Chemistry and Technology of Water-Soluble Polymers

Edited by C. A. Finch

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FOREWORD

This volume was conceived during the course of a Residential School organized by the Royal Society of Chemistry at Newnham College, Cambridge, in September 1981: it is a rewritten version of the course manual prepared for this School by the group of tutors who are now the authors contributing to this volume.

Although I have always been dimly aware of the existence and importance of water-soluble synthetic polymers, I first became directly involved with them several years ago in connection with studies of their effects on the nucleation of ice in undercooled water and on the growth and morphology of ice crystals. It became necessary to characterize samples of polyvinyl pyrrolidone, polyethylene glycol, hydroxyethyl starch and polyvinyl alcohol. After some correspondence with the manufacturers, I began to realize that they knew little about the physical properties of their products; our questions about molecular weight distributions or the degree and nature of any chemical modifications usually met with the response that these were difficult things to determine. What was obvious was that successive batches of material bought from the same source exhibited significant variability in some physical properties.When this was pointed out to the suppliers concerned, they usually regretted any inconvenience caused, but it was fairly clear that their control over their manufacturing processes was limited, as was also their knowledge of the properties of the finished products.

It began to dawn on me that to most self-respecting polymer scientists water, as a solvent, was anathema. The reason is not hard to discern: water does not fit into the framework of the accepted and acceptable theories which govern the behaviour of macromolecules in solution. On the other hand, alternative theories have not yet been developed. What is done instead is to make aqueous solutions fit the theory by using the technique of Procrustes' bed. Sooner or later, such fitting exercises tend to produce absurd values for some physical parameter or other.

To the biochemist, water is, of course, the only solvent worthy of consideration, because natural macromolecules exhibit their remarkable conformational properties only in aqueous media. Probably because of these remarkable properties, biochemists do not tend to regard proteins, nucleotides and polysaccharides as polymers in the way that real polymer scientists regard methyl methacrylate and polyethylene. The laws of polymer statistics hardly apply to native biopolymers.

Between these two powerful camps, lies the No-man's land of water soluble synthetic polymers: here, we must also include natural polymers which have been chemically modified. The scientific literature of these compounds is characterized by a large number of patents, which is usually a sign of little basic understanding, of 'know-how' rather than of 'know-why'. Many of the physical properties of such aqueous solutions are intriguing: the polymer may be completely miscible with water, and yet water is a 'poor' solvent, in terms of polymer parlance. Many of the polymers form thermoreversible gels on heating or cooling. The phenomena of exothermic mixing and salting-in are common features of such systems: neither can be fully explained by the available theories. Finally, the eccentric behaviour of polyelectrolytes is well documented.

Despite the lack of a sound physico-chemical foundation there is a general awareness of the importance of water soluble vinyl, acrylic, polyether, starch and cellulose derivatives, as witnessed again by the vast patent literature. They enjoy widespread applications in industries as diverse as pharmaceuticals, food, cosmetics, paper, leather, textiles, paints, mining, oil drilling, and in medicine. It was the aim of the Residential School to review such scientific basis as does exist for water soluble polymers and to bridge the gap that separates the scientific principles and the application technologies. The programme combined a series of state-of-the-art lectures with group discussion/tutorials on specialized aspects, and a panel problem solving session.

As course organizer and chief tutor I had never contemplated that the course manual would or should be published. Indeed, I felt that even a mention of eventual publication might scare off potential tutors. However, such was the enthusiasm of the group of tutors who assembled at Newnham College, that by a unanimous vote they decided to publish the course material in rewritten form: this volume is the result.

It is a pleasure to thank the Royal Society of Chemistry for permission to use the course manual as a basis for this publication, and Dr.A.D.Ashmore and Miss L.Hart for the smooth organization of the Residential School. The staff of Newnham College were also most efficient and courteous in dealing with the hundred-odd tutors and participants of diverse nationalities.

Felix Franks

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University of Cambridge

Cambridge
February 1982

PREFACE

Water soluble polymers have, for many years, received less than their share of the considerable scientific effort which has been devoted to the study of the structure and properties of the broad mass of macromolecular systems. The effect of this has been that the study of water soluble polymers has been something of a 'Cinderella' subject, in spite of the importance of the polymers in biological systems, foods, and industrial products where the advantages (and low cost) of water as a solvent can be employed.

Estimates of the scale of use of water soluble polymers are difficult to establish, since definitions are uncertain and variable (especially when foods are included), but it has been suggested that the total world production is probably over 5 M t/yr. Of this, some 80 - 90 % is carbohydrate-based (including starches and natural gums), with an additional 300,000 t/yr. of cellulose ethers, about 100,000 t/yr. of proteins, mainly gelatin, the remainder being synthetic polymers, the most important of which are polyvinyl alcohol and polyacrylamide (each of which are convenient designations for a group of copolymers, of varying composition). Water soluble polymers are, therefore, of considerable economic importance, and the industries in which they are used, including paper coating, textile sizing, detergent production, water treatment, and oil-well drilling , have a significant effect on our daily life. The extent to which water soluble polymers are applied in many different fields is indicated by the notably wide range of reference sources from which authors have drawn information in the following chapters.

Quite apart from the intrinsic interest of studies of water-soluble polymers, in scientific terms, the potential economic importance of increased knowledge of the behaviour involved presents many opportunities for more detailed and effective investigation of their properties and applications. The existing limitations of our knowledge (as indicated by Felix Franks in the Foreword) amply justify the studies reported in this volume, which is based, more-or-less closely, on the Course Manual of a Royal Society of Chemistry Residential School held in Cambridge. The book is intended to provide an insight into the scientific relationships which may exist between theoretical studies and industrial applications of these polymers. Because of the immense scope of water-soluble polymers, some limitations on the extent of the course were imposed - notably that the behaviour of water soluble polymers in biological systems and in foods should be omitted, in general, although certain aspects of these systems are considered in relation to other properties. This is particularly so in the various sections describing the characteristics and performance of water soluble polymers in pharmaceutical and medical applications (Chapter 2 (Warburton), and Chapter 12 (Ogston), which discuss, respectively, the rheology and the thermodynamics of such systems, whilst Chapter 16 (Hutchinson) describes their application). The basic types of synthetic water soluble polymers are reviewed and classified (Chapter 1 (Molyneux)),with special reference to their properties as polyelectrolytes, with some consideration of natural and semi-synthetic polymers, although the latter are discussed only in outline, except in relation to their cross-linking properties (Chapter 5 (Finch)). Methods of fractionation and characterization are described in Chapter 8 (Dietz). The reactions (including their kinetics) involved in the preparation of water soluble polymers (especially polyacrylamides) are detailed in Chapter 3 (Thomson), and more specifically, those of the relatively novel 'hydrogel' polymers in Chapter 4 (Kálal). These polymers, although they can be considered as water-swellable, rather than water soluble, are of considerable scientific and technical interest, especially in medical applications. The theoretical considerations in the study of water soluble polymers in solution, notably thermodynamics (Chapter 7 (Burchard)), thermo-reversible gelation (Chapter 6 (Borchard)), hydration effects (Chapter 9 (Franks)), and behaviour as polyelectrolytes (Chapter 10 (Mandel)) are described in a series of 'state-of-the-art' reviews which can be studied in relation to the later chapters describing some industrial applications. The importance of water soluble polymers in behaviour at the interface between the aqueous phase and materials dispersed within the phase in emphasized in several sections: the theoretical approach is mentioned in Chapters 11 (Robb), 13 (Vincent) and 14 (Napper). The practical application of these effects, especially in relation to polymer emulsions for industrial use, is described in Chapter 15 (Baily). Two other areas where the importance of the surface active properties of water soluble polymers is considered are noted in Chapter 18 (Gregory)(where the mode of action in flocculant systems, especially in water treatment, is mentioned), and in Chapter 19 (Graham) (where the complex considerations in the use of water soluble polymers in oil-well drilling and enhanced oil recovery are outlined).

In many of these topics,the industrial importance of the use of water soluble polymers is considerable, yet the gap between empirical knowledge and the available theoretical background remains wide (as Felix Franks points out in his Foreword). It is the intention of this book to attempt to reduce the size of this gap, both by pointing out to industrial scientists where relevant fundamental advances have been made, and to academic workers where empirical systems (sometimes in daily use) may be sufficiently tractable to be amenable to theoretical treatment.

Authors have made different approaches to the requirements of publication on the basis of notes originally provided for a Course Manual. In some cases, there has been little alteration of the material originally submitted in June 1981. In others, texts have been revised on the basis of the mutually constructive (and, sometimes, critical) comments made by other participants during the Course. Some authors, mainly those from industrial establishments, provided brief seminar notes before the Course, and have subsequently expanded these, with incorporation of material emerging during the seminars, into independent chapters. In all cases, the texts have been edited to a limited extent, to provide reasonable conformity of style and convention in accordance with the publisher's requirements.

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THE INTERFACE BETWEEN THE CHEMISTRY OF AQUEOUS POLYMER SOLUTIONS AND THEIR APPLICATION TECHNOLOGY

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INTRODUCTION

The Residential School on which this book is based had three general aims. These were, firstly, to summarize and systematize what is known about the properties and behaviour of water-soluble polymers; secondly, to review the present state of the scientific basis of this knowledge, and to place it into a general theoretical framework; and, thirdly, to bridge the gaps which currently divide these scientific principles from the application technology of these materials.

This first Chapter is intended to serve both as a prologue, in which the requisite background information is presented on the types and examples of water-soluble polymers most commonly used, and on their applications, functions, properties and behaviour, and also as a summary, to provide an overall view of the area and a framework of reference to place the specific topics discussed in subsequent chapters into their wider context.

TYPES OF WATER-SOLUBLE POLYMERS

In this section, we consider those types and examples of water-soluble polymers which are most important from both scientific and technological aspects. Polymers are conveniently classified according to their origin into three main types:

- natural polymers (biopolymers);
- chemically modified natural polymers (semisynthetic polymers);
- synthetic polymers.

In the present context, it is the last two types which are of the greatest interest: natural polymers have largely been excluded from detailed consideration in this book, to avoid becoming entangled in the purely biological aspects, although they will, nevertheless, be considered briefly in this section.

Table 1. presents a list of some of the most common synthetic homopolymers, with the most widely used nomenclature and acronyms. A general objective in the study of all these types of polymers is the investigation of the structural features which lead to the polymer being water-soluble, and the minimum change in circumstances which cause such a polymer to become water-insoluble. It is therefore helpful to consider the behaviour of closely related polymers - for example, those in which the monomer unit differs only by the loss or gain of a methyl or methylene group: most synthetic homopolymers of this related class which are water-insoluble, or at most only water-sensitive, are listed in Table 2.

From a correlation of the contents of these two Tables, it is evident that, in certain cases, the addition of the methyl or methylene group leads either to the complete loss of water solubility (PAA → PMA; PEO → P3MO; PMAA → PMMA; PVME → PVEE) or to a much reduced water solubility (PEO → PPO); however, in numerous other cases, water solubility is still retained on such an addition (PAA→ PMAA; PAAm → PMAAm; PV-OH → PVME; note also PAAm → PDMAAm; PAAm → PIPAAm, and PESA → PPSA, where the degree of substitution is greater), whilst in one case (PEO → POM) it is the loss of a methylene group which leads to the loss of water solubility.

Copolymers, whether they are available commercially or have to be produced by well-defined laboratory methods, give the potentiality of a much wider range of properties which is valuable, both from the scientific and the technological viewpoints. Some examples of synthetic copolymers, which are important in the present context, are listed in Table 3. It should be noted that several commercially available products which are named as homopolymers have, in fact, a copolymer character (e.g. 'PAAm' may actually be PAA-AAm, and 'PV-OH' may be PVAc-V-OH), where even the presence of a minor comonomer may influence the properties of the material in relation to water to a significant extent.

Studies on synthetic copolymers also serve to reveal, in a more sensitive fashion than with homopolymers, the structural features leading to water-solubility or water-insolubility.

Turning to the semisynthetic polymers, the most important examples of these that are water-soluble are the chemically modified forms of cellulose and starch, as listed in Table 4. These polymers are readily available commercially, and extensively used technically: however, they have received relatively little systematic study, and the interpretation and evaluation of those studies which have been carried out is made difficult by uncertainties in the degree of substitution and the distribution of the substitutent groups on the monomer units, and by the wide spread of molecular weight distribution of the commercially available grades of these materials.

As previously mentioned, the natural polymers have been purposely excluded from this review, for detailed consideration. However, it is appropriate to mention these materials briefly: some of the most important water-soluble polymers of this type are noted in Table 5. Many of these materials, indeed, have a wide technical application, often being used in competition, or even in conjunction, with the synthetic and semi-synthetic types. Furthermore, certain of the latter two types are applied as partial substitutes in various medical applications - e.g., as blood plasma extenders. As will be expected, much of the interest in the biopolymers lies in the investigation of their mode of action in their native environment, in cells and organisms; correspondingly, since the same scientific principles must govern the behaviour of all three types of water-soluble polymers, it is anticipated that studies on the synthetic types will lead to the establishment of satisfactory theories of macromolecular behaviour in aqueous systems which can be applied to understanding and clarifying those of the more complex biopolymers.

TECHNOLOGICAL ASPECTS

It is useful to introduce this area by considering an emulsion paint (latex paint) as a typical, and important, example of a water-based formulation containing water-soluble polymers. As is shown in Table 6, even such an apparently simple product as this may involve up to 17 types of constituents, although any one paint formulation will seldom contain all of those listed. In the paint there will therefore be a variety of particles dispersed in the aqueous phase, in which there may be dissolved anything up to three different water-soluble polymers and an even greater diversity of small-molecule solutes. In use, this type of system has to remain chemically and physically stable during extended periods of storage under a variety of conditions, including temperatures

Table 1. Some important water-soluble synthetic homopolymers[1-12]

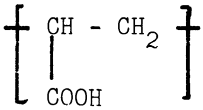
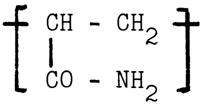
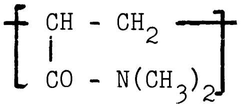
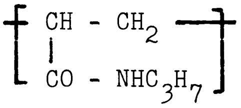
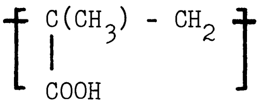
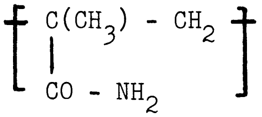
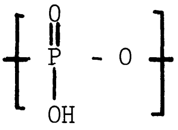
Group	Name	Acronym	Monomer unit	Type[a]
Acrylic Polymers	Polyacrylic acid	PAA	 $\left[\underset{\text{COOH}}{\text{CH}}-\text{CH}_2\right]$	WA
	Polyacrylamide	PAAm	 $\left[\underset{\text{CO}-\text{NH}_2}{\text{CH}}-\text{CH}_2\right]$	NI
	Poly-(N,N-dimethyl-acrylamide)[c]	PDMAAm	 $\left[\underset{\text{CO}-\text{N(CH}_3)_2}{\text{CH}}-\text{CH}_2\right]$	NI
	Poly-(N-isopropyl-acrylamide)[d]	PIPAAm	 $\left[\underset{\text{CO}-\text{NHC}_3\text{H}_7}{\text{CH}}-\text{CH}_2\right]$	NI
	Polymethacrylic acid	PMAA	 $\left[\underset{\text{COOH}}{\text{C(CH}_3)}-\text{CH}_2\right]$	WA
	Polymethacrylamide	PMAAm	 $\left[\underset{\text{CO}-\text{NH}_2}{\text{C(CH}_3)}-\text{CH}_2\right]$	NI
Inorganic Polymers	Polyphosphoric acid (Polymetaphosphoric acid)	PPA	 $\left[\underset{\text{OH}}{\overset{\text{O}}{\overset{\Vert}{\text{P}}}}-\text{O}\right]$	SA
Polyimines & oxides	Polyethylene imine[e]	PEI	$-[\text{NH-CH}_2\text{-CH}_2]-$	WB
	Polyethylene oxide (Polyethylene glycol, Polyoxyethylene)	PEO	$-[\text{O -CH}_2\text{-CH}_2]-$	NI
	Polypropylene oxide (Polypropylene glycol)[f]	PPO (PPG)	$-[\text{O -C(CH}_3\text{) - CH}_2]-$	NI

Table 1. (continued)

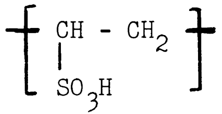
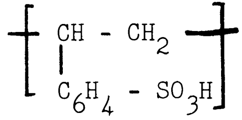
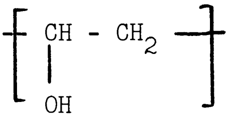
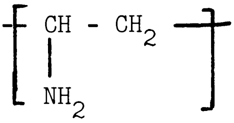
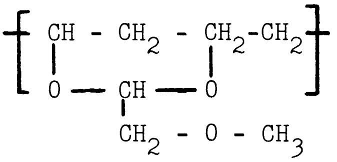
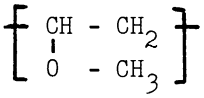
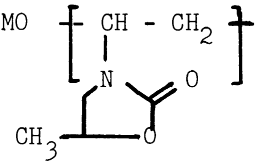
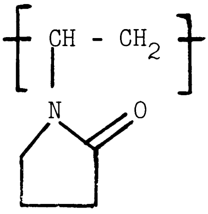
Group	Name	Acronym	Monomer unit	Type
Vinyl Polymers	Polyethylene-sulphonic acid[g]	PESA	 $-[\underset{SO_3H}{CH}-CH_2]-$	SA
	Polystyrene-sulphonic acid[h]	PSSA	 $-[\underset{C_6H_4-SO_3H}{CH}-CH_2]-$	SA
	Polyvinyl alcohol[i]	PV-OH (PVAL, PVAl)	 $-[\underset{OH}{CH}-CH_2]-$	NI
	Polyvinylamine	PVAm	 $-[\underset{NH_2}{CH}-CH_2]-$	SB
	Polyvinylmethoxy-acetal[j]	PVMA		NI
	Polyvinyl methyl ether	PVME	 $-[\underset{O-CH_3}{CH}-CH_2]-$	NI
	Polyvinylmethyl-oxazolidone	PVMO		NI
	Polyvinyl-pyrrolidone	PVP		NI

Table 1. (continued)

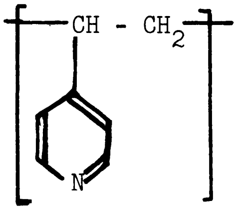
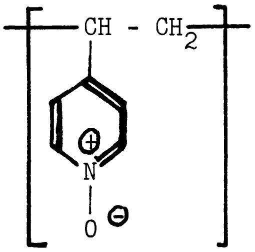
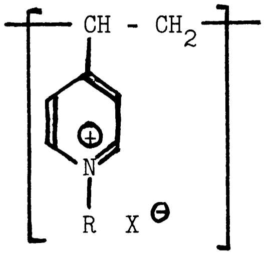
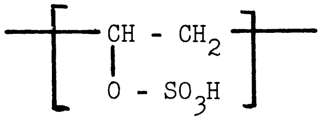
Group	Name	Acronym	Monomer unit	Type
Vinyl polymers (cont.)	poly-4-vinyl pyridine[k,l]	P4VP		WB
	Poly-4-vinyl-pyridine-N-oxide[k]	P4VPO		NI
	Poly-4-vinyl-N-alkyl-pyridinium salts[k,m]	P4VRPX		(SB)
	Polyvinylsulphuric acid[n]	PVSA	 $-[CH-CH_2(O-SO_3H)]-$	SA

Table 1. (continued): Notes

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a NI = Nonionic; SA = strong acid; SB = strong base; WA = weak acid; WB = weak base.

b Many commercial samples of 'polyacrylamide' are chemically modified forms, i.e., either partly hydrolyzed to give PAA-AAm (see Table 3), or, alternatively, modified to give them a cationic character.

c Chosen as a typical poly-(N,N-dialkylacrylamide) which has been studied in some detail[13].

d Chosen as a typical poly-(N-alkylacrylamide) which has been studied in some detail[14].

e Commercial samples of PEI are highly branched.

f Only oligomers of PPO with molecular weights less than about 2000 are water-soluble at normal temperatures.

g Commonly misnamed 'poly(vinylsulphonic acid)', with the corresponding acronym 'PVSA', leading to confusion in both respects with polyvinyl sulphuric acid.

h Samples of PSSA are commonly prepared by sulphonation of polystyrene (PS), where the substitution may be incomplete (i.e., giving PS-SSA - see Table 3) or excessive (giving more than one sulphonate group per ring).

i Many commercial samples of 'polyvinyl alcohol' are copolymers with vinyl acetate - see Table 3.

j Samples of PVMA commonly studied have been obtained from PV-OH with only partial acetalization - see Table 3.

k The corresponding 2-isomers (P2VP, P2VPO and P2VRPX) are also important.

l P2VP and P4VP are insoluble in the un-ionized (non-protonated) form.

m Samples may be only incompletely alkylated forms of the parent polymer (P2VP or P4VP).

n Samples of PVSA are generally prepared by sulphation of PV-OH, often with incomplete substitution (i.e., giving PV-OH - VSA - see Table 3).

Table 2. Some water-sensitive, marginally water-insoluble, and associated synthetic homopolymers.

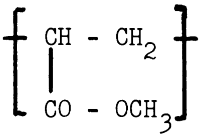
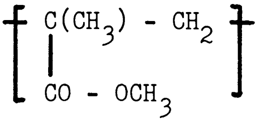
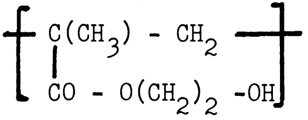
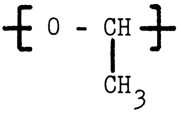
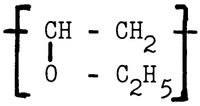
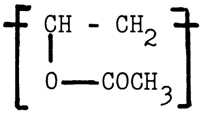
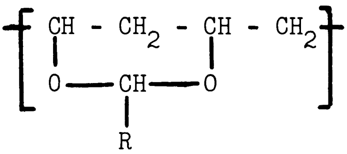
Group	Name	Acronym	Monomer unit
Acrylic Polymers	Polymethyl acrylate	PMA	 $\left[\begin{array}{l} CH - CH_2 \\ \mid \\ CO - OCH_3 \end{array}\right]$
	Polymethyl methacrylate	PMMA	 $\left[\begin{array}{l} C(CH_3) - CH_2 \\ \mid \\ CO - OCH_3 \end{array}\right]$
	Poly(2-hydroxyethyl methacrylate (Poly(ethylene glycol monomethacrylate)	PHEMA (PolyHEMA)	 $\left[\begin{array}{l} C(CH_3) - CH_2 \\ \mid \\ CO - O(CH_2)_2 -OH \end{array}\right]$
Polyoxides	Polyoxymethylene (Polyformaldehyde, Polyacetal)	POM	$\left[O - CH_2 \right]$
	Poly(trimethylene oxide) (Polyoxacyclobutane)	P3MO	$\left[O -(CH_2)_3 \right]$
	Polyacetaldehyde	PAC	 $\left[O - \underset{\substack{\mid \\ CH_3}}{CH} \right]$
Vinyl Polymers	Poly(vinyl ethyl ether)	PVEE	 $\left[\begin{array}{l} CH - CH_2 \\ \mid \\ O - C_2H_5 \end{array}\right]$
	Poly(vinyl acetate)	PVAC (PVAc, PV-OAc)	 $\left[\begin{array}{l} CH - CH_2 \\ \mid \\ O — COCH_3 \end{array}\right]$
	Poly(vinyl acetal)s e.g. formal (R = H) butyral(R = Bu)	PVFo PVBu	 $\left[\begin{array}{lllll} CH & - CH_2 - & CH & - & CH_2 \\ \mid & & \mid & & \\ O & — CH — & O & & \\ & \mid & & & \\ & R & & & \end{array}\right]$

Table 3. Some water-soluble and water-sensitive synthetic copolymers; Poly(m-Co-N).

Monomer M	Monomer N	Common methods of synthesis, special features, etc.
Acrylamide	Acrylic acid	Partly hydrolyzed PAAm: true form of many commercial samples of 'PAAm'.
Acrylic acid	Methyl acrylate	Partly hydrolyzed PMA, or partly methylated PAA.
Ethylene oxide	Propylene oxide	Block copolymers ('Pluronics' are surface active)
Maleic acid	Acrylic acid Alkenes Styrene Vinyl alkyl ethers	Alternating copolymers with maleic anhydride (subsequently hydrolyzed) as Monomer M; ethylene copolymer is the 'head-to-head' form of PAA; depending on the Monomer N, may show conformational transitions on ionization, like PMAA.
Methacrylamide	Methacrylic acid	Partly hydrolyzed PAAm, or by direct copolymerization.
Methacrylic acid	Methyl methacrylate	Partly hydrolyzed PMMA, or partly methylated PMAA; show conformational transitions on ionization like PMAA
Styrene	Styrene sulphonic acid	Partly sulphonated polystyrene; true form of many common samples of 'PSSA'.
Styrene	Vinyl pyrrolidone	Surface active copolymers
Vinyl acetal	Vinyl alcohol	Partly hydrolyzed PV-OH; true form of 'polyvinyl acetals' (methoxyacetal, formal, butyral, etc.).
Vinyl acetate	Vinyl alcohol	Partly hydrolyzed PV-OAc or partly acetylated PV-OH (distribution of comonomers is route-dependent);true form of many commercial samples of 'PV-OH'.
Vinyl acetate	Vinyl pyrrolidone	Water- insoluble forms solubilized by urea, etc.
Vinyl alcohol	Vinyl sulphuric acid	Partly hydrolyzed PVSA, or partly sulphated PV-OH; true form of many common samples of 'PVSA'.

Table 4. Some water-soluble and water-sensitive semisynthetic polymers (modified natural polymers)[2,3,11,12,15]

Cellulose derivatives:-

Simple ethers:

Methyl -	(MC)	
Ethyl-	(EC)[a]	
Hydroxyethyl-	(HEC)	
Hydroxypropyl-	(HPC)	
Carboxymethyl-	(CMC)	(cellulose glycollate)

Mixed ethers:

Ethylhydroxyethyl-	(EHEC)
Ethylmethyl-	(EMC)
Hydroxybutylmethyl-	(HBMC)
Hydroxyethylmethyl-	(HEMC)
Hydroxypropyl- -methyl-	(HPMC)

Oxidized cellulose

Starch Derivatives:-

Starch acetates	(SAC)	
Hydroxyethylstarch	(HES)	
Carboxymethylstarch	(CMC)	(Starch glycollate)

Other ionic starch derivatives : Phosphate, Sulphate, etc.
Oxidized starch (dialdehyde starch)
Aminoalkylstarch and other cationic derivatives.

Note a : Only those grades of ethylcellulose with rather low degrees of substitution are water-soluble at normal temperatures; grades with higher degrees of substitution may be soluble at lower temperatures.

which may range from the subzero to the tropical, and subject to contamination from the container and the atmosphere. Even after this, the paint must have the required rheological properties when it is being applied, whilst it must subsequently form a film which is coherent, adherent to the surface, and have the correct characteristics of colour, texture, weathering properties, and so forth.

Table 5. Some important water-soluble and water-sensitive natural polymers (biopolymers)[2,3,11,12,15]

Polysaccharides:

Acacia (Gum arabic)
Agar and agarose
Alginic acid and its salts
Carrageen (Chondrus; Irish moss) & Carrageenan
Dextran
Dextrin (British gum)[a]
Furcellaran
Ghatti gum
Heparin
Pectins, Pectinic acid, and their salts
Seed gums: Ceratonia (Locust bean gum), Fenugreek,
 Guar gum, Ispaghula, Psyllium, etc.
Starch (Amylose, Amylopectin)
Sterculia (Karaya gum)
Tragacanth (Gum tragacanth)
Xanthan gum

Proteins:

Albumen
Albumins
Casein
Collagen
Gelatins[a]
Enzymes
Gluten
Zein

Note a : Dextrin and gelatin are degraded (i.e., modified) forms of true natural precursors (starch and collagen, respectively)

These requirements illustrate the type of complex, multi-phase, multi-component system into which a water-soluble polymer may be incorporated in practice, also indicating the consequent diversity of reactions and interactions with which scientific concepts and theories must deal if they are to be applicable to the solution of technological problems.

From the more general viewpoint, the important areas of use of water-soluble polymers are listed in Table 7, whilst those applications are further analyzed into the corresponding main functions of the polymers in Table 8. Such an analysis is necessary for any particular application if we are to be able to understand why a polymer should be appropriate for that application, and even

Table 6. Types of constituents of emulsion paints (latex paints)[16]

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1. Water (~50 % of the whole system)[a]
2. Polymer particles (e.g. PV-OAc)[a]
3. Polymerization stabilizer[a,b]
4. Anionic surfactant[a]
5. Nonionic surfactant[a]
6. Polymerization initiator (residual)[a]
7. Pigment particles
8. Extender particles
9. Pigment dispersant[b]
10. Thickener[b]
11. Coalescent/plasticizer (for the polymer particles)
12. Anti-microbial agent (preservative)
13. Corrosion inhibitor
14. pH-Adjuster
15. Anti-foaming agent
16. Anti-freeze
17. Thixotropic agent

<u>Note</u> a : Constituents 2 - 6, and at least part of the water (Constituent 1), derive from the parent emulsion polymer latex.

b : Water-soluble polymer.

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more so when we have to decide which polymer would be suitable for solving some problem encountered with an established product, or for use in an entirely new type of product.

However, in correlating the contents of these two tables, it should be borne in mind that any one polymer may (from chance, or from design) fulfil a number of different functions at the same time - for example, in a disperse system such as an emulsion paint it may serve both to thicken or gel the continuous phase, and also, at the same time, it may have a more direct effect on stability by being adsorbed on to the particles. Furthermore, the polymer may have different functions at different stages in the 'life history' of the product - for example, incorporated into tablets of a drug, it will act in the essentially anhydrous state as a binder up to the point when the tablet is taken by the patient, whereupon it will go through various stages of swelling and dissolution by the body fluids as the tablet disintegrates, and the drug is absorbed by the body. Moreover, polymers may have unwanted functions - for example, they may complex in solution with small-molecule components (anti-microbial agents, anti-oxidants,

Table 7. Areas of use of water-soluble polymers[2,3,12,16]

1. Adhesives, bonding agents and glues
2. Agricultural and horticultural products
3. Asphalt emulsions and pitches
4. Bacteriological and microscopy media
5. Beverages and foods
6. Cements, concrete, plasters, ceramics and glazes
7. Containers and packaging
8. Cosmetics and toiletries
9. Detergents, emulsifier formulations, and laundry products
10. Dyeing pastes and other textile-treatment products
11. Electroplating and electrorefining solutions
12. Emulsion polymerization latices and related products
13. Explosives
14. Fire-fighting additives
15. Foamed-plastic products
16. Hydraulic fluids and lubricants
17. Inks, paints, and other surface coatings
18. Leather processing
19. Lithographic and reprographic materials
20. Marine and naval applications
21. Metal production and processing
22. Mining and mineral processing
23. Oil-well drilling and oil-recovery
24. Paper, paperboard and wallboard production
25. Pharmaceutical, dental and related products
26. Photographic films and related products
27. Scientific studies and laboratory techniques
28. Tobacco products
29. Water treatment (ground water, boiler-feed water, waste water, effluents, and sewage).

detergents, drugs, etc.), possibly reducing the activity of the component below the level desired; again, the water-soluble polymers serve a variety of useful functions in the paint as such (Table 6), but their consequent presence in the final paint film may have disadvantages, such as too great a hydrophilic character, and too ready a permeability to water vapour.

SCIENTIFIC ASPECTS

If we are to maintain the interplay between technology and science, the functions of these materials need to be further analyzed systematically into their physical and chemical features.

Table 8. Some functions of water-soluble polymers in their uses

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1. Thickening and gelling: bacteriological and microscopy media; cosmetics and toiletries; drilling muds for oil production; dye pastes (textile printing); foods; glazes; inks; latices; lubricants; paints; pharmaceuticals.
2. Stabilizing agents and suspensions: cosmetics and toiletries; detergent formulations; drilling muds for oil production; emulsion polymerization; foods; glazes; inks; paints; pharmaceuticals.
3. Flocculating and clarifying suspensions; beverages; mineral processing; water treatment.
4. Coatings, films and sheets: laundry bags; mould release agents; oil-resistant films; packaging (single-dose products); photographic films; temporary protective coatings; textiles (warp-size agents).
5. Solid-solid bonding; adhesives; agricultural and horticultural sprays; cements; ceramics; explosives; fertilizers; foundry cores and moulds; hair sprays; leather processing; paper production; pharmaceuticals.
6. Moisture retention (humectants): foods; leather processing; tobacco products.
7. Osmotic effects: blood-plasma substitutes; cryoprotectants.
8. Complexing: dye-levelling and dye-stripping (textiles); pharmaceuticals; tannin precipitation (beverages).
9. Turbulent-flow drag reduction: fire-fighting,marine and naval applications.
10. Crystal-growth modification: cryoprotectants; electroplating and electrorefining; foods; pharmaceuticals.

Table 9. lists the features which are important, in their experimental and theoretical implications, for the linking of scientific studies to technological applications. Many of these features are indeed common to all polymers, whether water-soluble or not, but it is nevertheless useful to have an extensive listing of this kind for the present more limited area.

Certain of these features have already been discussed as they apply to water-soluble synthetic polymers[6], and this particular area will receive more extensive treatment in a forthcoming monograph[7].

One feature mentioned in Table 9 which may not seem to be important in the present context is that of the solid state properties and behaviour. However, it should be remembered that, in many of their uses, these polymers start out in the solid state (e.g., in packaging applications for single-dose products), or finish up in the solid state (e.g. adhesives). Moreover, the values of the glass transition temperature, t_g, and the melting point, t_m, of these polymers are also important in drying, since the polymer has to be heated above either of them to optimise removal of the last traces of water - this is a limitation in attempts to use microwave heating for this purpose. Solid state properties also influence the water-sensitivity of the polymer - thus the apparently anomalous insolubility of POM is the consequence of strong crystal lattice forces involving the favourably oriented C-O dipoles, whilst the apparently paradoxical increase in the water-sensitivity of PV-OH on introducing a few hydrophobic acetate groups (especially marked if they are randomly distributed in the chains) is the result of their disruption of the crystal lattice of the solid homopolymer.

INTERACTION FORCES

The observed behaviour of these systems, i.e., that at the macroscopic level, will be controlled by that at the molecular level, particularly by the types and the relative strengths of the covalent forces between the various molecules and the molecular grouping present.

In the case of the solid polymer, poly(M), these are simply the interaction forces between the neighbouring (non-bonded) 'mer' units, which can be symbolized $M \sim M$; however, these will be different in any amorphous regions present from those in any crystalline regions (and in the second case they will also depend critically upon the lattice structure), so that the average energy (which determines, amongst other features, the water--sensitivity of the solid) will depend upon the structures and extents of these two types of regions.

When the polymer is dissolved in a solvent S, there will then be three main types on interaction, i.e., $M \sim M$, $S \sim S$ and $M \sim S$. Aqueous solutions of polymers (and, indeed, those of other solutes also) are often viewed as if they were controlled by effects which are different in principle from non-aqueous solutions; this viewpoint is apparently supported by the fact that, whilst the normal behaviour of non-aqueous polymer solutions is endothermic, dilution, and, consequently, precipitation of the polymer occurs (where it occurs at all) on cooling . The same behaviour is also shown by the aqueous solutions of a few polymers (e.g. PAA, PAAm, PMAAm), but in most other cases of aqueous polymer solutions, the dilution is exothermic and any precipitation occurs on heating.

