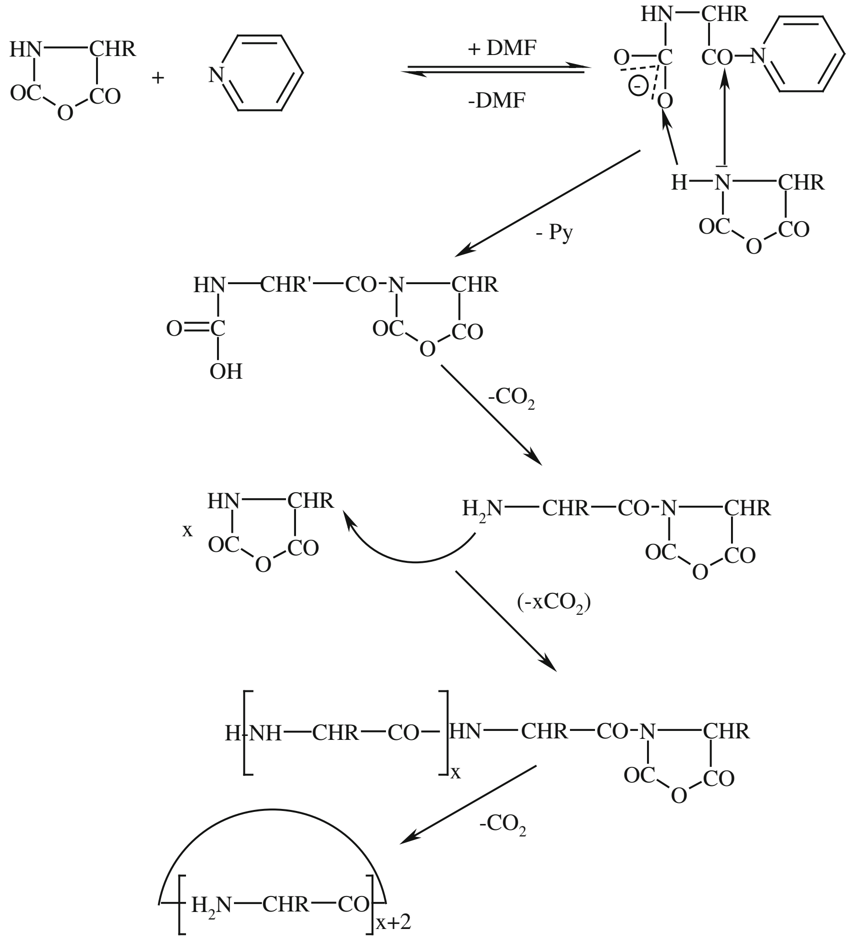
Table 15.1 Nucleophilic and nonnucleophilic polar solvents

Nucleophilic solvents	DC[a]	Nonnuclophilic solvent	DC[a]
Tetramethyl urea	23,1	Dichloromethane	8,9
N-Methylpyroluidone	33,7	Nitrobezene	34,8
Dimethylformamide	36,7	Sulfolane	44,0
Dimethylsulfoxide	48,9		

[a] Dielectric constant measured at 25 °C

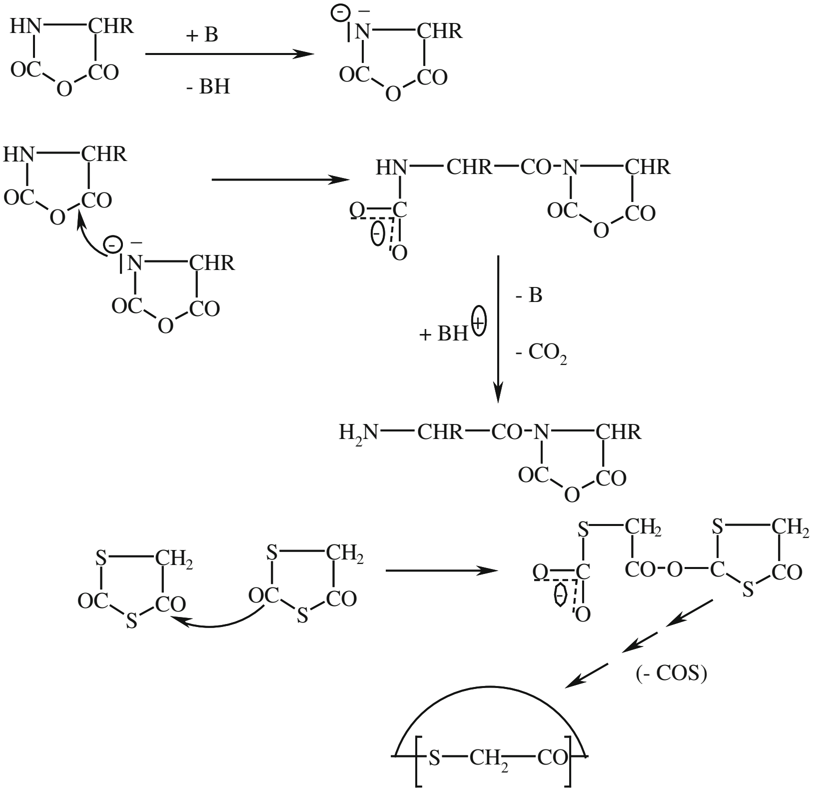


Formula 15.2



Formula 15.3

Surprisingly, it was found that also trialkylamines yield cyclic polypeptides, although a zwitterionic mechanism is excluded, because a nucleophilic attack on the carbonyl C-5 can for steric reasons not occur. As evidenced by model reactions [6–8], trialkylamines are basic enough to deprotonated NCAs, and the resulting NCA anion reacts with another NCA (see Formula 15.4). The ensuing ROP may proceed either by reaction of the amino end group with NCAs (amine mechanism) or by reaction of NCA anions with the N-acyl NCA chain end (activated monomer mechanism) [8–10]. Regardless which kind of propagation predominates, the resulting difunctional chains can cyclize (see Formula 15.4). Finally, it should be mentioned that two types of cyclic polypeptides are also formed, when NCAs are heated above their melting points, and initiation via zwitterions is highly probable, but clear-cut evidence and a detailed study of the polymerization mechanism is

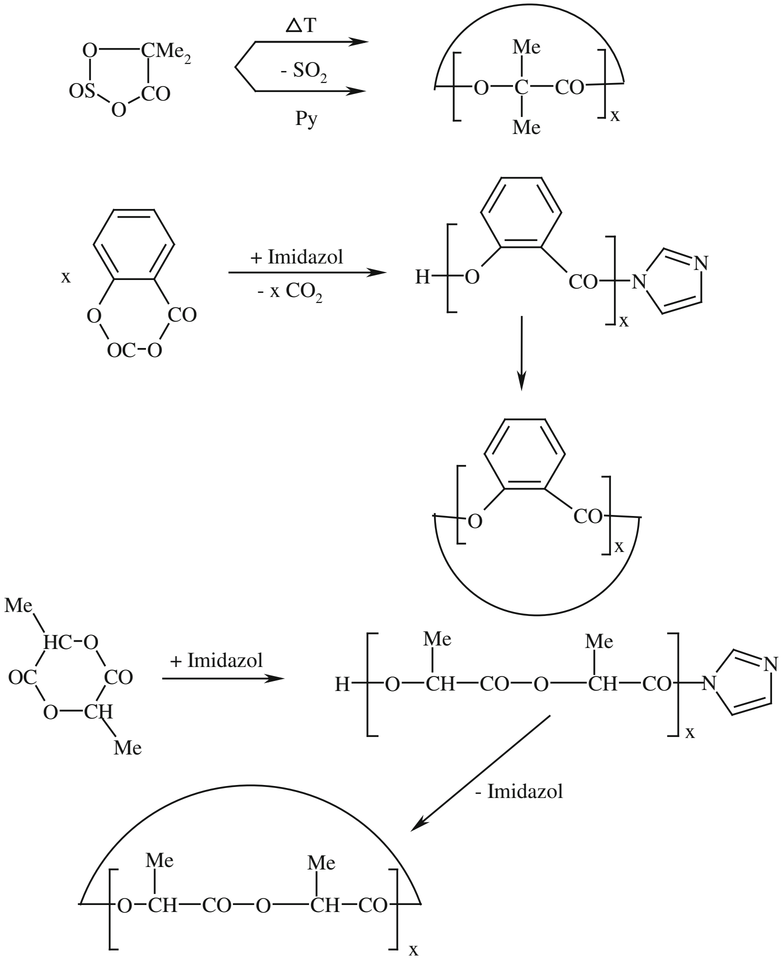


Formula 15.4

still lacking [11]. In summary, it was found that most catalysts and reaction conditions yield cyclic polypetides in contrast to what was assumed in the literature for almost 100 years.

Cyclic anhydrides and anhydrosulfides resembling the structure of NCAs react analogously. For instance, dithiolane-2,4-dione yields cyclic poly(thioglycolide) upon heating above 150 °C or when dissolved in pyridine at room temperature [12] (see Formula 15.4). The cyclic anhydrosulfite of a-hydroxy isobutyric acid (see Formula 14.5, top) also yields cyclic polyesters, and zwitterionic polymerizations are the most likely reaction mechanism [13]. However, Tighe et al. [14] postulate on the basis of kinetic measurements for the intermediate formation of an α-lactone. Yet, any spectroscopic evidence is lacking, and a characterization of the reaction products by MALDI-TOF mass spectrometry was not feasible at that time. In the case of the O-carboxyanhydride of salicylic acid imidazole-initiated polymerizations were studied, and in addition to cyclic polyesters linear chains having imidazolide end groups were identified by mass spectrometry (see Formula 15.5), so that the intermediate formation of these difunctional chains was definitely proven in this case [15].

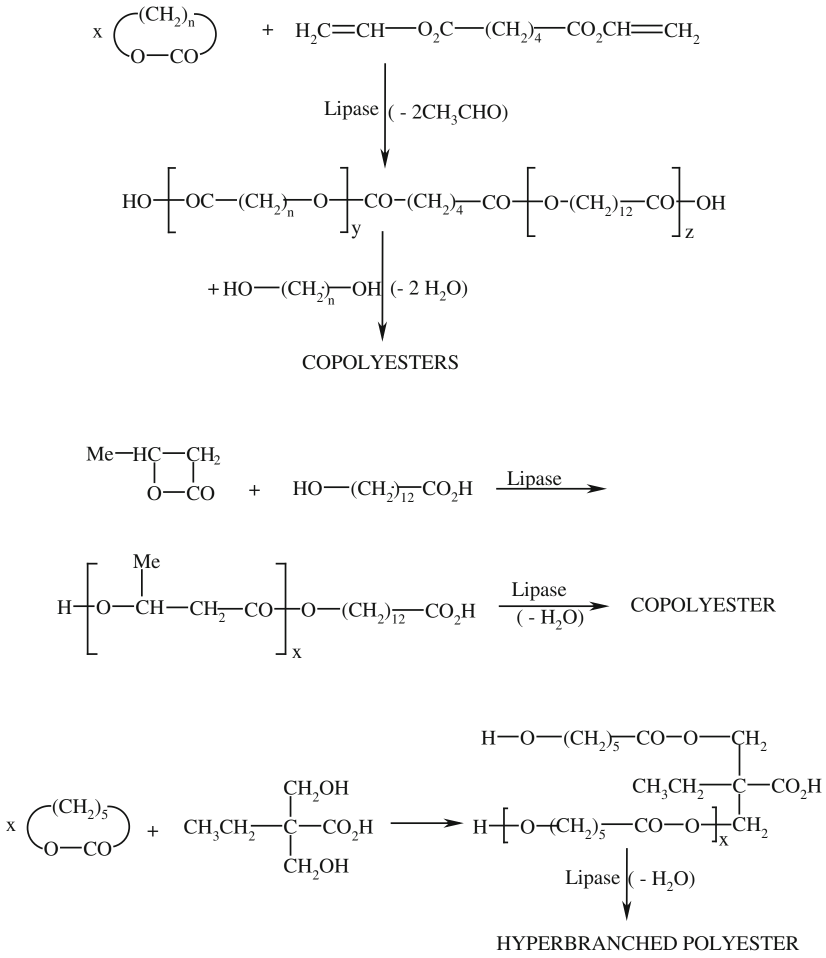
Imidazole also proved to be nucleophilic enough to initiate polymerizations of lactide in bulk. When the polymerization was conducted at 80 °C with meso-lactide (Tm = 52-54 °C) [16] or at 100 °C with L-lactide (Tm = 95-97 °C) [17] the reaction products mainly or exclusively consisted of even-numbered cyclic polylactides (see Formula 15.5). These results demonstrated that at relatively low temperatures and at reaction times of only a few hours the entire polymerization process was KC. Higher temperatures and longer reaction times favored equilibration, and thus formation of odd-numbered cyclics. At 150 °C/48 h equal amounts of odd- and even-numbered cycles were obtained [17]. In other words, imidazole-initiated polymerizations of lactides represent the rare case that a



Formula 15.5

polymerization can be changed from perfect kinetic to total thermodynamic control (Formula 15.5 bottom).

A quite different approach based on enzyme-catalyzed polymerizations was reported by three different research groups [18–20]. Kobayashi et al. used a lipase to catalyze ROPs of macrolides in the presence of divinyl adipate, whereby telechelic oligolactones having two CO_2H end groups were obtained (see Formula 11.6). Due to the addition of alkanediols the lipase also could catalyze condensation steps, but the characterization of the reaction products was extremely poor. Jedlinski et al. [19] polymerized ß-butyrolactone in the presence of *ω*-dodecanoic acid and assumed that the lipase also catalyzed condensation steps. Yet, only oligomers were obtained and characterization of their sequences and composition was again poor. Frey et al. [20] studied the same approach using 2,2-bis(hydroxymethyl)butyric



Formula 15.6

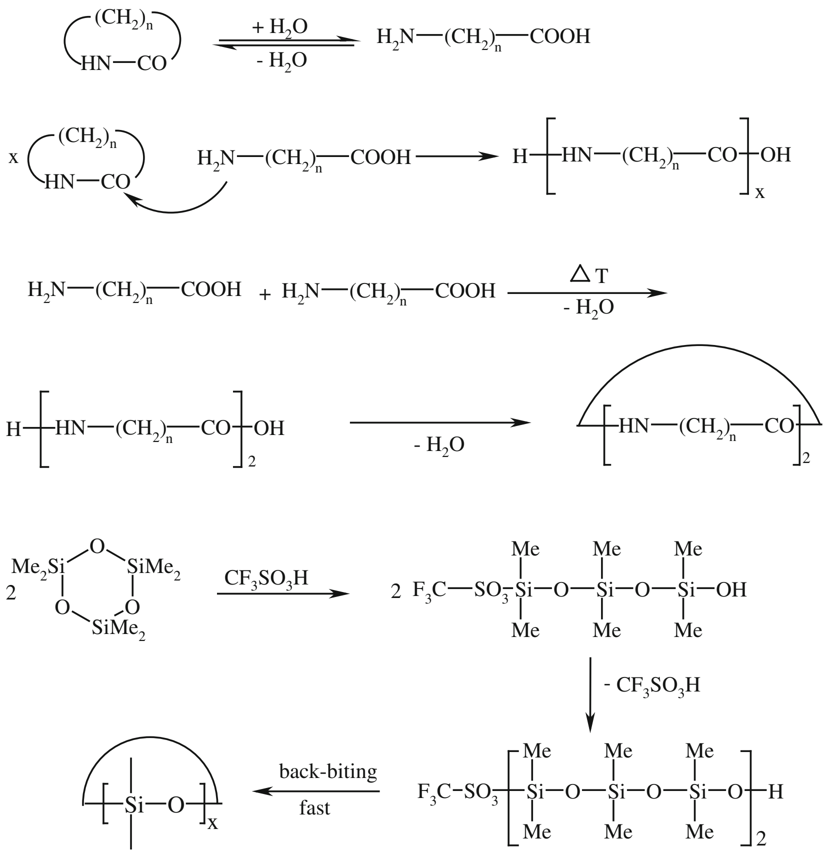
acid as initiator for the ROP of ε-caprolactone (see Formula 11.6, bottom). The simultaneous polycondensation yielded high molar mass hyperbranched copolyesters. Good results were again obtained, when $HfCl_4(THF)_2$ served as catalyst in refluxing toluene [21], but the molar masses remained low when lactide was used as monomer and condensation steps were almost absent [22].

15.2.2 Thermodynamically Controlled Polymerizations of Cyclic Monomers

The oldest examples of polymer syntheses involving simultaneous ROP and (poly)condensation under thermodynamic control are syntheses of aliphatic polyamides from ω-amino acids or from the corresponding lactams [23–27] (see also Chap. 2).To avoid misunderstandings, it should be emphasized that only those polymerizations of lactams are here considered, which are initiated and catalyzed by water or ω-amino acids. Furthermore, the reactions outlined in Formula 15.7 are not meant as an exhaustive description of the entire polymerization process. They should only illustrate a handful of typical ring-opening and condensation steps. The question to what extent ROP and condensation steps occur depends largely on the molar ratio lactam/water or lactam/ω-amino acid. When only ω-amino acids are used as monomers, as it was true for the first synthesis of polyamides in 1935 (Chap. 2) or for the technical production of Nylon-11, the vast majority of reactions are condensation steps. Since part of the ω-amino acids and oligopeptides will rapidly cyclize above 220 °C (a temperature range typically used for technical production) ring-opening steps will also occur (see Formula 15.7). When lactams are polymerized in bulk with small amounts of water, a small fraction of lactams will be hydrolyzed, and the resulting ω-amino acids make condensation steps, but the vast majority of all growing steps will, of course, be ring-opening reactions. Regardless which kind of monomer is used, at very high conversions (>99.8 %) the reaction mixture will mainly consist of cyclic oligo- and polyamides (see Chaps. 5 and 7).

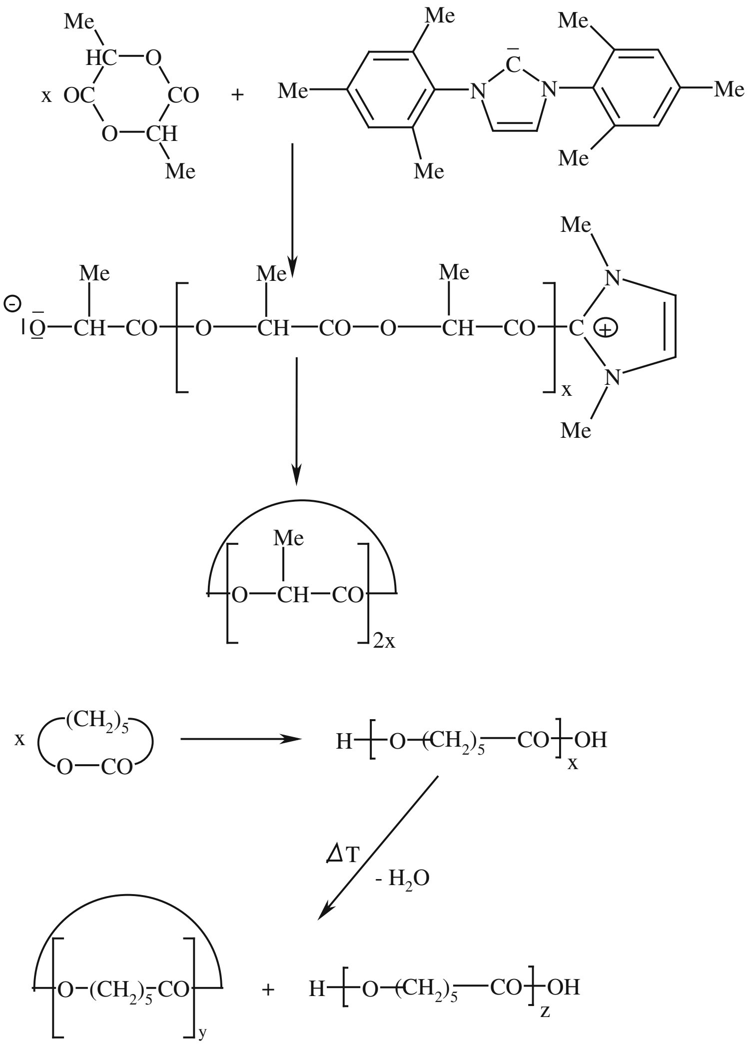
A quite different kind of polymerization combining ROP and condensation steps is the triflic acid catalyzed polymerization of hexamethyl cyclotrisiloxane [28–30] (see Formula 15.7). A rapid formation of cyclic tetra-, penta-, and hexasiloxane is followed by a slower equilibration yielding higher cyclic and linear polysiloxanes. These findings suggest that ring-opening yielding a linear trisiloxane having a triflate end group is the first reaction. Rapid condensation yields a linear hexamer, which enables back-biting with formation of cyclic tetramers, pentamers and hexamers, but no higher cyclics. The base-catalyzed polymerization and equilibration takes a quite different course, which does not involve condensation steps.

Furthermore, zwitterionic polymerizations of lactides and lactones catalyzed by a nucleophilic carbene need discussion. With the extremely nucleophilic imidazolidine carbene outlined in Formula 15.8. Waymouth et al. [31–35] achieved rapid



Formula 15.7

zwitterionic polymerizations of cyclic esters even at room temperature. Cyclic polylactides having Mn‘s up to 20 kDa (corrected values) [32] were isolated. Those authors presented a kinetic scheme characterized by a high rate of propagation and relatively slow rates of initiation and end-to-end cyclization. On the basis of these kinetic results and considering the rather low PDs (<1.5), these zwitterionic ROPs were classified as KCPs. However, the MALDI-TOf mass spectra of the polylactides revealed almost equal amounts of odd- and even-numbered cyclics proving that rapid “back-biting cyclization” was involved. In other words, the structure of the cyclic polylactides is thermodynamically controlled. As expected from anionic polymerizations of lactides and lactones [31, 32], the formation of alkoxide anions as active chain ends can cause side reactions, such as the formation of unsaturated end groups in the case of ß-lactones [23–38] or racemization of lactide. The latter side reaction was not reported because only rac.lactide was used as monomer.



Formula 15.8

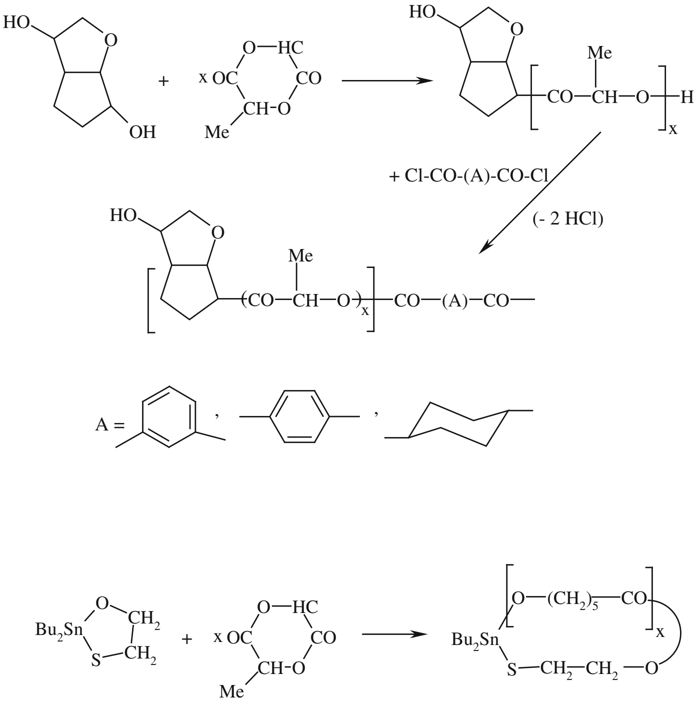
15.3 Two-Step Polymerizations

15.3.1 ROPs Yielding Linear Macromers

A few examples of ROPs yielding predominantly linear macromers, which were subjected to polycondensation in an immediately following reaction step, were recently reported by Kricheldorf et al. [38–41]. It is important for the attractivity of this approach as synthetic strategy that both steps are performed in a "one-pot procedure" using the same catalyst. Therefore, the first publication mainly dealed with optimization of the catalyst e-caprolactone served as monomer and water as initiator, so that polylactones having one CH_2OH and one CO_2H end group were obtained (see Formula 15.8). Both ROP and polycondensation were performed in bulk, and vacuum was applied to promote the polycondensation by removal of water. Poor results of the polycondensation step and side reactions were found, when metal triflates were used as catalysts at 100 °C. Metal bromides and iodides were excluded from that study to avoid side reactions, such as cleavage of alkyl-O bonds. A comparison of several metal chlorides at 140 °C revealed that $SnCl_2$ gave the best results. The difficulty to remove the liberated water from the viscous melt was the limiting factor for the conversion. Nonetheless, the Mn's obtained by ROP were enhanced by a factor up to 4, and a considerable fraction of linear oligomers were converted into cyclic oligomers and polymers (see Formula 15.8). Therefore, cyclization was another factor limiting the chain growth.