Table 9. Physico-chemical features of water-soluble polymers

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1. <u>Chemical features</u>
    - Synthesis reactions and their consequences
        - Rate and mechanism
        - Stereoregularity
        - Molecular-weight averages and distribution
        - Structural irregularities (end-groups, branching, etc)
    - Modification and conversion reactions
        - Copolymers from partial reaction
        - Route dependence of comonomer distribution
    - Chemical and biochemical degradation
        - 'Ageing effects' (especially high molecular wt. samples)
        - Inhibition of degradation in use
        - Environmental aspects
        - COD (Chemical Oxygen Demand)
        - BOD (Biochemical Oxygen Demand)
2. <u>Practical features</u>
    - Purification
        - Common contaminant
        - Solvent/non-solvent precipitation
        - Exhaustive dialysis
        - Electrodialysis (especially polyelectrolytes)
        - Chromatography (gel filtration, ion exchange, etc.)
    - Fractionation
        - Solvent/non-solvent fractionation
        - Gelfiltration chromatography
    - Handling
        - Avoidance of moisture pickup
        - Polyacids - contamination from metals, glass, etc.
        - Polybases - contamination from CO_2, etc.
3. <u>Structural and analytical features</u>
    - Characterization
        - Molecular weight averages
        - Molecular weight distribution
        - Stereoregularity
    - Identification
        - Physical methods
        - Chemical methods
    - Analysis of solid samples
        - Polymer content
        - Water content
    - Analysis of solutions for polymer content
        - Evaporation
        - Precipitation
        - Refractometry
        - Titration (especially polyelectrolytes)
        - Turbidimetry
        - Coloured complexes

Table 9. (continued).

Analysis of solutions for polymer content (cont.)
- Complex coacervates
- Spectroscopy (especially UV for aromatic complexes)

Copolymers
- Composition
- Comonomer distribution

4. Solid state properties

Physical and mechanical properties
- Density
- Elastic modulus, tensile strength, etc.
- Glass transition temperature, t_g (amorphous fraction)
- Melting point, t_m (crystalline fraction)

Crystallinity/amorphosity
- Relative extents of two forms
- Lattice structure of crystalline fraction

Spectroscopic and dielectric properties

Uptake of gases and vapours
- Equilibrium and thermodynamics (especially H_2O)
- Permeation kinetics (especially H_2O, O_2, CO_2)

Solid state complexes
- Amorphous complexes (e.g. PVP + I_2, drugs,...)
- Crystalline complexes (e.g. PEO + urea, drugs,...)

5. Solution behaviour (other solutes absent)

Aqueous solutions (dilute, concentrated, gels)
- Volumetric and thermdyanamic aspects
- Refractive index
- Viscosity and rheology
- Conformational effects
- Gelation behaviour

Non-aqueous solutions
- Comparison with aqueous solutions
- Uses (purification, characterization, etc.)

Mixed (aqueous + non-aqueous) solutions
- Comparison with aqueous solutions
- Preferential solvation
- Uses (purification, fractionation, etc.)

Partition behaviour (aqueous/non-aqueous systems)
- Relative solvent affinities
- Uses (especially polymer separation)

Solubility behaviour (phase equilibria)
- Effect of crystallinity and lattice forces in solid
- Comonomer distribution in colpolymers

Polyelectrolytes
- Ionization of polyacids and polybases
- Counterion binding in polysalts

Table 9. (continued).

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6. Solution binding with small-molecule cosolutes
    - Low cosolute concentrations (< 0.1 - 1 M.)
        - Specific effects (cosolute binding)
        - Binding isotherms
          Examples: detergents, drugs, dyes, I_2/I_3^-,...
    - High cosolute concentrations (> 0.1-1 M)
        - Generic effects ('salting out', etc.)
          Examples: simple salts, alcohols, ...
7. Solution interactions between polymers
    - Phase separation between polymers
        - Role of excluded volumes
        - Role of interaction forces
    - Phase separation by complex coacervation
        - Polyelectrolyte complexes
        - H-Bonded complexes (PEO, PVP, ... + PAA, PMAA, ...)
    - Homogeneous systems
8. Interfacial behaviour
    - Air/water interface
        - Adsorbed films
        - Spread films
    - Water/non-aqueous liquid interface
        - Adsorbed films
        - Spread films
        - Use in polarography (maxima suppressors)
        - Stabilization of emulsions
9. Water/solid interface
    - Adsorbed films (trains, loops, tails)
    - Adsorption isotherms
    - Anchored films
    - Effects on the stability of suspensions
    - Stabilization (e.g. 'steric' stabilization)
    - Destabilization (flocculation, coagulation, sensitization).

However, for all solutions, the observed behaviour is the result of a balance (often a delicate one) between the three types of interaction, involving the equilibrium

$$M \sim M + S \sim S \rightleftharpoons 2\ M \sim S$$

and only a small shift in this balance is needed for the behaviour to move from the 'normal' (nonaqueous) to the 'abnormal' (aqueous) type.

When a small molecule cosolute, A, is also present, then, in addition to the three types of interaction listed there will be tow more, i.e. A ~ S and A ~ M. When the A ~ M interaction is strong (relative to A ~ S and M ~ S) then even at low cosolute concentrations this can lead to 'specific effects', i.e., to binding (complexing) of cosolute to the polymer chain (although in practice this may involve a sequence of 'mer' units either 'chelating with' or 'enveloping' the cosolute molecule). Where no such direct interactions can take place, the 'generic effects' which appear only at higher cosolute concentrations probably arise indirectly from the perturbing effect of the cosolute molecule on the three original types of interaction.

With two polymers, poly(M) and poly(N), in the system with solvent S, then again the three basic interactions already listed will be joined by two others, i.e. M ~ N and N ~ S . Again, the observed behaviour will be the results of the balance between the five types of interaction force involved. Similarly, for a polymer 'poly(M)' at an interface I, there will be two extra types of interaction, I ~ M and I ~ S, and again the behaviour observed will be the result of the balance between the total of five types of interaction.

Even the picture outlined above will be a simplification of the true state of affairs, since these interactions will themselves be complex, being composed of various types of component noncovalent interactions (e.g. ion-dipole, ion-ion, van der Waals, hydrogen bonds, hydrophobic interactions) appropriate to the groups involved. Furthermore, these interactions must be expected to be sensitive at least to the immediate environment of the interacting pair. Thus, even in the case of a simple polymer solution, the strength of the M ~ S interaction must be expected to differ when the surroundings are the solvent molecules (i.e. in dilute polymer solution) from those when they are 'mer' units (i.e. in the uptake of solvent vapour by the solid polymer); this will be particularly marked where the solvent is water.

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THE RHEOLOGICAL CHARACTERIZATION OF CONCENTRATED SOLUTIONS AND GELS OF WATER-SOLUBLE POLYMERS

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INTRODUCTION

Rheology is the science of deformation and flow of matter under stress. Traditionally, the subject has been of interest in two different ways[1]. Physicists and mathematicians have been interested in the subject mainly from a behavioural point of view. If a rheological equation of state for the system of interest can be formulated which can reconstruct the rheological behaviour of that system under any deformation or flow regime in any apparatus, the goal is deemed to have been achieved. Since the behaviour in this sense need not be related to any particulate or molecular structure, it has been convenient for these rheologists to use continuum mechanics models for their analyses. However, another group of rheologists, e.g. chemists, physical biochemists, pharmacists, and food and paint technologists has sought to relate rheological behaviour to the physical chemistry of the system of interest. It is now widely considered that these two approaches can be reconciled and this will be discussed.

The present Chapter will be treated from the point of view of chemical structure related to rheology.Although the brief is a discussion of the rheology of water soluble polymers, it is considered that there is no particular virtue in restricting the discussions to specific instances of water soluble polymer behaviour where more general models are basically considered by theoreticians. If we remember that the solvent is not unimportant even in the rheology of silute solutions in the general solvent case, we have the added complication that, with water as a solvent, ions, and particularly H^+,OH^-, and the common alkali and alkaline earth metal ions play a crucial role. Molecular biologists have hitherto ignored the role of rheology as a controlling influence in cell processes which involve the shearing of macromolecular species in the concentrated cytoplasm.

When we move to concentrated solutions and gels the situation beomes very complex and a complete analytical solution is quite impossible. All we can do is look at the trends, where, in the usual scientific tradition, we keep all the variables constant except one, and gradually map out the entire behaviour in multidimensional space. Unfortunately, as indicated above, the number of variables is immense. We have, first, the chemical variables: polymer concentration; mean molecular weight; a dispersion of molecular weight index; the degree of chain branching; the degree of ionization (for electrolytes); solution pH; prevailing ionic strength, and the temperature.At the same time, we can vary the following rheological parameters: the shear stress; shear; shear rate: for continuous time assessment or under dynamic conditions we can input a small sinusoidally varying quantity of either stress or strain and monitor the other. We can even superimpose a small sinusoidal disturbance on continuous shear[2]. Added to all of this, we can have very complex behaviour in time.

Most concentrated solutions of polymers and their gels exhibit the phenomenon of viscoelasticity. In simple terms, this means that their inner structure displays a spectrum of characteristic times. These are expressed either as relaxation times or retardation times. The polymer system only comes to equilibrium during rheological investigation when the experiment has been conducted for a time significantly longer than the longest characteristic time. However, the simple type of viscoelastic behaviour does not display any experimental evidence of long term change in the system. When the test sample is allowed to recover it behaves in the same way again. On the other hand, many systems of interest to the industrial technologist, particularly water soluble polymers in concentrated solution, and their gels, undergo long term ageing, which is irreversible. Again, this ageing is of two kinds; it can be quite independent of the rheological treatment[3] where it is due to chemical change - e.g., cross linking, or enzymatic or other degradation. It can also be brought about by the rheological investigation itself.

It would be helpful to conclude this section with some elementary definitions: for a more detailed description the reader is referred to a standard rheological text or, in particular, to the handbooks produced for previous Postgraduate Schools of the Royal Society of Chemistry[4,5] .

Stress

The physical components of the stress tensor are nine in number and are denoted by σ_{ij} where i and j are cycled through 1 to 3. Stress is directed force (a vector) per unit area and the direction in space of the element of area is defined by the direction of its unit normal. Most rheological investigations are carried out under shear, where i $\neq$ j and although in principle there will be six different possible values, for isotropic materials there is usually only one, designated τ. The SI units for stress are Nm^{-2} or mNm^{-2}.

Strain

A similar argument can be upheld for strain. The shear components of strain are usually just referred to as shear γ. Strain is dimensionless. RATE OF STRAIN is $d\gamma/dt$ or simply γ. The units are s^{-1}..

Shear modulus

$$G = \tau/\gamma \quad Nm^{-2} \text{ or } mNm^{-2}$$

Newtonian viscosity

$$\eta = \tau/\gamma \quad Ns\ m^{-2} \text{ or } mNs\ m^{-2}$$

(It is interesting to note that, in the old CGS units, a centipoise is exactly equivalent to 1 mNs m^{-2} (SI); also, the viscosity of water at 20°C is almost 1 centipoise.)

Time functions

Under constant stress, the time dependent function of shear sodulus G(t) and its inverse function J(t) = 1/G(t), the time dependent shear compliance are also important.

Dynamic moduli

Under sinusoidal conditions of pulstance ω rads s^{-1} ($2\pi \times$ frequency) it is possible to define three dynamic functions[6].

$$G^{*}(\omega) = G'(\omega) + iG''(\omega)$$

$$J^{*}(\omega) = J'(\omega) - iJ''(\omega)$$

$$\eta^{*}(\omega) = \eta'(\omega) - i\eta''(\omega)$$

These quantities are two dimensional vectors in the general complex plane u + iv and the negative sign associated with the last term in the latter two arises directly as a consequence of the first definition.

Surface parameters

For those interested in very thin films of water soluble polymers (Ref.[5], pp. 186 - 206), the specialism of surface rheology may be of interest. Here, the above-mentioned parameters usually carry a subscript 's' and will have one less spatial dimension - e.g., J_s $m(mN)^{-1}$ for the surface compliance.

Rheological techniques

A variety of instrumental techniques is available for the materials of present interest. In a short chapter, it is not possible to give an exhaustive account but the important principle will be mentioned. The fundamentals behind the design of rheometers have been discussed in depth by Walters[7] and the instrumental techniques specific to the investigation of viscoelasticity are reviewed by Ferry[6]. Industrial techniques have been reviewed by Sherman[8], who has more recently made special reference to the food industry[9]. Surface rheological techniques have been considered by Warburton in Ref.[5] (pp.186 - 206). General techniques have also been adequately covered in the handbooks of previous Postgraduate Schools of the RSC[4,5].

INTERPRETATION OF RESULTS

Concentrated solutions

Concentrated solutions of water soluble polymers are, with few exceptions, non-Newtonian in flow properties. One of the earliest attempts to find a rheological equation of state for disperse systems was due to Ostwald in 1925[10]:-

$$\gamma = 1/\eta_p(\tau)^n$$

where η_p is a parameter corresponding to viscosity and n is some measure of internal structure. n equals one for Newtonian fluids and may be evaluated by taking logarithms when the expression is transformed into a linear equation. n has been referred to as the 'flow index', and it is clear that, when $n > 1$, the apparent viscosity increases with shear stress and when $n < 1$ it decreases with shear stress. For most concentrated polymer solutions, n is less than one and the shape of the apparent viscosity/shear rate curve is that shown in Figure 1.

Probably the most fundamental early approach to the problem of non-Newtonian viscosity based on the theory of chemical rate processes was put forward by Ree and Eyring in 1955[11].

This was based on an early theory of Glasstone et al. in 1941[12]. The Ree and Eyring theory has been applied to both emulsions and concentrated polymer solutions. Most systems can be simulated with three unit mechanisms. The rate processes are designated by hyperbolic sine functions of the shear rate, giving:-

$$\eta(\dot{\gamma}) = \sum_{n=1}^{3} (x_n/a_n)\sinh^{-1}(\beta_n\dot{\gamma})$$

Even with three basic mechanisms, the first of which is usually Newtonian, the rheological properties of the system will be characterized by nine constants:- x_1, a_1, β_1 ..... x_3, a_3, β_3. The curve fitting process to the experimental data is non-trivial and for statistical significance there would need to be at least 40 - 50 raw data per experiment.

From the experimentalist's point of view, the pseudo-plastic flow equation due to Cross in 1965[17] is more tracable and is based on a reasonable molecular model, giving a good fit to many sets of data for water soluble polymer solutions. Although Cross's original intentions were for the equation to be applied to the rheology of disperse particulate systems, the theoretical derivation makes it equally applicable to concentrated water soluble polymer solutions. The derivation of the equation rests on the argument that the flow entities, in this case macromolecule, can aggregate to form chains. The apparent viscosity of the ensemble of chains at a shear rate γ, is given by:

$$\eta(\dot{\gamma}) = \eta_\infty + BL(\dot{\gamma})$$

where B is a characteristic constant and $L(\dot{\gamma})$ is the length of the chain at the prevailing shear rate. η_∞ is the limiting viscosity at high shear rates. It is further conjectured that at any particular shear rate, the length of the chains is a dynamic constant determined by equal and opposite aggregation and de-aggregation kinetics. The aggregation process is only due to Brownian motion, whereas deaggregation is due to two mechanisms, one spontaneous and the other governed by the shear rate raised to an even power. The latter is a necessary restriction since the direction of shear is unimportant but the characteristic index of shear rate n does not need to be an integer and can be expressed as a fraction n = 2/m. This leads to the expression

$$L/L_o = 1/(1 + \alpha'(\gamma)^n)$$

where L_o is the length of the aggregated chain when the shear rate is zero and α' is a constant for the system. This leads to a final expression for the apparent viscosity:-

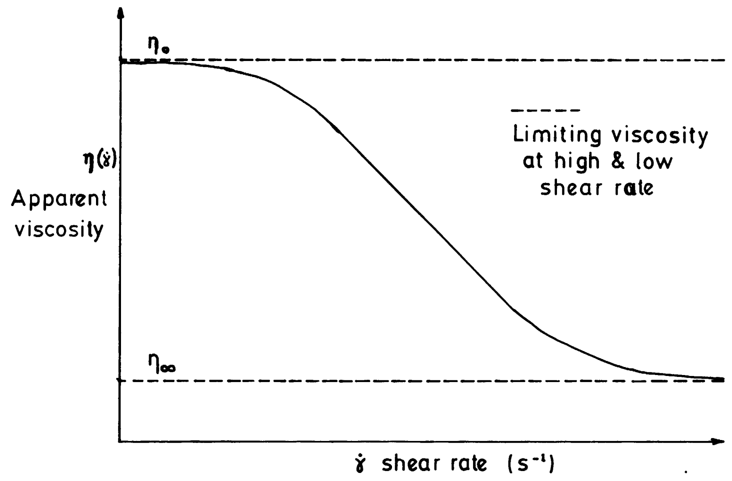

Figure 1. General dependence of apparent viscosity on shear rate for water-soluble polymer solutions.

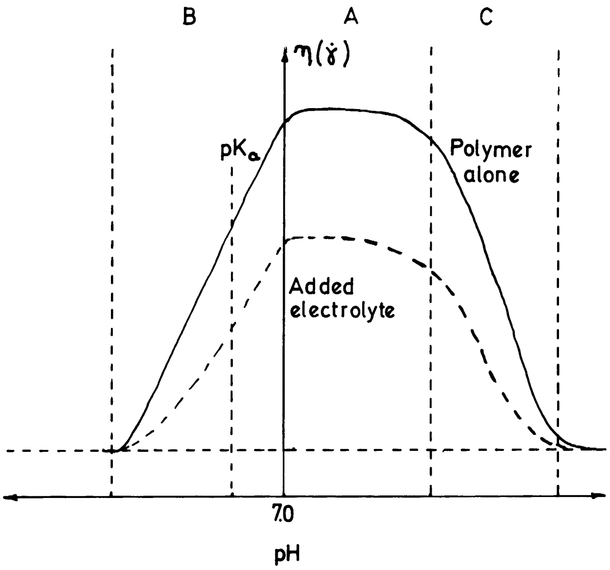

Figure 2. General dependence of apparent viscosity on hydrogen ion concentration and ionic strength for polyelectrolytes.

$$\eta(\dot{\gamma}) = \eta_\infty + (\eta_0 - \eta_\infty)/(1 + \alpha'(\dot{\gamma})^n)$$

For plotting purposes, and in order to evaluate parameters α' and n, which characterize the material, Cross suggests that, at high shear rates:-

$$\eta(\dot{\gamma}) - \eta_\infty \rightarrow (\eta_0 - \eta_\infty)/ (\alpha'(\dot{\gamma})^n)$$

hence, if η_∞ can be estimated, a plot of log $(\eta(\dot{\gamma}) - \eta_\infty)$versus $\log(\dot{\gamma})$ should give a straight line of slope n and intercept log $(\eta_0 - \eta_\infty)/ \alpha')$ on the ordinate.

When the water soluble polymer is a polyelectrolyte, pH and ionic strength play a dominant role at all shear rates. It is now no longer possible to display the whole rheological behaviour at one polymer concentration on a two dimensional graph. If we assume that,at a fixed shear rate the size of the polyelectrolyte molecule is a function of the degree of ionization α, (α is in no way related to α' above) we can,at least qualitatively, sketch out the shape of the apparent viscosity/pH relationship for, say, an anionic polyelectolyte (see Figure 2.).

In region A of this Figure,the ionic strength is assumed to be low, but, as hydrogen ions are added to the ionized polymer, the degree of ionization is gradually depressed, according to the approximate relationship

$$\mathrm{pH} = \mathrm{p}K_a + \log(\alpha/(1 - \alpha))$$

Ideally, a separate value for the $\mathrm{p}K_a$ should be used for each acidic site in the polyelectrolyte, but this is impracticable. However, if, as is often the case, all the sites represent, say, the same uronic acid and equivalent weight of the polyelectrolyte is quite high, e.g. >1000, the above simple expression operates well. Thus, as we progress into further acidity, in region B, the polyelectrolyte molecule, originally over-extended due to the attached anionic charges, will contract, lowering the apparent viscosity. However, there is another mechanism by which the polyelectrolyte molecule will contract - the formation of a strong ionic atmosphere around the ionic sites as the ionic strength is increased. So, if we start again at pH 7 and add hydroxyl ions, and, of course, the metal ions that go along with them, the ionic strength will build up, the polyelectrolyte sites will be shielded and the molecule will contract, giving the region of falling apparent viscosity C in Figure 2. Of course, if the ionic strength is maintained high over the entire pH range, the overall height of the curve will be lowered, as shown with the dotted curve.

In fact, the fully ionized and unshielded polyelectrolyte molecule will always have a larger relative viscosity than a corresponding uncharged polymer in solution and the degree to which its viscosity will be unchanged will depend on three main considerations:-

(i) the degree of substitution of the ionic sites;
(ii) the flexibility of the polymer chains;
(iii) the amount of entanglement between the neighbouring chains.

POLYMER NETWORKS

Most of the classical work on gels of water soluble polymers was carried out on gelatin gels by Ferry[14] and Ward and Saunders[15]. Static values of the shear modulus of gels may be obtained using a formula almost identical to Poiseuille's Law of capillary flow. The gel is cast in the lower part of a U-tube and pneumatic pressure is applied to one limb. The deflection of the meniscus of the gel gives the shear modulus G directly[16]. If the frequency dependence of the dynamic shear modulus G* is required, transverse shear wave propagation can be used, as shown by Ferry[17] and by Goodwin[18]. If the fraction of the critical damping distance travelled by the shear wave during one oscillation is small, then

$$G' = V^2\rho$$

where ρ = the density of the gel, and V is the velocity of the wave propagation through it. Measurements of both the static modulus and the real part of the dynamic modulus show that gels usually increase their rigidity with time, eventually reaching an equilibrium value G_∞ after a very long time. The shear modulus of gelatin gels appears to be approximately proportional to the square of the polymer concentration, according to Cumper and Alexander[19], whilst they show that these gels are weakened by the increase of ionic strength, I :-

$$G_o = G (1 - 0.77 \sqrt{I})$$

G_o is the modulus of the gel without salt. Sucrose and glycerol increase the rigidity of the gel. Plots of $G/(\text{conc.})^2$ for gelatin fall off almost linearly with temperature, becoming zero at 30^o. The shear modulus of gelatin gels is very dependent on molecular weight. Ferry[20] found that

$$G^{\frac{1}{2}}/(\text{conc.})$$

was a linear function of molecular weight, being approximately zero below a molecular weight of 20,000.

Recently, some work on the rigidity of polysaccharide gels has been carried out by Mitchell and Blanchard[21], particularly for gels of alginate and pectate. Experimentally, they have measured the Young's Modulus E of cylinders of the gels in compression, using an Instron Model 1140. Making fundamental calculations of the Helmholtz free energy F as a function of the distribution function W(r) of the end-to-end length for the chain vector, $\underline{r}$, they found that the chains only obey Gaussian statistics if the degree of polymerization is greater than 1000. Agreement between theory and experiment is good.

SURFACE AND INTERFACIAL RHEOLOGICAL BEHAVIOUR

The surface rheology[5] of water soluble polymers is proving to be of great interest in the investigation of both emulsion stability and the architecture of microcapsules[22]. Water soluble polymers in solution tend to be adsorbed at both aqueous/air and aqueous/oil interfaces. Although the polymers are hydrophilic in nature, and would not be expected to be surface active, nevertheless the polymer chains in solution normally carry a sheath of loosely attached aligned water which can be discharged at the interface. This will happen when the polymer chains hit the interface in the course of ordinary random kinetic motion. This leads to an overall increase in the entropy ΔS_s for the system polymer-water at the interface and a consequent lowering of the surface free energy ΔG_s according to the thermodynamic relationship:-

$$\Delta G_s = \Delta H_s - T.\Delta S_s$$

where ΔH_s is the change in surface enthalpy (generally) small and T is the absolute temperature. Hence, the polymer absorption is thermodynamically favourable. For moderately concentrated polymer solutions, up to, say, 5 % w/v, the surface of interfacial polymer films are essentially molecular multilayers. The surface rheological techniques are particularly useful in detecting whether the interfacial film is elasticoviscous (LIQUID) or viscoelastic (SOLID) in nature. It was originally thought that all elasticoviscous films were rheologically stationary in nature. This would have meant that, after the initial film formation by diffusion from the bulk, which is 90 % complete in the first 5 - 10 minutes, there could have been no further change. However, recent work on a polyelectrolyte containing carboxylate residues[23] has shown that further pH dependent changes in film surface viscosity can take place for a further time of more than half-an-hour. This is thought to be due to a change in the dielectric environment for the polyelectrolyte chain in going from the bulk to the surface.

Most of the viscoelastic (SOLID) interfacial films so far investigated are decidedly non-stationary in nature (i.e., 'growing' films) and, although a successful kinetic theory has been published specifically for biopolymers[24], there is no reason to believe that the theory, which is entirely general in nature, would not apply to all water soluble polymers.

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METHODS OF POLYMERIZATION FOR PREPARATION OF WATER-SOLUBLE POLYMERS

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INTRODUCTION

Water-soluble polymers may be grouped under three main headings:

(i) naturally occurring;

(ii) semi-synthetic, in which inherently insoluble polymers are modified by suitable chemical treatment in order to disturb their normal structures and enhance their interaction with water;

(iii) completely synthetic polymers which are produced by condensation, addition, or ring-opening polymerization.

The most commercially important examples of this group are the polymers of acrylamide and its C- and N-substituted derivatives, acrylic and methacrylic acids, N-vinyl amines, cyclic and vinyl ethers. The present chapter will deal with completely synthetic polymers and, in view of their commercial importance and the considerable amount of work published, will concentrate mainly on the free radical polymerization of the acrylamides, and acrylic and methacrylic acids, with the aim of describing the present state of the art, discussing, where possible, the chemical principles involved.

Such polymerizations are generally assumed tofollow the usual sequence of initiation, propagation, chain transfer, and termination steps. Conventional kinetic analysis leads to the usual. relations:

$$R_p = -d[M]/dt = \frac{k_p}{k_t^{\frac{1}{2}}} \cdot R_i^{\frac{1}{2}}[M]$$

and

$$(\bar{P}_n)^{-1} = (\bar{P}_{n_o})^{-1} + C_m + C_i\frac{[\text{Init}]}{[M]} + C_s\frac{[S]}{[M]}$$

where R_p and R_i are the rates of polymerization and initiation, respectively, k_p and k_t are the velocity coefficients for propagation and termination, C_i, C_m and C_s are the transfer constants for initiator, monomer and chain transfer agent at concentrations of $[\text{Init}]$, $[M]$, and $[S]$ respectively. $\bar{P}_{n_o}$ and $\bar{P}_n$ are the number average degrees of polymerization in the absence and presence, respectively, of chain transfer agent.

The actual relationships observed in practice are, of course, strongly influenced by the various complicating factors which occur. Typical examples of such effects are radical caging, radical and monomer complexing, conformational effects in the growing chains, degradative transfer, the nature of the initiation step, etc. Complicating effects are frequently encountered in copolymerization as well as in homopolymerization, and have been the subject of much study and speculation.

A considerable effect is also exerted by the polymerization temperature. This is further complicated if the polymerization is carried out under approximately adiabatic conditions, as is often the case. For polymerizations obeying the above equations, it is easily shown that:

$$E_{ov} = E_i/2 + E_p - E_t/2$$

where E_i, E_p, E_t and E_{ov} are the energies of activation for initiation, propagation, termination and the overall polymerization respectively. The value of $E_i/2$ is usually considerably greater than that of $(E_p - E_t/2)$, so E_i makes a very significant contribution to the value of E_{ov}. A high value of E_i, coupled with a high heat of polymerization, therefore leads to considerable temperature variation if a polymerization is carried out under approximately adiabatic conditions. This, in turn, significantly affects the polymer degree of polymerization, and its distribution.

ACRYLAMIDE

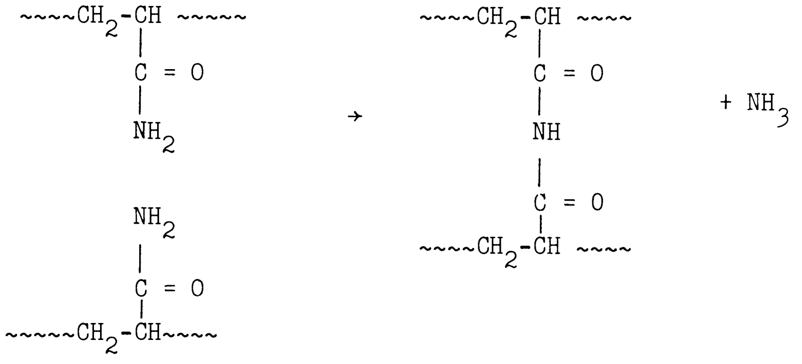
Acrylamide and its C- and N-substituted homologues readily polymerize by free radical mechanisms in the absence of oxygen. Several detailed literature reviews of the subject have appeared[1-10].

At high pH, anionic initiation yields poly-β-alanine (nylon 3) by a hydrogen-transfer mechanism[11]:

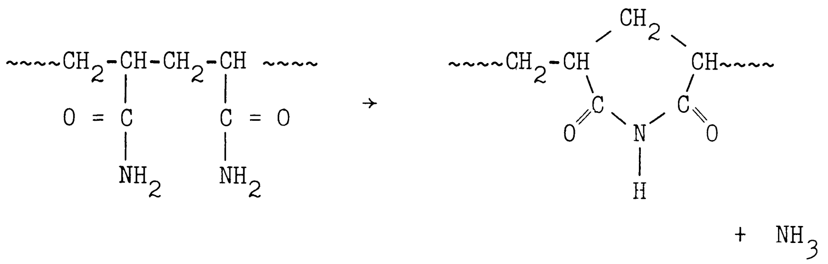
$$\mathrm{B{:}^{\ominus}} + \mathrm{CH_2{=}CH{-}CO{-}NH_2} \rightarrow \mathrm{B{-}CH_2{-}\underset{\cdot\cdot}{\overset{\ominus}{C}}H{-}CO{-}NH_2} \rightarrow \mathrm{B{-}CH_2{-}CH_2{-}CO{-}\underset{\cdot\cdot}{N}\overset{\ominus}{H}}$$

etc.

At low pH and high temperature, imidization occurs[12]:



If intermolecular imidization occurs, the product is insoluble, but this is not necessarily the case if the reaction is intramolecular:



INITIATION METHODS

The major methods of free radical initiation are:

(i) thermal or photolytic decomposition of an initiator (sometimes in the presence of a promoter);

(ii) redox initiation;

(iii) physical excitation of monomer in bulk or solution.

Photolytic decomposition often presents practical problems: thermal decomposition of a heat-sensitive compound is usually preferred. Unfortunately, however, common initiators require the use of temperatures rather higher than are convenient for easy dissipation of heat resulting from the relatively high exothermicity of an acrylamide polymerization[13] ($\Delta H = - 82.8$ kJ mol^{-1} in aqueous solution). One method of overcoming this problem is by the addition of a 'promoter' which lowers the energy of activation of the decomposition process, thus giving higher rates and a lessened temperature dependence. An equivalent approach is to use a redox initiation system. The individual components of the latter system are quite stable but react rapidly when mixed at relatively low temperatures. The major difficulty with such systems is the rapid disappearance of the redox system components and the possoble effect of chain transfer, etc., on the degree of polymerization of the product. Rapid consumption of redox initiator components may lead to a cessation of polymerization before complete conversion of monomer to polymer. Continuous addition of the redox components is not usually possible because of the high viscosity of the polymerizing system.

An alternative approach has been to combine a redox system with a heat-sensitive initiator. In this case, the approximately adiabatic polymerization is initiated during the first stage of the process by the redox system: as the temperature rises, the heat-sensitive compound becomes the radical source, as the redox system becomes exhausted.

The above are the major commercial methods of initiation employed in the polymerization and copolymerization of acrylamide and its analogues. Initiation methods involving physical excitation of monomer in bulk or solution are,however, becoming of increasing technical importance. They include electron-beam irradiation[14], electrolytic initiation[15-18], plasma polymerization[19], high pressure, shear and mechano-chemical methods[20-23], ultrasonic[24], photo-sensitized[25,26], and high energy radiation methods[27]. Polymerization can also occur in the solid state[28,29].

SINGLE COMPONENT INITIATORS

A large number of heat and light-sensitive compounds suitable for use as initiators is available. An excellent review by Sheppard and Kamath[30] has recently appeared. Amongst the many compounds suggested are the following:

Inorganic peroxides: Various persulphates[31] (sometimes promoted by metal ions, such as Cu^+, Ag^+)[32], peroxy-diphosphate[33], nitrogen peroxide[34].

Organic peroxides: A wide range of diacyl[36], dialkyl[37] peroxides[35], hydroperoxides[38] and peroxy-esters[39] is available. A major disadvantage of the use of peroxides is the likelihood of trace impurities and chain transfer agents, etc. acting as reductants, so forming redox couple systems inadvertently.

Organic azo-compounds[40]: Bis-(cyanoalkyls)[41], bis(cyanocarboxylic acids)[42], bis(alkylamidines)[43], α-amino-acetic acid derivatives[44] are widely used. These have the advantage of usually being less susceptible to the effects of solvent and impurities, and are therefore less likely to cause initiation problems. The introduction of polar substituents increases water-solubility and, in recent years, various workers have reported data for many such initiators[45].

Metal complexes: Ce(IV)[46], Co(III)[47-49], Mn(III)[50,51], Fe(III)[52], Ni(II)[53] and Cu(II)[54] have been reported in the literature.

REDOX INITIATORS

Many long-established systems are still used, including, for example, persulphate coupled with metabisulphite[55], sulphite[56], thiosulphate[57] and Fe(II)[58]. Hydrogen peroxide is coupled with hydroxylamine[59], Fe(II)[60], etc. More recent work has concentrated on the attack on particularly susceptible groups. Persulphate has been used to oxidize the S - H group of water-soluble mercaptyls such as cysteine hydrochloride[61], thioglycollic[62], thiomalic[63] and thiolacetic[64] acids, 2-mercaptoethylamine[65], 2-mercaptoethanol[66], etc.

Attack on a number of amino-substituted oxidants has been studied. Examples are the attack of persulphate on dimethylamino-propionitrile[67], β-morpholinopropionamide[68], urea[69], and silver aminoacetate[70].

Oxidation by acidic permanganate of a number of carboxylic acids has been reported. Examples are oxalic[72] (which inhibits persulphate initiation), malic[73], tartaric[74], ascorbic[75], glycollic[76], lactic[77] and mercaptosuccinic[78] acids.

Ce(IV) has been used as an oxidizing agent with glycerol[79], pinacol[80], thioglycollic acid[81], 2-mercaptoethanol[82], thiomalic acid[83]and l-cysteine[84]. Other recently studied systems include vanadium(V)/cyclohexanone[85], Mn(III) acetate/diglycollic acid[86], Fe(II)/chlorate[87], Cu(II)/bisulphite[88], bromate/thioglycollic acid[89] and $Li_4P_2O_7$/silver nitrate[90], etc. A review by Nyak and Lenka[91] very comprehensively covers the field of redox systems.

'Promoted' systems, which have been mentioned above, include systems such as benzoyl peroxide/dimethyl aniline[92-94] and Co(II) chloride/dimethylaniline[95]. These are effectively redox systems: reference to their mechanisms of operation is made later in the Chapter.

MECHANISM OF INITIATION

Many accounts of the elucidation of the initiation mechanisms of a wide range of initiators have been published[93,96-98] . Fission of the relatively labile O - O bond is the usual route to radical production in the case of the peroxides. C - N bond rupture is the typical route in the case of the azo-compounds. Decomposition maye be affected by the solvent[99]. As an example, low pH favours the non-radical decomposition of persulphate, whilst azo-bis(isobutyronitrile) is comparatively insensitive to pH difference[96].

Addition of 'promoters' to increase the rate of decomposition of the initiator is commonly practised. In general, such addition leads to decreased energy of activation. The amine-promoted decomposition has been exploited to a limited extent in acrylamide polymerization[92-94] . A redox mechanism has been reliably confirmed and the increased rate of decomposition has been ascribed to distortion of the peroxidic bond, due to the formation of charged intermediates. It is also found that the presence of electron-donor groups on the amine and electron-acceptor groups on the peroxide enhance the rate of decomposition.

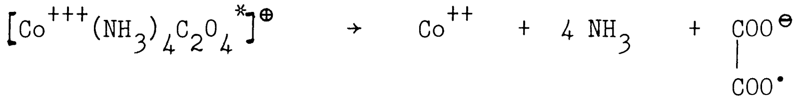
Initiation by metal complexes can follow very diverse mechanisms. The reaction depends upon the metal ion involved, its associated ligands, the monomer, the reaction medium, and the specific interactions between the various species. Decomposition often yields radicals originating from the ligands present. Typically, at pH < 4, sodium bis(diethanolamine)cobalt(III) decomposes according to[48]:

$$[Co(DEA\text{-}2H)_2]^{\ominus} + 2\,H_3O^{\oplus} + H_2O \rightarrow [Co(DEA\text{-}2H)(H_2O)_3]^{\oplus} + (C_2H_4OH)_2\overset{\bullet}{N}H$$

and (ammine-oxalato)cobalt(III) complexes decompose photochemically by way of the excited intermediates[47]:

$$[Co^{+++}(NH_3)_5HC_2O_4{}^{*}]^{\oplus} \rightarrow Co^{++} + 5\,NH_3 + HC_2O_4^{\bullet}$$

and,

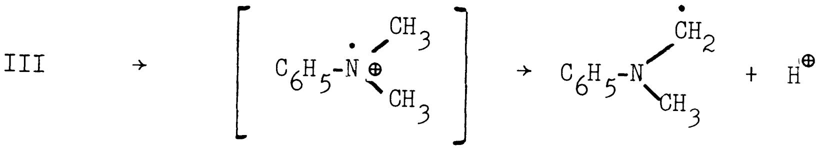


$$[Co^{+++}(NH_3)_4C_2O_4{}^{*}]^{\oplus} \rightarrow Co^{++} + 4\,NH_3 + \begin{array}{l} COO^{\ominus} \\ | \\ COO^{\bullet} \end{array}$$

In many cases, however, initiators involving metal ions behave as redox systems. This is apparently the case in the cobalt(II) chloride/dimethylaniline system[95] for which the proposed mechanism is analogous to that of the peroxide/amine system mentioned above:

$$[Co(H_2O)_6]^{\oplus\oplus}2\,Cl^{\ominus} + n\,ACM \rightleftharpoons \underset{\text{II}}{[Co(H_2O)_{(6-n)}(ACM)_n]^{\oplus\oplus}2\,Cl^{\ominus}} + n\,H_2O$$

$$\text{II} + DMA \rightleftharpoons \underset{\text{III}}{\left\{[Co(H_2O)_{(6-n)}(ACM)_n]^{\oplus\oplus}\,2\,Cl^{\ominus}\;....\;DMA\right\}}$$



Mechanisms have been proposed for many redox systems: these vary widely in their complexity. Fe(II)/persulphate and Fe(II)/hydrogen peroxide systems are fairly straightforward. The former is thought to proceed via[58]:

$$Fe^{++} + S_2O_8^{--} \rightarrow Fe^{+++} + SO_4^{-\bullet} + SO_4^{--}$$

$$SO_4^{-\bullet} + Fe^{++} \rightarrow Fe^{+++} + SO_4^{--}$$

$$SO_4^{-\bullet} + H_2O \rightarrow HSO_4^{-} + OH^{\bullet}$$

$$SO_4^{-\bullet} + M \rightarrow$$

$$OH^{\bullet} + M \rightarrow$$

and persulphate/mercaptyl systems are thought to follow a similar mechanism[61-66] :

$$S_2O_8^{--} + RSH \rightarrow RS^{\bullet} + SO_4^{-\bullet} + HSO_4^{-}$$

$$SO_4^{-\bullet} + RSH \rightarrow RS^{\bullet} + HSO_4^{-}$$

$$2\ RS^{\bullet} \rightarrow RS\text{-}SR$$

$$RS^{\bullet} + M \rightarrow$$

$$SO_4^{-\bullet} + M \rightarrow$$

Both systems are affected by pH, the former displaying a rate maximum around pH 4[100], due possibly to ionic strength effects coupled with the increasing importance of a non-radical decomposition route at low pH. The mercaptyl-containing systems display a reduction in rate with increase in pH. This has been ascribed to the consequent increase in the degree of ionization and the reduction in concentration of RSH:

$$RSH \rightleftharpoons RS^{\ominus} + H^{\oplus}$$

Systems which employ combinations of oxidizing agents coupled with amino-substituted oxidants resemble[67-71], in general, the 'amine-promoted' initiators previously mentioned[92-94]. In such systems, decomposition of an intermediate complex leads to production of radicals.

Oxidation of carboxylic acids by acidified permanganate is very complex and mechanisms are highly specific to each acid[72-78]. Highly reactive Mn(III) is generally claimed to be involved and is thought to result from the disproportionation of Mn(II) and Mn(IV). The initiating radicals are usually fragmented species originating from the relevant carboxylic acid. It is usually essential to maintain a sufficiently low pH to ensure that the MnO_2 remains in solution.

Ce(IV) oxidations[79-84] seem to follow the pattern of complex formation followed by decomposition to yield initiating radicals:

$$R + Ce(IV) \quad Complex \rightarrow R^{\bullet} + Ce(III) + H^{+}$$

$$R^{\bullet} + M \rightarrow$$

DEPENDENCE OF POLYMERIZATION ON TEMPERATURE

The effect of temperature variation in an adiabatic polymerization has already been mentioned. It was pointed out that this is controlled mainly by the energy of activation of the initiation process, which is of great importance in determining the overall energy of activation of the entire process. Table 1 lists such data for a few common initiators only, since there are extensive compilations in the literature. These values are seen to lie within fairly narrow limits, but decomposition rate is very sensitive to the value of the energy of activation for the decomposition (E_d).

Table 1. Thermal decomposition of initiators[92,96].

Initiator	$A_d(s^{-1})$	E_d(kJ)	10-hour half-life temperature (°C)
Persulphate	6×10^{16}	140	69
Benzoyl peroxide	$\sim 3 \times 10^{14}$	125	73
AIBN	1.6×10^{15}	129	64
CAT 78[101]	1.6×10^{15}	125	55

A more practically useful quantity for comparing initiators is the '10-hour half life temperature'[30]. This is the temperature at which 50 % of the initiator is consumed in 10 hours. Clearly, 'CAT 78' (2,2'-azobis(2-amidinopropane)hydrochloride) is the most rapidly decomposing of the initiators quoted. In general, a useful rule of thumb is that the temperature chosen should be that at which the half life is equal to the time of reaction.

Redox and 'promoted' polymerizations usually, but not always, display lower energies of activation than do single component initiators. This is apparent from the data of Table 2. Rationalization of such data is not easy, however. The most surprising feature is, of course, the negative values displayed by a few of the initiators. Decrease in rate with increase in temperature is not commonly encountered in free radical polymerization. The phenomenon in these cases has been ascribed to entropy effects on termination between primary and polymer radicals[48,51,54].

PROPAGATION AND TERMINATION

The propagation process is significantly affected by the nature of the polymerization medium, by pH, solvent, presence of salts, complexing agents, surfactants, etc., all of which exert a strong influence on the rate of polymerization and on the nature of the produce. Results of such studies are sometimes contradictory and reproducibility is not always good. A comprehensive review by Kurenkov and Myagchenkov[103] has recently appeared. There is also a considerable volume of Japanese literature, which has not been included in this review.

EFFECT OF pH

Table 3 shows that the velocity coefficients for propagation and termination in aqueous solution both increase with fall in pH. The variation is such, however, that the ratio $k_p/k_t^{\frac{1}{2}}$ remains substantially constant. As a result, the rate of polymerization is virtually constant provided that the initiation process itself is independent of pH. Dainton et al.[104] suggested that the variation in k_p and k_t is the result of change in reactivity due to alkaline hydrolysis of the amide group,repulsion between reactant species and change in conformation and mobility of the growing radicals.

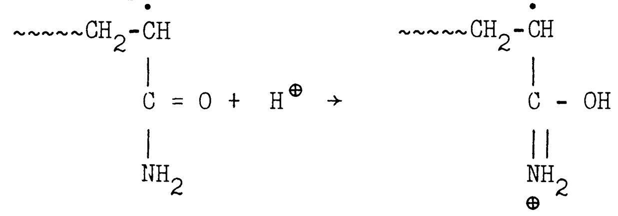
Table 2. Overall energy of activation for polymerization of acrylamide using various initiator systems.

Initiator	E_{ov}(kJ)	Reference
Persulphate/mercaptoethanol	134	66
Persulphate/thioglycollic acid	126	62
Permanganate/malic acid	83	73
Permanganate/glycollic acid	78	76
Permanganate/tartaric acid	78	74
Persulphate	$\sim$70	92,96
Permanganate/pyruvic acid	66	114
Permanganate/lactic acid	65	77
Azo-bis(isobutyronitrile)	$\sim$62	92,96
Benzoyl peroxide	$\sim$62	92,96
CAT 78 (2,2'-azobis(2-amidino-propane)hydrochloride)	$\sim$62	101
Permanganate/oxalic acid	50	72
Permanganate/thiourea	48	71
Persulphate/cysteine hydrochloride	41	61
Persulphate/2-mercapto-ethylamine	41	65
Permanganate/ascorbic acid	41	75
$CoCl_2$/dimethylamine	39	95
Persulphate/lactic acid	33	64
Chlorate/sulphite	31	102
Permanganate/mercaptosuccinic acid	28	78
Hydrogen peroxide/hydroxylamine	27	59
Bromate/thioglycollic acid	26	89
Ce(IV)/L-cysteine	20	84
Na bis(diethanolamine)/Co(III)	-28	48
bis 2-(2-hydroxyethylamino) exotho Cu(II)	-53.3	54
Mn(III)/bis(diethanolamine)	-87	51

Table 3. Effect of pH on kinetic parameters in ACM polymerization[104,105]

Source	pH	k_p x 10^{-4} (dm^3 mol^{-1} s^{-1})	k_t x 10^{-6} (dm^3 mol^{-1} s^{-1})	$k_p/k_t^{\frac{1}{2}}$	Temp. (°C)	A_p x 10^{-7}	E_p (kJ)	A_t x 10^{-10}	E_t (kJ)
Dainton[104]									
	1.0	1.72	16.3	4.3	25	-	-	-	-
	5.5	0.6	3.3	3.3	25	-	-	-	-
	13.0	0.4	1.0	3.0	25	-	-	-	-
Abkin[105]									
	7.0	7.9	660	3.0	30	0.8	11.7	6.8	11.7
	13.0	5.8	200	4.1	30	2.2	15.0	0.1	4.2

Abkin et al.[105] (Table 3) reported a decrease in E_p as the pH changes from 13 to 7. These workers explained this mainly in terms of the increasing extent of protonation of the amide group with decrease in pH:

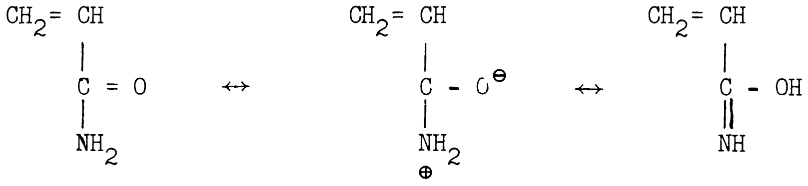


$$\sim\sim\sim\sim\sim CH_2-\dot{C}H(-C(=O)-NH_2) + H^{\oplus} \rightarrow \sim\sim\sim\sim\sim CH_2-\dot{C}H(-C(-OH)=\overset{\oplus}{N}H_2)$$

The consequent localization of the unpaired electron by the positive charge on the nitrogen atom would be expected to lead to an increase in the reactivity of the growing radical and thus a decrease in E_p with decrease in pH. It may be presumed that this effect more than compensates for charge-repulsion effects which would also be expected to increase with fall in pH and would therefore give an increase in E_p.

Despite the expected increase in k_t being, in fact, observed, the value of E_t, surprisingly, increases as the pH falls. This has been ascribed to increased repulsive forces between the terminating radicals. The larger value of k_t is thus a consequence of the marked increase in A_t at lower pH values. Changes in shape, size, and nature of the growing radicals will undoubtedly affect entropy of activation with significant effects.

Copolymerization studies, which are discussed below, have led to the suggestion that pH-controlled keto-enol tautomerism may be responsible for the effect[106,110]:



$$CH_2=CH-C(=O)-NH_2 \leftrightarrow CH_2=CH-C(-O^{\ominus})-\overset{\oplus}{N}H_2 \leftrightarrow CH_2=CH-C(-OH)=NH$$

Unfortunately, copolymerization studies in general have not clarified the situation. Many of the studies of the effect of pH carried out using aqueous phase copolymerization techniques have involved ionogenic comonomers whose behaviour is also pH-dependent. Values obtained for the ratio $k_p/k_t^{\frac{1}{2}}$ are very much greater than for most monomers (for example, 0.01, 0.04, and 0.12 for styrene, methyl methacrylate, and vinyl acetate polymerization, respectively, at 25°C.). The high value of this ratio is responsible for the rapid rate of polymerization and high molar mass polymers obtained from acrylamide.

EFFECT OF MONOMER CONCENTRATION

Studies using different initiators, solvents, and monomer concentration ranges have indicated values of 1 to 1.5 for the dependence of rate of polymerization on monomer concentration[103]. Explanations for such values are usually in terms of radical caging, monomer complexation, diffusion control, solvent transfer, etc., although these suggestions have been criticised[111]. In this context, too, the proposals of Chapiro involving 'matrix' and oriented polymerizations, which are discussed later, cannot be ignored[112,113].

EFFECT OF POLYMERIZATION MEDIUM

Homogeneous polymerization of acrylamide is usually carried out in the aqueous phase. The presence of additives can extert a profound effect and can yield information about the component processes involved.

Organic reagents such as alcohols, acetone, dimethylsulphoxide (DMSO), and tetrahydrofuran (THF) generally depress k_p, k_t, R_p and $\bar{P}_n$ and, at some stage, may cause polymer precipitation, according to many workers[61,62,65,66,72-74]. Abkin et al.[105] have been very active in the field, and have shown that the rate of polymerization varies with the nature of the solvent in the following order:

Rate in the presence of: water > formamide > dimethylsulphoxide

Table 4. shows some of their results. Dioxan (DO) and THF also exert a significant effect but, unfortunately, cause precipitation of the polymer is they are present in amounts greater than 10 %. For reasons of brevity, discussion will be restricted to the DMSO/water systems. It is clear that, as the polymerization medium changes from water to DMSO, the rate of polymerization decreases despite the increase in rate of initiation by azo-bis(isobutyronitrile). This is a consequence of the compensating increase in the value of $k_p/k_t^{\frac{1}{2}}$. By means of inhibition and non-stationary state measurements, these workers were able to obtain individual values for k_p and k_t in each solvent at a range of temperatures. Relevant data are presented in Table 4. These workers also studied the importance of the various monomer, solvent, and

Table 4. Effect of DMSO on the aqueous phase polymerization of acrylamide[105] ($R_p = k_{ov}[AIBN]^{\frac{1}{2}}[ACM]$)

mole fraction DMSO	$k_{ov} \times 10^4$ (40°C)	$k_i \times 10^6$ (40°C)	$k_p \times 10^{-4}$ (30°C)	$k_t \times 10^{-8}$ (30°C)	E_p(kJ)	$A_p \times 10^{-7}$	E_t(kJ)	$A_t \times 10^{-10}$
0 (pH = 7)	19.3	0.34	7.9	6.6	11.7	0.8	11.7	6.8
0.10			4.3	3.5	15.9	2.4	10.9	2.87
0.12			4.0	3.2	16.3	2.6	10.9	2.3
0.35			1.9	0.8	18.8	3.3	10.9	0.57
0.62			0.70	1.0	20.5	2.4	7.9	0.23
1.00	4.4	1.6	0.37	1.7	25.1	7.8	0	0.017
0.10 (DO)			3.3	2.3	17.6	3.4	10.5	1.5
0.10 (THF) (extrapol-ated)	1.6 (bulk)	10 (bulk)	1.9	1.4	19.2	5.0	10.9	1.2

and radical interactions by cryoscopy, heat of solution, NMR, reactant and product solution measurements. The conclusions reached were:

(a) Monomer-solvent interactions are stronger in water than in DMSO, as shown by the greater endothermicity of the dissolution in the case of the former, and, also, by NMR studies. Cryoscopic measurements indicated that, in DMSO, acrylamide exists largely as dimer, whilst in water it is monomeric. The additional energy required to decompose the dimers therefore contributes to the higher value of E_p for systems containing a greater proportion of DMSO.

(b) Radical-solvent interaction is thought to give donor-acceptor complexes with DMSO acting as a much stronger donor than water towards the polyacrylamide acceptor radical. These complexes display lower reactivity than the un-complexed radicals because of electron delocalisation. Such an effect may thus be expected to lead to larger values for E_p and E_t in systems containing higher proportions of DMSO. By contrast, the possibility of proton-donation by water may result in protonated radicals of enhanced reactivity, so lowering the values of E_p and E_t with increasing water concentration.

(c) The presence of solvents such as DMSO is thought to produce conformational effects by causing tighter coiling of the growing polyacrylamide radical than is the case in water. Abkin et al.[105] provided evidence of this by reporting a significant reduction in the intrinsic viscosity of a given polyacrylamide when DMSO was present in the solvent used in its determination. Access of monomer to the growing radical end is hindered in the presence of DMSO and the rate of propagation is consequently reduced. Although a reduction in the value of A_p might be anticipated under such circumstances, this is not observed. This parameter, however, is often anomalous in polymerization studies, and may be a consequence of mutual compensation between E_p and A_p. These workers also found that the temperature coefficient of viscosity of a polymer solution is greater in DMSO than in water, indicating that the radical conformation, and therefore its reactivity, is more temperature-dependent in the former. Such an effect would also be expected to lead to a higher value of E_p.

The consequence of these effects thus explains the observation that the activation energy for propagation increases as the solvent increases as the solvent medium changes from water to DMSO.

The relative independence of k_t on the nature of the medium is also seen to be a consequence of the above phenomena. The termination process might be expected to be enhanced by reduction of radical coil size in the presence of DMSO. This should permit radical ends to be more easily found by each other and therefore lead to an increase in the value of k_t. By contrast, the decrease in radical reactivity caused by complexation should lead to a decrease in value of k_t. Presumably these opposing effects compensate each other and yield a value of k_t which is fairly insensitive to solvent composition. Close inspection of the data shows that k_t does in fact pass through a minimum. Abkin et al.[105] showed that this corresponds to a maximum in the graph of viscosity versus mole ratio of DMSO/water. They therefore suggested that diffusion control of the termination reaction is a contributory factor. Auto-acceleration is a characteristic feature of such polymerizations and stirring is claimed to depress the rate of polymerization by enhancing the rate of termination[114]. Strictly speaking, A_t and E_t rather than the velocity coefficients should be compared for the various solvent systems, but these quantities are somewhat unreliable for termination steps in polymerization reactions.

Table 5. includes heat of polymerization data for acrylamide. The greater value of ΔH for polymerization in water is mainly due to the higher energy of the acrylamide monomer in water, compared with the dimer in DMSO and to the looser radical coil, and, therefore, the greater extent of solvation of the polymer chains in water.

Table 5. Effect of solvent on heat of polymerization (kJ mol^{-1})

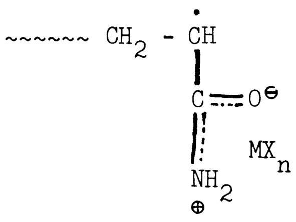
Monomer	Organic solvent	Aqueous phase	Ref.
Acrylamide	~59	83	107
Methacrylamide	35	58	107
Acrylic acid	59	77	105
Methacrylic acid	57	66	108,109
Fluoroacrylic acid	54.3	55.6	105

Saini[110] has used a different approach to examine solvent effects. He copolymerized acrylamide (M_1)with styrene (M_2) and methyl methacrylate (M_2) respectively and observed significant changes in r_1 with change in solvent from dioxan to ethanol[110a]. Similar effects were observed when methacrylamide was used as monomer[110c]. With NN'-dimethylacrylamide, no solvent effect was observed[110b]. To explain these observations, Saini proposed the keto-enol tautomerism previously mentioned, and suggested that the solvent effect in the case of acrylamide and methacrylamide was due to the effect of different dielectric constants on the position of the equilibrium and consequently on the monomer and radical reactivities. The absence of solvent effect in the case of NN'-dimethylacrylamide was ascribed to the impossibility of the tautomerism in this case, because of the absence of N-substituted H-atoms.

Another important factor involved in solvent effects is, undoubtedly,chain transfer. A few studies have been reported[115-117], and there is no doubt, for instance, that methanol[115] markedly reduces polymer molar mass. Although the effect has been ascribed to chain transfer, the possibility of similar effects to those of DMSO must be considered. This has, in fact, been suggested by Misra[74] who has claimed that alcohols decrease the area of a strong hydration layer in aqueous medium resulting in more rapid termination. It has also been suggested[118] that glycerol acts by enhancing H-bonding between acrylamide monomer and radical. In addition, dioxan, acetic acid,etc., may affect rate of polymerization and polymer molar mass by the formation of 'pluri-molecular aggregates'[112,113]. Clearly, change in the polymerization medium may lead to change in solvation, monomer orientation, size of growing radical coil, chain transfer, complexation and chemical nature of the reacting species. Factors such as these are presumably involved in the effect of various additives described in the patent literature. Examples of these factors include improved solubility and reduced gelling characteristics of polyacrylamide produced in the presence of certain ketones, alcohols, glycols, gluconates, etc. Long-chain additives such as polyethylene oxides, polyvinyl alcohol, alkylene oxide/polyamine adducts, etc. possibly depend on monomer alignment for their effect.

INORGANIC SALTS

The presence of inorganic salts in the polymerization medium also causes complicated effects. Interaction with the solvent is of great importance. For example[119], in aqueous solution, lithium bromide has no effect, whilst in DMSO the rate of polymerization increases threefold and then decreases on further addition of LiBr: DMSO/water mixtures give intermediate results. Other salts give similar results: for example, in DMSO, the effect is in the sequence $CaCl_2$ > LiCl > LiBr. The rate effect was ascribed to complex formation which was confirmed by infra-red and NMR studies. Species of the type:



are likely to enhance reactivity by localisation of the unpaired electron.. Stability constants are thought to lie in the order $k_{CaCl_2} > k_{LiBr}$ and are also thought to be greater in DMSO than water. The passage of the curve of the rate of polymerization, plotted as a function of salt concentration, through a maximum is ascribed to the rate enhancement effect described above, followed by the decreasing possibility of aquation, with further increase in salt concentration, causing the radical coil undergoing polymerization to tighten and so have lower reactivity.

In contrast, many salts have a depressing effect on rate and degree of polymerization. There are some contradictions in the literature, but these may arise from the use of different initiators, solvent systems, etc. It appears that KCl, Na_2SO_4, NaF, NH_4Cl, NaCl, and $(CH_3)_4NI$ usually, but not inevitably, depress both rate and degree of polymerization and extent of conversion[61,62,65,66,73,74]. Mn(II) salts usually increase rate[62,66,81], etc., by the disproportion process mentioned above. These effects are generally thought to occur by virtue of complex formation or by factors associated with ionic strength, although they are probably highly specific - for example, persulphate initiation is said to be totally suppressed by the addition of oxalate ions[62] - presumably as a result of complex formation. Copolymerization behaviour is also significantly affected by the presence of such salts[120,121].

EFFECT OF SURFACTANTS

These effects[103] are very varied and depend upon the type and concentration of the surfactant relative to the critical micelle concentration and the concentration of the other reactants. Coulombic forces and hydration phenomena are thought to be the main factors influencing rate and degree of polymerization. Alternatively, improved component diffusion may favour formation of reactive complexes. The explanations of particluar effects are usually fairly specific, and few generalizations can be made.

NATURE OF THE TERMINATION PROCESS

Under normal circumstances, second order termination is observed in acrylamide polymerization in a wide range of solvents. Dainton and Tordoff[122] suggested combination as the predominant mechanism, but Suen and Rossler[123] claimed that measurements of unsaturation supported disproportionation. Cavell[125] suggested that end-group imidization precedes disproportionation. There is, however, evidence of first order chain termination by oxidative termination with certain metal ions, for example Fe(III)[124,125] and Ce(IV)[79]. Typically, the reaction would be:

$$\sim\sim\sim\sim\sim\sim CH_2-\dot{C}HR + Fe(III)(aq) \rightarrow \sim\sim\sim\sim\sim CH = CHR + Fe(II)(aq) + H^{\oplus}$$

If this reaction is significant, it will lead to reduction in rate and degree of polymerization. The use of an EDTA/Zn(II) complex with the ability to sequester Fe(III) but not Fe(II) has recently been patented[126] as a method of eliminating the problem of oxidative termination in redox systems involving Fe(II).

Radical stabilization by complexation is claimed to affect the termination process seriously in certain cases. In extreme cases, termination is prevented , and 'living radical polymerization' results[127-129]. This results in considerable post-polymerization with increase in degree of polymerization but no change in the number of molecules. 'Aged' Cr(II)/benzoyl peroxide/dimethyl formamide and $ZnCl_2$/1-butenethiol systems both produce this effect. Although work has tended to concentrate on methyl methacrylate polymerization, acrylamide is reported to behave similarly in the presence of the former system[129].

SUBSTITUTED ACRYLAMIDES

Methacrylamide (MeACM)[130] and NN'-dimethylacrylamide (NN-di-Me-ACM)[131] have been most widely studied. Polymerization and copolymerization methods are similar to those for acrylamide. Comparison of results is difficult because of the different polymerization conditions. Some of the limited data available is listed in Table 6[104,130-135]. Methyl substitution on the α-carbon atom generally leads to reduction of radical reactivity in vinyl polymerization through steric hindrance and hyperconjugation. This is evident from the values of k_p but not from k_t.Clearer evidence comes from Dainton and Sisley's study[136] of the copolymerization of methacrylamide (M_1) with acrylamide (M_2), which gave values of 1.1 ± 0.2 and 0.74 ± 0.11 for the monomer reactivity ratios r_1 and r_2 respectively. Combination with the k_p values in Table 6 shows that the polyacrylamide radical is 25 times more reactive than the methacrylamide radical (towards acrylamide monomer) whilst acrylamide monomer is 1.35 times less

Table 6. Velocity coefficients for polymerization of substituted acrylamides.

Monomer	$k_p \times 10^{-4}$	$k_t \times 10^{-7}$	$k_p/k_t^{\frac{1}{2}}$	temp. (°C)	pH	Ref
ACM	1.72	1.63	4.2	25	5.5	104
NN'-diMeACM	1.1	3.8	1.78	50	?	131
N-t-butyl-ACM	-	-	0.63	25	?	132,133
MeACM	0.08	1.65	0.2	25	~4	130
NN'-dialkyl- -disubst.-MeACM	Do not undergo free radical polymerization					134,135

reactive than methacrylamide monomer (in attack by polyacrylate radicals).

The low value of $k_p/k_t^{\frac{1}{2}}$ for methacrylamide polymerization is responsible for the lower rate and degree of polymerization observed with this monomer. This is further influenced by enhanced monomer transfer because of the stability of the allylic radical formed by hydrogen-abstraction from methacrylamide monomer. The effect of N-substitution has received less attention, possibly becuase of difficulty in purifying and handling the monomers. North and Scallan[131] have reported kinetic parameters for the coplymerization of NN'dimethacrylamide (Table 6.). Comparison with data for acrylamide and methacrylamide is difficult, since the studies on these monomers were carried out in aqueous solution whilst, although not specifically stated, it appears that North and Scallan's measurements were carried out on bulk monomer. The very considerable effect of solvent has already been discussed. Examination of the results would suggest, however, that, in this case, radical reactivity is lowered by N-substitution.

Several workers have reported studies of copolymerization of monomers such as NN'-dimethylacrylamide[131,110b, 106], NN'-di-n-butylacrylamide[137], N-t-octylacrylamide[137], N-n-octylacrylamide[137], NN'-diacetoneacrylamide[138], and even more complex substituted acrylamides[139] with styrene, methyl methacrylate, etc. Results are difficult to compare because of different solvents and conditions, but, in general, N-substitution appears to reduce monomer reactivity, di-substitution by linear groups being more effective than mono-substitution by larger bulkier groups. These conclusions conflict with the prediction that the electron-withdrawing N-substituent should enhance the reactivity of the vinyl double bond to free radical attack. Until data obtained under identical circumstances are available for direct comparison, the nature of the influence of N-substitution will remain equivocal. Since, however, combination of N- and C-substitution can totally prevent polymerization as in the case of NN'-dialkyl methacrylamides[134,135], it seems probable that N-substitution results in radical stabilization as a result of steric hindrance. It is likely, however, that the effect observed is strongly influenced by the nature of the solvent.

HEAT OF POLYMERIZATION

Strain induced in the polymer chain by α-methyl substitution, together with hyperconjugation in the monomer are the main reasons for the lower heat of polymerization of methacrylamide compared with acrylamide (Table 5.). The lower value observed in benzene solution is attributed to dimerization of amide molecules in non-polar solvents (association energies 17 - 30 kJ mol^{-1})[105]. These bonds must be broken before polymerization can occur and cannot re-form to the same extent because of steric factors. The monomer state is thus more thermodynamically stable in non-polar than in aqueous media, thereby giving lower values of ΔH.

METHODS FOR POLYMERIZATION OF ACRYLAMIDE

Problems commonly encountered in the polymerization of acrylamide include the evolution of heat and its dissipation, rapid temperature rise, highly viscous or gelled product adhering to the apparatus, isolation of pure polymer in a convenient form (the monomer is neuro-toxic), initiator depletion before completion of polymerization, etc. In addition to well-established procedures, recent attempts to overcome these problems include:

(i) Spraying a mixture of acrylamide and initiator into a heated reaction chamber, sometimes containg an atmosphere of sulphur dioxide[140,141].

(ii) Addition of a volatile organic liquid to provide evaporative cooling and thereby increase the degree of polymerization[142-144].

(iii) Polymerization in thin layers and sometimes on a cold surface[142,145-147].

(iv) Use of a batch reactor which contains heating and cooling compartments[148].

(v) Continuous polymerization on a conveyor belt which progressively curls to give polymers with U-shaped or circular cross-sections[149] In an alternative system, a hot rotating disc may be used, where the polymerization and drying takes place before removal by scraper[150]

(vi) Polymerization in a reactor lined with a polythene bag[151] or silicone coating[152] to prevent polymer sticking to equipment.

(vii) Polymerization in the presence of solid particles to give speciality products for column packing, etc.[153]

(viii) Reactant-loss compensation techniques (either batch or continuous)[154-156]; use of combinations of light-sensitive and insensitive initiators, or initiators which are heat-sensitive over different ranges[157,158]; control of initiator-release by coating initiator with paraffin wax, which slowly melts as reaction proceeds[159].

(ix) Attempts to overcome mixing problems include a system of feed-pipes and baffles which eliminate clogging[160]; various specially-designed reaction columns[161,162] and a device involving rotating horizontal tubes designed to create a vortex[163].

(x) Various procedures for carrying out emulsion and mixed solvent solution polymerizations[164-167]. The advantages of heterogeneous systems, particularly water-in-oil emulsions, are lower viscosity, non-adhering polymer beads, absence of gelling and easier heat dissipation. Xylene or tetrachloroethylene are the preferred organic phase for bead production, with fuel oil or paraffin hydrocarbon being used for dispersions. With mixed solvent systems, polymer precipitation permits easy product recovery.

ACRYLIC AND METHACRYLIC ACIDS

Polymerization of acrylic and methacrylic acids may be carried out in both aqueous and non-aqueous media[4]. Both polymers precipitate from the latter as powders[1,168]. Polyacrylic acid remains in aqueous solution, whilst polymethacrylic acid precipitates from water but re-dissolves on cooling. Similar initiators and polymerization methods may be used[169,170] as for acrylamide, although grafting onto other polymers is more important. Rates and kinetic parameters are highly sensitive to polymerization conditions.

EFFECT OF pH

Several workers[171-174] have shown that the rate of polymerization in aqueous solution is markedly affected by pH. Fig. 1., due to Kabanov et al.[174] shows that, as the pH increases, the rate of polymerization of acrylic acid decreases to a minimum

Table 7. Kinetic data for effect of pH on the polymerization of acrylic and methacrylic acids[174] ($23^{\circ}C$)

Monomer	pH	$k_p \times 10^{-4}$	$k_t \times 10^{-8}$
Acrylic acid	acidic[105]	~ 3.0	1.8
	7.9	0.065	2.6
	7.9(1.5 M NaCl)	0.315	2.6
	11.0	0.66	2.1
	13.6	0.25	2.25
Methacrylic acid	acidic[105]	0.500	0.1
	8.8	0.067	2.1
	13.6	1.95	2.25

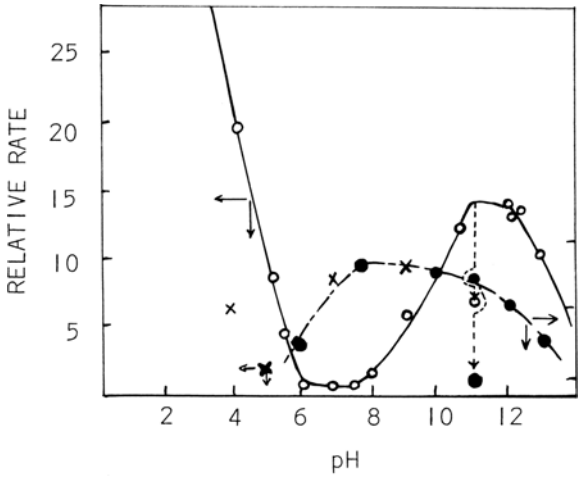


Figure 1. Polymerization of acrylic acid in aqueous solution at $60^{\circ}C$[174]

—○—○—○— Relative rate of polymerization

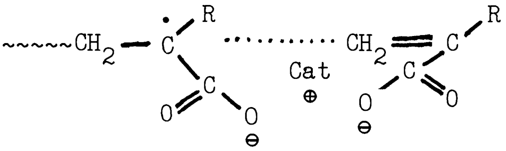
-·-●-·-●-·-●-. Viscosity of polyacrylic acid model sample

× r_1 for AA/NVP copolymerization[182] (L.H.scale for absolute values)

——→ Effect of addition of electrolyte.

then increases to a maximum around pH 11 before decreasing again with further increase in pH. Similar behaviour was observed in the case of methacrylic acid. Other workers have reported similar effects, but, in general, the agreement is qualitiative rather than quantitative. Kabanov et al.[174] measured k_p and k_t - their values are shown in Table 7. These demonstrate that the variation in rate is due principally to changes in k_p, since k_t is relatively insensitive to pH. Different factors are thought to become involved as the pH changes. The initial decrease in rate of polymerization with increase in pH from 1 to 7 has been ascribed to increasing charge-repulsion as a result of the increasing degree of ionization of growing radical and monomer.