In a second part of that study [39], the polycondensations were conducted in concentrated chlorobenzene or xylene solutions to remove the water by azeotropic distillation. Slightly, higher molecular weights were obtained and a higher degree of cyclization. Furthermore, it was found that the polycondensation does not involve transesterification, what means that almost all cyclics were formed by end-to-end cyclization and not by "back-biting".

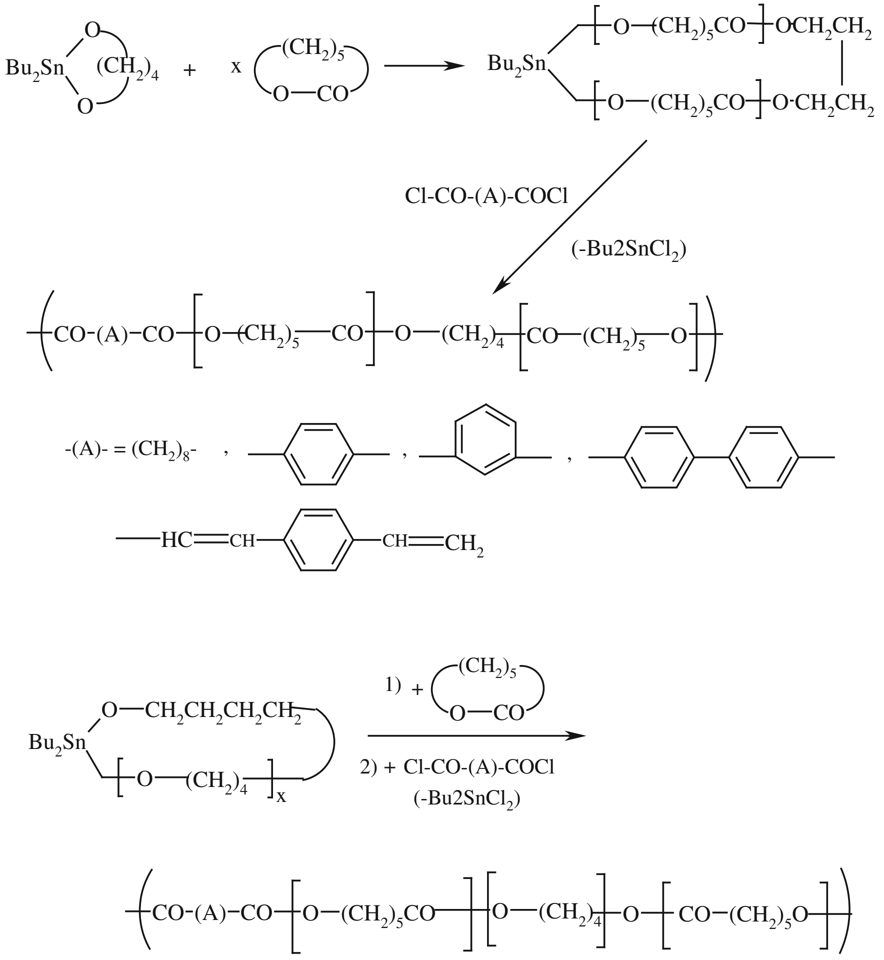
On the basis of these results, a new class of polyesters was prepared having an attractive combination of properties: transparency due to an amorphous character, biodegradability due to the presence of lactic acid units, high glass-transition temperatures (80−180 °C), and compositions mainly based on monomers from renewable resources. The preparation of these polyesters was performed in such a way that isosorbide was used as initiator for an oligomerization of L-lactide. The resulting OH-terminated oligomers were polycondensed with dicarboxylic acid dichlorides in refluxing chlorobenzene or xylene [40, 41] (see Formula 15.9). $SnCl_2$ served as catalyst for both polymerization steps. Copolyesters having an extremely broad MWD were obtained, and DPs above 10 were found in individual cases. The MALDi-TOF mass spectra evidenced that in the observable mass range below 5 kDa all reaction products were cycles. These results indicated: (a) that the reaction conditions were nearly ideal allowing for very high conversions, (b) that the chain growth was mainly limited by cyclization, and (c) that the random sequences of the comonomers were obtained. The high PDs were partially a consequence of the high extent of cyclization, but a low degree of branching might have contributed to the high PDs. The Tg's and thermostabilities decreased with higher contents of lactide, which favor, on the other hand, higher rates of biodegradation. In summary, the properties may be controlled by systematic variation of the composition [40, 41].



Formula 15.9

15.3.2 ROPs Yielding Cyclic Macromers

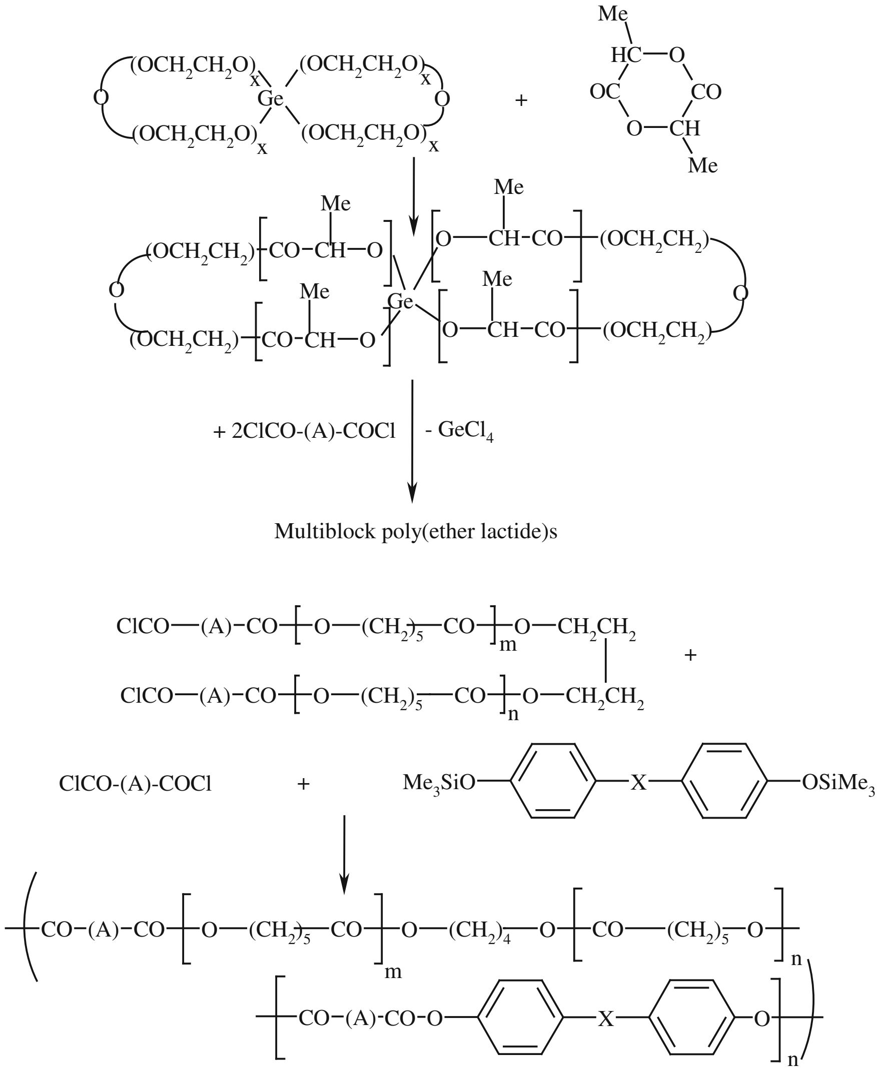
As demonstrated by Kricheldorf and coworkers [42–46], cyclic tin alkoxides (see Chap. 9) are excellent initiators for the ROP of lactides and lactones. Due to the cyclic structure of these initiators, these ROPs are in fact ring-expansion polymerizations (REPs, see Formula 15.9 bottom, and 15.10, top), and the first short note on such a REP [42] was in fact the first report on a successful REP at all. However, REPs of cyclic esters are not limited to cyclic tin alkoxides, they were also realized with spirocyclic germanium alkoxides [47] and cyclic bismuth alkoxides [48]. As already discussed in Chap. 9, cyclic tin alkoxides react rapidly and exothermically with (di)carboxylic acid chlorides, whereby dibutyltin chloride is liberated. When the Bu_2Sn-containing polylactones are condensed with dicarboxylic acid dichlorides, homopolyesters containing a few aliphatic or aromatic “guest monomers” are obtained [49] (see Formula 15.10). Successful polycondensations also work with bis(4-chlorothiophenyl)esters of dicarboxylic acids [50], because the Sn–S bond is more stable than the Sn–O bond, and the elimination of $Bu_2Sn(SC_6H_4Cl)_2$ contributes to the driving force of the polycondensation.



Formula 15.10

When bisphenol-A bis chloroformiate was used as reaction partner of the cyclic macromers, carbonate groups were incorporated into the “guest–host” polyesters [51].

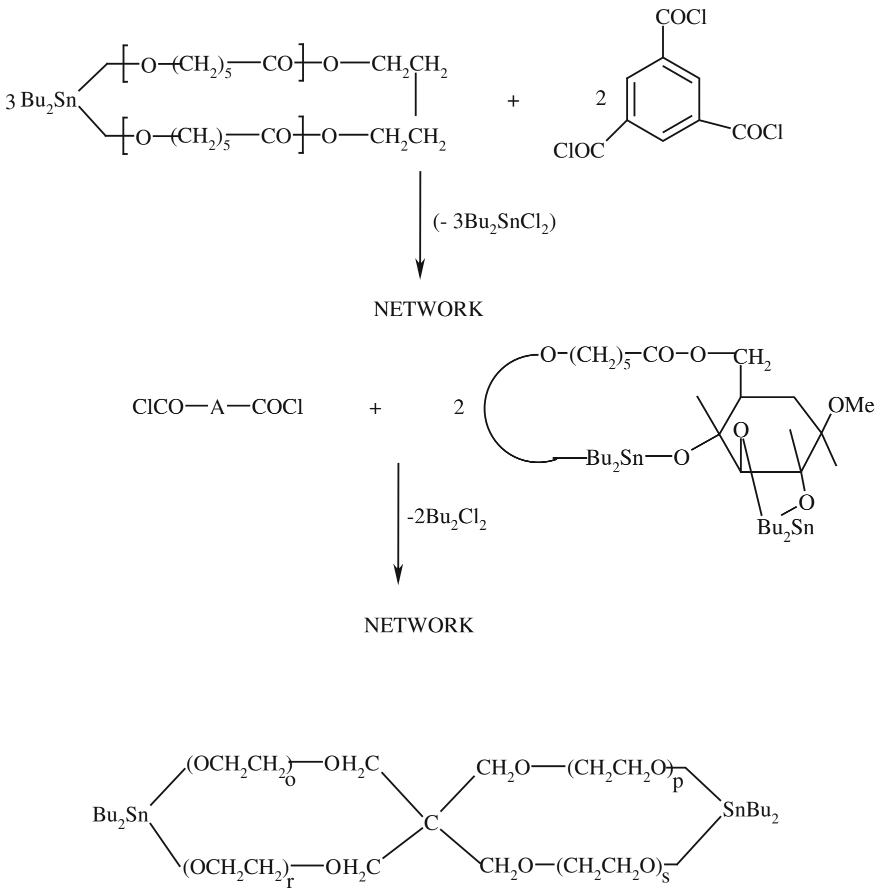
This approach also enables syntheses of various multiblock copolyesters. Two strategies were elaborated. First, a polymeric cyclic initiator was prepared, for instance from oligo- or poly(ethylene glycol)s [52] or from poly(tetrahydrofuran diol)s. The subsequent REP of a lactone (see Formula 15.10, bottom) or of lactide (see Formula 15.11, top) yielded, in turn, multiblock poly(ether ester)s [53, 54]. As demonstrated in Formula 15.11, this strategy may involve spirocyclic Ge-initiators [54]. Another variant of this strategy was realized in such a way that in the first step acyclic amorphous copolymer was prepared from ε-caprolactone and



Formula 15.11

trimethylene carbonate. After complete conversion, L-lactide was incorporated and a cyclic triblock copolyester was obtained [55], because no transesterification occurred.

Polycondensation with sebacoyl chloride yielded the desired multiblock copolyester. Such multiblock copolymers consisting of a crystalline "hard" block and an amorphous "soft" block show the typical mechanical properties of thermoplastic elastomers [53, 55].