Acrylic acid monomer is a typical weak acid which undergoes ionization, with a pK_a of 4.2. Polyacrylic acid ionization is a more complicated process[175-177], since partial ionization imparts a negative charge to the polyion and lessens the ease with which subsequent hydrogen ions are released. This results in a variable pK_a for the polyacid which is usually considerably higher than the single pH-independent value for the ionogenic monomer. Consequently, the degree of ionization at a given pH is greater for the monomer than for the polyacid. It has been shown that the time required for an ionization process ($\sim 10^{-9}$s)[178] is several orders of magnitude less than that for an addition step ($\sim 10^{-4}$ s) in a free radical polymerization. It is likely therefore that the behaviour of the polyacid radical will be similar to that of the 'dead' polymer molecule. These ionization phenomena lead to progressive changes in charge and reactivity of the reacting species , interactions of which are presumably responsible for the initial decrease, followed by a somewhat flat minimum in Fig. 1. between pH 1 and pH 8, and for the virtual independence of k_t on pH. In support of this, it has been calculated that monomer ionization is virtually complete by pH 7, whilst radical ionization is not complete until pH 9 - 10. Fig. 1. also shows that, as the pH increases from 8 to 11, the rate of polymerization increases significantly, and the kinetic data in Table 7 again demonstrate that this is due almost entirely to increase in k_p. This increase is thought to be due to the effect of sodium-ion binding:



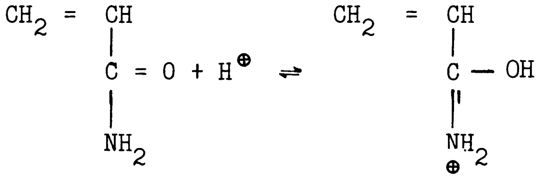
This reduces charge-repulsion between the reacting species by a shielding effect and also assists the reaction processes by affecting steric placement, so enhancing reaction rate. There is also the possibility of stereoregular placement as an additional effect. The increased radical coiling which might be expected to result from the lessened charge-repulsion would, of course, be compensated to some extent by the increase degree of ionization of the radical over this region.

Finally, Fig. 1 shows that above pH 11, the rate of polymerization decreases sharply and this decrease is seen from Table 7 to be associated with decrease in the value of k_p. Kabanov et al.[174] have ascribed this reduction in k_p to collapse of the polymer radicals under the influence of the high ionic strength due to the addition of sufficient alkali to produce the required pH. Over this region, ionization is complete and substantial shielding will permit coiling of the radicals. Access of monomer will be hindered and reduction of k_p and rate of polymerization would be expected.

Kabanov et al.[174] reported convincing evidence for their conclusions. Addition of high concentrations of sodium salts was found to increase the value of k_p by a factor of 5 at pH 7.9 but to reduce the rate considerably at pH 11. Sodium ion binding is presumably effective in extending the chain in the former case, chain-collapse is enhanced in the latter. Also included in Fig.1. are viscosity data, which give strong support to these points, even to the extent of showing that addition of electrolyte at pH 11 causes a sharp reduction in intrinsic viscosity and, presumably, the size of the polymer molecule.

The explanation of the chain-collapse phenomenon has been criticised[179] on the grounds that the ionic strengths involved[173] are too low. Unfortunately, the behaviour of polyacids in solution at pH > has received little study. Mandel has suggested that chain-collapse is due to more complex reasons. He has speculated on the possibility of high pH affecting the 'quality' of the solvent, possibly by bringing it closer to θ-conditions[179].

pH effects have also been investigated by copolymerization studies and similar conclusions have been reached. Fig. 2. shows the results of two groups of workers[180,181] for the variation in the monomer reactivity ratios r_1 and r_2 in the copolymerization of acrylamide (M_2) and acrylic acid (M_1). Explanation of these results involves the equilibria:



$$CH_2{=}CH{-}C({=}O){-}NH_2 + H^{\oplus} \rightleftharpoons CH_2{=}CH{-}C(OH){=}NH_2^{\oplus}$$

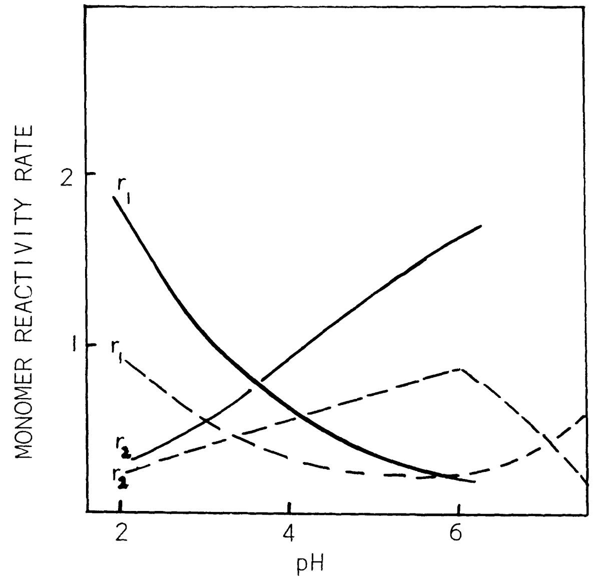
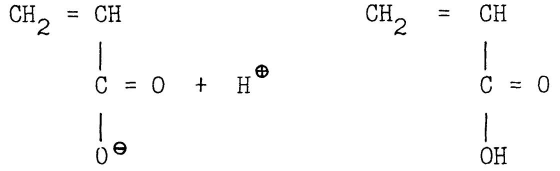


Figure 2. Effect of pH on aqueous phase copolymerization of acrylic acid (M_1) and acrylamide (M_2)

———— Cabaness et al.[180]

------- Ponratnam and Kapur[181]

and



$$\begin{array}{c} CH_2 = CH \\ | \\ C = O \\ | \\ O^{\ominus} \end{array} + H^{\oplus} \qquad \begin{array}{c} CH_2 = CH \\ | \\ C = O \\ | \\ OH \end{array}$$

The other factor involved is variation of radical reactivity (due to resonance contributions) in the sequence:

$$-COOH > -COO^{\ominus} \sim -CONH_2 \quad \text{and} \quad -C(OH)\overset{\oplus}{N}H_2 > -CONH_2$$

monomer reactivity displaying the opposite order.

At low pH, the low value of r_2 could be a consequence of the protonated acrylamide monomer being of lower reactivity than un-dissociated acrylic acid. As the pH increases, the degree of protonation decreases and the extent of the ionization of the acid increases. The observed increase in r_2 with increase in pH suggests that the expected increase in acrylamide reactivity is greater than the corresponding increase in acrylic acid reactivity. It is not clear whether this effect is due to the different equilibria or to the chemical nature of the species involved.

The variation of r_1 with pH is much more easily explained. In this case, attack of the two monomers on the polyacid radical is being compared. As the pH increases, the charge on acid monomer and radical is becoming greater, whilst the charge on the acrylamide monomer is decreasing. Charge-repulsion will therefore increase in the former case, leading to a reduction in the numerator of the expression for r_1. The resonance effects described above will reinforce this trend and the observed decrease in r_1 will result.

Similar studies have been carried out on other systems. For example, Ponratnam and Kapur[182] have studied the acrylic acid (M_1)/ N-vinyl pyrrolidone (M_2) copolymerization in the aqueous phase, which is rather simpler since the latter monomer is only very slightly basic and is less susceptible to protonation. These results are shown in Fig.1. Variation in r_1 closely parallels the variation in R_p referred to above. Values of r_2 are small, indicating the very low reactivity of N-vinyl pyrrolidone monomer. Results for methacrylic acid indicate similar behaviour, in general, to that observed for acrylic acid[183].

EFFECT OF POLYMERIZATION MEDIUM

Polymerization of acrylic and methacrylic acids is also highly sensitive to the nature of the polymerization medium. Several copolymerization studies have been reported which emphasize this phenomenon - typically, the above-mentioned paper[182] indicates that, in bulk toluene and dimethylformamide, r_1 values are 1.3, 0.48 and 0.67, respectively, for the copolymerization of the acrylic acid/ N-vinyl pyrrolidone system. However, the most intensive study of solvent effects, by Abkin et al.[105,184] (see Table 8) shows the very significant solvent effect with acrylic acid, and the virtual absence of effect with fluoroacrylic acid (FAA). As with acrylamide, as discussed above, these effects are believed to be due to monomer dimerization, complex formation, and radical chain conformation. The presence of the highly electronegative fluorine atoms in FAA is thought to reduce radical reactivity by delocalization of the unpaired electron, to hinder the formation of complexes with DMSO, and to eliminate dimer formation. The other major effect of the

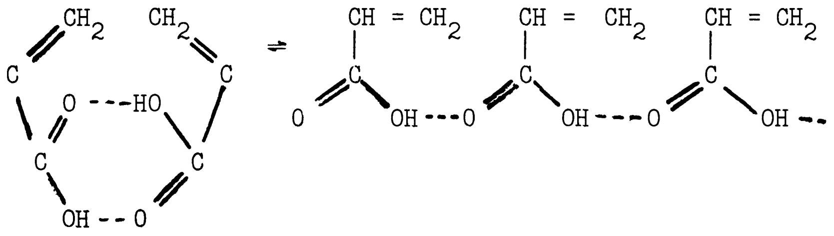
Table 8. Effect of DMSO on acrylic acid and fluoroacrylic acid polymerization[105]

	Acrylic acid		Fluoroacrylic acid	
	Water	DMSO	Water	DMSO
$k_p \times 10^{-4}$(30°C)	3.19	0.076	0.36	0.11
$k_t \times 10^{-8}$(30°C)	1.8	0.2	0.9	0.5
$A_p \times 10^{-8}$	0.6	47	0.6	0.66
E_p (kJ)	13.0	33.4	18.8	21.7
$A_t \times 10^{-8}$	1.8	0.2	2.0	1.0
E_f (kJ)	0	0	2.5	1.7

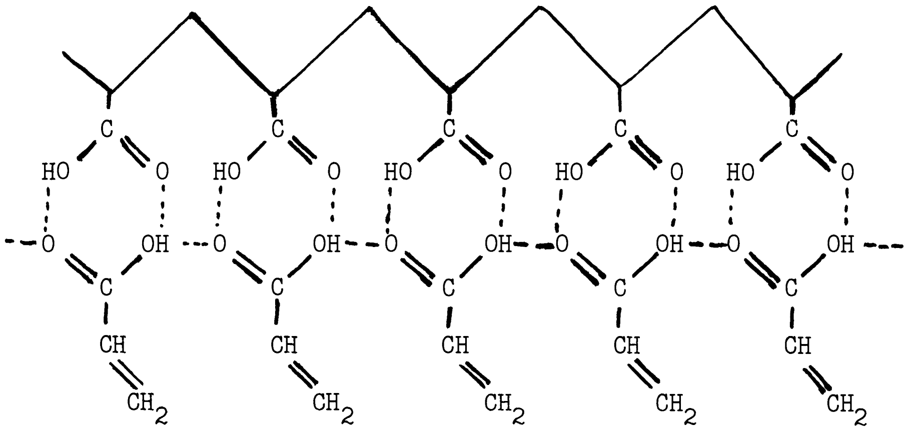
fluorine atoms is to produce very stiff radical diols because of their mutual repulsion. As a result of these factors, the kinetic constants are much less sensitive to the nature of the solvent. Similar effect are apparent from energy of activation and frequency factor data.

These conclusions are further supported by the data in Table 5. for heat of polymerization. With acrylic acid, the heat of polymerization is significantly lower in DMSO than in water, because of monomer dimerization in the former and solvation of the polymer in the latter case. Neither effect is apparent with FAAm so the heat of polymerization is almost the same in both solvents. It is also worth mentioning in this context that the main reason for the generally greater exothermicity of the polymerization of acrylic acid compared with methacrylic acid is the greater strain in the methyl-substituted polymer back-bone in the latter case.

Chapiro[185,186] has suggested that hydrogen-bonding may be involved in the solvent effects in the polymerization of acrylic acid, acrylamide, acrylonitrile, etc., observing that the rate of polymerization and stereoregularity of polyacrylic acid are unaffected by dilution with up to 20 % by volume of H-bonding solvents, whilst non-polar solvents (hexane, toluene, etc.) cause these parameters to decrease abruptly. He suggested that this effect is due to the influence of the solvent on the dimer-oligomer equilibrium of acrylic acid molecules in solution:



Non-polar solvents favour existence of the dimer, whilst polar solvents lead to formation of the linear oligomers or 'pluri-molecular aggregates'. In the latter, the double bonds are in an organized narrow zone, so that when an initiation step takes place, leading to high rate of polymerization and degree of stereoregularity. Viscosity and infra-red measurements support the existence of such structures in the monomer. Chapiro further suggested that the presence in solution of polyacrylic acid already formed in the reaction provides a'template' to induce suitable orientation of the pluri-molecular aggregates in a 'matrix polymerization, leading to auto-acceleration and tactic polymer:



Such behaviour is in fact observed and the resulting polymer, which crystallizes readily, is not entirely stereoregular, but is thought to consist of syndiotactic blocks interspersed with atactic segments. Chapiro[186] has estimated that the relative rates of the matrix/oligomer/dimer processes are approximately 85/14.5/1 in the case of acrylic acid, although the effects are not observed with methacrylic acid. He has extended his work to acrylamide polymerization with similar conclusions.

The copolymerization studies of Kerber[187] also support these ideas, showing that the monomer reactivity ratios correlate with the tendency of the solvent to form hydrogen bonds with the monomers, rather than with the charge on the reacting species.

N-VINYL PYRROLIDONE (NVP)

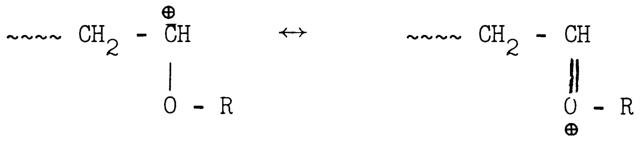
N-Vinyl pyrrolidone[188,189] polymerizes and copolymerizes readily by free radical initiators in the absence of oxygen. AIBN is the preferred initiator, since persulphate and organic peroxides react rapidly with the monomer, and are very rapidly removed[190]. Although NVP has been studied to only a limted extent, there is undoubtedly a significant solvent effect. Senogles and Thomas[191] showed that addition of water to the bulk monomer increase the rate of polymerization until about 25 % (v/v) is present: after this, the rate decreases steadily. Solvents such as isopropanol, methanol, ethyl acetate, etc., do not have this rate-enhancement effect. They attributed the effect to reactive complex formation between water and N-vinyl pyrrolidone monomer or radicals. Progressive addition of water increases complex formation, which reaches a concentration maximum before subsequent dilution. Addition of the other solvents does not produce complexes, and does not increase the rate of polymerization. Viscosity measurements suggest that only in water are complexes formed.

OTHER WATER SOLUBLE POLYMERS

For the sake of completeness, brief reference will be made to the more important water-soluble polymers produced by ionic means. The hydrogen-shift polymerization of acrylamide to give poly-β-alanine has already been mentioned. Other important monomers producing water soluble polymers are:

VINYL ALKYL ETHERS[192,193]

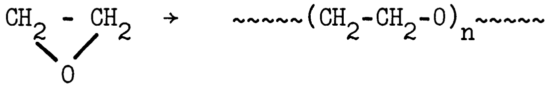
These may be polymerized in bulk or in inert solvent, using cationic catalysts (Lewis acids, such as boron trifluoride-etherate). Co-ordination catalysts give stereoregular products. The polymerizing ion is resonance-stabilized:



$$\sim\sim\sim\sim \mathrm{CH_2} - \underset{\displaystyle \mathrm{O-R}}{\overset{\oplus}{\mathrm{CH}}} \quad \leftrightarrow \quad \sim\sim\sim\sim \mathrm{CH_2} - \underset{\displaystyle \underset{\oplus}{\mathrm{O}}-\mathrm{R}}{\overset{}{\mathrm{CH}}}$$

When R is branched, short-chain, or non-aryl, reactivity is increased. The only water-soluble example of these polymers is that in which R represents CH_3.

ETHYLENE OXIDE(CYCLIC ETHER)[194,195]



The usual catalysts employed are:

(i) Species with metal-oxygen bonds;

(ii) Alkaline earth compounds; and

(iii) Miscellaneous anionic and cationic sources.

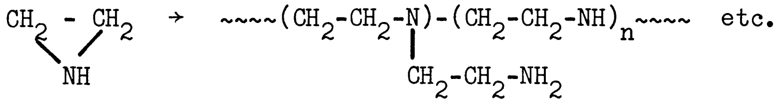
Typical examples are:

- Metal alkoxides, such as $Al(OR)_3$, etc., activated by metal chlorides, iron-based catalysts (the reaction product of $FeCl_3$ and propylene oxide, containg the Fe-O bond) in ethereal solution.
- Sr, Ca, or Ba carbonates, which must contain adsorbed water (possibly enough to form an adsorbed monolayer as the optimum amount).

The degree of polymerization of the product increases with conversion, so a step-wise mechanism is suggested.

ETHYLENE IMINE[196,197,198]

Polymer is formed by the acid-catalyzed reaction:



CONCLUSIONS

This chapter has concentrated on the free radical-initiated formation of water-soluble polymers. The polymerization of acrylamides and acrylic acid has been discussed in detail because of the technical importance of the polymers, and the considerable amount of work carried out on these systems. The factors controlling the various processes are subtle. The size, shape, chemical nature, interaction between the various species and the reactivity of the interacting entities are apparently controlled by the monomers present, the solvent and its condition,temperature, reactant concentration, solvent viscosity, dielectric constant, etc. It is not surprising that results from different workers are often in quantitative, if not qualitative, disagreement.

There is much scope for further fundamental study to be carried out to clarify this situation. It has been said that 'water as a solvent is anathema'. If polymer scientists persist in its use, then they must accept the consequences!

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WATER SENSITIVE CHEMICALLY CROSS-LINKED GELS

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SUMMARY

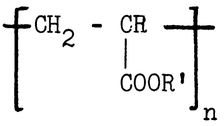
The principal properties and available information on hydrogels prepared by synthetic methods are reviewed. Hydrogels made from natural polymers are not discussed.

INTRODUCTION

The simplest definition of a hydrogel is ' a network which swells in water'[1]. According to another definition[2], a hydrogel can be defined as a polymeric material possessing ability to swell in water and retain a significant fraction (typically, 20 %) of water within its structure, but will not dissolve in water. The definition offered by Silberger[3] is still more detailed, taking into account the potential instability of the system formed by the swollen network and its surroundings where the temperature, pressure or chemical composition of the surroundings is changed. Hence, hydrogels are characterized by a pronounced affinity of their chemical structure towards water in which they do not dissolve, but merely swell. This is due to the existence of cross-links which, at least in water, bind macromolecules or their segments either by permanent bonds (definite chemical links) or through more extensively organized regions (effective cross-links). The latter are formed by bonds of sufficiently long life that changes in structure do not occur, or only occur very slowly under stress.

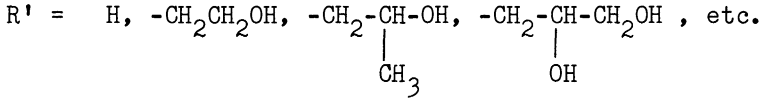
STRUCTURE OF SYNTHETIC HYDROGELS

A number of synthetic polymers behave as hydrogels. The largest group comprises the homopolymer and copolymer derivatives of methacrylic and acrylic acids:



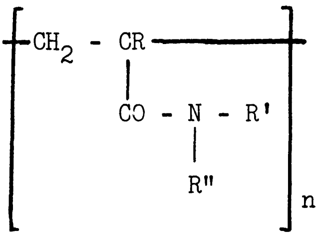
$$\left[CH_2 - \underset{COOR'}{\underset{|}{CR}} \right]_n$$

where R = H, CH_3, Na



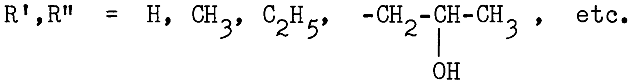
$$R' = H,\ -CH_2CH_2OH,\ -CH_2-\underset{CH_3}{\underset{|}{CH}}-OH,\ -CH_2-\underset{OH}{\underset{|}{CH}}-CH_2OH\ ,\ \text{etc.}$$

or derivatives of acrylamide:



$$\left[CH_2 - \underset{CO - \underset{R''}{\underset{|}{N}} - R'}{\underset{|}{CR}} \right]_n$$

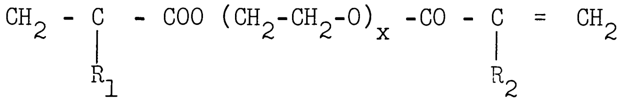
where R = H, CH_3



$$R',R'' = H,\ CH_3,\ C_2H_5,\ -CH_2-\underset{OH}{\underset{|}{CH}}-CH_3\ ,\ \text{etc.}$$

These polymers swell more or less in water, depending on the hydrophilicity of the side group. If the hydrophilicity of the side group is insufficient to dissolve the whole molecule in water, swelling takes place only in the aqueous medium. As would be expected, a further increase in hydrophilicity leads to water-soluble polymers.

Polymers such as polyvinyl pyridine, poly n-vinylpyrrolidone, or polyvinyl alcohol are water-soluble, and behave as hydrogels only if they are cross-linked chemically. The most common cross-linking agents are derivatives of ethylene glycol dimethacrylate :



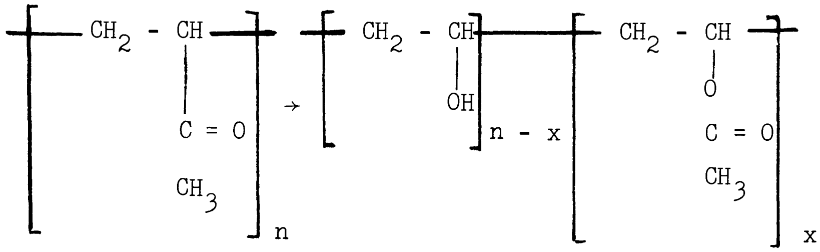
$$CH_2 - \underset{R_1}{\underset{|}{C}} - COO\ (CH_2\text{-}CH_2\text{-}O)_x\ \text{-}CO - \underset{R_2}{\underset{|}{C}} = CH_2$$

or methylene-bis-acrylamide:

$$CH_2 = CH.CO.NH - CH_2 - NH.CO.CH = CH_2$$

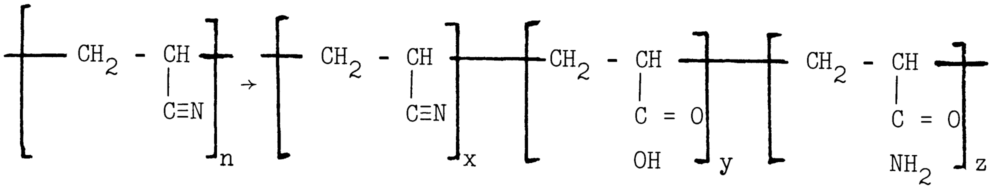
Amongst other properties, the copolymerization of hydrophilic and hydrophobic monomers also allows the control of hydrophilicity. The relative hydrophobicity of the usual chemical cross-linking agents also affects the overall hydrophilicity of the hydrogel formed, which may, of course, be raised by exchanging the cross-linking agent for a more hydrophilic compound. It must be remembered that, with hydrogels formed by chemical cross-linking, the copolymers obtained depend on the constraints of the copolymerization system, especially with respect to the possible inhomogeneity of composition of the copolymer formed, particularly if the copolymerization parameters differ from each other.

Polymer-analogous reactions yield copolymers (or terpolymers) with various hydrophilic sequences of different length. An example can be seen in poly(vinyl alcohol), formed by the incomplete hydrolysis of poly(vinyl acetate):



$$\left[CH_2 - \underset{\underset{CH_3}{\underset{|}{C = O}}}{CH} \right]_n \rightarrow \left[CH_2 - \underset{OH}{\underset{|}{CH}} \right]_{n-x} \left[CH_2 - \underset{\underset{CH_3}{\underset{C = O}{\underset{|}{O}}}}{CH} \right]_x$$

and of hydrolyzed polyacrylonitrile:



$$\left[CH_2 - \underset{C{\equiv}N}{\underset{|}{CH}} \right]_n \rightarrow \left[CH_2 - \underset{C{\equiv}N}{\underset{|}{CH}} \right]_x \left[CH_2 - \underset{\underset{OH}{C = O}}{\underset{|}{CH}} \right]_y \left[CH_2 - \underset{\underset{NH_2}{C = O}}{\underset{|}{CH}} \right]_z$$

where the remaining nitrile sequences yield some more extensively organized regions preventing complete dissolution of the products of hydrolysis. At the same time, the hydrophilicity of sequences of both polyacrylic acid and of polyacrylamide is extremely high[10].

The chemical character of hydrophilic groups differs not only in affinity to water, but, equally important, in the polarity. This makes the character of some gels either completely neutral - e.g. poly(2-hydroxyethyl methacrylate) (PHEMA), or polymers of glucose and sucrose methacrylates[11]- acid, and capable of ionization - e.g. polyacrylic and polymethacrylic acids and their copolymers - or basic, such as polyvinylpyridine and its copolymers and derivatives. Negatively and positively charged macromolecules mixed together can form water-insoluble, but swelling, complexes, which behave as hydrogels[12,13].

It is quite clear that a number of other macromolecular compounds with different chemical structure exist, which in water behave as hydrogels. Some blends also behave as hydrogels - e.g. a composite formed from 2-hydroxyethyl methacrylate and fibrous collagen[14].

PREPARATION

Most monomers used in the preparation of synthetic hydrogels are water-soluble, which makes possible the use of bulk and solution polymerization, whilst at the same time reducing the application of emulsion and suspension polymerization. The latter method is applied in the preparation of macroporous hydrogels with a high degree of cross-linking, and hence with a low degree of swelling in water[15]. The high polarity of hydrophilic groups on the one hand, and their relatively high reactivity in various polycondensation reactions on the other, impede the use of ionic or polycondesnation methods.

Owing to their high degree of hydration as water-plasticized polymer networks, the hydrogels have, in fact, a low mechanical strength: the more water they contain, the more their strength decreases. This property often unfavourable affects the practical application. For this reason, coating techniques have been developed, allowing the deposition of a thin layer of the hydrogel on substrates such as other polymers with better mechanical properties, including glass and carbon fibres. The simplest technique consists of dipping in a solution of the polymer. The hydrophilic character of the layer thus formed often does not provide a sufficient adhesion: in particular, it is likely to crack during drying. Various techniques of grafting of hydrophilic polymers on to surfaces have been tested[2] which ensure a chemical bond between the hydrogel and the substrate. This increases the mechanical cohesion between both layers, especially if the hydrogel layer is sufficiently thin. The surface of the substrate is activated by irradiation with accelerated electrons, atomized gas plasma, by γ-irradiation, with Ce^{4+} ions, by U.V. irradiation of the photosensitizer, or through the formation of peroxides.

Fabrics have often been used in order to strengthen the mechanical properties of hydrogels. Depending on conditions, hydrogels can be prepared in various forms, such as transparent optically pure blocks and films, porous sponges, or almost unswellable porous beads. The transparency and the type and degree of macroporosity (if any) are particularly affected by the degree of solubility of the polymer in the monomer or in the solvent if present, by the amount of the cross-linking agent,,or by the compounds producing the porosity. The suspension polymerization of hydrophilic monomers resulting in porous beads is also affected by other factors, especially by interfacial tension[16].

SWELLING OF GELS

The swelling function of gels has been the object of thermodynamic analysis[17].

Swelling is the most important property of hydrogels, and is a practical consequence of the affinity of the chemical structure of the hydrogel to water. Since the hydrogel cannot dissolve, it appears to take up water. During swelling, the volume of the hydrogel increases up to equilibrium, at which the chemical potentials of water in the gel, and of water surrounding the gel are balanced. As the network swells, the polymer chains are elongated and exert a force in opposition to swelling. The network acts as a pressure generating device. The osmotic pressure (π) attributed to the polymer is the driving force of swelling. The swelling process distends the network and is counteracted by the elastic contractability of the stretched polymer network (p). Contractability of the network tends to expel the water. At equilibrium, swelling of nonionogenic hydrogels is the swelling pressure (P) equal to zero[4].

$$P = \pi - p$$

Concentration of water in the gel can be adjusted by suitable contracting or expanding the distance between cross-links by coiling or uncoiling the macromolecular segment chains. The configuration of the network in its swelling equilibrium situation is the reference unstressed nondistorted configuration[3].

Swelling pressure can be defined as the pressure exerted by a gel when swelling is constrained, but swelling solvent is available. If there are no obstacles to swelling, water will enter in the hydrogel until the water chemical potential as in hydrogel environment is matched: zero value of the swelling pressure is reached at the same time.

Since swelling depends on the osmotic pressure, and thus on the water chemical potential in outside solution, the degree of swelling depends on the type and concentration of solutes in solution. Some solutes may also penetrate into the hydrogel network and somehow interact with network segments. This will probably affect the contractability of the network. For example, ion partitioning in gel has been observed for cellulose[18], cross-linked dextrans[19,20], and poly(2-hydroxyethyl methacrylate)[21]. Other solutes are too bulky to penetrate into the network. Since dissolved compounds in the surroundings of the gel always alter the water chemical potential, the degree of swelling is altered each time.

In a study[4] mentioned above, Refojo pointed out, using highly-swollen hydrogels based on poly(2,3-dihydroxypropyl methacrylate) (polyglycerol methacrylate) that inorganic salts,

Table 1. Equilibrium swelling of poly(2,3-dihydroxypropyl methacrylate - methacrylate) gels in different solutions

Solute	Concentration	% of equilbrium weight in H_2O
NaCl	0.9	36.7
$CaCl_2$	1.3	37.6
urea	1.63	59.3
glucose	5.51	47.05
serum	-	26.82
serum ultrafiltrate	-	39.05
vitreous	-	30.35

or large or small organic molecules, at concentrations up to 5 % decrease the degree of equilibrium swelling compared with that achieved in pure distilled water, as shown in Table 1.

The different degree of swelling of the same neutral hydrogel in distilled water, saline solution, or in tears is of practical importance when hydrogels are used as surgical implants, soft contact lenses, etc.

Refugo has also shown that similar hydrogels for which equilibrium swelling had been reached in distilled water are dehydrated in dextran solutions. Since the dextran molecule employed in these experiments had an average size of about 270 Å, but the average pore diameter of the hydrogels used is about 12 Å, so no penetration of dextran macromolecules into the hydrogel network seems likely: hence, partial dehydration is a result only of the balancing of the water chemical potential throughout the system.

In general, it can be said that hydrogels can, with comparative ease, lose water by evaporation. this is accompanied by network contaction. During the gradual evaporation of water, the water chemical potential in the hydrogel increases. This can be demonstrated by the increasing osmotic and mechanical pressure needed for the compression of the hydrogel to an identical, partly dehydrated, state.

So far, neither the character of the interaction between water and the segments of the macromolecular network in hydrogels, nor the water structure in hydrogels has been givin an unambiguous explanation. Using measurements of the 'freedom of water' and of permeability, some workers have suggested that water present in ahydrogel has a structure partly different from that of water in bulk water, or, more precisely, that the order relative to that of bulk water is different. According to measurements of the water activity versus hydrogel hydration, it is concluded that water in the hydrogel can be divided into 'free' water and ' bound' water. The former has approximately the same vapour pressure as liquid water. In this, it differs from the latter, which is present in the hydrogel in an amount up to 25 - 30 %, and possesses a lower water activity. In considering its amount, it is suggested that 'bound' water is identical with that in which Lee, Jhon and Andrade assigned as 'bound' and 'interfacial' water. The remainder of the water of hydration in the hydrogel is 'free' or 'bulk' water[22]. Water in hydrgels has also been distinguished as free liquid, capillary or pore retained liquid and polymer absorbed liquid[5,23,24].

Other workers, however, referring to measurements of sorption isotherms and heat capacities, have concluded that the binding of water in hydrogels, either on to hydrophilic groups in the side-chain, or on to hydrophilic groups in the main chain is no stronger that intermolecular bonds in pure liquid water. It is emphasized that attention should be paid to the possible change of physical state (from glass to a viscoelastic system) which may occur on adding water to the polymer[25].

Assuming that part of the water in the hydrogel is highly structured, it is possible to employ another way to describe the osmotic, swelling, and viscoelastic behaviour of gel networks. The solubility theory modification of the classical Flory theory is proposed to explain the osmotic and swelling behaviour of gel networks. In describing the viscoelastic behaviour of hydrogels, three functions, governed by the three types of water, are used to explain the stress-strain relations in the rubbery region[6]:

Effect of pressure. As previously noted, elastic contractability creates a force counteracting the penetration of the water into the hydrogel. It is understandable, therefore, that the equilibrium degree of swelling depends on the degree of compression of the gel under a mechanical pressure. Under certain circumstances water exudes from the swollen hydrogel until equilibrium is reached. Highly hydrated hydrogels (jellies) (over 90 % water) lose much water with comparatively low compression, sometimes with only the pressure of their own weight. This occurs with some hydrogels of poly(2,3-dihydroxypropyl methacrylate). Hydrogels of poly(2-hydroxyethyl methacrylate), which, in the equilibrium swelling condition conatin about 40 % of water, may also lose water due to long-term compression, but the pressures required are much higher[4].

Effect of ionizable groups. Polymer networks which behave as hydrogels but contain ionizable groups behave in a more complex way. Swelling of such hydrogels depends on the degree of ionization of the groups. This is known especially for carboxylic groups, notably in copolymers ofacrylic or methacrylic acid. Basic groups affect the degree of swelling to a lesser extent[7].

Permeability. The permeability of poly(2-hydroxyethyl methacrylate) membranes has been studied by several authors[8,26,27,28]. It is generally accepted that the structure of the membrane-forming gel depends on the amount of the cross-linking agent. At low concentrations of the cross-linking agent, 'voids' (some kind of minute pores) are present, making possible the transport of water and solutes. The membrane then acts as some sort of network[8]. At high concentrations of the cross-links, the minute pores are not formed, or they are already too small. The transport of water and of relatively small molecules is, however, still possible, by employing the partition of dissolution mechanism. Under certain circumstances, both mechanisms can operate. The presence of 'voids' of free volume also explains why, at the beginning of swelling of dry hydrogels, a much greater initial amount of water is taken into the gel than would be anticipated from the linear swelling measurement alone[8,29]. It appears that pores are quickly filled with water before the gel is able to produce any linear expansion. This view has also been adopted for some biopolymers[6,30].