Formula 15.12

The second strategy combines three reaction steps in a“one-pot procedure”. The first step is a REP of a lactone using a small cyclic tin alkoxide. The resulting cyclic polylactone is then condensed with a 10-fold excess of a dicarboxylic acid dichloride, whereby telechelic polylactones having acid chloride end groups are formed. The mixture of these telechelics and the excess of the dicarboxylic acid dichloride were, in turn, polycondensed with silylated diphenols [56, 57] (see Formula 15.11, bottom). Despite reaction temperatures up to 230 °C, transesterification was not observed. Depending on the structure of the diphenol, amorphous aromatic blocks having high Tǵs or crystalline and liquid-crystalline blocks [57] were obtained. Therefore, this strategy allows for an flexible access to multiblock copolyesters having a broad variety of physical and mechanical properties.

The combination of REP and polycondensation also allows for an easy preparation of biodegradable networks with good control of pore-size, flexibility of the chain segments and rate of biodegradation. Again two synthetic strategies were elaborated. The first strategy is based on bicyclic (spirocyclic) initiator derived from the methyl glycoside of glucose [58] (see Formula 15.12, top), or from ethoxylated pentaerythritol [59] (see Formula 15.12). After REP with a lactone or lactide in situ polycondensation with dicarboxylic acid dichlorides or phosphoric acid chlorides yielded the desired networks.

The second strategy starts out from REPs with monocyclic tin alkoxides. The resulting cyclic polylactones were in situ condensed with trifunctional acid chlorides [60] (e.g., trimesoyl chloride, see Formula 15.12). For a variant of this strategy cyclic A-B-A triblock copoly(ether ester) consisting of a central poly(ethylene oxide) block and two L-lactide blocks were used as reaction partners of trimesoyl chloride [61]. This variant allows one to optimize the compatibility of the chain segments with hydrophilic or hydrophobic drugs, and it allows one to tailor the rate of hydrolytic (bio)degradation. Such networks may be useful as containers for controlled drug release, and promising results in this direction were reported [61].

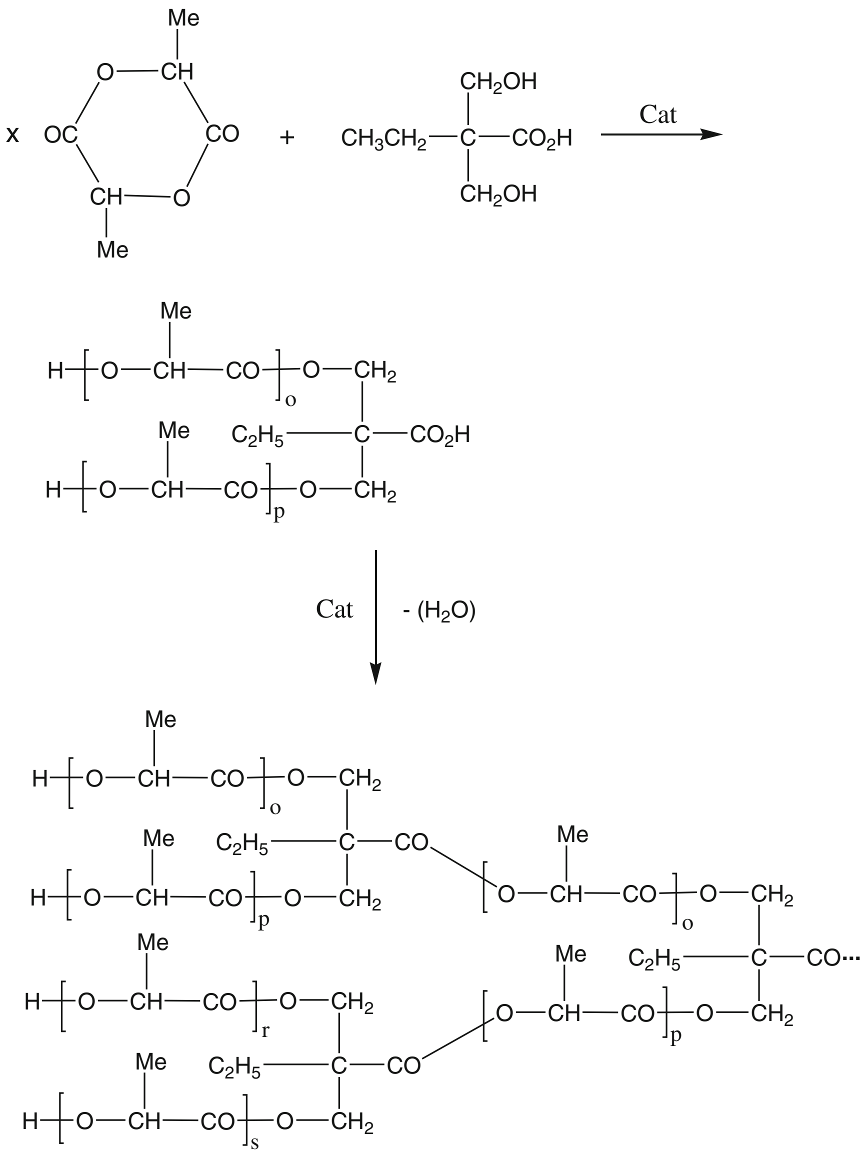
15.3.3 Syntheses of Hyperbranched (hb) Polyesters

After the year 2000, a handfull of papers has appeared describing attempts to prepare hb polylactones or polylactides via ROP in combination with in situ polycondensation. All these papers have in common that bis(2-hydroxymethyl)butyric acid (BHBA) served as trifunctional branching comonomer. The reaction pathway is exemplarily illustrated for lactide as cyclic monomer in Formula 15.13. The first step is a ROP yielding a linear polyester having two OH end groups and one pendant CO_2H group. The second step consists of a polycondensation process yielding the hb architecture along with water as byproduct.

A first attempt in this direction was described by Frey et al. [62]. who used ε-caprolactone as monomer and a commercial, immobilized lipase as catalyst. The polymerizations were conducted at 85 °C, where a rapid ROP followed by slower polycondensation was observed.

The lactone/BHBA ratio was varied over a broad range. The incorporation of BHBA was lower than expected from the feed ratio, and only low Mn‘s (<5 kDa) were found for lactone/BHBA ratios < 10/1. In other words, only few condensation steps and correspondingly low degrees of branching were achieved.

Choi and Kwak [63] studied the same monomer combination, but tin(II)2-ethylhexanoate ($SnOct_2$) was used as catalyst for the ROP, and the linear polyester with pendant CO_2Hgroup was isolated prior to polycondensation. Toluene sulfonic acid served as catalyst for the polycondensation, and the water was removed with a stream of argon or in vacuo. From careful Mn measurements those authors concluded to have 8.3, 5.1, and 3.3 branching points per polymer for lactone/BHBA ratios of 5, 10, or 20.



Formula 15.13

Frey et al. [64] resumed their studies of the ε-caprolactone/BHBA system using chemical instead of enzymatic catalysts. Either $HfCl_4(THF)_2$ or diphenylammonium triflate (DPAT) served as catalyst for both ROP and polycondensation. These catalysts were known from previous work of other authors, who had studied $a_2 + b_2$ polycondensations [65, 66]. Toluene or 1,2-dichloroethane were used as reaction media enabling azeotropic removal of water. With both catalysts 2–4 times higher molecular weights were achieved than with lipase. The highest Mn's were obtained with DPAT, but formation of ether groups was observed, when the temperature exceeded 80 °C. Unfortunately, those authors never corrected their Mn data, although it is known from numerous research groups that polystyrene-calibrated SEC measurements of aliphatic polyesters heavily overestimate the real molecular weights.

Finally, Frey et al. [67] studied the combined ROP and polycondensation of L-lactide and BHBA (see Formula 15.13): $SnOct_2$ served as catalyst for both, ROP and polycondensation. However, those authors ignored, that this tin compound, although an excellent transesterification catalyst, is a poor esterification catalyst. For lactide/BHBA ratios < 20/1 only low molecular weights (200−5,000 Da) were obtained, when a correction of the reported SEC data is taken into account. Frey et al. themselves admitted that only two or three BHBA units were incorporated. Since one BHBA unit forms a CO_2H end group, this means that only one or two branching points existed in a polymer. In other words, those polylactides had in fact a star-shaped rather than a hb architecture.

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Chapter 16
Condensative Chain Polymerization

16.1 Definitions

The term condensative chain polymerization (CCP) was coined and approved by the IUPAC. It defines polymerizations which show all the typical kinetic features of a chain growth polymerization, whereas the individual growing steps involve an elimination (condensation) reaction quite analogous to a true polycondensation. The typical features of a CCP are the following ones:

(1) Only one kind of growing steps occurs, namely the reaction between monomers and active chain end. If the monomer itself is activated by a catalyst or not, does not matter for this definition.
(2) Cyclization reactions do not compete with chain growth.
(3) The DP (Mn) may be controlled by addition of a reactive initiator.
(4) Molecular weight distributions are relatively narrow, and dispersities around 1.1 may be achieved.
(5) Sequential copolymerizations yield perfect block copolymers.

CCPs do not play a role for technical production of polymers, but they are particularly important and interesting, because almost all biopolymers (perhaps with exception of lignin) are prepared by living organisms via CCPs. It is a fascinating aspect of evolution that all syntheses of polymers during the period of prebiotic evolution were based on polycondensations, whereas the appearance of living organisms is characterized by the appearance of CCPs. The following text is subdivided into three sections: (A) biomonomers, (B) cyclic monomers, and (C) linear monomers.

16.2 Biomonomers

Not all syntheses of biopolymers were fully elucidated, and therefore, only those syntheses which are well understood will shortly be discussed [1, 2]. The chain growth of proteins is managed by living cells in "bioreactors" called ribosomes.

H. Kricheldorf, *Polycondensation*, DOI: 10.1007/978-3-642-39429-4_16,

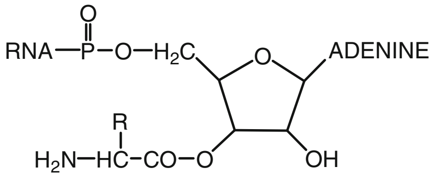
The individual amino acids playing the role of monomers, are activated in the form of ribose esters (see Formula 15.1). The enzyme "peptide transferase" transfers the growing peptide chain activated as ester of t-RNA (transfer ribonucleic acid) to the amino group of a new amino acid fixed to the ribose end group of another t-RNA which continues this reaction pathway. In contrast to CCPs in the laboratory the byproduct split off in the growing step is a relatively large molecule, namely a t-RNA having a molar mass in the range of 25–30 kDa. Another RNA, the messenger-RNA provides the information of the sequence and quantity needed for the 20 proteinogenic amino acids which are copolymerized in a normal protein. The mRNA is a copy of a DNA strand in the gene of a living cell. The driving force for the chain growth is the transformation of an ester group in the thermodynamically more stable peptide group, which is an exothermic reaction.

For the biosynthesis of polysaccharides not the chain end but the monomers are activated. As outlined in Formula 16.1 for glucose the carbon in the highest state of oxidation (here C-1) is connected to a diphosphate group of a nucleoside. Uridine is the most widely used nucleoside for this purpose. The activated glucose is transferred to an OH-group of the last monomer unit of the growing chain, so that a new glycoside bond is formed. This growing step is per se slightly exothermic, but the driving force (both the Gibbs free energy and the reaction enthalpy) can be enhanced by hydrolysis of the pyrophosphate group which is an anhydride of phosphoric acid. The biosynthesis of ribonucleic acids (RNA) and deoxyribose nucleic acid (DNA) follows a similar strategy. The monomer, a nucleoside triphosphate (see Formula 16.1) may be considered as an activated nucleotide. The growing step involves liberation of a pyrophosphate group, the hydrolysis of which is exothermic and irreversible shifting the equilibrium of the growing step in direction of the polymer chain. This synthetic strategy also holds for the biosynthesis of natural rubber. 2-Methyl-1-butenyl-4-pyrophosphate serves as monomer and dimethylallyl pyrophosphate as primer (initiator). Liberation and hydrolysis of the pyrophosphate group generates the driving force.

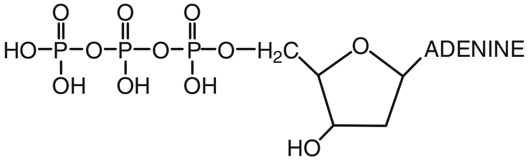
The activation of ß-hydroxybutyric acid which is the monomer for the biosynthesis of the poly(ß-oxybutyrate) which serves as a food stock in numerous bacteria, is effected in a different way. The carbonyl group is attached to coenzyme-A, and thus, activated in the form of a CO–S bond.