SURFACE PROPERTIES

To complete the description of the most important properties of hydrogels, the wettability of hydrogels, and, consequently, their surface properties in an aqueous medium, should be mentioned. Considering its importance, this problem has been studied rather fully[5,9]. Although hydrogels in the swollen state contain a considerable amount of water, this does not mean that their surface must always be completely hydrophilic. The character of the surface depends on the history of preparation of the hydrogel. This applies not only to synthetic hydrogels[31], but also to gelatine[32,33] or agarose. It has been found that the wettability of hydrogels is primarily determined by the nature of the polymer, and also by the segmental mobility of the polymer chains at the gel boundary. It is assumed that during contact with water that the wettability of the hydrogel may vary from more hydrophobic to more hydrophilic. This is made possible by segment mobility and amphipatic character of the polymer chains at the gel boundary which also explains differences between the so-called advancing and receding contact angle measurements. More hydrophobic groups can be exposed and lined up at the surface when it is exposed to water vapour and more hydrophilic sites can be exposed to the adjacent liquid water phase[9].

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CHEMICAL MODIFICATION AND SOME CROSS-LINKING REACTIONS OF WATER-SOLUBLE POLYMERS

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1. INTRODUCTION

Many chemical reactions of water-soluble polymers are possible, depending on the presence of reactive groups attached to a polymer chain able to combine with other water-soluble polymers (polymeric or otherwise) under conditions which do not significantly degrade the polymer. Since the property of water solubility implies the presence of a substantial number of polar groups in the molecule, the potential and, indeed, the actual degree of complexity of chemical behaviour is considerable. It is therefore worth establishing some simple principles, common to most water-soluble polymers, which describe the actual or possible cross-linking reactions. In general, and with a considerable degree of over-simplification, 'chemical modification' can be considered as a part-way stage towards the cross-linking which results in a more rigid, and possibly less soluble, molecular structure.

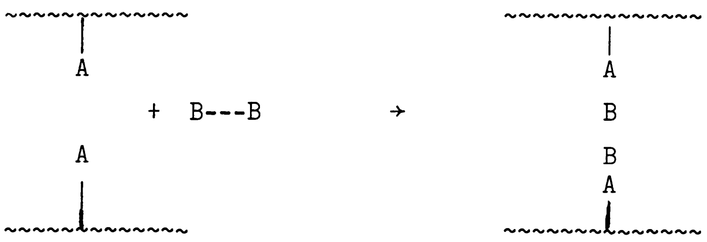
Only too many chemical reactions are potentially possible: most problems arise from the competing reactions which can occur between different molecular species, to a greater or lesser extent, and the resulting interactions. The principal possible reactions will now be considered in general terms.

2. CROSS-LINKING WITH FUNCTIONAL GROUPS

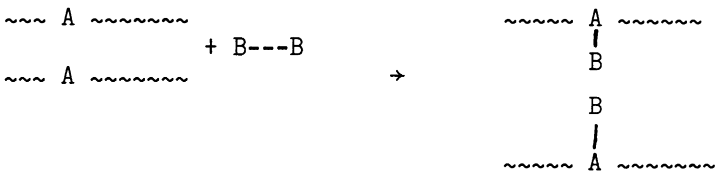
Polymers with pendant or back-bone functional groups may be cross-linked by typical organic chemical reactions involving functional groups. Schematically, the basic reactions are:-

a. Use of difunctional group B - B

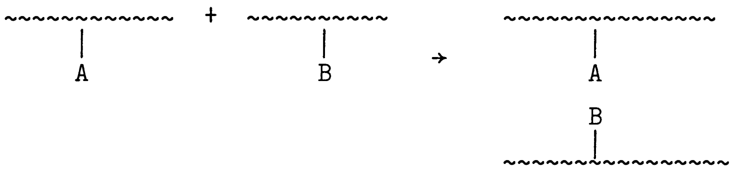
i. Reactive groups pendant to back-bone:-



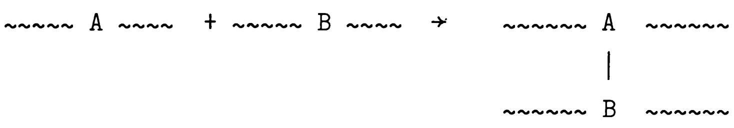
ii. Reactive groups part of backbone:-



iii. Linking between reactive polymers:-



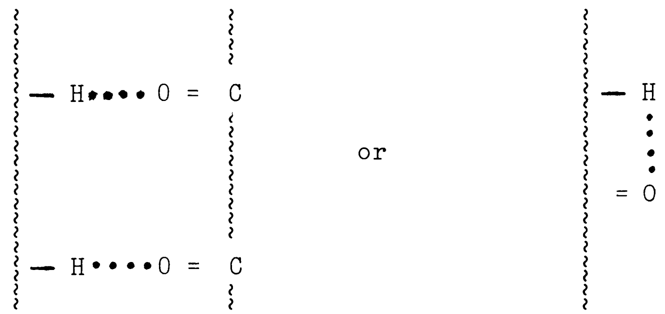
or, possibly,



The mechanism of the formation of the ~A---B~ bond may be either by condensation or addition or, sometimes, by ionic reaction.

3. CROSS-LINKING BY HYDROGEN BONDING

There are many possible variations on the basic theme of either inter- or intra-molecular bonding represented by:



4. EFFECTS OF CROSS-LINKING ON THE PHYSICAL PROPERTIES OF POLYMERS

Much of the theoretical work published on the relationship between cross-linking structure and polymer properties has been concerned with hydrocarbon polymers in hydrocarbon solvents - notably, the speciality synthetic rubbers, especially butyl rubber, which is a copolymer of isobutene with a small amount (below 3 %) of isoprene. Although not specifically applied to the chemistry of water soluble polymers, some of the concepts are common to all organic polymers. The physical properties of a cross-linked polymer, in relation to those of the starting polymer, are affected by:-

i. The molecular weight (and the molecular weight distribution) before cross-linking;

ii. The degree of spatial order in the molecule (which may be considered in relation to the degree of crystallinity);

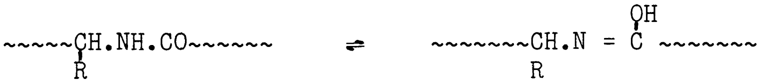
iii. The degree of cross-linking - i.e., the number (and nature) of the cross-links, their flexibility, and their relation to the chain-length of the starting polymer.

The classical theory[1,2] (Flory-Stockmayer) of gel formation (discussed in more detail by Borchard in Chapter 6) may also be considered, broadly, as a form of cross-linking, possibly reversible by physical change (rather than chemical bond-breaking) makes two approximations - the absence of substituent effects, and the absence of cyclization through intermolecular effects and reactions. The importance of these has been considered by Gordon[3] who has taken the view that both effects are, in practice, about equal.

5. PRINCIPAL TYPES OF WATER-SOLUBLE POLYMERS

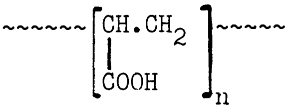
All water-soluble polymers include a significant number of polar groups in sterically exposed positions on the polymer chain (see Molyneux, Chapter 1). By far the greater number of such polymers contain hydroxyl groups, notably carbohydrates and their derivatives (which are the most common class of organic polymers), and the synthetic polyhydroxyl polymers, such as polyvinyl alcohols, which are also mentioned in Chapter 17 .

The basic structure of the proteins may be represented by



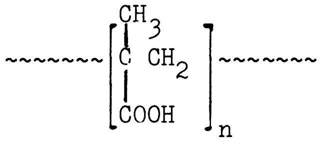
$$\sim\sim\sim\overset{}{\underset{\mathrm{R}}{\mathrm{CH}}}.\mathrm{NH.CO}\sim\sim\sim \rightleftharpoons \sim\sim\sim\underset{\mathrm{R}}{\mathrm{CH}}.\mathrm{N} = \overset{\mathrm{OH}}{\mathrm{C}}\sim\sim\sim$$

where the side chain, R , may also contain hydroxyl, amino, or carboxyl groups. Other water-soluble polymers may also contain carboxyl groups, as in the many polyelectrolytes. Typical examples, discussed in more detail elsewhere in this book, include:-



$$\sim\sim\sim\left[\underset{\mathrm{COOH}}{\mathrm{CH}}.\mathrm{CH_2}\right]_n\sim\sim\sim$$

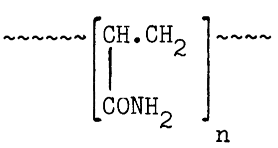
and



$$\sim\sim\sim\left[\underset{\mathrm{COOH}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\ \mathrm{CH_2}\right]_n\sim\sim\sim$$

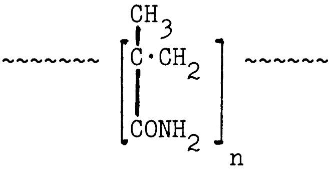
polyacrylic acid polymethacrylic acid

and the corresponding amides, such as



$$\sim\sim\sim\left[\underset{\mathrm{CONH_2}}{\mathrm{CH}}.\mathrm{CH_2}\right]_n\sim\sim\sim$$

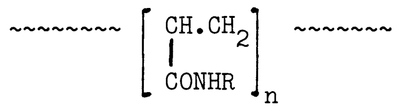
and



$$\sim\sim\sim\left[\underset{\mathrm{CONH_2}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdot\mathrm{CH_2}\right]_n\sim\sim\sim$$

polyacrylamide polymethacrylamide

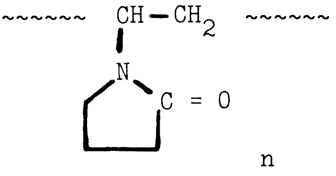
Substitution can also take place on the N- atom, as in:-



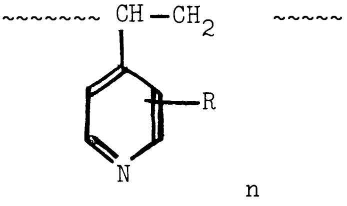
$$\sim\sim\sim\left[\underset{\mathrm{CONHR}}{\mathrm{CH}}.\mathrm{CH_2}\right]_n\sim\sim\sim$$

poly-N-alkylacrylamide

Other N-containing water-soluble polymers include



and

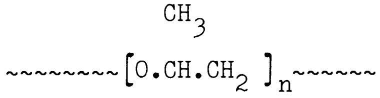


polyvinylpyrrolidone

polyvinylpyridine and derivatives

Polymers based on the presence of an oxygen or nitrogen atom in the main backbone include:-

~~~~~~~ $[O.CH_2.CH_2]_n$ ~~~~~~ polyethylene oxide



$$\sim\sim\sim[O.\overset{CH_3}{CH}.CH_2]_n\sim\sim\sim$$

polypropylene oxide

~~~~~~~~ $[NH.CH_2.CH_2]_n$ ~~~~~ polyethylene imine

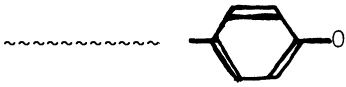
The principal side-chain groups which occur in water-soluble polymers are:-

~~~~~~~~~~~~~~ OH

(also

$$\sim\sim\sim\sim\ \underset{R}{CH}.OH$$

and



OH)

~~~~~~~~~~~~~~ COOH

~~~~~~~~~~~~~~ $CONH_2$

~~~~~~~~~~~~~~ NH_2

~~~~~~~~~~~~~~ $CONR_1R_2$ (R_1,R_2 = H or alkyl)

~~~~~~~~~~~~~~ SO_3H

Each of the above groups provides potential sites for cross-linking reactions, as discussed below. Before considering these reactions in detail, it is worth indicating some of the theoretical approaches to the general problem of determining the degree of cross-linking, or cross-linking density.

6. DETERMINATION OF CROSS-LINKING DENSITY

Cross-linking density is a key factor in establishing the relation between the molecular structure and the properties of a polymer. In general, most theoretical studies of this reaction have been concerned with the relatively simple systems of water-insoluble hydrocarbon polymers, without polar side-groups, in hydrocarbon solvents. Comparatively little discussion outside the present volume (see, especially, Franks (Chapter 9) and Borchard (Chapter 6)) has been published on the structure of cross-linked polar polymers in water, in spite of their obvious industrial and biological importance. A brief account of the relevant theory, as far as it exists, for polymers in general (not specifically water-soluble polymers) will now be outlined.

Flory[4] pointed out that: 'In cross-linking, the larger the molecule becomes, the greater the cross-linking expectancy, because of the increased number of potential cross-linkable units'. He considered that the general conditions for the formation of infinite networks are:

- infinite structures are only possible in systems possessing structural units, some of which are capable of joining with more than two other units;
- complex molecules must be generated with the capacity to combine with each other; so
- the expected number of elements in a molecule united to other molecules must exceed two.

The cross-linking density may be determined in non-polar systems:

- before gelation, by measurement of the sol fraction, or volume swelling, by determination of intrinsic viscosity, if the basic data on the properties of the polymer before cross-linking are available;
- by measurement of the elastic and stress-strain behaviour of suitable specimens of polymers.

The intrinsic viscosity before the formation of gel[5] is used in:

$$\frac{\eta_0 - \eta_\pi}{\eta_0} \cdot \frac{1}{\pi} = \frac{\sqrt{2}}{\sqrt{N_m}}$$

from which

$$N_m = 2\left(\frac{\pi\,\eta_0}{(\eta_0 - \eta_\pi)}\right)^2$$

where

η_0 = i.v. of open-chain polymer
η_π = i.v. of cross-linked polymer
N_m = number of statistical chain elements
π = molecules of cross-linking agent

The gels produced on cooling of water soluble polymer solutions, which are reversible (see Borchard, Chapter 6) can be considered as reversibly cross-linked networks, in which the cross-linking function is due to hydrogen bonding. The gelatin gels are amongst the best characterized of these systems[6], where the density of cross-linking depends on the configuration of the helical chain of the protein, and the distribution of the side-chain substituents of the amino-acids (see below), which can affect the spatial characteristics of the molecules (Figure 1).

The theory of the cross-linking density of gelled systems, notably vulcanized rubbers in hydrocarbon solvents, has been discussed by Flory and Reiher[7], who suggested that

$$\text{Moles of cross-linked units per gm. of polymer} = \frac{V_r + \chi V_r^2 + \ln(1 - V_r)}{d_r \cdot V_o (V_r^{1/3} - \tfrac{1}{2} V_r)} = \frac{1}{M_c}$$

$$\text{where} \quad V_r = \frac{\text{swollen polymer volume}}{\text{total cross-linked polymer volume}} = \frac{1}{1 + q}$$

For water soluble polymers, these expressions can be simplified,

$$\text{when} \quad q = \frac{w_s}{w_g}$$

where

d_r = density of polymer
w_s = weight of solvent in gel
w_g = weight of gel
V_o = molar volume of water
χ = polymer/solvent interaction parameter
M_c = molecular weight between cross-links

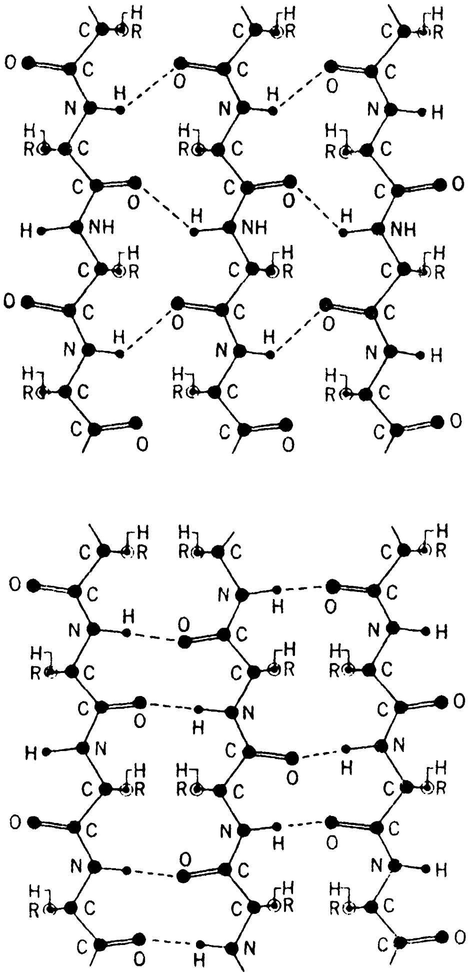


Figure 1. Gelatin gels - schematic representation of hydrogen bonding between multiple helical chains of proteins.

Other types of molecules are considered by Borchard (Chapter 6), who also lists the different types of gels which have been described by Flory[8]. Most water soluble polymers fall into the class of gels which are mainly disordered, with regions of local order. At the 'melting' point of the gel, this order is lost, and a viscous solution containing the polymer in a random spatial distribution is formed. The process of order-disorder can be repeated, but it appears to be difficult to measure the degree of local order in the cross-linked zones in relation to the surrounding disordered solution (see Borchard (Chapter 6) Figure 1). Systems similar in concept, if not in detail, to the cross-linked zones with local order, depending on the hydrogen bonding of polypeptide molecules, can also be conceived for polysaccharides, probably with single or multiple-chain helices (Figure 2). These concepts have been considered mainly in relation to the structure and properties of biologically important molecules (see Borchard (Chapter 6) References 50 - 57), where it is possible, by detailed structural analysis, to obtain some information on the number, and likely position, or hydrogen bonds in the ordered molecule - which, however, may not be water soluble under the conditions of investigation. However, it must be said that there appears to be no current theory which provides a satisfactory explanation of the relations between the structure, degree of cross-linking, and properties of water soluble polymers in general. Considering the importance of solubilization-insolubilization phenomena of polymers in both biological and industrial processes, this position is both remarkable and regrettable.

The reactions of water soluble polymers with small molecules may result in chemical modification or cross-linking. Some of these reactions will now be considered.

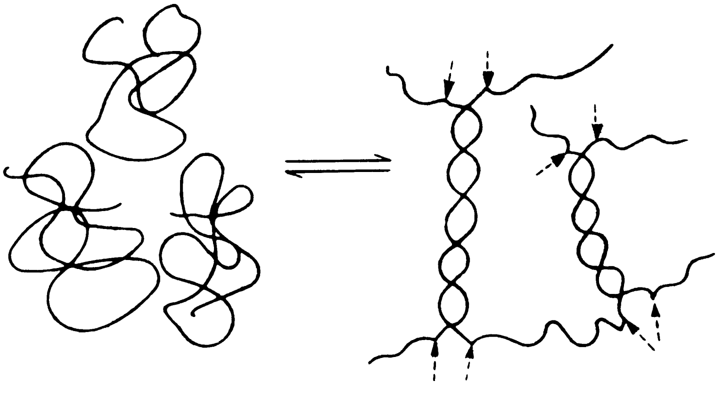
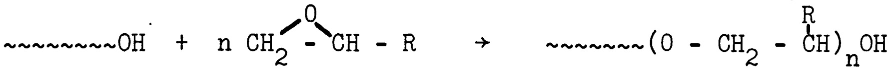


Figure 2. Junction zones of a typical gel (carrageenan). (The arrows indicate galactose sulphate or disulphate residues replacing anhydrogalactose units: these residues break up the regular helical structure).

7. CHEMICAL REACTIONS OF WATER SOLUBLE POLYMERS

The chemical reactions of water soluble polymers - both inter- and intra-molecular - are the foundation of many applications in industrial processes, where these polymers are required to have altered properties, of which the most significant are,probably, altered surface activity, or increased water resistance.

Most reactions of water soluble polymers involve the addition of small molecules to extend side-chains, such as ethoxylation:



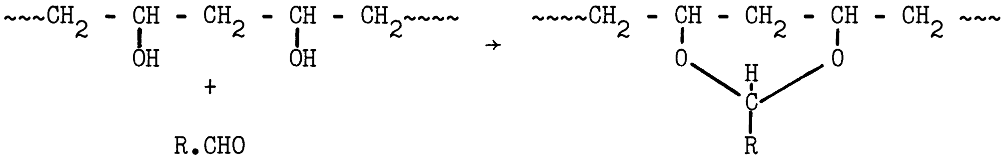
$$\sim\sim\sim\sim\sim\sim\sim\sim OH + n\, \overset{O}{CH_2 - CH} - R \rightarrow \sim\sim\sim\sim\sim\sim\sim (O - CH_2 - \overset{R}{CH})_n OH$$

However, the reactions of aldehydes with hydroxy-containing polymers are more complex, since the aldehydes used may include:

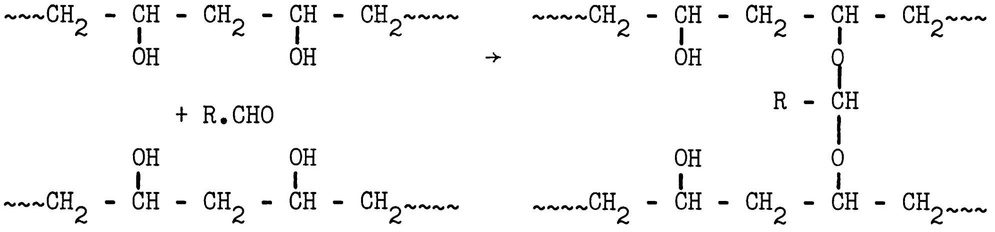
monofunctional	$HCHO$	formaldehyde
	CH_3CHO	acetaldehyde
	etc.	
difunctional	$OHC.CHO$	glyoxal
	$OHC.\ CH_2.CHO$	glutaraldehyde
	etc.	
also		dialdehyde starch

A typical example of this reaction is the acetalization of polyvinyl alcohol (see below)which can occur in different ways:-

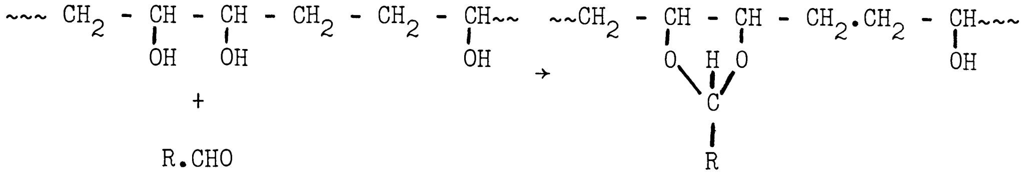
a. intramolecular acetalization of 1,3-glycol groups.



b. intermolecular acetalization



c. Intramolecular acetalization of 1,2-glycols



$$\sim\sim\sim CH_2-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_2-CH_2-\underset{OH}{\underset{|}{CH}}\sim\sim \;\; \underset{R.CHO}{+} \;\; \rightarrow \;\; \sim\sim CH_2-\underset{O}{\underset{|}{CH}}-\underset{O}{\underset{|}{CH}}-CH_2.CH_2-\underset{OH}{\underset{|}{CH}}\sim\sim\sim \quad \underset{\underset{R}{|}}{\overset{O\;H\;O}{\diagdown\,|\,\diagup\atop C}}$$

The stereochemistry of the reaction products obtained (the most important of which is polyvinyl formal, used in wire coating and in lamination of vehicle windscreens) is indicated in Figure 3.

The reaction of monofunctional aldehydes with amines commence with the formation of an N-methylol polymer:-

$$\sim\sim\sim\sim\sim\sim NH_2 \quad + \quad HCHO \quad \rightarrow \quad \sim\sim\sim\sim\sim\sim NH.CH_2OH$$

Most polymer of this nature are highly reactive, with a tendency to condense with another similar molecule, with loss of water:

$$\sim\sim\sim\sim\sim NH.CH_2OH \;+\; HOCH_2,NH\sim\sim\sim\sim \rightarrow \sim\sim\sim NH.CH_2.O.CH_2.NH\sim\sim\sim \quad + \; H_2O$$

For more convenient reaction conditions, the corresponding ether may sometimes be employed, with an acidic catalyst (usually p-toluenesulphonic acid), so that the reaction rate can be controlled.

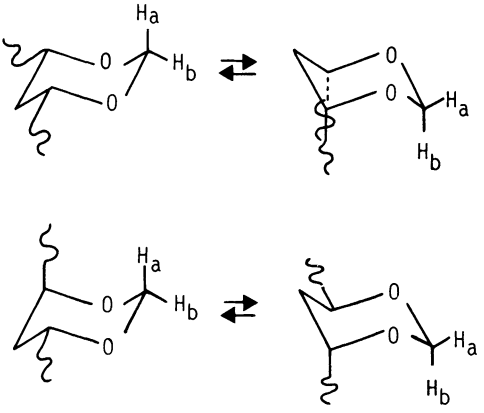
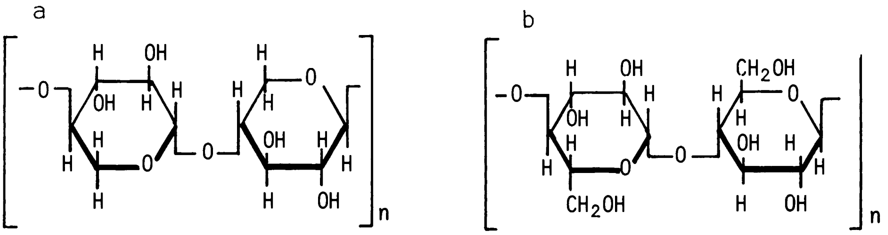
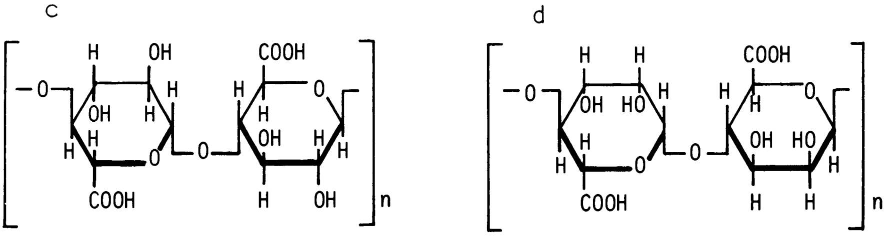


Figure 3. Stereochemistry of formals of polyvinyl alcohol

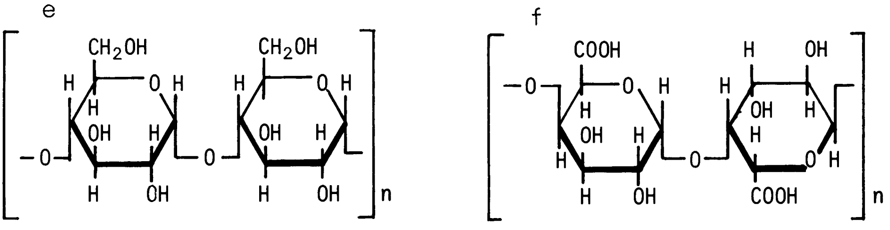
Many other water soluble polymers are based on the carbohydrate structures indicated in Figure 4, with the principal common feature, from the point of view of chemical reactivity, of the presence of large numbers of hydroxyl groups. Typical examples, ignoring for the present the effects of different chain lengths, and degrees of chain branching, show a pattern of reactive groups in the pairs of pyranose units, where xylan (Figure 4(a)) is the simplest molecule, followed by cellulose (Figure 4(b)) (where OH is partly replaced by -CH$_2$OH), then polyglucuronic acid (Figure 4(c)) (where -CH$_2$OH is replaced by -COOH), alginic acid (Figure 4(d)) (where -OH is replaced by -H), amylose (figure 4(e)) (which is the sterically opposed form of (b)), and polygalactouronic acid (Figure 4(f)) (which is the sterically opposed form of (c)).



Xylan Cellulose



Polyglucuronic acid Alginic acid



Amylose Polygalacturonic acid

Figure 4. Carbohydrate polymers

The reactions of cellulose, as a hydroxyl-group containing polymer, are legion: many of them are exemplified by the well-studied chemistry of the reactions of cotton, developed for the established processes of stiffening and improvement of the crease-resistance of fabrics. Although cotton is not, of course, water soluble, many of these reactions can, or could be, applied to starch and other related water soluble polymers.

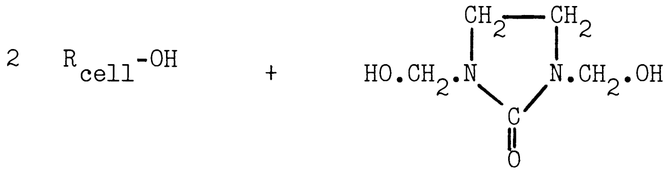
8. REACTIONS OF CELLULOSE AND STARCH[9-13]

The basic molecule is R_{cell}-OH - typically, cotton.

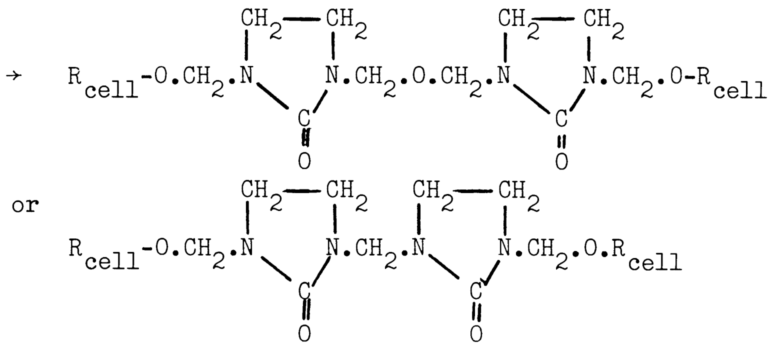
With formaldehyde, as above, using a strong acid catalyst, the basic cross-linking reaction takes place:-

$$2\ R_{cell}\text{-OH} \xrightarrow{H^+} R_{cell}\text{-O.CH}_2\text{.O-}R_{cell}$$

Alternatively, using bifunctional reagents, with <u>methylol</u> groups, cross-linking can occur with either methylene or ether links. Typically:-

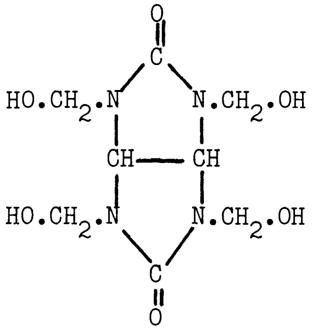


bis-methylolethylene urea

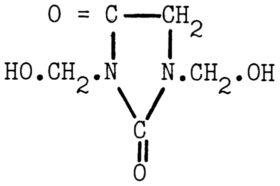


With cotton, the optimum cross-linking effect (in terms of desired fabric performance) is obtained with 11 % of reagent, corresponding to one methylol group per cellobiose unit.

Other methylol compounds used include:-



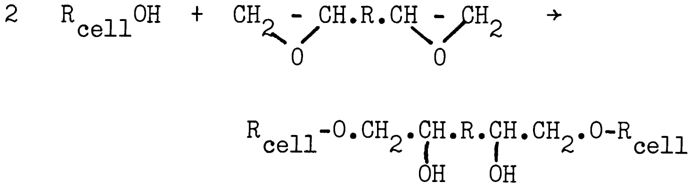
Tetramethylol acetylene
urea



dimethylolhydantoin

and many other compounds[11]

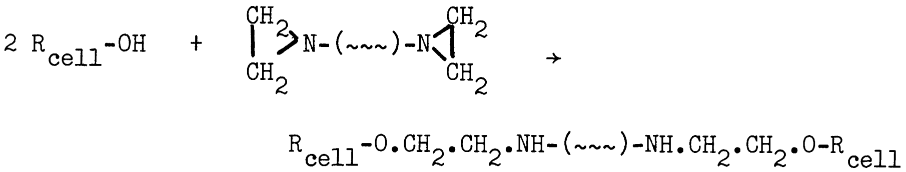
Reactions with epoxides (especially diepoxides, such as butadiene diepoxide), apart from the main reaction:-



$$2\ R_{cell}OH + CH_2\text{-}CH.R.CH\text{-}CH_2\ (\text{two epoxide }O) \rightarrow R_{cell}\text{-}O.CH_2.\underset{OH}{CH}.R.\underset{OH}{CH}.CH_2.O\text{-}R_{cell}$$

can have several side reactions (see also protein reactions, below).

Reactions with the analogous derivatives of ethylene imine have been used in the paper coating industry for insolubilization and improvement of the wet strength of the product, e.g.:-



$$2\ R_{cell}\text{-}OH + (CH_2)_2{>}N\text{-}(\sim\sim\sim)\text{-}N{<}(CH_2)_2 \rightarrow R_{cell}\text{-}O.CH_2.CH_2.NH\text{-}(\sim\sim\sim)\text{-}NH.CH_2.CH_2.O\text{-}R_{cell}$$

Typically, -(~~~)- is

$-CH_2.CH_2-$

$-CH_2.CH_2.O.CH_2.CH_2-$

$-CO.NH(CH_2)_6NH.CO-$

$-OOC.R.COO-$ etc.

The reactions of sulphones take place under easily controllable and reversible conditions:

e.g.	$(CH_2 = CH)SO_2$	divinyl sulphone
	$(HOCH_2CH_2)_2SO_2$	bis(2-hydroxyethyl)sulphone

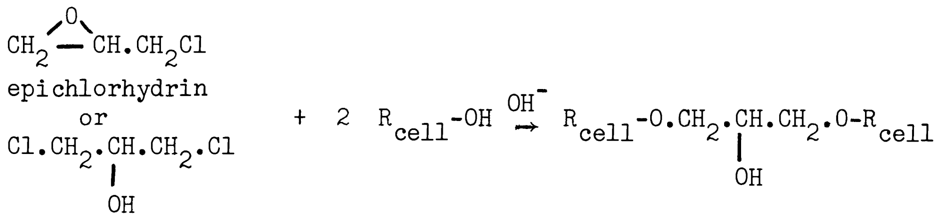
$$2\ R_{cell}\text{-}OH \ + \ HO.CH_2.CH_2.SO_2.CH_2.CH_2.OH$$

$$\overset{OH^-}{\rightleftharpoons} \ R_{cell}\text{-}O.CH_2.CH_2.SO_2.CH_2.CH_2.O\text{-}R_{cell} \ + \ 2\ H_2O$$

Reactions with labile chlorine compounds occur in alkaline conditions:-

$$2\ R_{cell}\text{-}OH \ + Cl - R - Cl + 2\ NaOH \ \rightarrow \ R_{cell}\text{-}O.R.O\text{-}R_{cell} \ + 2\ NaCl$$

e.g.



epichlorhydrin

or

$$Cl.CH_2.\underset{OH}{CH}.CH_2.Cl \ + \ 2\ R_{cell}\text{-}OH \ \xrightarrow{OH^-} \ R_{cell}\text{-}O.CH_2.\underset{OH}{CH}.CH_2.O\text{-}R_{cell}$$

9. STRUCTURE AND CROSS-LINKING REACTIONS OF PROTEINS

Gelatin, the hydrolytic degradation product of the triple helix of collagen, the protein of connective tissue[6], gels by hydrogen bonding. The basic protein structure is shown in Fig.5 (a more detailed account of gelatin gel structure is given by Stainby[14]). Side chain substituents depend on collagen source and on method of extraction: the amino-acids are common to all collagens, but differ only in proportion. Table 1 shows typical amino-acid distributions, indicating that most have hydrocarbon side-chains, which are chemically unreactive under conditions which do not cause cleavage of the main polymer chain. Reactive side-chains are carried on the following amino-acids:-

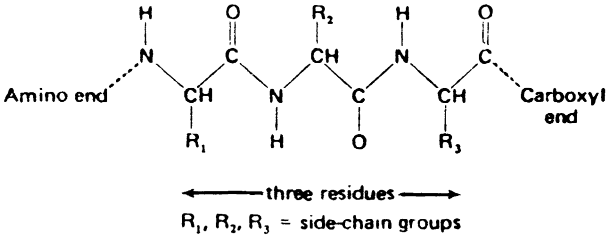


Figure 5. Basic structure of the protein chain.

Table 1. Side chain groups in gelatin.

Amino-acid	Side-chain structure	Number occurring in 1000 residues		
		Limed hide gelatin	Limed ossein (bone) gelatin	Limed pigskin gelatin
Amide NH_2	see Note 1	7.5	15.7	40.8
Alanine	$-CH_3$	112.0	116.7	110.8
Glycine	-H	333	335	326
Valine	$-CH(CH_3)_2$	20.1	21.9	21.9
Leucine	$-CH_2CH(CH_3)_2$	23.1	24.3	23.7
*iso*Leucine	$-CH(:CH_2)CH_2CH_3$	12.0	10.8	9.6
Proline	see Note 2	129.0	124.2	130.4
Phenylalanine	$-CH_2C_6H_5$	12.3	14.0	14.4
Tyrosine	$-CH_2C_6H_4OH$	1.5	1.2	3.2
Serine	$-CH_2OH$	36.5	32.8	36.5
Threonine	$-CH(OH)CH_3$	16.9	18.3	17.1
Arginine	$-(CH_2)_2NH.C(:NH)NH_2$	46.2	48.0	48.2
Histidine	imidazolylmethyl	4.5	4.2	6.0
Lysine	$-(CH_2)_4NH_2$	27.8	27.6	26.2
Aspartic acid	$-CH_2COOH$	46.0	46.7	46.8
Glutamic acid	$-(CH_2)_3COOH$	70.7	72.6	72.0
Hydroxyproline	see Note 2	97.6	93.3	95.5
Hydroxylysine	$-(CH_2)_2CH(OH)NH_2$	5.5	4.3	5.9
Methionine	$-CH_2CH_2.S.CH_3$	5.5	3.9	5.4

Notes: 1. The amount of amide ammonia present in a gelatin depends on the pre-treatment of the collagen source. This treatment can be either acid or alkaline, and will bring about a degree of hydrolysis of the side chain amide groups present. Prolonged alkaline treatment will bring about an almost complete loss of amide ammonia, whilst brief acid treatment leaves the amide groups almost intact.

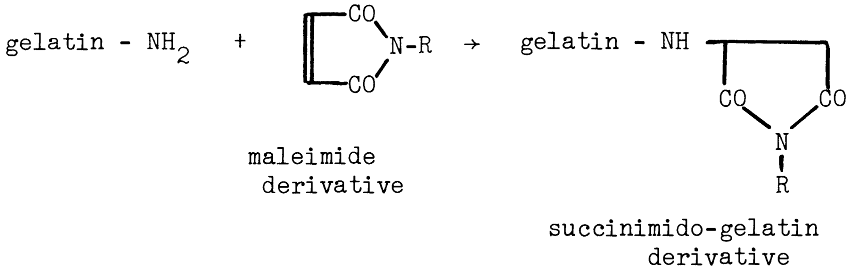
2. Proline contains a bridging $-CH_2-$ group on the main chain whilst hydroxyproline contains the corresponding -CH(OH)- . Both amino-acids are specific to collagen and its derivatives, and provide a significant increase in main-chain rigidity, and gelling power.

Serine	-	primary -OH
Threonine) Hydroxyproline)	-	secondary -OH
Tyrosine	-	phenolic -OH
Aspartic acid) Glutamic acid)	-	-COOH
Lysine	-	$-NH_2$
Arginine	-	- guanidinyl $-C(:NH).NH_2$

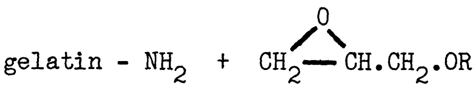
Many chemical modification reactions of these side-chains have been studied: they fall into the general categories of:-

A. Removal of side-chains.
The guanidyl group of arginine may be removed by strong alkaline hydrolysis, using sodium hydroxide with hypobromous acid or sodium in liquid ammonia, whilst the amino-groups may be removed by nitrous acid (the traditional Van Slyke method for the determination of amino-acids).

B. Substitution on side-chains.
  i. Amino-group substitution.
    a. Acetylation, using acyl halides or anhydrides;
    b. Sulphonation, using substituted sulphonyl halides;
    c. Formation of urea derivatives, using, e.g. phenylisothiocyanate, C_6H_5SCN;
    d. Aromatic substituted amino-derivatives - e.g. 1-fluoro-2,4-dinitrobenzene (Sanger's reagent[16]);
    e. Other active hydrogen derivatives, including triazines used as dyes[17] and as dye-couplers in colour photography[18];
    f. Carbamoylation[19];
    g. Reaction with double bonds
      - grafting with acrylic polymers (using, e.g. free radicals), also



h. Reaction with epoxides

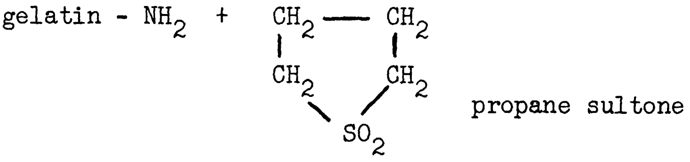


$\rightarrow$ gelatin - $NH.CH_2.CH(OH).CH_2OR$

$\rightarrow$ gelatin - $N(CH_2.CH(OH).CH_2OR)_2$

A similar reaction occurs with propylene oxide and alkali.

j. Reaction with sultones



$\rightarrow$ gelatin - $NH.(CH_2)_3.SO_3H$

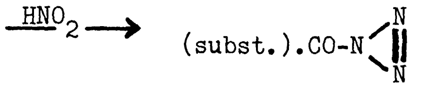
k. Guanidinylation[20]
-reconversion of ornithine to arginine, using O-methylisothiourea (the hydrogen sulphate salt, $CH_3O.C(=NH).NH_2.H_2SO_4$, is used to modify the lysine residues):-

gelatin- $(CH_2)_3$ $-NH_2$ + $CH_3O.C(=NH).NH_2$

$\rightarrow$ gelatin - $(CH_2)_3.NH.CH(=NH).NH_2$

l. Carboxylazide modification (mainly used for dye-couplers in colour photography[21]:-

(subst.)$.COOC_2H_5$ $\xrightarrow{H_2N.NH_2}$ (subst.)$.CO.NHNH_2$



$$\xrightarrow[\text{gelatin - OH}]{\text{gelatin - NH}_2} \quad \begin{matrix}\text{gelatin - NH.CO - (subst.)}\\ \text{gelatin - O.CO - (subst.)}\end{matrix}$$

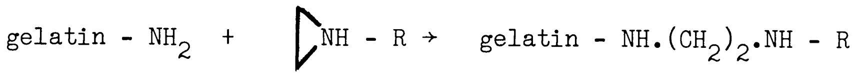
ii. Carboxyl group substitution
  a. Methylation - partial esterification;
  b. Carbodiimide reactions[22] to introduce novel substituents

$$\text{gelatin - COOH} + \text{R - N = C = N - R'}$$
$$\rightarrow \text{gelatin - CO.OC }(=\overset{+}{\text{N}}\text{HR})\text{NH - R'} + \text{NH}_2\text{.CH}_2\text{.COOCH}_3$$
$$\rightarrow \text{gelatin - CO - NH - CH}_2\text{ - COOCH}_3 + \text{H}^+ + \text{R.NH.CO.NH.R'}$$

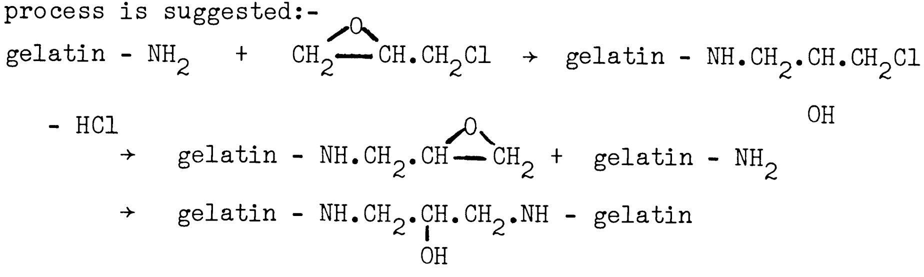
iii. Hydroxy groups
  a. Carboxyl azide modification - see i. (k) above.
  b. Esterification, especially by sulphuric acid, sulphates, or sulphonates;
  c. Acylation[20]

Cross-linking reactions of gelatin have been studied in considerable detail, mainly in relation to the hardening of photographic gelatin films[23,24,25] and other coating applications where insolubilization is required, such as the manufacture of security paper. Many of these reactions represent difunctional 'equivalents' of the modification reactions indicated in the preceding sections. Those reactions involving the -NH_2 and the primary -OH groups are the most widely investigated. The more important reactions include those with :-

- acid anhydrides and halides, especially the more complex compounds, such as terephthaloyl chloride;
- activated halogen hardeners, such as NN'-dibromoacetyl- and NN'-dibromopropionyl derivatives of hydrazine, dimethyl hydrazine, ethylene or propylene diamine, and urea[26];
- active double bond hardeners, such as sulphones, especially divinyl sulphone (see cellulose, above);
- aziridines, typically



  Many substituted aziridines have been claimed for use as photographic gelatin hardeners[27];
- Epoxides[28], especially epichlorhydrin, where a two-stage reaction process is suggested:-



The epoxide ring isvery reactive, so a number of compounds containing two or more epoxide rings, such as butadiene diepoxide, react readily, not only with gelatin, but with other polymers bearing carboxyl groups or hydroxyl groups (see cellulose above). Amino-group linkages with epoxides are stable to hydrolytic action[28].

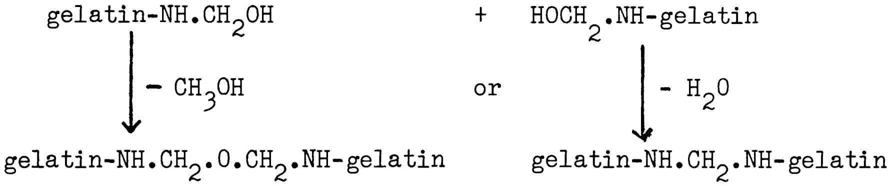
- di- and polyisocyanates: the use of bisulphite adducts of isocyanates has been claimed for the increase of gelatin viscosity, presumably by cross-linking[29]

C. Aldehyde and ketone cross-linking.

Formaldehyde is probably the most widely used hardening agent for gelatin[23]. The probable mechanism of reaction is, initially, the formation of a methylol substituent at the amino-groups:-

$$\text{HCHO} + \text{gelatin} - \overset{+}{N}H_3 \rightleftharpoons \text{gelatin-NH.CH}_2\text{OH} + H^+$$

In very dilute solution, it can be assumed that this reaction does not proceed further, because of the distance between molecules. Upon addition of further formaldehyde, there appear to be two possible routes for the cross-linking stage of the reaction:-



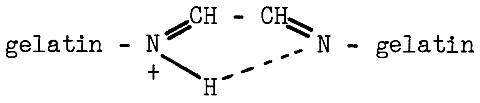
$$\text{gelatin-NH.CH}_2\text{OH} + \text{HOCH}_2\text{.NH-gelatin}$$

$$\xrightarrow{-\,CH_3OH} \text{gelatin-NH.CH}_2\text{.O.CH}_2\text{.NH-gelatin} \quad \text{or} \quad \xrightarrow{-\,H_2O} \text{gelatin-NH.CH}_2\text{.NH-gelatin}$$

In large scale use, formaldehyde suffers from the problems of odour and difficulties of control of the reaction rate, although it is much less expensive than dialdehydes such as glyoxal, OHC.CHO, glutaraldehyde, $OHC.CH_2.CHO$ and polyformals[30], which are more easily handled. It has been suggested by Courts and Holman[31] that, for the dialdehydes, $OHC.(CH_2)_n.CHO$, the effectiveness of cross-linking is in the order

$$n = 1 < n = 2 < n = 3 < n = 4$$

For photographic gelatin is has been reported that succinaldehyde and, especially, glutaraldehyde, are outstanding in their hardening activity, and glutaraldehyde is stated to react as much as 3600 times faster than formaldehyde with gelatin[32,33]. Evidence from kinetic studies on the mechanism of glyoxal hardening (and, presumably, cross-linking) suggests[34] the possibility of a partially stabilized cross-link of the type

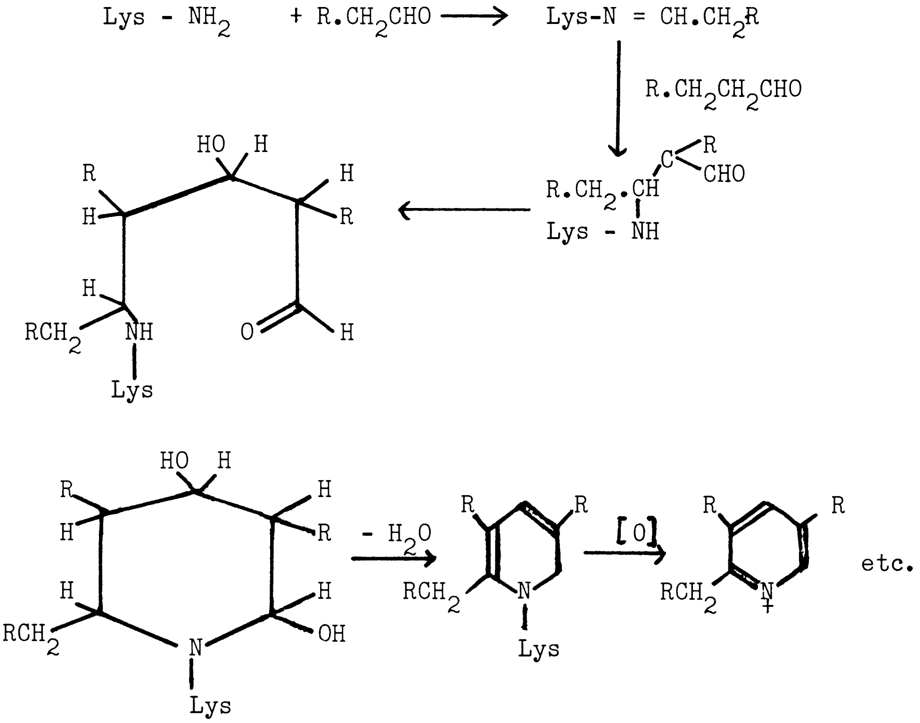


Glutaraldehyde is more active than succinaldehyde in photographic developer solutions[23], possibly due to a formation of a relatively stable cyclic complex with the sulphite present.

Studies of the reactions of dialdehydes with gelatin, collagen and other proteins suggests that[35,36]:-

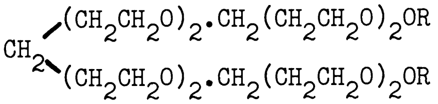
- lysine and hydroxylysine are the amino-acids which are mainly involved;
- two or more aldehyde molecules are sometimes involved in a single cross-link;
- most, if not all, the cross-links formed are stable to boiling water and dilute acid. Studies of the formation of the cross-links of the protein elastin, and of lysyl residues, suggest that, with glutaraldehyde, cyclic pyridinium compounds may be formed[23]:-

  (R = $-CH_2CH_2CHO$)



- the fact that glyoxal can only form the aldimine (-CH = N -) may account for its hydrolytic instability[35].

Other useful aldehyde reacting compounds include paraformaldehyde and its reaction products with hexamethylene tetramine (see cellulose, above) and with diethylene glycol:-



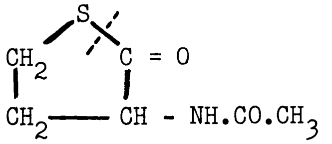
$$CH_2\begin{cases}(CH_2CH_2O)_2.CH_2(CH_2CH_2O)_2OR\\(CH_2CH_2O)_2.CH_2(CH_2CH_2O)_2OR\end{cases}\quad (R = H \text{ or } CH_2OH)$$

Polymeric aldehydes include compounds such as the cleavage products of polysaccharides by periodate, of which a typical example is dialdehyde starch (Figure 6).

As an alternative approach, there are several methods of introducing suitable cross-linkable side-chain functions into the gelatin molecule, in which cross-linking can be achieved by relatively mild and controllable reaction conditions, Sulphonate esters act as alkylating agents: a large variety of bis(methane sulphonates) are effective as gelatin hardeners[38], which undoubtedly operate by alkylation of gel - NH_2 . Bis(sulphonyl halides) behave similarly, forming - $SO_2.NH$ - linkages[39].

Sulphide groups can be introduced on to the lysine amino-groups by reaction with a thiolactone:-

gelatin - NH_2 +



N-acetylhomocysteine thiolactone

→ gelatin - $NH.CO.CH(CH_2CH_2SH).NH.CO.CH_3$

Mild oxidative conditions, such as exposure to air, cause cross-linking by the formation of intermolecular disulphide bridges (or, at high dilution, intramolecular bridges will be formed prefrentially). The process is reversed by reduction.

Vinyl side-chains have been introduced by treatment with several different reagents, e.g.:-

gelatin - NH_2 + $OCN.CH_2.CH_2.O.CO.CH = CH_2$

acryloxyethylisocyanate

→ gelatin - $NH.CO.NH.CH_2.CH_2.O.CO.CH = CH_2$

Other 'reactive' side groups include those in photographic gelatin hardening systems based on triazines[40,41], notably those

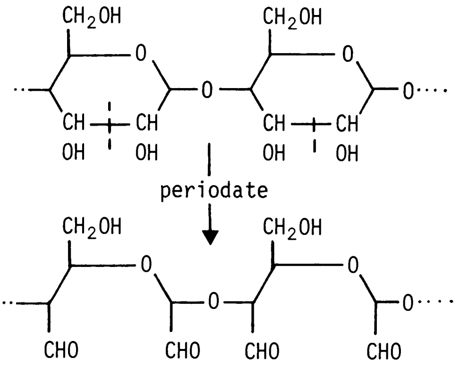
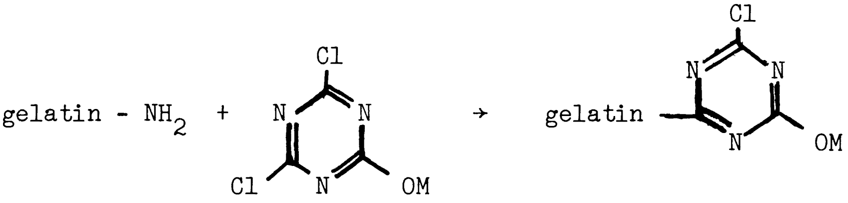


Figure 6. Formation of dialdehyde starch.

using the water soluble salt of 2,4-dichloro-6-hydroxy-s-triazine:-



(M = H, or alkali metal ion)

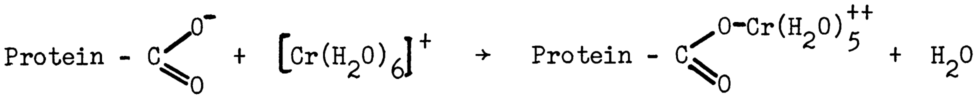
Cross-linking reactions of this type appear to occur exclusively with the ε-amino-group of lysine. Treatment of this reactive polymer with a polymeric amine (including gelatin) causes loss of the labile Cl atom, with formation of covalent cross-links of the 2-hydroxy- or 2-metaloxy-s-triazine-4,6-diylamino- structure. Many variations of these reactions with triazines with bulky aromatic side-chains have been suggested, which produce gelatin-derived polymers with interesting coacervation properties, potentially or actually useful in the formation of microcapsules.

Indeed, the phenomenon of coacervation of gelatin by natural polyacidic and polyphenolic natural compounds, such as gum arabic (see, e.g.[42]), pectins and tannins is an important example, in both scientific and industrial terms, of the cross-linking of a water soluble polymer by non-covalent bonds. This coacervation, essentially dependent upon cross-linking by hydrogen bonds, is employed, for example, in the production of microcapsules for carbonless copying paper and other applications[43].

Gelatin forms many polyelectrolyte complexes (these are discussed in more general terms by Mandel in Chapter 10) of considerable commercial significance, including those with metaphosphates (in foods) and in photographic applications, and with polysaccharides. It has been noted[44] that, whilst covalent cross-linking of gelatins does not usually cause the product to separate in aqueous solution, there are many examples (including the above) of non-covalent types of compounds with which this can occur, especially in dilute solution.

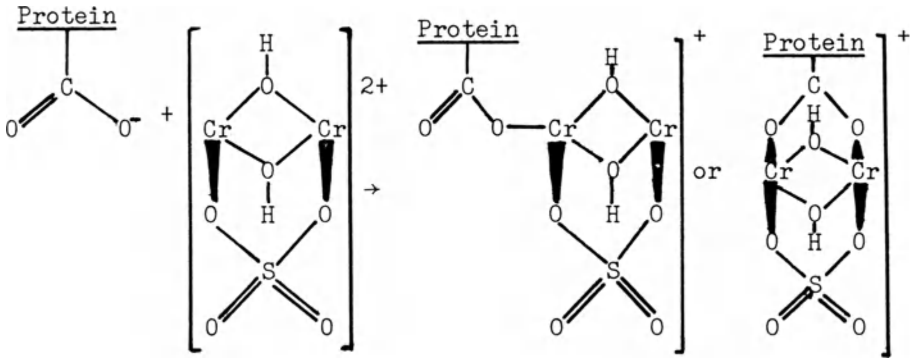
10. CROSS-LINKING REACTIONS INVOLVING METAL IONS

The cross-linking reactions of metal ions with proteins have been studied in detail, with particular interest in the tanning reactions of leather, especially by chromium salts, with the object of insolubilizing the fibrous water swellable, if not water soluble, protein structure. Whilst there is considerable uncertainty, in many cases, about the details of the structures formed, the basic type of complex is believed to involve the side-chain carboxyl groups (of aspartic and glutamic acids) is the terminal carboxyl groups attached to the protein chain:-

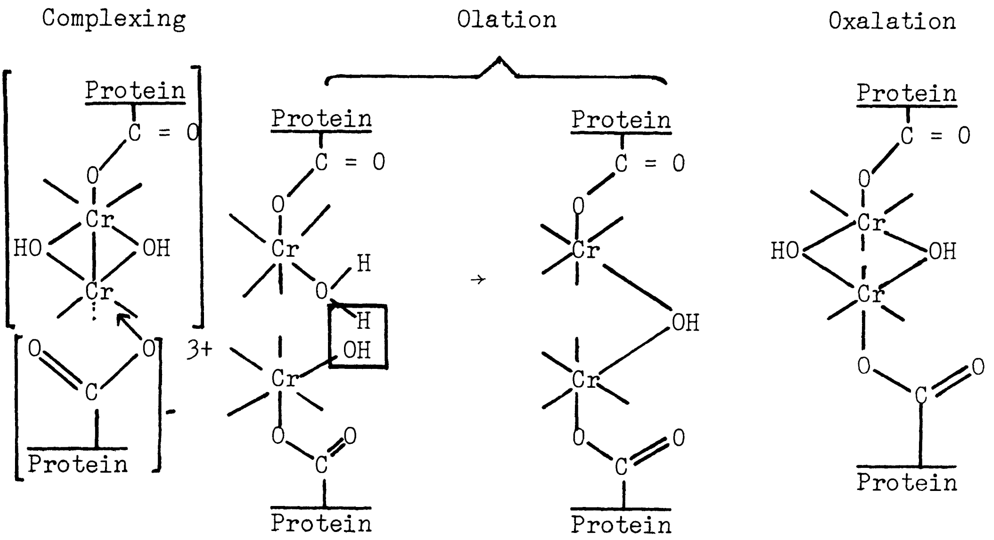


$$\text{Protein - C}\overset{\text{O}^-}{\underset{\text{O}}{<}} + [\text{Cr(H}_2\text{O)}_6]^+ \rightarrow \text{Protein - C}\overset{\text{O-Cr(H}_2\text{O)}_5^{++}}{\underset{\text{O}}{<}} + \text{H}_2\text{O}$$

which, in spatial terms, can be shown as:-



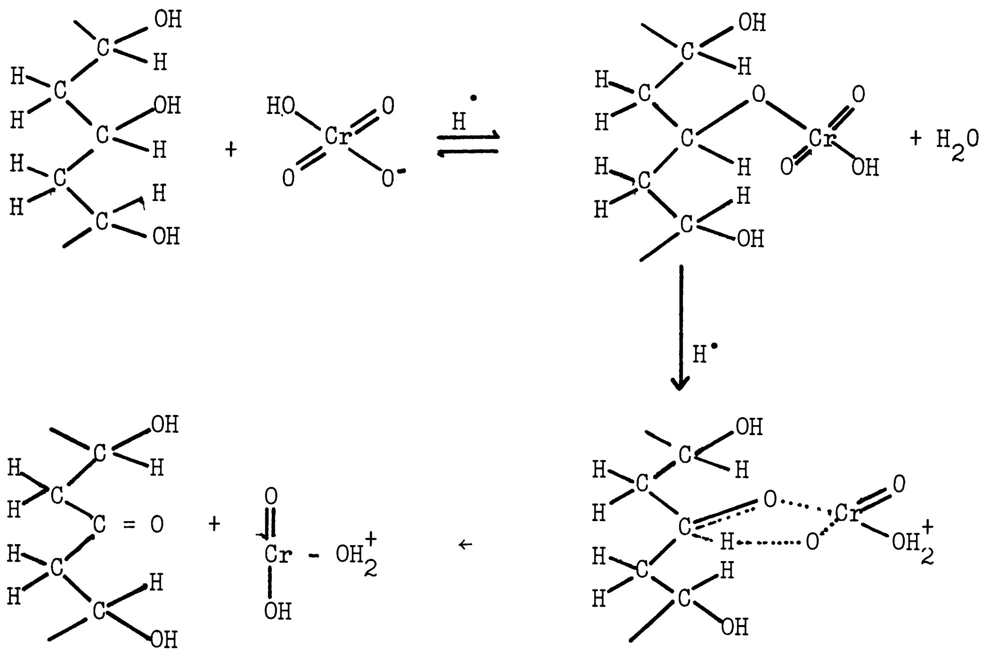
with, probably, cross-linking as in:-



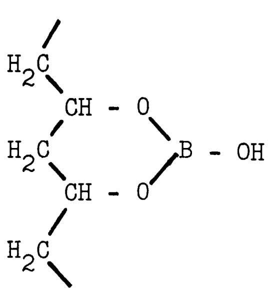
Reactions with metal complexes have been postulated for many polymers with hydroxyl side groups. Competing reactions may take place, as exemplified by oxidation of a secondary alcohol by Cr^{6+}:-

$$
\begin{array}{llll}
(1) & R_1R_2CHOH + Cr^{VI} & \rightarrow & R_1R_2C = O + Cr^{IV} \\
(2) & Cr^{VI} + Cr^{IV} & \rightarrow & 2\ Cr^{V} \\
(2') & Cr^{IV} + R_1R_2CHOH & \rightarrow & R_1R_2CHO + Cr^{III} \\
 & R_1R_2CHO & \rightarrow & R_1CHO + R_2^{\bullet} \\
 & R_2^{\bullet} + O_2 & \rightarrow & RO_2^{\bullet} \rightarrow \text{autoxidation reactions} \\
 & R_2^{\bullet} + Cr^{VI} + H_2O & \rightarrow & R_2OH + Cr^{V} + H^{+} \\
(3) & Cr^{V} + R_1R_2CHOH & \rightarrow & R_1R_2C = O + Cr^{III}
\end{array}
$$

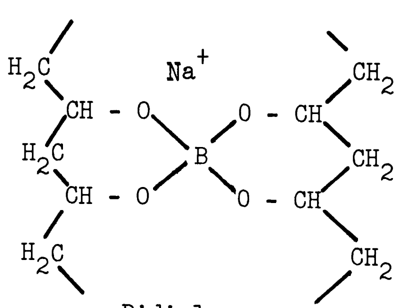
A similar type of reaction is thought to take place in the formation and decomposition of the chromate ester of polyvinyl alcohol:-



Polyvinyl alcohol (see also Chapter 17) forms many other complexes, notably those with borates: under suitable pH conditions these complexes result in irreversible gelling in aqueous solution. The exact pH conditions at which gelling can occur appears to vary with the structure of the polyvinyl alcohol: most of the relevant data has been reported for commercial polymers. For these polymers, information on the degree of chain branching (which is affected by the conditions of polymerization of the polyvinyl acetate from which the polyvinyl alcohol is obtained[45]) and the 1,2-glycol content (also dependent on the polymerization temperature[46]) is rarely available. It may be assumed that different borates[47] will also form different complexes, such as the monodiol and didiol types:-



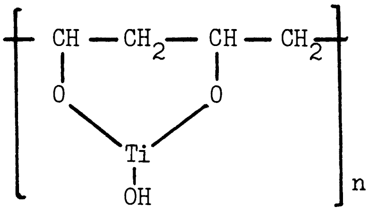
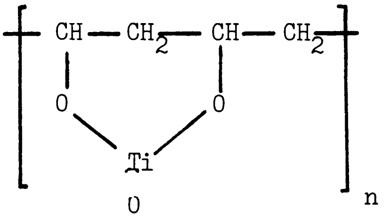
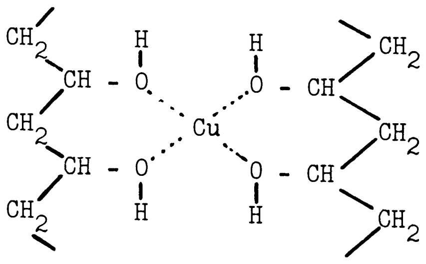
Monodiol



Didiol

Other metal salts will also form similar complexes, some of which have been investigated for their effect on the gelling properties, with increased water resistance and tendency to insolubilization. Some of these are shown in Table 2.

Table 2. Some reactions of polyvinyl alcohol with metal salts (for detailed references see[46])

Gelling agent	Product
$Ti(OCH(CH_3)_2)_4$ + lactic acid	
$TiO(SO_4)$	
Ti^{3+}, VO^{2+} compounds	Gel
$KMnO_4$(pH sensitive)	
$TiCl_3$	Gel
Ammonium vanadate	Gel
Inorganic oxidizing agents (e.g. $K_2Cr_2O_7$) + secondary amines + amphoteric metal chlorides (e.g. phenyl-β-naphthylamine + $AlCl_3$ or $SnCl_2$	Improvement of water resistance of polyvinyl alcohol plasticized with glycerol
Cu salts (at pH 7 - 9)	

Many of these reactions are obviously possible with the many other hydroxyl-containing polymers, such as cellulosics, but do not appear to have been studied, although it is likely that some take place in the more complex systems containing water soluble polymers, such as emulsion paints and some water-based adhesives (see, e.g. Baily in Chapter 15). Another group of polymers which should show reactions of generally similar type are the water--swellable hydrogel polymers and related compounds which are similar, in many properties to natural polymers such as gelatin, alginates, agar, etc., within theoretically, a wide variation of properties with many possible copolymer ratios of a relatively small number of monomers. These are considered in more detail by Kálal in Chapter 4 .

This outline of the principal cross-linking reactions of water-soluble polymers leaves many areas unconsidered (especially in the field of polymers in biological systems) where the complexity of the systems involved makes for formidable difficulty in rigorous study. Many systems have received only cursory investigation, from a strictly scientific aspect, yet have considerable industrial and commercial importance. In some of these cases, it may be possible, by taking the example of other systems studied in more detail, to extend our insight into other, related, polymer reactions and structure-property relations: a great many of these fascinating topics remain to be investigated.

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THERMOREVERSIBLE GELATION

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It is well known that in dilute solutions linear polymers tend to form aggregates, whilst in concentrated solutions gels are formed, if the temperatures of the systems are chosen appropriately. Although, in some cases, it may be difficult to distinguish a liquid (sol) from a solid (gel), Hermans attempted to define a gel as a coherent system of at least two compounds, which exhibits mechanical properties characteristic of a solid, where both the dispersed component and the dispersion medium extend themselves continuously through the whole system[1].

The most striking property of a gel is its rigidity, which is described by the static or dynamic moduli for different kinds of deformation. On the molecular level, an 'infinite network' of macroscopic dimensions must be present in gels to explain the stability of their shape, when external forces are applied[2]. In classifying gels, Flory differentiates into four types[3]:-

1. Well-ordered lamellar structures, including gel mesophases, such as soap gels and clays. The forces between the lamellae may be elctrostatic or dipolar.
2. Covalent polymer networks, which are completely amorphous. Examples are vinyl - divinyl copolymers, vulcanized rubbers, the protein elastin, alkyd and phenolic resins, and silica gel.

3. Polymer networks formed by physical aggregation. These are predominantly disordered, but with regions of local order. The primary molecules, by means of which the network is built up, are usually of linear structure, and of finite size. The network junctions are multiple stranded helices, bundles of chains, or crystalline regions. The microcrystals may be regarded as cross-linkages of a high functionality, which is the number of possible linkages per junction.
4. Particulate disordered structures, such as flocculant precipitates, which usually consist of particles of large geometric anisotropy, e.g. disordered network-like accumulations of fibrils,as in V_2O_5-gels, followed by gels formed by aggregation of proteins, both fibrillar and globular.

Examples of both synthetic and natural polymers which are components of a gel system include polysaccharides[4-9] - such as chitin, cellulose, cellulose-derivatives, and starches - polypeptides, such as collagen and its der ived product gelatin[10-26], polyacrylonitrile[28,29], polyvinyl alcohol[30-33], polyvinyl chloride[34-37], mixtures of isotactic and syndiotactic poly methylmethacrylate[38-40], and more complex systems, including polymer solvent and dyestuff mixtures[41,42].

Most of the polymers mentioned above belong to Type 3. The gels are mainly in the disordered state, favouring rubber-like elasticity, with regions of local order, probably in the junction zones. Upon increasing the temperature a transition takes place. At the gel melting temperature, T_m, the gel loses its rigidity and a viscous polymer solution is formed. Lowering the temperature below T_m, the gel formation process, or the gelation, begins again. This thermally induced process may be repated several times, where the physical quantities such as comples shear modulus are changing with time, always in the same manner, under isothermal conditions. This process is called thermoreversible, although we know that gel formation, or ageing, as it is often called, is an irreversible process. A striking exception to the gelation process just described is shown by aqueous solutions of O-methylcellulose, which gel when they are heated[43]. These gels lose their structure upon cooling, and do not belong to Type 3.

Gels of natural polymers have widespread biological functions, for example in animal connective tissues, and in the walls of plant cells. They also have many commercial applications, notably in foodstuffs, cosmetics, photographic films, paper, and pharmaceutical formulations.

Investigations of the primary structure of polymers with a high tendency to form gels indicate that the general principle may, in the most simple representation, be that of an alternating copolymer of the type of:

a) $R\text{-}(\text{-}A\text{-}B\text{-})_m R'$ or b) $R\text{-}(A_i\text{-}B_i\text{-}C\text{-})_n R'$

where R and R' are the chain ends, A, A_i, B, B_i, and C are different monomer units, and m and n are the number of repeating monomer units. Araki[44] and O'Neill[45] established the structures of two gelling polysaccharides, agarose and κ-carrageenan, which belong to type a). Residue B is D-galactose in agarose, or its 4-sulphate in κ-carrageenan: the residue A is 3,6-anhydro-L-galactose in agarose or its D-enantiomer in κ-carrageenan. Rees was able to show that the polysaccharide κ-carrageenan could not entirely be described by a completely alternating structure, because in a single chain the repeating units A - B are replaced to a certain extent by slightly different chemical species like $A^* - B$ or $A - B^*$. This is called a masked repeating structure[9,46]. This type of structure is also applicable to a large number of seaweed polysaccharides and many mucopolysaccharides[8].