16.3 Cyclic Monomers

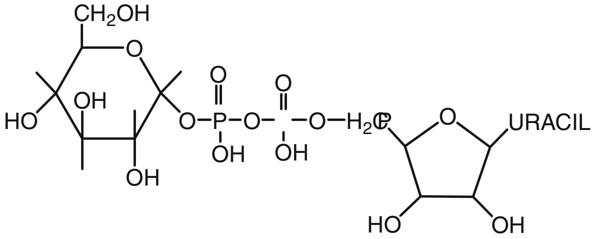
The oldest example of a CCP in a laboratory are polymerizations of α-amino acid N-carboxyanhydrides (NCAs, 2,5-dioxo-oxazolidines, see Formula 16.2). Synthesis and polymerization of these amino acid derivatives were first described by Leuchs and coworkers in the years 1906–1908 [3–5]. The existence of long covalent polymer chains was not accepted by the scientific community at that time, and poly(α-amino acid)s which are insoluble in almost all organic solvents were difficult to characterize. Therefore, Leuchs abandoned this working field after three



activated
amino acid



Nucleotide: Adenosine triphosphate



UDPG

Glycose activated by uridine diphosphate

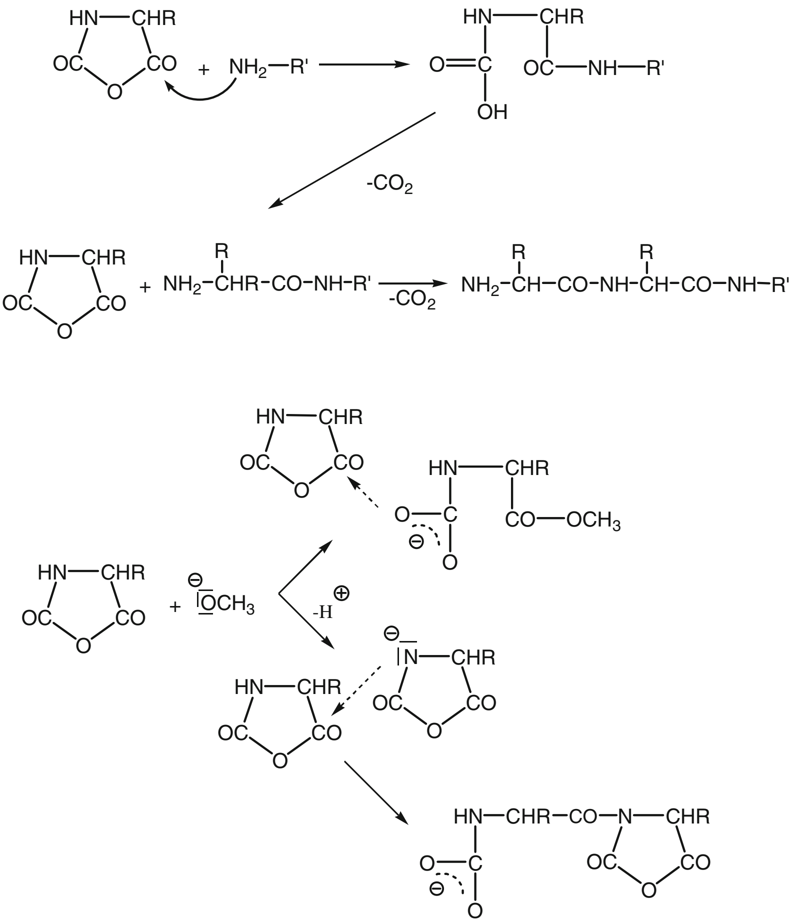
Formula 16.1

publications, and systematic studies began in 1925 with the work of Wesley et al. [6–10]. Meanwhile, several hundreds of publications dealing with syntheses and/or polymerizations of NCAs have appeared, and a detailed presentation of all results is far beyond the scope of this subchapter. Only the most important aspects of the various polymerization methods will be discussed below, and the interested reader is referred to a dozen of review articles and books that were published over the past 6 decades [11–22].

The best understood and most widely applied polymerization mechanism is the so-called "amine mechanism" (see Formula 16.2, top). The propagation proceeds by reaction of NCAs with the amino end group of the growing peptide chain. The target of the nucleophilic attack is the carbonyl C-5, because C-2 is less reactive due to the delocalization of the electrons from the neighboring N-atom. As recently demonstrated by MALDI-TOF mass spectrometry [23] this polymerization method yields perfectly linear chains with little or no sideractions. If high molecular weights cannot be achieved in this way, physical problems (see below) and not side reactions are responsible for the failure. The "amine mechanism" can be initiated by various protic nucleophiles, such as water, alcohols, mercaptans, primary amines, and sterically nonhindered aliphatic secondary amines. For preparative purposes primary aliphatic amines are preferentially used, because they are slightly more nucleophilic than amino end groups. Therefore, the initiation step is faster than the growing steps, and all initiator molecules will react in the beginning of the polymerization. Provided that the polypeptide stays in solution, the DP will increase with the M/I ratio and with the conversion quite analogous to any other living polymerization.

Regardless, which initiator or catalyst is used, the course of the polymerization and the efficiency of the chain growth is strongly influenced by the physical properties of the peptide chains. All –CO–NH– groups have in inert reaction media a high tendency to form H-bonds with each other. Therefore, all oligopeptides having DPs < 10 associate via intermolecular H-bonds and precipitate from the reaction mixture in the form of ß-sheet lamellae. The further course of the polymerization depends on whether the soluble fraction can grow beyond a DP of 10 and form a-helices or not. In the case of helicogenic amino acids high molar masses (Mn > 20 kDa) may be achieved, because the active end group of the a-helix remains accessible to NCAs even after precipitation, and thus, the helical chains can continue to grow, albeit at a lower rate than in solution. However, a good control of the DP and narrow MWDs can only be achieved, when the polypeptide stays in solution. Therefore, most mechanistic and preparative studies were performed with γ-Bzl-L-Glu-NCA or N^{ε}-Z-L-Lys-NCA, because their polymers are soluble in polar inert solvents, such as DMF. In the case of non-helicogenic amino acids all oligo and polypeptides precipitate as ß-sheet lamellae and the chain growth suffers a "physical death" due to steric hindrance (s. Ref 18, Chap. 4). In those cases, quantitative conversion and Mn's > 10 kDa are usually not obtained.

To illustrate the various preparative applications of primary amine-initiated polymerizations the following enumeration may suffice [22]. In addition to simple homopolymers, block copolymers may be prepared by sequential copolymerization of two or more different NCAs. Mixtures of two or more different NCAs yield copolypeptides having a nearly (but rarely a perfectly) random sequence. Random and blocky stereocopolymers may be prepared from D- and L-NCAs. D Initiation with diamines yields telechelic polypeptides having two amino end groups which may serve as macroinitiators for syntheses of A-B-A triblock copolymers. Telechelic polymers having a different type of backbone may, of course, also act as macroinitiators. Grafting of polypeptides is feasible, when polymers having pendant amino groups (e.g., polylysine) are used as macroinitiators. Even natural



Formulas 16.2

proteins, such as bovine serum albumin, were used as polymeric initiators. Such graft copolypeptides were widely used to elucidate the immunogenicityof natural polypeptides and proteins [24–26]. Finally, the preparation of star-shaped polypeptides from multifunctional initiators and the modification of various surfaces doped with amino groups (e.g., by 3-aminopropyl trimethoxysilane) should be mentioned.

A special case represents CCPs of NCAs in the solid state initiated by primary amines. NCAs are unstable upon storage, and therefore, they are not commercial. Contamination with strong electrophiles such as PBr_3, $SOCl_2$, or carboxylic acid chlorides, stabilize the NCAs suggesting that the solid-state polymerization (SSP) is usually initiated by nucleophiles. Water fixed to the surface of NCA crystals via H-bonds certainly plays a key role for the low stability on storage. Primary amine-initiated polymerizations of NCA crystals were studied by Kanazawa et al. [22, 27–30]. Such polymerizations are highly interesting from a theoretical point of view, because they require a change of the crystal lattice, but they are not attractive for preparative purposes because only yield low or moderate molecular weights. Finally, it should be noted that polymerizations in water were studied in connection with the concept that NCAs might have played a significant role in prebiotic evolution [22, 31].

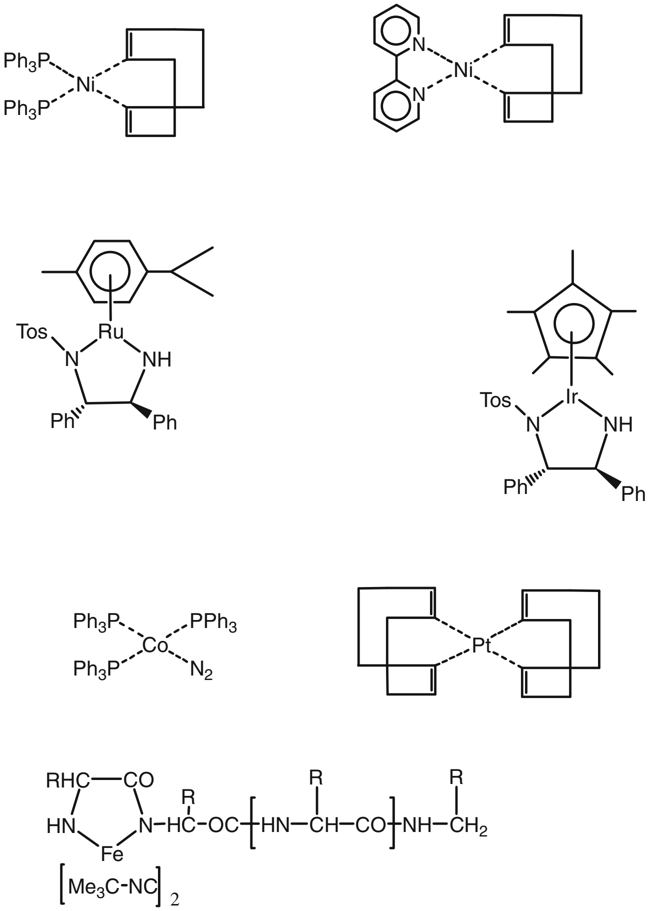
Secondary amines also yield linear polypeptides, when their nucleophilicity is not reduced by steric hindrance (e.g., dimethylamine or piperidine). Imidazole is an exception mainly yielding cyclic polypeptides. Cyclic polypeptides are also formed by sterically hindered secondary amines and by tertiary amines. Thermal polymerizations also yield cyclic polypeptides. Mechanisms and preparative aspects of all these polymerizations are discussed in Chap. 15.

Numerous publications were devoted to the catalytic activities of metal alkoxides and various metal salts. Sodium methoxide found considerable interest, because high molecular weights were achieved by Blout and Karlson with NCAs yielding soluble polypeptides [15–18, 32]. Alkoxides can, in principle, react with NCAs in two different ways (see Formula 16.2). Either they react as nucleophiles with C-5 (route (a)) initiating an anionic CCP, or they react as bases (route (b)). The reaction of NCA anions with the N-acly-NCA chain end was called “activated monomer mechanism”. The formation of high molecular weight polypeptides was attributed to this mechanism, but clear cut experimental evidence for this hypothesis is missing. LiCl is another catalyst which found great interest [18, 33] for both, mechanistic and preparative studies.

A new class of initiators and a new polymerization mechanism yielding linear polypeptides was recently elaborated by Deming et al. [21, 22, 34–36]. The research group studied complexes of zero-valent metals of the eights group of the Periodic Table (see Formula 16.3).

Regardless which metal or ligand was used, the reaction with NCAs resulted in the formation of peptide chains having an activated amino end group in the form of a metal complex (see Formula 16.3, bottom). With NCAs yielding soluble polypeptides, Deming et al. elaborated a variety of useful preparative applications. First, homopolymers having low dispersities (Ds around 1.2 ± 0.1) were obtained. Second, a control of the chain length via the M/I ratio was feasible. Third, sequential copolymerizations yielded two and triblock copolymers having narrow MWDs of all blocks. Fourth, A-B-A triblock copolymers based on a central poly(alkenamer) segment were prepared [33]. However, it should be kept in mind that the problems resulting from the association and precipitation of most polypeptides are not eliminated by variation of the initiator.

In addition to NCAs numerous related heterocycles capable of CCP were prepared. At first, the thio-analogs of NCAs should be discussed (see Formula 16.4, top). Syntheses and reactions of 2-thioxo-5-oxothiazolidine(a) were first prepared by Cook and Levy [37], but no polymerization experiments were performed. Thiazolidone-2,5-diones ((b), NTAs or TADs) were synthesized by four research groups [38–41] beginning with the work of Bailey, but again no

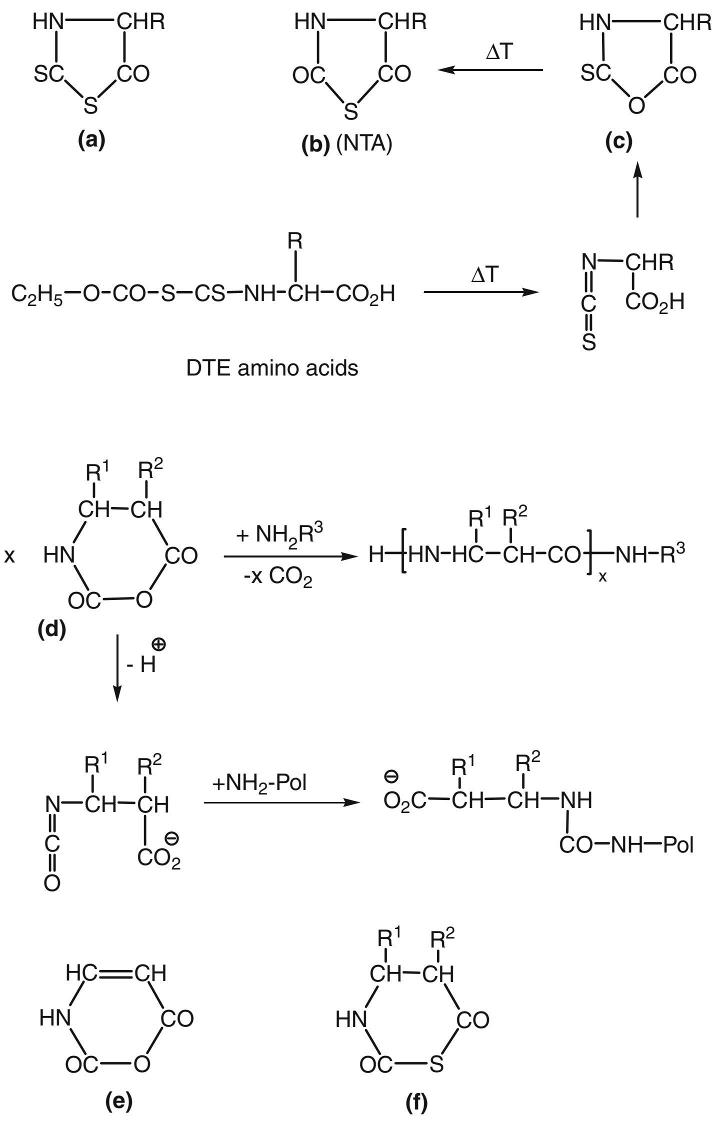


Formulas 16.3

information their polymerizability was disclosed. When compared to NCAs the NTAs are characterized by a lower sensitivity to hydrolysis and greater stability on storage. A first report on the polymerization of NTAs was focused on grafting of peptide chains on wool [42].

Systematic studies using primary and tertiary amines as initiators or catalysts were performed by the author [43–45]. Comparisons of NCAs and NTAs under identical conditions revealed that NTAs gave lower yiels and lower molecular weights under all circumstances. A recent reinvestigation [46] using MALDI-TOF mass spectroscopy did not reveal side reactions when n-hexylamine was used as initiator. Therefore, the question, why NTAs give lower yield and DPs remained unanswered.

Research on 2-thiopxo-5-oxazolidones (see Formula 16.4, ©) began with the work of Higashimura et al. [47–50] on DTE-amino acids. Those authors obtained high yields and seemingly molar masses above 10 kDa upon heating and originally



Formulas 16.4

believed that the DTE-amino acids react via a normal polycondensation process. Yet, later [50] they observed the intermediate formation of a-isothiocyanato carboxylic acids and their cyclization and proposed the reaction pathway outlined in Formula 16.4 top. In other words, the 2-thioxo-5-oxazolidones were now considered to be the true monomers which yield the polypeptides by CCP. This interpretation was later confirmed by the author, who found a new approach to the synthesis of 2-thioxo-5-oxazolidones [51, 52]. These relatively unstable monomers partially polymerize on heating and partially isomerize to the more stable NTAs. Since their syntheses involve a high risk of racemisation, and since they are more cumbersome than syntheses of NCAs they are not of great interest for the preparation of polypeptides.

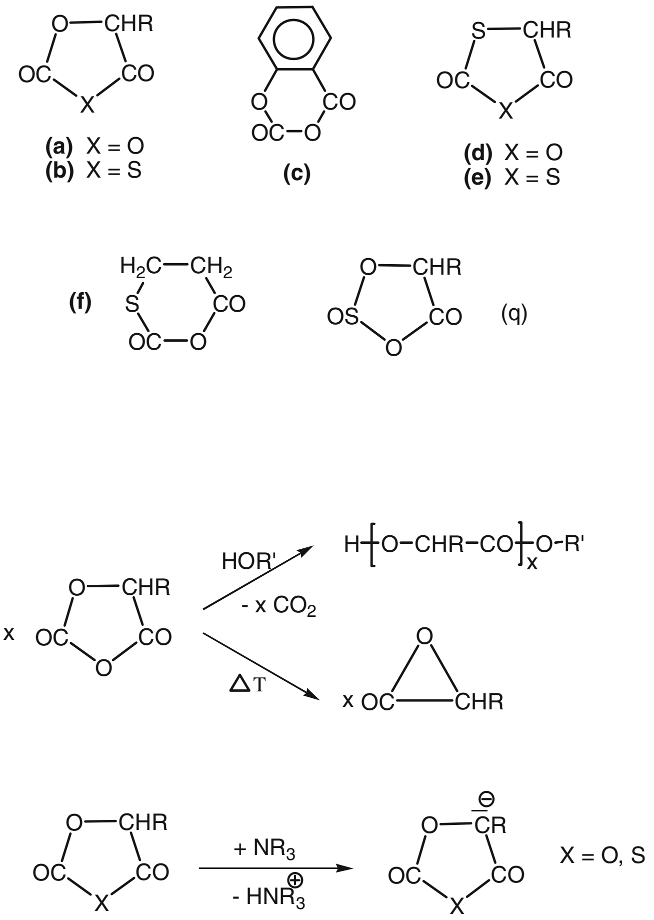
Since 1954 N-carboxyanhydrides were also prepared from ß-amino acids [53–61]. These syntheses included ß-NCAs of N-substituted amino acids. CCPs initiated by water, primary amines, tertiary amines were conducted. Characteristic for all amine-initiated polymerizations was the deprotonation of the NH group followed by formation of ß-isocyanato carboxylic acids which react, in turn, with amino end groups (see Formula 16.4). An analogous side reaction occurs in thermal polymerizations. Due to these termination steps DPs > 60 (Mns > 10 kDa) were never obtained [54, 60]. Cleaner polymerizations yielding higher DPs may be achieved with N-substituted ß-NCAs [57]. ß-NCAs having a double bond in the ring (see Formula 15.4e), including the NCA of o-amino benzoic acid, are not polymerizable.

Cyclic carboxyanhydrides and anhydrosulfides are also known from hydroxyl carboxylic acids (see Formula 16.5a, b). OCAs (a) were first prepared by Davies [62], but not polymerized. OCAs are sensitive to moisture and unstable on storage like NCAs. The few publications dealing with their CCP suggest [63–65] that Mn's > 10 kDa are difficult to achieve.

Smith and Tighe [63] postulate for thermal polymerizations the intermediate formation of a-lactones, but kinetic data alone cannot prove this hypothesis. Thermal and pyridine-catalyzed polymeizations of salicylic OCA (c) gave low molar mass polyesters due to cyclization [66, 67].

Apparently, no information is available on the polymerization of the corresponding OTAs (see Formula 16.5b).

The cyclic anhydrides and anhydro sulfides of a-mercapto carboxylic acids are the 2,5-dioxo-1,3-dioxathiolanes and 2,4-dioxo-1,3-dithiolanes (Formula 15.5d, e). Syntheses and preliminary polymerizations were first described by Schöberl [68] followed by more detailed studies of Elias et al. [69, 70] and of the Kricheldorf and Bösinger [71]. It was found that neither acidic catalysts nor protic nucleophiles initiate the polymerization, whereas bases, such as tert-amines were highly effective. From kinetic measurements of thermal polymerizations, Tighe et al. [72] concluded that an intermediate formation of α -thiolactones takes place. An alternative interpretation is discussed in Chap. 14. The dithiolanes (e) first described by Kricheldorf et al. [73] were more stable against hydrolysis and heat, but surprisingly they were also more reactive against bases. Their base catalyzed CCPs were faster, gave higher yields and higher molar masses [72, 73]. Pyridine amd heat-induced polymerizations yielded cycles as discussed in Chap. 15. The author also synthesized the six-membered 2,4-dioxo-1,3-dithiane (f) and found that tert. amines are again good polymerization catalysts [74].



Formulas 16.5

Finally, cyclic anhydrosulfites of a-hydroxycarboxylic acids (1,3-dioxa-2-tholane-4-one-2-oxides, see Formula 16.5g) need to mentioned. First syntheses and polymerization experiments were reported by Blaise et al. [75] as early as 1922. Systematic studies of this highly reactive class of monomers began about 40 years later [76–88]. Tighe et al. concentrated their kinetic studies on thermal and alcohol-initiated polymerizations. They found that increasing size and number of substituents do not stabilize these heterocycles [83]. They concluded that the first step of a thermal polymerization is a decomposition into SO_2 and an α -lactone (compare OCAs in Formula 16.5). Another interpretation of thermal and pyridine-catalyzed polymerizations is presented in Chap. 15.

16.4 Linear Monomers

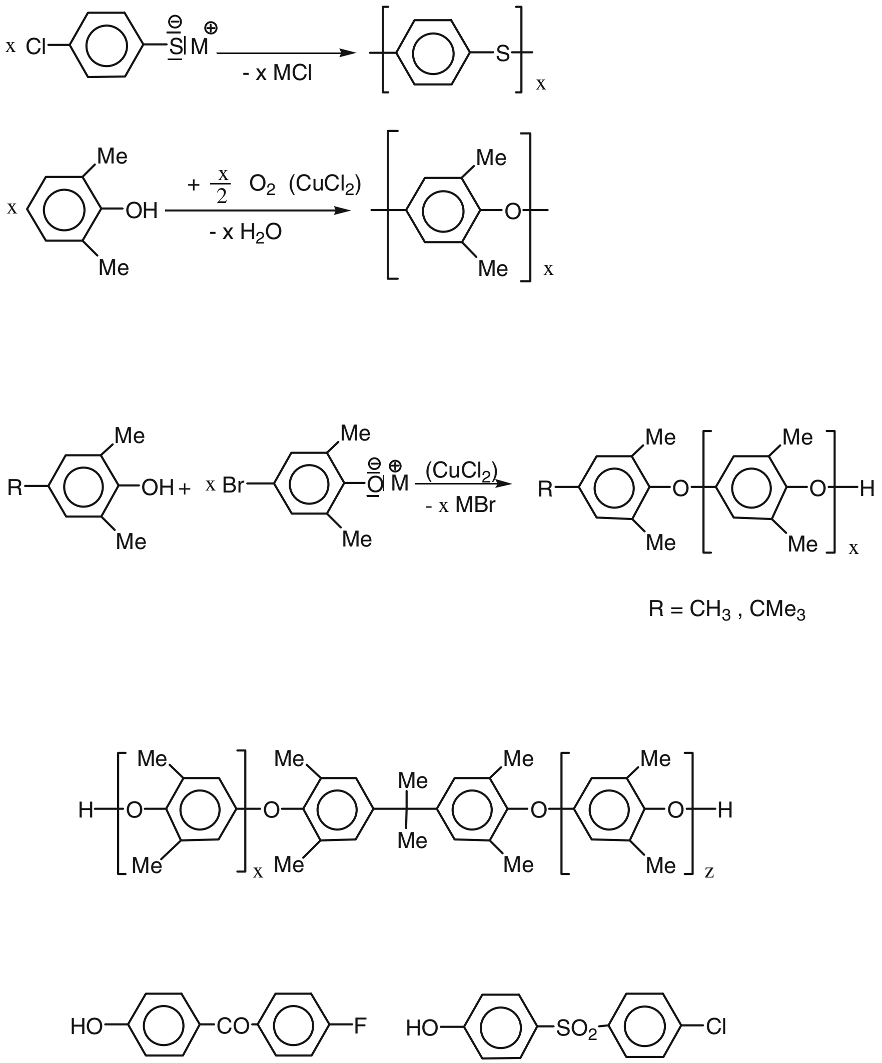
The first report of CCPs of linear monomers concerned dehydrohalogenation of para-halophenols and para-halothiophenols; Lenz et al. [89, 90] studied polymerizations of alkali metal salts of 4-halothiophenols as part of a broader study on preparation and technical production of poly(phenylene sulfide) (see also Chap. 8). In agreement with a cationic radical mechanism, the reactivity of the haloatoms decreased in the order J > Br > Cl > F. Furthermore, it was found that chain growth and monomer consumption did not agree with the Carothers equation and high oligomers were formed at low conversion. These polymerizations were performed in solution, but the poly(phenylene sulfide) precipitated from the reaction mixture and the chain growth continued in the solid state, albeit a 50–100 times lower rate [90].