The primary structure of the α_1-chain of collagen may be approximately described by the formula of type b) in replacing C by the peptide residue of glycine. Along the polypeptide chain each sequence may have different amino-acid residues for A_i and B_i. Heidemann <u>et</u> <u>al</u>. have shown, in a series of papers[47,48], that oligomers of the collagen type with strictly alternating sequences of the terpolymer type A - B - C form aggregates in solution.

When considering a part of a gel forming synthetic polymers containing the mono-substituted vinyl monomer unit, it may be regarded as a copolymer of two different stereoisomeric sequences but the same kind of monomer. It is well-known that in atactic polymers there is no regular structure, and there is no tendency to gel or to crystallize.

In addition to the above, a further type of thermoreversible copolymeric primary stucture should be noted: this is represented by the following arrangement of blocks $-(A)_m-$ and $-(B)_n-$ in sequence:

c) $R\text{-}(A)_m\text{-}(B)_n\text{-}R'$

The sufficient and necessary condition for gel formation is a transition of one of the blocks to domains, where the macro-Brownian motion of polymer chains in not free, which means that chains cannot move along each other. The micro-Brownian motion of the polymer chains (the changes of position of the remaining type of blocks) must be free or only partly hindered[49]. The transition may be caused by themally induced glass transition, a partial crystallization

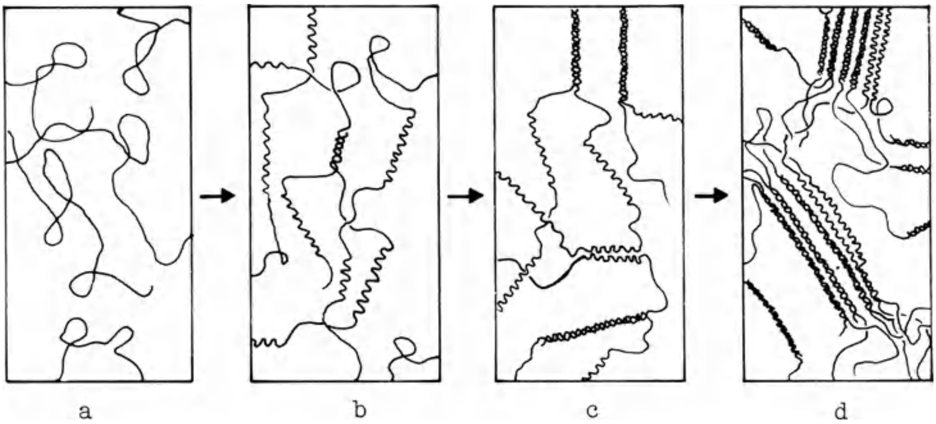

Figure 1. Schematic representation of the coil-helix transition:
(a) state of coiled macromolecules;
(b) partial transformation to helices and double helices;
(c) double helix formation and aggregation of single helices;
(d) final state.

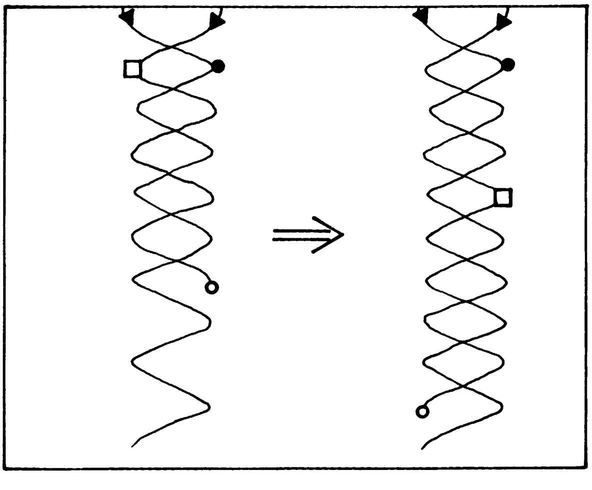

Figure 2. Screw pattern of two helices of equal sense and handedness[9].
Schematically: (○) end and (□) marked atom of helix 1.
(●) atom of helix 2.

or an intermolecular ionic bonding of chains of one of the blocks. The latter can be achieved by addition of a third component to the polymer solution, such as divalent ions - e.g. Ca^{2+} in the form of salts in polysaccharides[9]. In this case, the gel structure is lost if the divalent cations are exchanged with monovalent alkali metal ions such as Na^{+}. This transition is not necessarily thermo-reversible.

It should be mentioned that crystallization from solution is always a phase transition, which means that phase equilibria can be described by the conditions for heterogeneous equilibria. Kinetic processes during isothermal crystallization are nucleation and growth of the nuclei. This kind of phase transition must be clearly distinguished from a transition in a single phase where a polymer coil transforms to a helix.

The common feature of the secondary and tertiary structure of gelling copolymers like polysaccharides and polypeptides seems to be their capability to form single and double helices, where two or more chains are involved. The coil-helix transition, which occurs even in extremely dilute solutions, is an intramolecular transformation in homogeneous phase. The equilibrium transition is a cooperative intrachain reaction. Helical structures in macromolecules have been successfully calculated using statistical mechanical methods or potential function calculations[55-57]. Double and triple helices have been assumed as modes explaining the dense packing of polymer strands in the crystalline structure in agreement with results of X-ray diffraction analysis and further conditions, such as intra- and interchain hydrogen-bonding. Structures of this kind have been predicted to occur in the crystalline state and in the dilute regime[55]. It is therefore important to have details of the packing of strands in the polymer crystal and changes in the structure when solvent water is added.

The manner in which double or triple helices are formed in solutions of linear macromolecules is not yet exactly known, although different proposals have been made for the reformation of the collagen fold in gelatin solutions, giving rise to junction zones[13,14]. For the gelation of agarose, a similar mechanism leading to a double helix arrangement was assumed[8]. In the later stages of helix formation a lateral aggregation similar to that found in gelatin solutions is probable. This is demonstrated in Fig.1a) - 1d), where schematically a transition from a solution of polymer coils to partly helical macromolecules is considered to be the first step. In the second step, the principal effect is the double helix formation, which takes place under the conditions mentioned by Rees, so that only a chain end has sufficient mobility to form either a double helix with another chain end, or with helical sequence inside a second chain. This leads to the general conclusion that the double helix formation at chain ends corresponds to a functionality of f = 2. The branching of chain end to a middle sequence of a second chain corresponds to a functionality of f = 3. In the third step, a lateral packing of single and/or double helices is assumed, leading to ordered regions. According to Hosemann, there is a difference in principle between the long range order in the low molecular crystals and high molecular crystal structures, so he introduced the concept of a microparacrystal[68,69].

From experimental evidence, it is known that the structure which has developed during the first period of gelation is not stable[21]. Consequently, a further mechanism for the enhancement of local order has to be postulated. This process has to be compatible with diffusion processes discussed in relation to polymer systems in the liquid state. From studies of the tack of elastomers, we conclude that polymer coils move by a replication of their chain ends, as predicted by DeGennes[58-61]. Such a movement was suggested for a double helical structure of the magnesium salt of a chemically modified ι-carrageenan by Rees when the relative humidity was increased[9]. This is shown in Fig. 2, where the twisting of two helices is shown for 3/2 turns. It is seen that, with such a mechanism, and because of non-helical sequences inside the macromolecule, the double helical sequences can be prolonged without the necessity of winding two chains (helices) around each other. However, from potential calculations, it is doubtful whether such a cooperative change of position is probable.

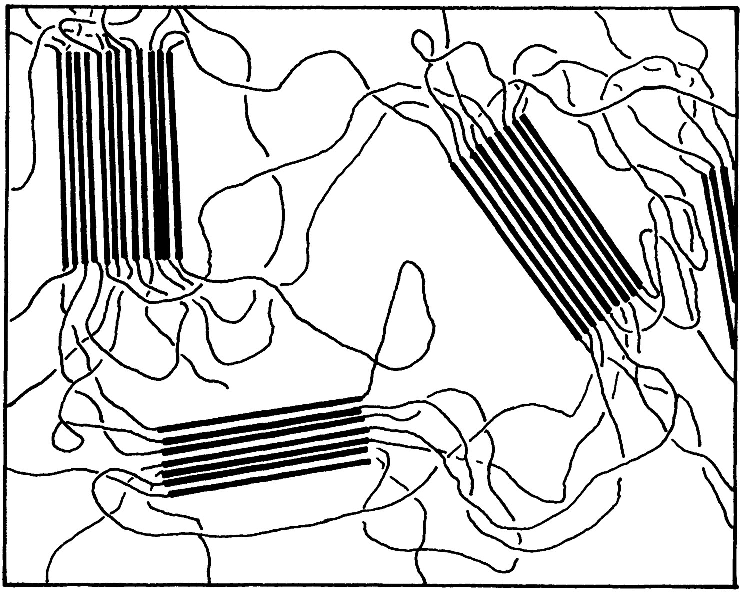

Figure 3. The model of a fringe micelle; crystalline region.

A model for the copolymer crystallization was described many years ago by Hermann, Gerngross and Abitz[62]. Called the fringe micelle model, it allows for network formation, because the non-crystallizing block sequences mainly tie different microcrystallites, as schematically presented in Fig.3. Very little is known of the sense of the sequences in the crystalline regions, their average size, size distribution, the number of linking chains, free chain ends, and rings, etc. in testing a model, it is desirable to have a maximum of information on the molecular level in order to decide whether a theory is applicable at all, or how a theory has to be developed to include structural findings.

For a better understanding of thermal gelation, we can present some phenomenological aspects in a temperature-concentration diagram shown in Fig. 4. The polymer in the solvent-free state is supposed to be only partially crystalline, which is the case in the block copolymer described above. Additionally, we assume that the solvent is not part of the crystal lattice of the copolymer, which leads to a state diagram wirh a eutectic point. The equilibrium melting curve of the polymer in solution is the liquidus curve (LC), which ends in the eutectic point (E), where it meets the second liquidus curve, which describes the melting of the solvent. According to the differences in the melting points of polymer and solvent, this point is shifted to low polymer concentrations. If a homogeneous solution of the initial mass fraction y_p^o is cooled from $T < T_m$ to the temperature T_1 a gel is formed if the concentration y_p^o is above the critical value for network formation, $y_{p,cr}$.
If crystallization alone governs the process, we would expect the solvent free polymer to coexist with the solution, which is indicated by two open circles. In reality, we observe, after some time, a 'gel' phase of a total concentration y_p'', which, by diffusion, excludes a solution of concentration y_p', which merely may be pure solvent.

In many cases, the gel phases are very turbid, which results from the fact that the solution with concentration y_p' is embedded in the gel phase, when the polymer network is formed so quickly that a separation of solution or solvent and the network, called syneresis, has not taken place. We have, therefore, to distinguish between crystalline domains, swollen amorphous network regions, and included solution or solvent not being part of the network. The amount of included solution depends on the concurrent processes of crystallization and diffusion. The overall polymer concentration in this case does not correspond to the polymer concentration of the network part.

Apart from this difficulty, it should be emphasized that, in addition to the crystallization equilibrium, we have to deal with a swelling equilibrium as soon as the network has been set up. In a pure crystallization equilbrium it is known that, on addition of solvent to a crystal, a solution is obtained. The superposition of crystallization and swelling equilibrium renders the system immune to dilution, because the crystalline regions are in a surrounding of high polymer content and the amorphous cross-linked polymer chains in the network cannot form a dilute solution. The only way to come to the state of high solvent content at a given temperature T_1 is to heat the gel to the state of solution, to add solvent and to cool again to T_1.

These considerations are confirmed by results in the system water-polyvinyl alcohol (PV-OH). After isothermal gelation at T_1 (see Fig. 4) the swelling curve (SC) has been determined in the temperature range $T < T_1$ in about one week. Starting from y_p'' the same value was found after the temperature cycle. After several months at T_1 the swelling curve was shifted to higher polymer concentrations, as shown by the arrow[30]. From this, and from the results of module measurements[10,25,31,38,39], calorimetric measurements[23,26], electron microscopic investigations[20], and measurements of the optical rotation[15,31], it is concleded that crystallization inside a physical network is a very slow process. It is open to question whether a true equilibrium, which is characterized by an absolute minimum of the free enthalpy of the system, can be attained.

The arrow in Fig. 4 indicates the direction in which the concentration changes during the irreversible process inside the cross-linking system. A crystal once formed at a temperature T_1 always melts at higher temperatures, so hysteresis must occur. This is schematically demonstrated for the swelling curve in Fig. 5, where the arrows indicate that on cooling and heating different traces are found in the temperature near the liquidus curve. In this figure we have shown the phase diagram of a polymer undergoing a helix-coil transition at the temperature T_{tr}. The temperature range in which this transition takes place had been shaded. In the concentration range $y_p < y_{p,cr}$ and for the temperatures $T_{LC} < T < T_{tr}$ between liquidus curve and transition range, double or triple helix formation leads to a branching of macromolecules. Above the critical concentration for network formation, $y_p > y_{p,cr}$ networks are formed, where no superposition of crystallization is expected. Starting at an initial concentration y_p^o, at temperature T_1 the isothermal crystallization increases the cross-linking density of the network which will shift the swelling curve to higher concentration.

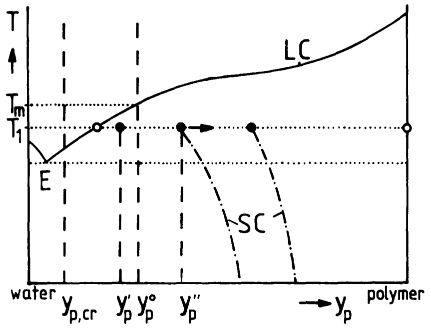

Figure 4. State diagram of a water-polymer system.
T = temperature
T_1 = crystallization temperature
E = eutectic point
T_m = crystal melting temperature
LC = liquidus curve
y_p = mass fraction of polymer
SC = swelling curve
$y_{p,cr}$ = critical mass fraction for network formation
y_p^o, y_p', y_p'' are mass fractions of the polymer concerning the overall concentration and the concentration of the coexisting phases ' and ".

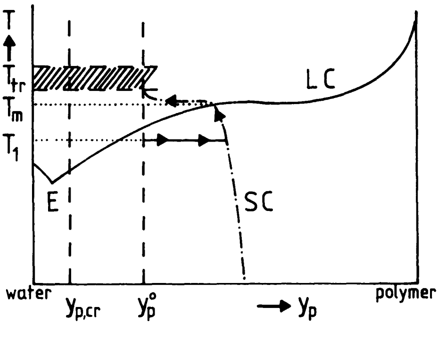

Figure 5. State diagram of a water-polymer system.
T = temperature
T_l = crystallization temperature
E = eutectic point
T_m = crystal melting point
LC = liquidus curve
y_p = mass fraction of polymer
SC = swelling curve
y_p^o = overall polymer concentration
$y_{p,cr}$ = critical concentration for network formation
T_{tr} = transition temperature of the coil-helix transformation

From these considerations, we conclude that gelation processes have to be studied in temperature and concentration regions where we can expect a single mechanism to be found. Detailed information on the state diagram of a system is therefore necessary. Only two simple cases have been mentioned, but it is known that other systems exist with a superposition of demixing and crystallization. These more complex cases are not treated in this paper.

CONCLUSION

Theoretical approaches which have been applied to different systems under certain assumptions will now be summarized. In the classical theory of gelation, the gel point of a polymerizing system is considered to be the point at which a three-dimensional network, infinite in extent, first appears[62]. For the cross-linking of linear macromolecules, with an arbitrary initial size distribution, Stockmayer has shown that, at the gel point, the fraction of cross-linkable units, which have actually formed cross-links is inversely proportional to the weight-average degree of polymerization of the original macromolecules, and to the fraction of monomer units carrying groups of forming cross-links[63].

Eldridge and Ferry assumed a chemical equilibrium between the free cross-linking loci on a macromolecule to form a binary association starting from the gel point equation of Stockmayer[64]. Gordon and co-workers refined the Flory-Stockmayer theory by application of the cascade theory including cyclization and nearest neighbour substitution effects[18]. They applied this theory to gelatin gels and concluded that the number of chains involved in individual cross-linking was probably two or three. DeGennes has criticized the classical approach[65]. The behaviour of polymer systems near the gelation point is found to correspond to critical properties of fluids and magnets which are well described by the new scaling theory.

The crystallization theory of copolymers has been derived by Flory and slightly modified by Takahashi and coworkers[66,67].

In systems containing water-soluble polymers especially, it is also necessary to consider polyelectrolytes, which are strongly influenced by the ionic strength of added salt and the pH-value of the solution. In network formation, there is a distribution of ions between gel and solution, which can be described by the Donnan equilibrium[2].

A generally applicable theory covering all the aspects of behaviour which have been mentioned does not yet exist.

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SOLUTION THERMODYNAMICS OF NON-IONIC WATER-SOLUBLE POLYMERS

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Non-ionic water soluble polymers exhibit solution properties which often differ strikingly from those of other polymers in organic solvents. The reasons for this difference in behaviour are not fully understood. This presentation is intended to gather together some details of the uncommon properties, rather than to be an in depth interpretation of the data. Three questions will be discussed:-

(1) Which quantities can be measured ?
(2) What is the state of polymer solution theories and how are they able to present an appropriate interpretation of the behaviour of aqueous solutions ?
(3) What are the reasons for the deviations in behaviour ?

EXPERIMENTAL TECHNIQUES

Solution properties are evidently governed by thermodynamic interactions between different macromolecules, by the polymer conformation, and by intramolecular interaction between segments of the same molecule. Only the intermolecular interactions are discussed here. The relevant parameters can be obtained by three kinds of measurements:-

(i) direct measurement of the heat of mixing;
(ii) measurement of the chemical potential, and
(iii) measurement of the temperature-concentration phase diagram.

The <u>heat of mixing</u> ΔH can be measured directly with a sensitive differential calorimeter. After measuring the dependence of ΔH on the volume fraction of the polymer $\phi_2 = v_2/v = \bar{v}\,c$, where c is the weight concentration, and $\bar{v}$ is the partialspecific volume of the polymer, the partial heat of dilution and of solution can be determined by the common rule

$$\Delta H_1 = \partial\Delta H/\partial n_1 = (\partial\Delta H/\phi_2)(\partial\phi_2/\partial n_1) \qquad (1)$$

with a similar equation for ΔH_2, where n_1 and n_2 are the numbers of mole of the solvent and the solute respectively.

The <u>chemical potential</u> $\Delta\mu_1$ of the solvent is related to the Gibbs free enthalpy of mixing ΔG_m by

$$\Delta\mu_1 = \mu\Delta G_m/\partial n_1 \qquad (2)$$

Three principal techniques for determining $\Delta\mu_1$ are known:-

(i) vapour pressure;
(ii) osmotic pressure;
(iii) light scattering measurements.

<u>Vapour pressure measurement</u>: Thermodynamics show that

$$RT\ln(p/p_o) = \Delta\mu_1 \qquad (3)$$

where p and p_o are the vapour pressures of the solvent at a certain concentration, and of the pure solvent, respectively.
For ideal solutions

$$\Delta\mu_1 = RT\ln X_1 \qquad (4)$$

where $X_1 = n_1(n_1 + n_2)$ is the mole fraction of the solvent. Polymer solutions usually deviate strongly from this ideal behaviour, and Eqtn. (4) has to be replaced by

$$\Delta\mu_1 = RT\ln a_1 = RT\ln X_1 f_1 \qquad (5)$$

where a_1 is the solvent activity, and f_1 is the activity coefficient.

Various principles for measurement of p/p_o have been developed. They are discussed in detail by Tompa[2]. Vapour pressure measurements are appropriate for concentrated solutions but fail in the dilute region, where p becomes very close to p_o. Figure 1 represents typical curve of the solvent activity, as a function of the mole fraction X_1.

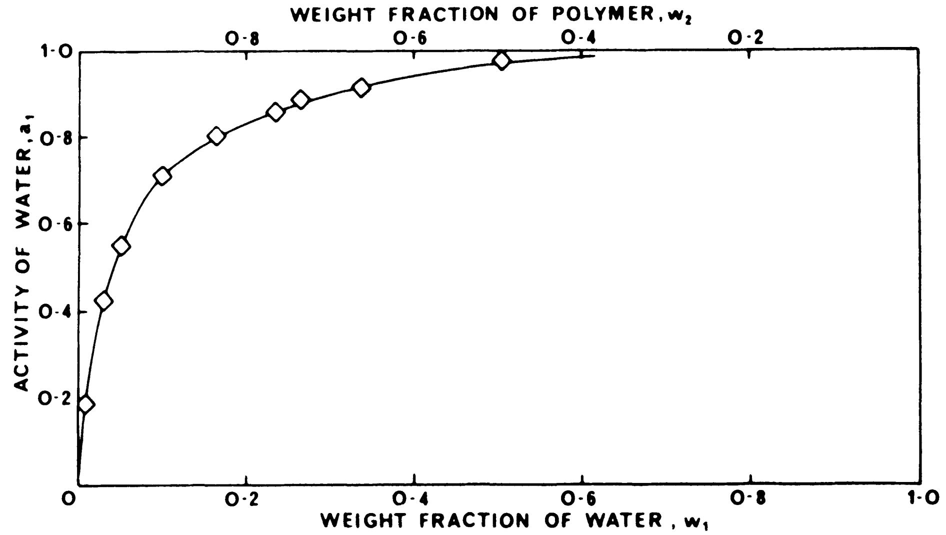

Figure 1. Solvent activity a_1 versus weight fractions of solvent w_1 and polymer w_2 for the water-polyoxyethylene 5000 system at 65°C. Reference 3.

Measurements of the osmotic pressure: The osmotic pressure is related to the chemical potential by

$$\pi V_1 = - \Delta\mu_1 \tag{6}$$

where $V_1 = M_1/\rho$ is the molar solvent volume, M_1 its molecular weight, and ρ the solvent density. The osmotic pressure depends on the concentration, and can be expressed as a virial expansion series

$$\pi = RTc(1/M_n) + A_2c + A_3c^2 + \ldots \tag{7}$$

where M_n is the number average molecular weight of the solute. The first virial coefficient ($= 1/M_n$) describes the ideal behaviour and the higher coefficients the interaction between two, three, etc. macromolecules respectively. With Eqtn. (7), a virial expansion of the chemical potential is obtained when inserted into Eqtn. (6), which is equivalent to the activity formalism. Osmotic measurements are particularly suited for concentrations up to 20 %.

Light scattering: The scattering intensity is related to the concentration gradient of the chemical potential by[5]

$$R_o = i_o r^2/I = - KcV_1RT/(\partial\Delta\mu_1/\partial c) \qquad (8)$$

where K is an optical constant describing the contrast between solvent and solute and R_o is the Rayleigh ratio of scattering (i_o) to primary beam (I) intensities and r the distance of the detector from the centre of the scattering cell. Extrapolation to zero scattering angle has to be carried out. Thus, $\Delta\mu_1$ can be obtained by integration of Kc/R_o over the applied concentration region[5].

The heat and entropy of dilution are obtained by standard practice from the temperature dependence of $\Delta\mu_1$:

$$\Delta H_1 = \partial\Delta\mu_1/\partial(1/T) \qquad (9)$$

$$\Delta S_1^{ex} = \partial\Delta\mu_1/\partial T - \Delta S_1^{id} \qquad (10)$$

where $\Delta S^{id} = RT \ln X_1$ is the ideal entropy of dilution and ΔS_1^{ex} the excess entropy of dilution.

Phase diagrams are usually determined by light scattering phenomena. When the temperature of a phase separation is approached, the solutions exhibit intense scattering of light. This visibly observable phase transition is called the cloud point. Thermodynamically the cloud point is the co-existence temperature for the two phases at thermodynamic equilibrium. Figure 2. shows a rather uncommon example of the cloud point curve of polyoxyethylene in water[6].

The coexistence curve has a different shape and position compared with the spinodal curve, which is the absolute instability curve. The spinodal condition is given by

$$\frac{\partial\Delta\mu_1}{\partial\phi_2} = 0 \qquad (11)$$

For many years, the spinodal curve was considered to be unmeasureable since it is necessary to pass through a region of decreasing metastability. Recently, however, Scholte has recognized[5] that the spinodal curve can be determined by plotting the reciprocal scattering intensity versus 1/T and extrapolating to zero value of KC/R_o. With the recent development of the pulse induced critical

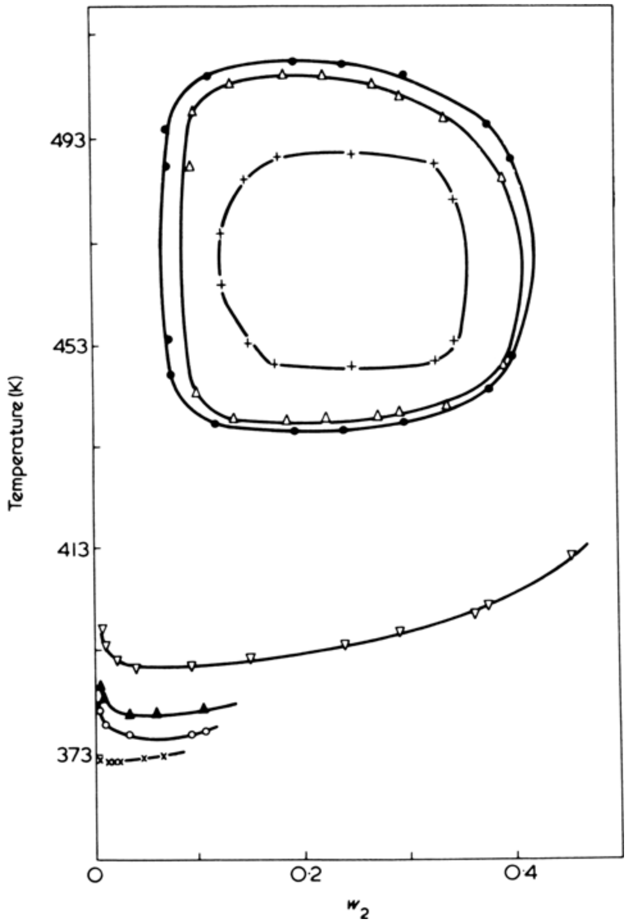

Figure 2. Phase diagram of six polyoxyethylene samples in water[6] M_w = 2.18 x 10^3 to M_w = 1020 x 10^3.

light scattering instrument (PICS)[7,8] rapid measurements can also be performed in the metastable region prior to droplet formation, thus improving the accuracy considerably. Recording the spinodals yields the largest number of parameters for a polymer solution, but has not yet been carried out widely.

THEORY

The basis of almost all interpretation of solution properties is the well-known Flory-Huggins (FH) theory[1]. According to this theory, the chemical potential is given by

$$\Delta\mu_1 = RT\{\ln(1 - \phi_2) + (1 - 1/x_n)\phi_2 + \chi\phi_2^2\} \qquad (12)$$

This equation is composed of two different parts. The first two terms have combinatorial character and result from the number of different ways of placing long chain molecules of polymerization degreee x_n (number average) and solvent molecules on a lattice. This part of the equation remains the same for all types of flexible polymer molecules but depends, of course, on the chain length. The last term in Eqtn. (12) describes the interaction between molecules and must be proportional to the squared volume fraction ϕ_2^2. In the older Flory theory, the interaction parameter, χ, was considered being concentration independent. This conclusion arises from the incorrect assumption that the number of solvent contacts equals the polymer volume fraction, whilst, in fact, the surface fraction, Θ, should be used. The surface and volume fractions are related by

$$\Theta = \frac{(1 - \gamma)}{1 - \gamma\phi_2}\phi_2 \qquad (13)$$

where $\gamma = 2/Z$ in the lattice theory and $\gamma = 1 - \sigma_2/\sigma_1$ in the off lattice model and σ_2 and σ_1 the surfaces per unit volume of the of the polymer and solvent, respectively. Using the surface fraction rather than the volume fraction for the interaction, it is found that there is a concentration dependent parameter, χ, where

$$\chi = \chi_1(1 - \gamma)/(1 - \gamma\phi_2)^2 \qquad (14)$$

Experimentally, a value of $\gamma \cong 0.3$ has been determined for polystyrene in cyclohexane, which is quite close to $\gamma = 1/3$ for a simple cubic lattice. Figure 3. shows the result of the concentration dependent χ of polystyrene in cyclohexane at 35°C (theta state) as an example of very good agreement[10].

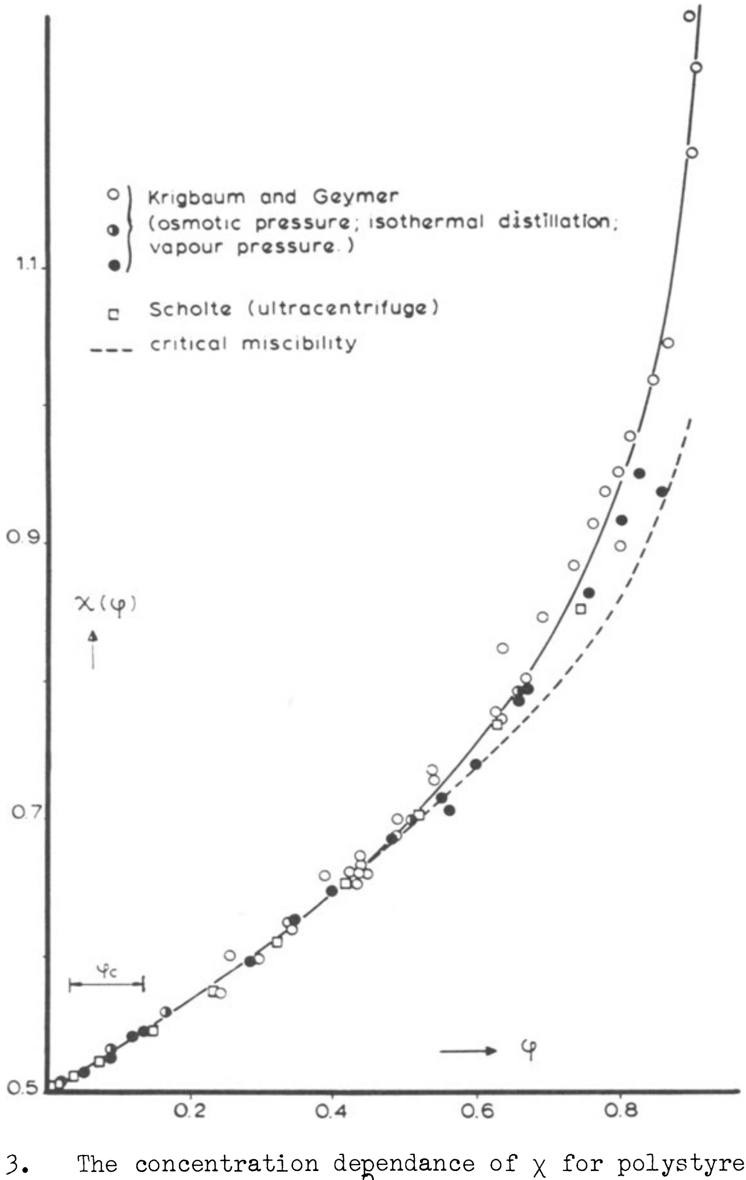

Figure 3. The concentration dependance of χ for polystyrene in cyclohexane at 35°C. Reference 10.

Expansion of the FH equation in terms of the weight concentration c yields the second virial coefficient

$$A_2 = \frac{\bar{v}_2}{\bar{v}_1} (1/2 - \chi) = \frac{\bar{v}_2}{\bar{v}_1} \psi_1 (1 - \theta/T) \qquad (15)$$

where

$$\psi_1 = \frac{1}{R} \frac{\Delta S_1^{ex}}{\phi_2^2} \qquad (16)$$

The χ_1 parameter (at infinite dilution) is temperature dependent and may be written as

$$\chi_1 = \beta_o + \beta_1/T \qquad (17)$$

where β_o and β_1 are related to the excess entropy of dilution and the heat of dilution. It should be noted that positive β_o corresponds to negative entropy, whilst positive β_1 corresponds to a positive heat of dilution (endothermic solution[1]). In the classical FH theory, only endothermic solutions are predicted[1,2] : the solvent power is reduced with decreasing temperature and in some cases a θ-state is attained, where A_2 becomes zero, and a pseudo-ideal behaviour is observed. However, the higher virial coefficients do not vanish in general.

The phase coexistence curve is obtained using the condition that the chemical potentials for the polymer and the solvent must equal in both phases

$$\Delta\mu_1' = \Delta\mu_1'' \qquad (18a)$$

$$\Delta\mu_2' = \Delta\mu_2'' \qquad (18b)$$

Application of these conditions involves serious numerical problems. The spinodal curve, on the other hand, is easily obtained in an analytic form by applying Eqtn. (11). The dependence of the spinodal decomposition temperature on the volume fraction is given by

$$T_{sp} = \frac{\beta_1(1 - \gamma) (1 - \phi_2)\phi_2}{\{\phi_2 - (1/x_w) (1 -\phi_2)\}(1 -\gamma\phi_2)^3 - \beta_o(1 -\gamma) (1 - \phi_2)\phi_2} \qquad (19)$$

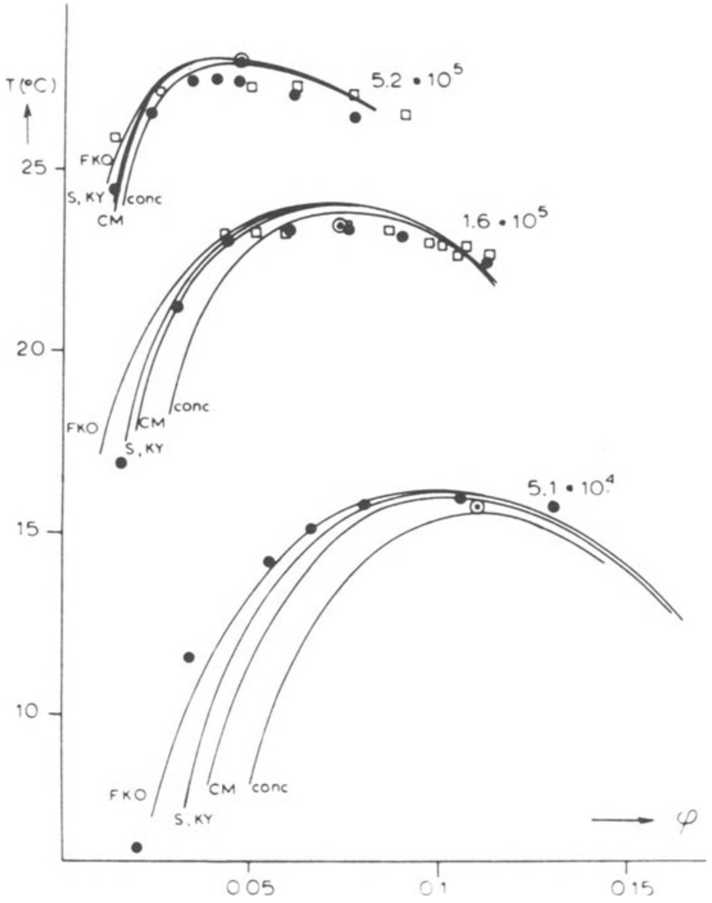

Figure 4. Spinodals of three polystyrene samples in cyclohexane[11]

Where the weight average degree of polymerization has to be used for a polydisperse system. Figure 4. shows, as a typical example, the measured spinodals for several polystyrene samples in cyclohexane[11]. Fitting these curves with Eqtn.(19) gives all the desired solution parameters. However, the FH theory is not correct for low concentrations where the behaviour of isolated macromolecules starts to govern the solution thermodynamics. Konigsveld et al.[11] successfully combined both solution models in a bridging theory where a very satisfactory agreement between experiment and theory was achieved.