Despite the complex mechanism, these polymerizations showed the characteristic features of CCP of aromatic monomers. The delocalization of electron density from the nucleophilic (anionic) “a”-function to the electrophilic “b”-function across the aromatic ring (mesomeric effect) considerably reduces the electrophilicityof the monomer relative to the “b”-end group of oligomers and polymers. This means, that the first step, namely the reaction between two monomers, is the slowest step of the entire polymerization process.

The oxidative polymerization of 2,6-dimethylphenol (invented by Hay et al. [91], see also Chap. 8) and the polymerization of potassium 4-bromo-2,6-dimethylphenoxide (see Formula 16.6) have both the character of CCPs. The former CCP needs oxygen as reaction partner and a Cu^{1+} amine complex as catalyst. Heitz et al. [92] observed that contrary to a normal polycondensation high oligomers were formed at low conversions, and he formulated a speculative radical-cation mechanism. The CCP of 4-bromophenoxide salts needs Cu^{2+} or other oxidizing metal ions as reaction partners and also involves a radical-cation mechanism [93]. When 4-methyl- or 4-tert.butylphenol are added as initiators, linear chains having one OH end group are formed, whereas addition of tetramethyl bisphenol yields telechelic polyethers (see Formula 15.6).

Control of Mn was feasible below 10 kDa and DPs < 1.5 were found. Higher molar masses with little control via the M/I ratio were obtained from other initiators [94–97]. Numerous polymerizations of metal salts of various halophenols were reported by several research groups beginning with the work Torey and Hunter in 1911 [98]. In many cases, more than one haloatom was attached to the phenol and branching or other side reactions occurred. The hypothesis of CCP versus polycondensation was not discussed. A detailed review of all these polymerizations has been published [99].

Whereas all aforementioned CCPs are characterized by a radical mechanism, syntheses of aromatic polyethers via CCPs involving normal nucleophilic substitution at activated C–Cl or (better) C–F bonds were also reported. The reactivities of 4-oxo-4′-fluorobenzophenone and 4-oxo-4′-chlorodiphenylsulfone (see Formula 16.6, bottom) were examined by a research group of ICI [100–103]. Although oxide anion



Formulas 16.6

and C–X bond were separated by two aromatic rings and a CO or SO_2 group, the reactivities of C–F was reduced by a factor of 10 and that of C–Cl by a factor of 20 relative to the C–X end groups of the oligomers. On the basis of these results, Yokozawa et al. [104] studied polymerizations of 4-oxo-4′-fluorodiphenylsulfone (Formula 15.6a). Using a more electrophilic initiator, only linear chains with low PD were obtained indicating a perfect CCP. Further CCPs were conducted by the same research group with a new monomer (see Formula 16.7b) [105–108]. Since oxide anions and C–F bond are attached to the same benzene ring, the mesomeric effect is here particularly effective. By means of a more electrophilic initiator, Ds as low as 1.1 were achieved. Using polystyrene containing an activated C–F end group, two-block copolymers or miktoarm star copolymers were also synthesized by this approach [109].

Further studies of the Yokozawa group concerned CCPs of aromatic polyesters. At first, polymerizations of 4-trimethylsiloxybenzoyl chloride and its anion (see Formula 16.7), first reported by Yokozawa et al. [110] were studied Yet the insolubility of poly(oxibenzoate) in all inert solvents prevented a satisfactory characterization of the reaction products [111]. Therefore, a new class of monomers (see Formula 16.7d) was synthesized. The aliphatic side chains rendered the polyesters soluble in various inert solvents, and the activated heterocyclic amid group eased purification by recrystallization To prevent transesterification the polymerization temperature had to be lowered to 30 °C [112, 113].

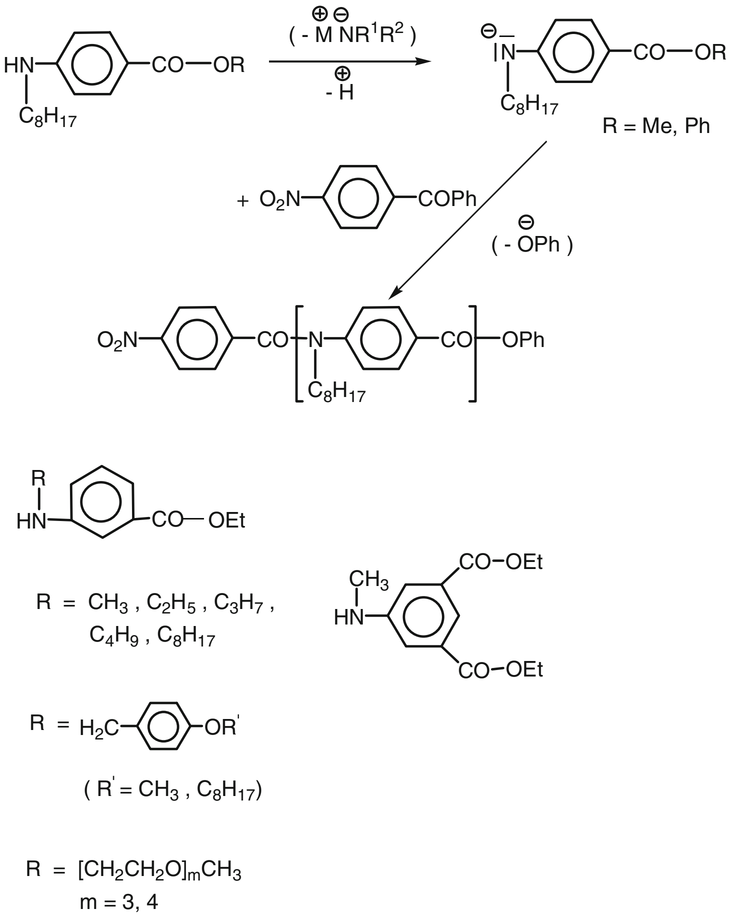
Most of the work of the Yokozawa group was dedicated to CCPs of monomers yielding soluble N-alkyl polyaramides [114–117]. At first monomers derived from 4-aminobenzoic acid were studied (see Formula 16.8, top). Deprotonation by a metal amide yielded nitrogen anions which deactivated the ester groups of the monomers, so that with an electrophilic initiator perfect CCPs were obtained (typically in THF at 20 °C). The ethyl esters of N-alkyl-3-amino benzoic acid also proved to be useful monomers. The transmission of electronic effects via the π-electrons is relatively weak in this case, but it is supported by a positive inductive effect.

Due to the shorter distance between amino and carbonyl group. In addition to numerous homopolesters having low DPs two-block copolymers either containing 3- and 4-aminobenzoyl units or different substituents or a block having a different backbone were prepared. Star-shaped polyamides were obtained from multifunctional initiators, and hyperbranched polyamides from diethyl 5-(N-methylamino)isophthalate (see Formula 16.8) [118]. Various details of all these CCPs were presented and discussed in two review articles [119, 120] and in five more recent publications [112–125].

16.4.1 Catalyst-Transfer Polymerizations

Syntheses of fully conjugated aromatic polymers by C–C coupling from dihaloaromatics frequently proceed via CCP involving migration of the catalyst to the active chain end. A typical example is syntheses of poly(alkyl thiophene)s as outlined in Formula 16.9 each growing step involves elimination of MgBrCl, but the Ni-catalyst migrates to the new chain end forming an activate end group. Formally the catalyst also plays the role of an initiator, so

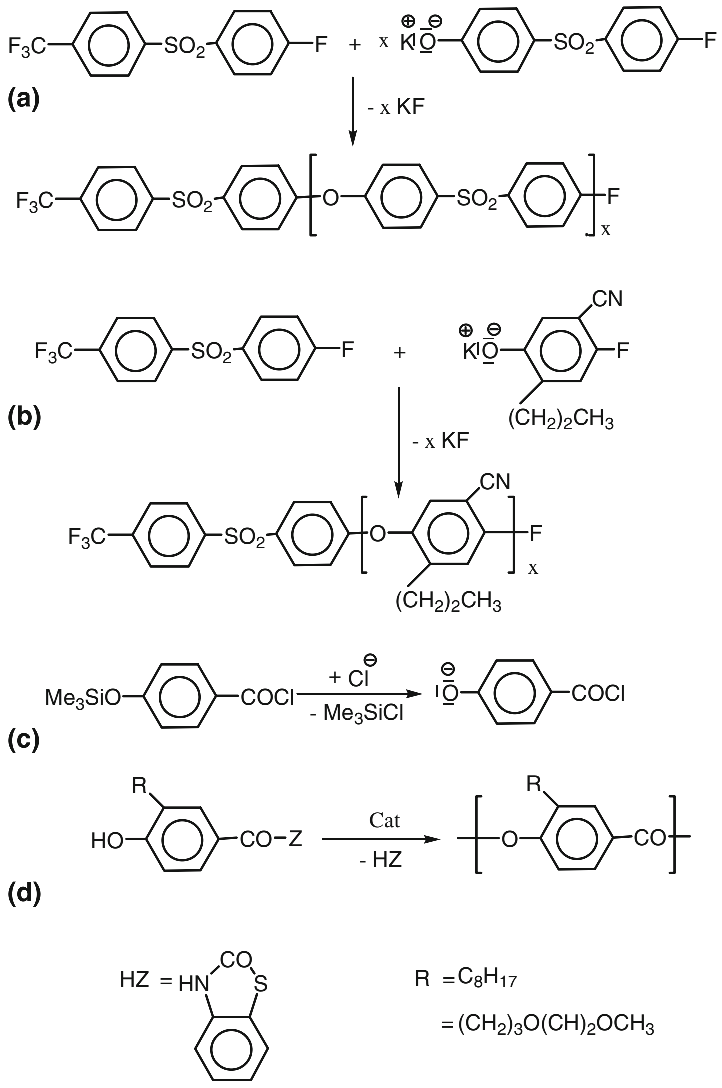
that the DPs parallel the M/I ratio. Furthermore, Yokozawa et at. [126, 127] obtained PDs as low as 1.1 under optimized reaction conditions, whereas high DPs were reported in the original work of McCullough [128, 129]. Both research groups explored and improved the polymerization of dihalo thiophenes in various



Formulas 16.7

directions. The influence of different ligands and the influence of different substituents (R in Formula 16.9) were studied, but clean CCPs were not achieved in all experiments. McCullough modified the chain ends with functional groups. Various block copolymers were prepared from thiophenes having different substituents and grafting on glass plates modified with polystyrene was performed (for details see review [120]).

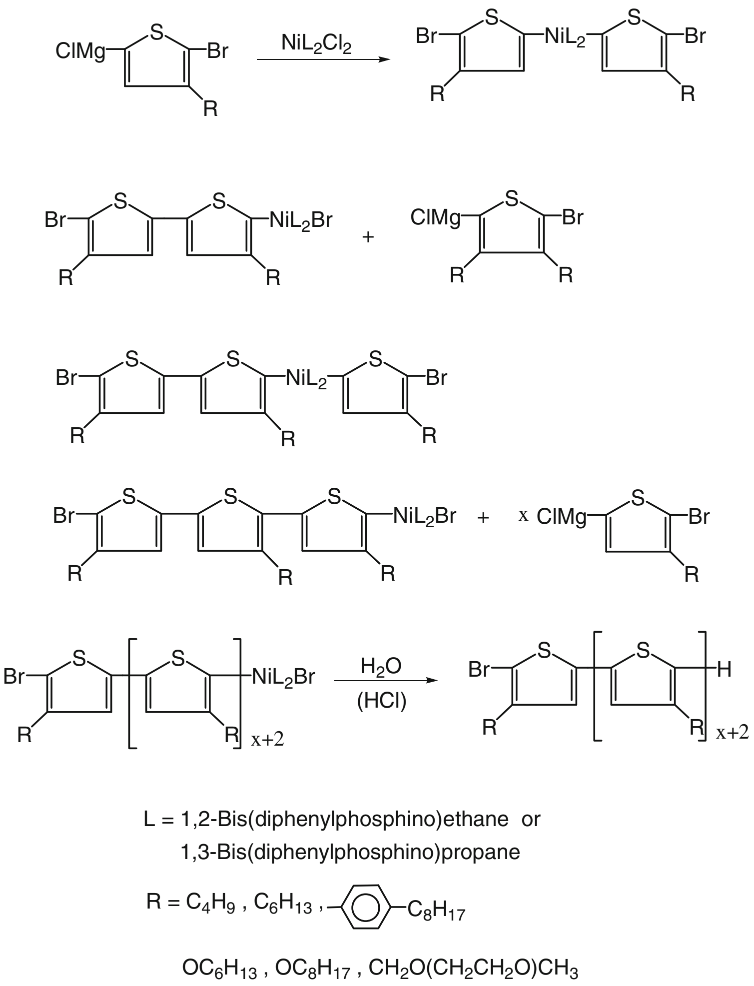
In an analogous way, soluble substituted poly(p-phenylene)s were prepared from substituted benzene rings functionalized with MgCl and Br in para position (see Formula 16.10). It proved to be necessary to add LiCl in addition to the Ni-catalyst to achieve low DPs (1.17–1.27) and Mns up to 36 kDa [130]. Furthermore, it was feasible to synthesize diblock copolymers, when the poly(p-phenylene) was prepared first and used as a macroinitiator for thiophene monomers. The same approach also allowed to perform CCPs of 2,5-dihalo N-hexylpyrrol, but again



Formulas 16.8

careful optimization of additives and reaction conditions was necessary to achieve low PDs, and the successful preparation of diblock copolymers [131, 132] (see Formula 15.10). Finally, Pd- and Ni-catalyzed polymerizations of fluorine monomers should be mentioned. CCP with catalyst transfer was only observed for the boron-activated monomer (see Formula 16.10) [133].

The Ni-catalyzed polymerizations of the dibromomonomer (d) took a complex course and yielded high PDs [134, 135]. All these conjugated polymers have in

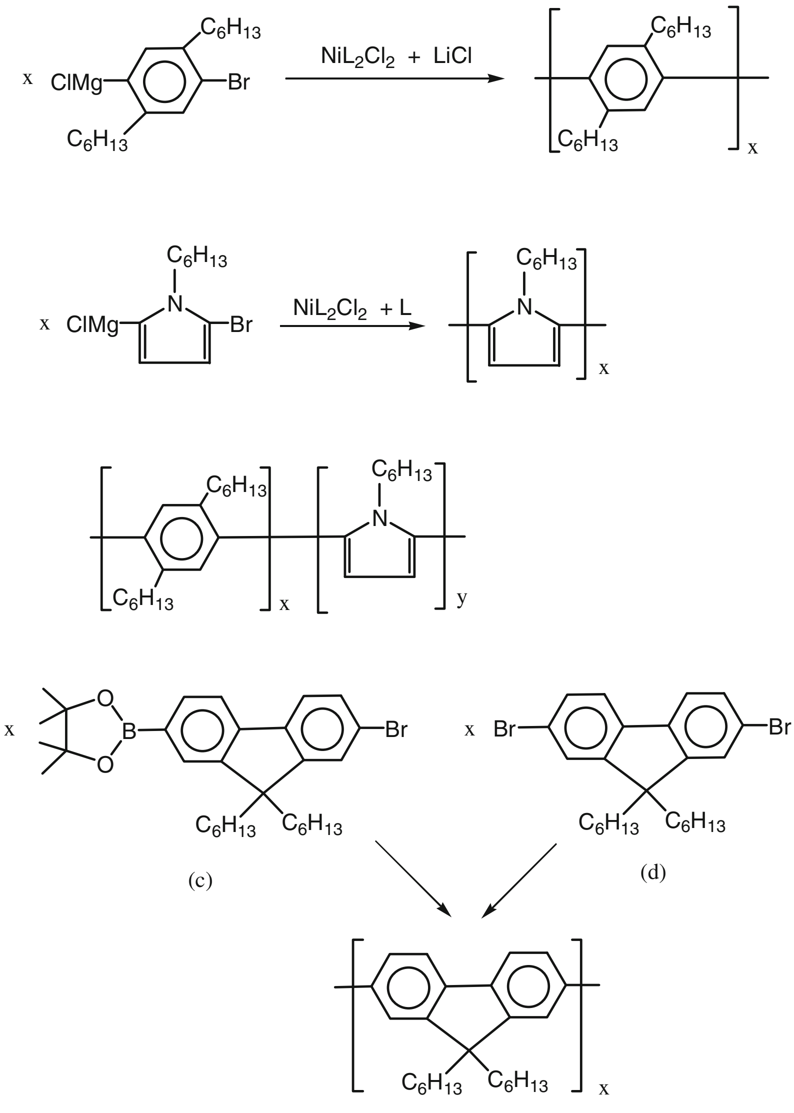


Formulas 16.9

common that the chain stiffness prevents formation of cyclic oligomers, so that their absence cannot serve as indication of a successful CCP.

16.4.2 Various Monomers

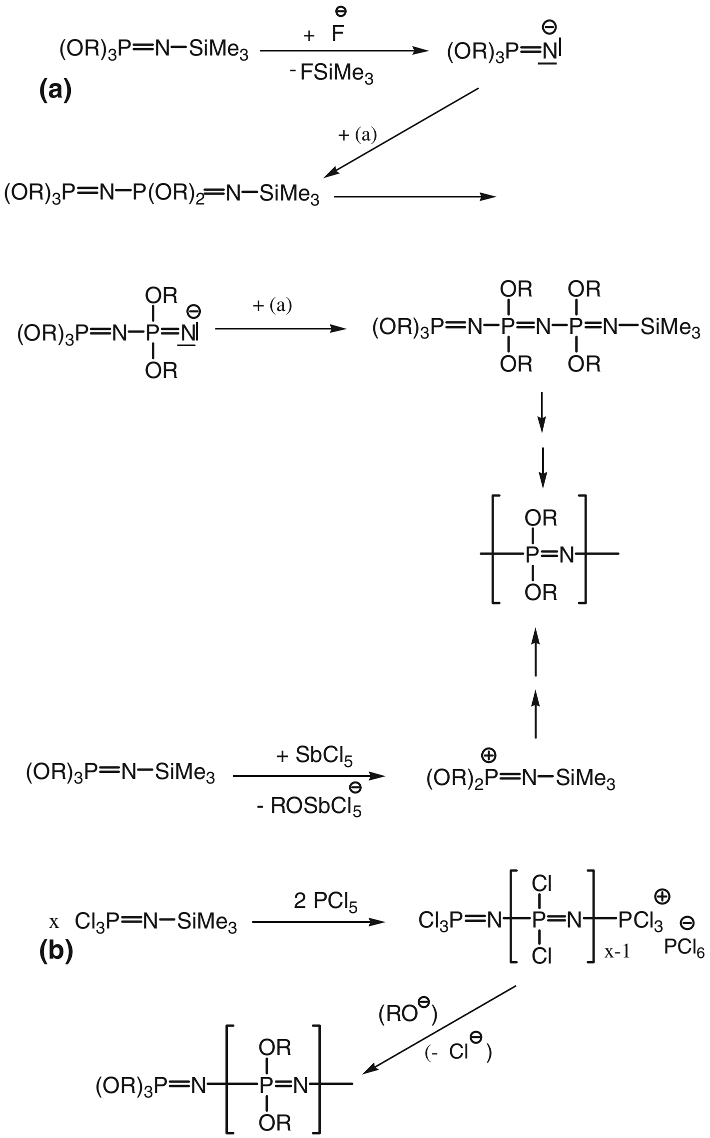
Polymerizations of N-trimethylsilyl phoporanimines (see Formula 16.11a, b) were explored as a new approach to the synthesis of poly(phosphazene)s. An anionic



Formulas 16.10

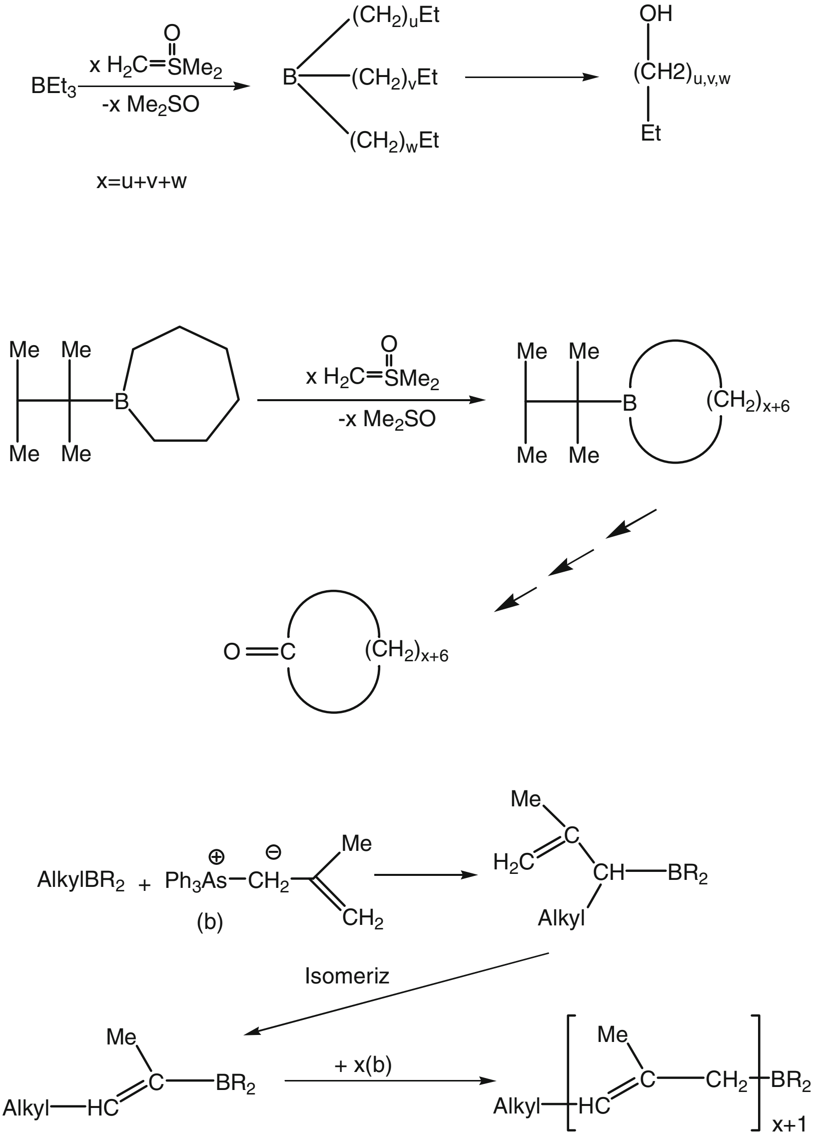
mechanism involving elimination of ROSiMe$_3$ in each growing step was formulated (see Formula 15.11)

and studied by Matyjazewski et al. [136–139]. Only moderate Ds around 1.5 were obtained, and since MALDI-TOF mass spectrometry was not available at that time, presence or absence of cyclic oligomers was not elucidated. The same research group also studied cationic polymerizations catalyzed by SbCl$_5$ and obtained lower Ds (1.25) with Mn's in the range of 10–50 kDa [139]. Cationic



Formulas 16.11

polymerizations of the trichloro phosphoranimine (b) were explored by Allcock et al. [140–142] using PCl_5 as catalyst. Again high Mns (up to 100 kDa) and Ds < 1.3 were achieved. A new synthesis of monomer (b) and subsequent cationic polymerization were reported by Wang [142]. Several publications also dealed with syntheses of block and graft copolymers as discussed in review [120].



Formulas 16.12

Furthermore, CCPs of “ylides” need mentioning. The research group of Shea has extensively explored polymerizations of dimethylsulfonium methylide ((a) in Formula 16.12) initiated by aliphatic boranes [143–148]. The ylide inserts into the B–C bond and creates a new reactive B–C bond by elimination of dimethylsulfoxide, Depending on the work-up procedure OH-terminated linear or star-shaped alkanes were isolated. The control of the DP and the low dispersities (1.04-1.17) agreed with the character of a living polymerization. With cyclic boranes ring-expansion polymerizations were realized. Similar CCPs Similar CCPs were performed by Moskowski et al. [149, 150] an arsonium ylide ((b) in Formula 14.12 and alkylboranes as initiators. The reaction mechanism involves a sigmatropic rearrangement of the reactive species prior to the fixation in the polymer backbone. Block copolymers of two different ylides were also described. Finally, it is worth noting that complex polymerization processes involving CCPs were discussed in Chaps. 9 and 15.

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