COMPARISON WITH AQUEOUS SOLUTIONS

The FH theory works satisfactorily for non-polar polymers dissolved in non-polar solvents. For these solutions, both β_o and β_1 are positive (i.e. $\Delta S_1{}^{ex} < 0$; $\Delta H_1 > 0$) and the θ-state and phase separation are correctly predicted to occur upon cooling. However, aqueous solutions of non-ionic polymers exhibit several significant deviations which may be listed as follows:-

1. Some solutions show phase separation on heating and sometimes even closed loops of non-miscibility, i.e. on heating after phase separation the solution clarifies again at very high temperatures. Typical examples are polyoxyethylene[6] and polyvinyl alcohol (PV-OH) with some residual acetate groups[12] (see Figure 1);
2. Other polymers tend to aggregate, and show gelation upon heating, or on cooling, or even only on standing (methyl cellulose[13], PV-OH, starch and amylose)[14];
3. The χ-parameter increases slightly with ϕ_2 in some cases, but passes through a maximum and then decreases gradually at higher concentrations (e.g. polyvinyl pyrrolidone[15]) (see Figure 5). In other cases (e.g. polyoxyethylene, polyvinyl acetal)(see Figure 6) the χ-parameter increases as predicted by the FH theory but decreases rapidly when $\phi_2 > 0.85$ to 0.9;
4. The heat of dilution is generally negative (i.e. exothermic solutions), and changes proportional to $(1 - \gamma\phi_2)^{-2}$ up to a certain volume fraction as predicted by theory, but the ΔH_1 curve passes through a minimum and starts to increase[16], as shown in the example of Figure 7.

POSSIBLE REASONS FOR THE DEVIATIONS

Polyoxyethylene has attracted special interest because phase separation is observed both on cooling and on heating, and in some cases a closed loop of immiscibility is observed, whereas at present only phase separation on cooling is understood in the FH theory. Two attempts at a quantitative interpretation of this effect have been undertaken:

i. Application of the Prigogine-Patterson theory[17,18], and
ii. Application of the quasi-chemical approximation for two different sites of interaction of the polymer with the solvent[19].

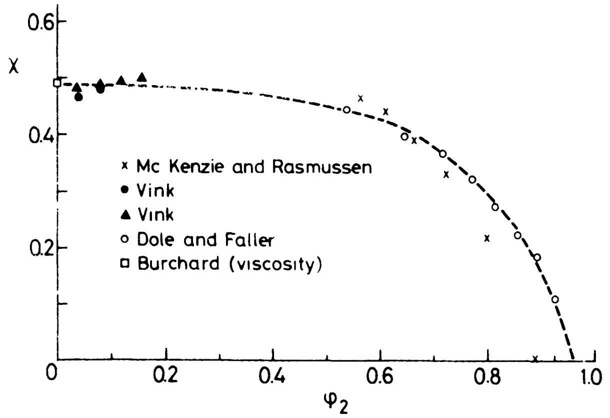

Figure 5. χ as a function of ϕ_2 for polyvinyl pyrrolidone in water[15].

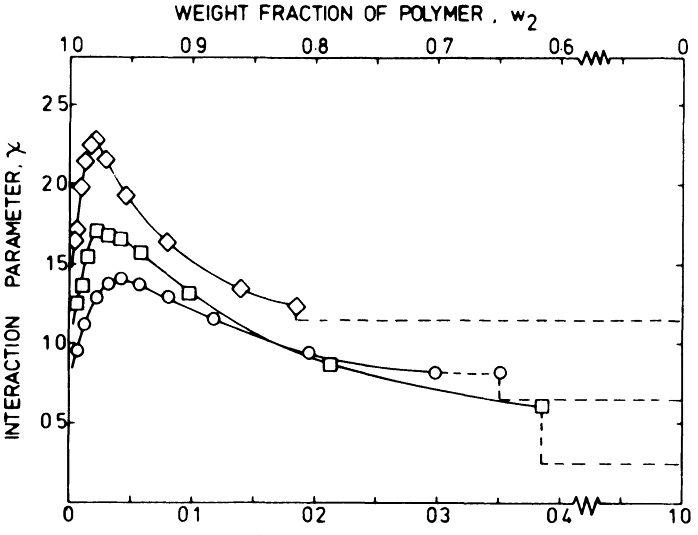

Figure 6. χ-dependence on ϕ_2 for polyvinylmethoxyacetals.

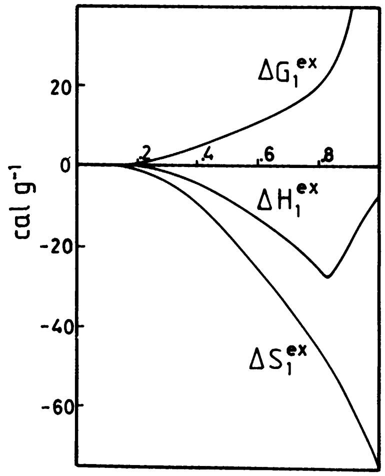

Figure 7. Excess thermodynamic functions for polyoxyethylene at 180°C

In the Prigogine-Patterson theory, phase separation results from the difference in the thermal expansion of the solvent and the solute. Near the liquid-gas critical point of the solvent, the thermal expansion of the solvent can become appreciably large whilst that of the polymer remains restricted since the units are covalently linked together. The number of contact pairs therefore decreases beyond a critical value. However, aqueous solutions already show phase separation at temperatures well below the critical point of water[6]. In the case of high molecular weight polyoxyethylene, the lower critical solution temperature (LCST) lies at 95°C, even below the boiling point of water[20]. Hence, the Prigogine-Patterson model has to be discarded as a description of non-ionic polymers in water.

Barker's approach[19] is based on the particular structure of water-soluble chains with their two different groups, or chain elements, of opposing properties: the hydrophilic, and the non-polar hydrophobic behaviour. The hydrophilic groups are responsible for the solubility of the polymer and are strongly hydrated. Different types of measurements[21,22] revealed that the ether oxygen in polyoxyethylene and the polar >N - C = O group in polyvinyl pyrrolidone bind, on average, about three molecules of water. In a simple sense, the non-polar sections of the chains are considered to have strong repulsion potentials with respect to the water molecules. In this picture, therefore, the thermodynamic properties of non-ionic polymers in water are a simple balance between these two opposing interactions.

Barker[19] has attempted a quantitative treatment of solutions according to this picture on the basis of the so-called quasi-chemical approximation. His approach has been successful in one case where a closed loop of immiscibility could be predicted. Unfortunately, this case is restricted to a polar polymer in a non-aqueous polar solvent, where the thermodynamics are determined by orientation of the solvent molecules around the solute. This causes a fairly pronounced negative entropy of dilution and a negative heat of dilution. Aqueous solutions, however, exhibit a much stronger negative excess entropy of dilution which often exceeds the always positive contribution of the combinatorial part in the Flory-Huggins theory, with a result that the overall entropy of dilution becomes negative. Although Barker's treatment could be improved a little and extended to copolymers (as the water-soluble chains can be considered in principle - e.g. methyl cellulose, or an incompletely deacetylated (partially hydrolyzed) polyvinyl alcohol), it appears unlikely that a satisfactory description of aqueous solutions can ever be achieved by this technique.

THE HYDROPHOBIC INTERACTION

All polymer solution theories mentioned so far neglect the highly ordered structure of water[23]. In addition, it has been shown, mainly by studies of the uncommon behaviour of the heat capacity as a function of temperature, that this order is increased by the addition of low molecular weight hydrophobic compounds. This increased order of the solvent in the immediate vicinity of the solute causes a highly negative entropy of dilution, ΔS_1. This entropy contribution dominates the solution properties for hydrophobic compounds and makes the excess chemical potential

$$\Delta\mu_1^{ex} = \Delta H_1^{ex} - \tau\Delta S_1^{ex} \qquad (20)$$

more and more positive with increasing temperature. The magnitude of the negative value of ΔH_1^{ex}, i.e. the hydrophilicity of the compound, determines whether phase separation on heating can be achieved or not.

A more detailed model has been developed[24,25] which can explain the increase in order of water by the dissolved hydrophobic compound. Briefly, water molecules have four sites for a strong H-bond interaction. As a result, they can form large clusters which, however, have a very short life time: the clusters quickly decompose and are reformed. If a moderately hydrophilic compound is added, some water molecules will hydrate certain groups - the ether oxygen in polyoxyethylene chains, for example. This interaction may be less strong than that between pure water molecules, which has the cooperative effect that the interaction between the other three sites of water are strengthened, so enlarging the size of clusters. It is therefore the cooperative increase in order of water which causes the decrease of solution power rather than the special interaction between non-polar groups. This whole mechanism is called 'the hydrophobic interaction'.

EVIDENCE FOR HYDROPHOBIC INTERACTION FOR POLYOXYETHYLENE SOLUTIONS

Whilst the existence of a hydrophobic interaction can be shown beyond doubt for low molecular weight compounds, it is difficult, in the present state of knowledge, to prove this type of interaction conclusively for non-ionic polymers. The difficulties arise mainly from the lack of reliable measurements of the aqueous solution properties as functions of temperature (there are more data available for the concentration dependence at room temperature). Recently, some light scattering measurements on a polyoxyethylene of molecular weight of 20,000 have been carried out in water in the temperature range of 20 to 90°C[26]. A gradual decrease of the second virial coefficient with temperature was observed, and a θ-temperature of 102 ± 7° was found by extrapolation of $A_2 \rightarrow 0$. This value agrees well with the lower critical solution temperature of about 110°C, as was found for polyoxyethylene of $M_w = 30,000$[27]. This increase of A_2 is fully in line with the concept of a hydrophobic interaction.

AGGREGATION

The light scattering measurements from polyoxyethylene have shown another surprising effect. In spite of the low molecular weight of 20,000, a very pronounced angular dependence and a much higher weight-average particle weight of $M_w = 260,000$ was observed, which indicated the presence of large aggregates. The aggregation increased by a factor of 100 when the temperature was raised to 60°C, above which the molecular weight began to decrease. The aggregation was found to be reversible on cooling. In addition, striking minima and maxima occurred in the angular distribution of the scattered light at higher temperatures. Figure 8. shows a Zimm plot of the polyoxyethylene solution at 40°C. The position of the first maximum allows an estimation of the aggregate size; the particles have radii of about 200 nm, a value that agrees well with the radius of gyration at low but not at higher temperatures. Details are given in the original paper[26].

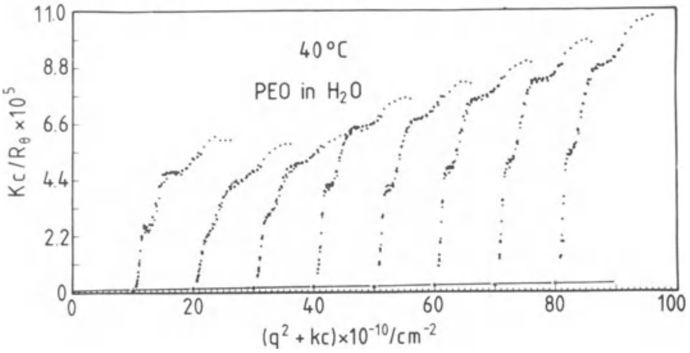

Figure 8. Zimm-plot of a polyoxyethylene (M_{GPC} = 21,400) in water at 40°C. The light scattering was performed at 8 concentrations, ranging from 0.25 % to 2.0 %. Measurements were made at the wave-lengths λ_0 = 546,436, and 365 nm respectively[26].
$q = (4\pi/\lambda)\sin\theta/2$.

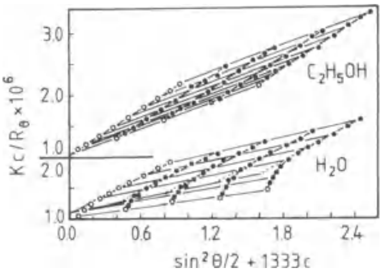

Figure 9. Comparison of light scattering measurements from polyvinyl pyrrolidone in ethanol and water at 20°C. The downturn in the Zimm-plot of the aqueous solution indicates association (see reference 28).

Similar, but less pronounced aggregation, was observed with polyvinyl pyrrolidone[28]. Figure 9 shows the Zimm-plot of the same sample in ethanol and water. The particles were found to have radii of about 270 nm which did not change when the molecular weight of the polymer was increased. Only the weight fraction of aggregates increases with M_w.

A conclusive explanation of these effects, which seem to be common to non-ionic solutions, is not yet possible, but it is tempting to make some speculations. The complex mechanism of the hydrophobic interaction finally has the effect of driving the polymers together. The overall solution power may be good, but there will still be a finite probability that some chains are brought fairly close together such that they interpenetrate each other and form several contact points. If the polymers have OH-groups, then H-bonds can be formed which act as cross-links and which may hold the chains together in the form of a microgel. At higher concentration, the interpenetration increases and a real gel may be formed. The probability for contacts between different chains should increase with increasing temperature, since the solution power is decreased, and gelation may take place on heating, if the concentration is larger than the overlapping concentration c^* [29]. This effect has been observed for both methyl cellulose[13] and incompletely deacetylated polyvinyl alcohol[12]. Starch shows different behaviour[30 - 32], probably because of the tendency to form crystallites.

The situation with polymers like polyoxyethylene and polyvinyl pyrrolidone is more complicated, since these chains have no groups which can form donot H-bonds. However, in both cases a layer of strongly bound water (about 3 molecules of water for each polar group) has been reported[21,22]. Thus, in aqueous solutions, the polymers may be, in fact, considered as water-coated chains, which are now provided with the functional groups for the aggregation via H-bonds. One can that the formation of cross-links produces a negative contribution to A_2, such that phase separation should occur. However, the number of cross-links is certainly low compared with the other groups which are solvated, and therefore the contribution to A_2 will be very small.

CONFORMATION

It is conceivable that the high degree of structuring of water in the vicinity of the polymer may result in an unusual chain conformation. Such possible perturbation of the random coil behaviour has been little studied in the past. Some indications of such an effect are seen in the data for the polyvinyl pyrrolidone and polyoxyethylene solutions. The intrinsic viscosities of the former in ethanol and water are very similar[28]:-

$$[\eta]_{ethanol} = 1.31.10^{-2}\ M^{0.72} \quad ;\ ml.g^{-1} \qquad (21)$$

$$[\eta]_{water} = 1.26.10^{-2}\ M^{0.70} \quad ;\ ml.g^{-1} \qquad (22)$$

However, the mean square radius of gyration in each case show an uncommon molecular weight dependence in water, with an exponent of only 0.98, which is even lower than for a θ-solvent. Polyoxyethylene shows much lower unperturbed dimension in o.45 M K_2SO_4 than in pure water[33]. This again may be taken as an indication of hydrophobic interaction, since the addition of a strong electrolyte changes the water structure completely, and the hydrophobic interaction breaks down.

PVP:

$$\langle S^2 \rangle = C\ M^{1.23} \qquad \text{ethanol} \qquad (23)$$

$$\langle S^2 \rangle = C\ M^{0.98} \qquad \text{water} \qquad (24)$$

Characteristic ratio:

Polyoxyethylene:

$$C_\infty = 7.5 \qquad \text{water} \qquad (25)$$

$$C_\infty = 4.9 \qquad 0.45\ M\ K_2SO_4 \qquad (26)$$

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FRACTIONATION AND CHARACTERIZATION OF WATER-SOLUBLE POLYMERS

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INTRODUCTION

The molecular structure of polymers is very complex, and characterization is never an easy task. Characterization is important scientifically, as it relates to mechanisms of polymer formation and degradation, and technically, as it relates to industrially significant properties of polymers. Thus the effectiveness of polyacrylic acid in the inhibition of boiler scale depends on molar mass, and the rate at which polymer solution can be pumped through rock in oil reservoirs is critically dependent upon the number and size of the largest solution species present.

There are so many sources of molecular heterogeneity that a complete description of a polymer sample would be quite impractical. Even for a homopolymer of a monosubstituted alkene, one needs to consider degree of polymerization, branching (short and long chain), tacticity and mode of monomer addition (head-to-head, tail-to-tail). Copolymers introduce the further complications of comonomer sequence. In principle, a polymer sample can be described in terms of the distribution of each of those structural variables. In practice, we must be content with a partial characterization of one or two of these variables.

Nearly all producers or users of water soluble polymers wish to know more about the structure of the materials. In this chapter, an overview is presented of the most important methods of polymer characterization as they apply to water soluble polymers. Most of the methods available were developed in application to polymers of relatively simple molecular structure that are soluble in non-polar solvents. Water soluble polymers present more difficulties for a number of reasons: solutions often contain persistent molecular aggregates, particularly when the molar mass is high; polymer adsorption on filters, membranes, column materials and glassware frequently intrudes; electrostatic effects with polyelectrolytes complicate many measurements; and few reference samples are available to facilitate comparison of results and refinement of techniques.

Molecular characterization of polymers employs techniques of two general kinds. Short-chain branching, mode of monomer addition and some features of comonomer distribution are best investigated by techniques such as infra-red spectroscopy and nuclear magnetic resonance spectroscopy, which are sensitive to local chemical structure. Molecules that differ in degree of polymerization and long-chain branching, on the other hand, are often indistinguishable chemically and spectroscopically; characterization of these features depends on polymer solution properties. This Chapter deals mainly with the latter type of characterization.

MOLAR MASS AND ITS DISTRIBUTION

The most fundamental structural variable in synthetic polymers is the degree of polymerization - the number of monomer units linked together. The degree of polymerization is inferred from measurements of polymer molar mass.* Synthetic polymers are invariably heterogeneous in molar mass, and are characterized by molar mass distributions (MMD). For a sample containing n_i molecules of molar mass M_i and mass $m_i = n_i M_i / N_o$, molar mass distribution can be described in two equivalent ways by relating respectively n_i and m_i to M_i. The former relation is called the number distribution and the latter the mass distribution of molar mass. Classical means of molar mass measurement yield average values when applied to polymers. The number-average molar mass $\bar{M}_n$, is the mean of the number distribution. The mass-average molar mass $\bar{M}_m$, is the mean of the mass distribution. The ratio $\bar{M}_m/\bar{M}_n$, the 'polydispersity' is a convenient index of heterogeneity in molar mass.

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* The older term 'molecular weight' is deprecated in the International System of Units. Molar mass has units kg/mol and symbol M. For mathematical operation the dimensionless relative molecular mass is convenient; its symbol is M_r.

An ideal homogeneous sample has a polydispersity of unity. Polymers made by 'living anion' polymerization have polydispersities around 1.1 and are loosely termed monodisperse. Water soluble polymers of this kind can be made directly from ethylene oxide and indirectly by the controlled sulphonation of polystyrene made by anionic polymerization. Commercial water soluble polymers have polydispersities in the range 3 - 8.

PREPARATIVE FRACTIONATION

The more homogeneous the polymer, the more simple its characterization. The production from a whole polymer of subsamples which are more homogeneous that the starting polymer is termed fractionation. Fractions are used in relating properties to structure, and in testing polymer theory, which usually refers to ideally homogeneous polymer: fractions often offer the closest practical approach to this objective. Characterized polymer fractions serve also as polymer reference samples, which have an important role in transferring scales of molar mass measurement between laboratories.

There are two general methods for producing fractions of water soluble polymers. The first depends upon the controlled phase separation which occurs when increasing amounts of a miscible non-solvent or salts are added to a dilute polymer solution. Homopolymer of high molar mass partitions preferentially into the concentrated polymer-rich phase. The efficiency of fractionation is low, and complete separation of a whole polymer into fractions of similar low polydispersity requires tedious refractionation procedures. For the production of small fractions of high molar mass, however, this classical procedure remains the method of choice. The 'Polymer Handbook' lists references to successful fractionations. Theoretical models are available which give some insight into the fractionation process: since they begin with a polymer of known MMD, however, their predictive value is small. For copolymers, the partitioning in phase separations is dominated by chemical differences, and little fractionation by molar mass occurs. Polymers such as polyethylene oxide and polyvinylpyrrolidone, which are soluble in both water and organic solvents, can be fractionated in the latter, often with greater success. Crystalline polymers, such as polyethylene oxide and isotactic polyvinyl alcohol are fractionated, in terms of their molar mass, only above their crystalline melting point.

The principal alternative to fractionation by phase separation is preparative size-exclusion chromatography (SEC), which is also, and less aptly, known as gel filtration and gel permeation chromatography (GPC). A sample of the dissolved polymer is added to a stream of solvent flowing through a column packed with a porous solid. If the pores are of sizes similar to those of polymer molecules in solution, the larger molecules may be excluded from the smaller pores and so pass through the column more rapidly. The sample emerges dilutes, and sorted in inverse order of molecular size. Dissolved molecules so large that they are totally excluded from the porous substrate emerge at a retention volume V_o, which is a measure of the interstitial fluid volume of the column. Dissolved molecules so small that they penetrate all the pores of the substrate emerge at a retention volume $V_o + V_i$, where V_i represents the total pore volume. Dissolved molecules of intermediate size emerge at retention volumes which vary approximately linearly with the logarithm of molecular size.

Column materials for aqueous size exclusion chromatography (Table 1.) have improved significantly since the introduction of cross-linked dextran gels ('Sephadex') in 1959. The porosity of these gels depends on controlled swelling in aqueous media; they lack dimensional stability, particularly when the pores are large, so that the chromatographic behaviour is poorly reproducible. Cross-linked polyacrylamide and agarose, poly(acrolylmorpholines) and poly(2-hydroxyethylmethacrylate) (see Chapter 4) offer some improvement in dimensional stability, but all suffer from inconsistency of commercial supply. Rigid inorganic materials, controlled pore glass and silica gel, are dimensionally stable, but their high-energy surfaces often retain polymer by adsorption, so that size separation is degraded. Coating the inorganic solids

Table 1. Column materials for preparative size-exclusion chromatography (SEC).

Structure	Trade name	Hazards
Cross-linked dextran	Sephadex	Dimensional instability
Cross-linked polyacrylamide	BioGel	↑
Cross-linked agarose	Sepharose	↕
Poly(acrolylmorpholines)	Enzacryl	↕
Poly(2-hydroxyethylmethacrylate)	Spheron	↕
Poly(vinyl alcohol)/ether	Toyo pearl	↕
Silica gel) coated	Porasil	↓
Porous glass) coated	Merckogel CPG	Risk of adsorption

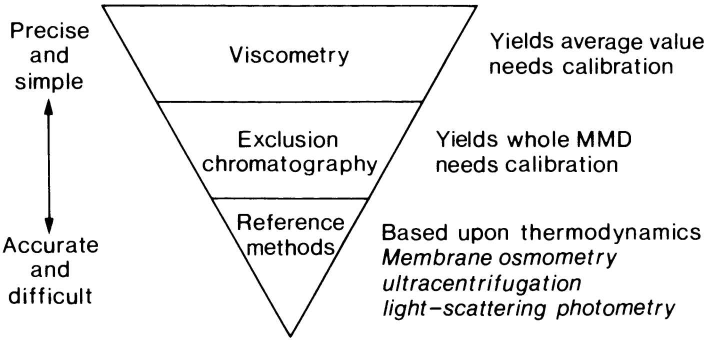


Figure 1. The hierarchy of molar mass measurement.

with silanes or polyethylene glycol reduces adsorption, but there is growing scepticism concerning published reports of the stability of the coatings and, indeed, of the organic solid itself during aqueous chromatography. The latest addition to the list of packing materials for preparative SEC is 'Toyopearl' - a proprietary gel made by polymerization of hydrophilic monomers and containing ether and hydroxyl groups; impressive claims are made for its stability and resolution. All of the column materials are available in ranges of pore size, so that it is possible to tailor a column to particular fractionation. It should be noted that the claimed ranges of molar mass separated often refer to globular proteins, and therefore greatly overestimate the range for synthetic polymers.

The efficiency[1] of fractionation in SEC increases with dilution, so that sharp fractions are best produced cumulatively from repeated separations; dimensional stability of the substrate is particularly important, therefore. If the concentration of whole polymer is increased (and the viscosity therefore raised) fractionation is degraded first at large dilution volumes. It is prudent to use electrolyte of moderate ionic strength (say, 0.1-M. salt) to suppress electrostatic interactions between polymer and substrate, which will degrade fractionation by size.

Fractionation by SEC reflects the degree of polymerization, long-chain branching, tacticity (marginally), and chemical heterogeneity, all of which determine molecular size in solution.

MOLAR MASS MEASUREMENT

The metrology of polymer molar mass features in every text on polymer science, and needs no detailed elaboration here. Instead, the relation between the methods of measurement will be described, indicating the special features of their application to water soluble polymers. Polymer molar mass can be measured by a variety of methods, which have a hierarchical relationship (Fig. 1.). The triangular shape emphasizes the fundamental role of the reference methods, membrane osmometry, light scattering photometry, and ultracentrifugation.

All three reference methods are based securely in thermodynamics, and yield absolute determinations in the sense that molar mass is derived from measurements of the fundamental physical quantities of mass, length and time. Each method depends on relating equilbrium differences of concentration in dilute solution to the osmotic work needed to produce them, and thereby to solvent activity. At infinite dilution, solvent activity can be equated with mole fraction, so that solute (polymer) mole fraction, and, hence, molar mass follow. Extrapolation to infinite dilution employs virial polynomials. When applied to a polydisperse polymer sample, each reference method yields a characteristic average molar mass. These points are summarized in Table 2.

Table 2. Basis of measurement by the reference methods.

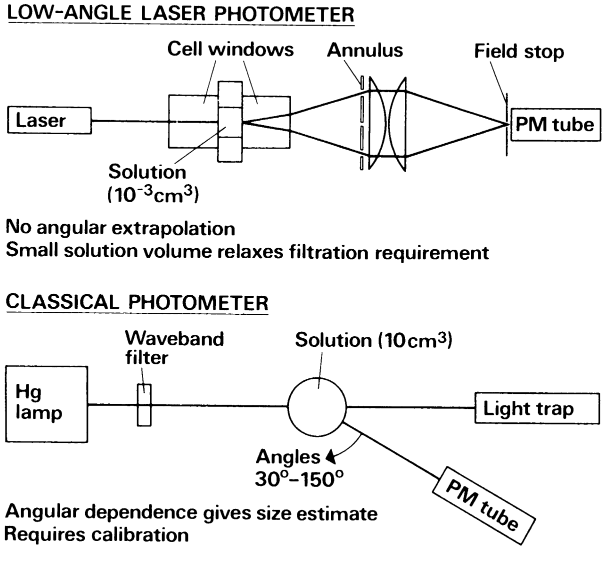
Method	Equilbrium concentration difference		Average Molar Mass
	Establishment	Measurement	
Membrane osmometry	Semipermeable membrane	Pressure developed	$\bar{M}_n$
Ultracentrifugation	Centrifugal field	Radial concentration profile	$\bar{M}_m$
Light-scattering Photometry	Spontaneous fluctuations	Scattering by refractive fluctuations	$\bar{M}_m$

Reference Methods

The reference methods are demanding of time and expertise, and are in established use in few laboratories. Their application to water soluble polymers introduces some features not always clear from texts that emphasize characterization of non-polar molecules. First, and most generally, it is essential to suppress polyelectrolyte effects by working with solutions containing an excess of simple electrolyte: unless electrostatic interactions are suppressed in this way, the relation of osmotic work to molar mass via a virial expansion is invalid.

Turning now to details of the specific methods, modern membrane osmometers measure the pressure needed to prevent net transport of solvent through a membrane and are capable of rapid measurements (~ 10 minutes) in non-polar solvents. Equilibrium is reached with aqueous solutions much more slowly (1-2 hr.) Instruments employing pressure transducers are more effective with aqueous solutions than those which follow solvent transport by the movement of an air bubble in a capillary. In general, membrane osmometry yields reliable results only with fractionated polymer.

Interest in light-scattering photometry has been stimulated by the recent introduction of instruments which measure the acattered intensity at low angles of scatter (Figure 2.). This avoids the necessity of extrapolating to zero angle of scatter data collected over a wide angular range by conventional photometers, but at the


LOW-ANGLE LASER PHOTOMETER

No angular extrapolation
Small solution volume relaxes filtration requirement

CLASSICAL PHOTOMETER

Angular dependence gives size estimate
Requires calibration

Figure 2. Light-scattering photometry.

price of a loss of information concerning molecular size: radius of gyration can be inferred from the angular dependence. Exclusive reliance upon measurements at low angles is open to error for two reasons: firstly, molecular aggregates are not uncommon, and dominate scattering at low angles, and, secondly, it is more difficult to eliminate scattering from extraneous dust in aqueous solutions than in non-polar solvents. Most of the dust is organic in origin and the refractive index contrast is higher in aqueous solutions. The angular dependence of scattering gives valuable information concerning both interferences.

Ultracentrifugation is traditionally the tool of the biochemists, and has not been applied widely to synthetic polymers. Analysis of polydisperse non-ideal solutions requires considerable effort. The difficulties of other means of characterization of the molar mass distribution of water soluble polymers are reviving interest in ultracentrifugation. The radial distribution of a polydisperse solute at equilibrium in a centrifugal field can be calculated from the molar mass distribution. The reverse derivation[2] is an 'ill-posed' mathematical problem: unavoidable experimental errors give rise to catastrophic oscillations in the calculated MMD. Techniques have been developed to circumvent this difficulty, and been applied to polysaccharides[3]. In the more straightforward measurement of mass-average molar mass, ultracentrifugation is much less sensitive than light-scattering photometry to extraneous dust.

Solution Viscosity

Most characterizations of water soluble polymers related to molar mass are carried out by capillary solution viscometry. The inadequacy of this characterization is well known: viscosity is an average of the molar mass distribution, and polymer samples with similar viscosities may differ signifcantly in other respects. Molar mass information derived from viscosity depends for its validity upon the reference methods: in the language of metrology, the viscometric characterization is traceable to them via the empirical Mark-Houwink relation:

$$[n] = KM^{\alpha} \tag{1}$$

where $[n]$ is the limiting viscosity number derived usually from capillary viscometry and K and α are empirical constants for a given polymer under specified solution conditions. These constants are established experimentally with a series of fractions characterized by the reference methods: agreement between published values for water soluble polymers leaves much to be desired. The reliance upon Mark-Houwink relations is so widespread that it is worth considering some likely reasons for the discrepancies: knowledge of these reasons assists critical selection from the published values.

The Mark-Houwink relation applies strictly to linear homologous samples. For a polydisperse sample, the molar mass in Eqtn.1 is the viscosity-average, $\bar{M}_v$. For a series of samples such that $\bar{M}_m/\bar{M}_v$ is a constant, the relation takes the form:

$$[n] = K_1\bar{M}_m^{\alpha} \qquad (2)$$

It should be noted that the exponent is unchanged but the K-value will differ in the ratio $\bar{M}_m/\bar{M}_v$. It is difficult, in practice, to establish that the ratio $\bar{M}_m/\bar{M}_v$ is constant for a series of fractions. Evidence of similar polydispersities or similar breadths of size-exclusion chromatograms is to be preferred, but is rarely available in published work. If the series of fractions is such that the ratio $\bar{M}_m/\bar{M}_v$ changes monotonically with M a relation of the form of Eqtn. 2 may fit the experimental results closely, but the parameters K and α will have no wider validity. It is also desirable to consider two factors which may give rise to low values of the measured $[n]$, especially at high molar mass: firstly, the polymer size in solution - a molecule with long-chain branching is more compact than its linear isomer, and so has a smaller viscosity. Secondly, the non Newtonian viscosity, which is common for polymers of high molar mass, should be noted, since a shear rate (~ 200 s^{-1}) in conventionaly capillary viscometry is large enough to lower the viscosity significantly below the zero-shear value needed for Mark-Houwink correlations. A further source of disagreement lies in the insensitivity of the logarithmic least-squares fitting procedure used to derive K and α. For the same reason, it is unwise to extrapolate beyond the calibrated region. Finally, theoretical predictions[4] suggest that, over a wide range of M, the logarithmic form of Eqtn. 1. is non-linear.

Analytical Size-exclusion Chromatography

The principle of the chromatographic separation of polymers by size in solution was described above. The analytical use depends upon separating a small sample (~mg) and using instrumental means (Fig.3) to relate polymer concentration to elution volume. If characterized samples are available for the polymer type of interest, a calibration can be established which relates elution volume to molar mass. Available calibrants are listed in Table 3. Figure 4. shows examples of chromatograms and calibrations established[4] with the polyvinyl alcohol reference samples. When no calibrants are available for the polymer of interest, the principle of 'universal calibration' may be used. For many polymers in non-polar solvents, elution volume in size-exclusion chromatography is determined by hydrodynamic volume, which, in simple polymer theory, is proportional to the product $[n]M$. Mark-Houwink parameters can be used, therefore, to interconvert

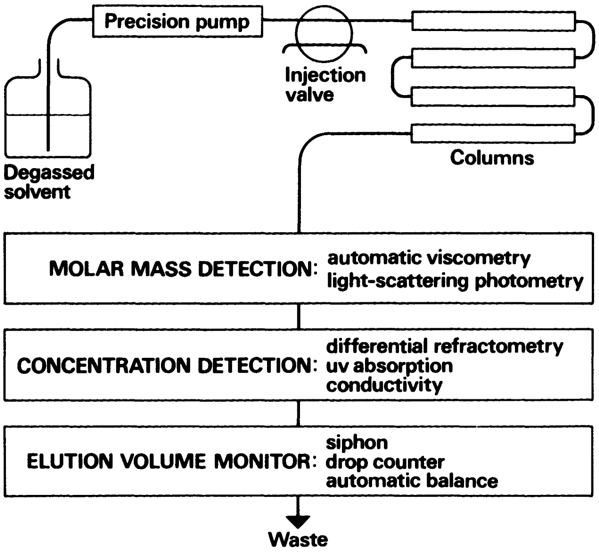


Figure 3. Analytical size-exclusion chromatography.

Table 3. Calibrants for aqueous size-exclusion chromatography

Polymer type	$\frac{\text{Molar mass}}{\text{kg/mol}}$	$\frac{\bar{M}_m}{\bar{M}_n}$	Source
Polystyrene sulphonic acid	1.8 - 1200	1.1	Pressure Chemical Co.
Dextran	10 - 500	1.6	Pharmacia
Poly(vinyl pyrrolidone)	10 - 360	?	Fluka
Polyacrylamide	3000 - 6000	2.0 - 2.4	McMaster University
Polyvinyl alcohol	20 - 400	1.2 - 1.5	National Physical Laboratory
Polyethylene oxide	20 - 1400	1.1	Toyo Soda Co.

calibrations. The extension of universal calibration to aqueous systems has been made for a few combinations of polymers[5,6] .

Measurement of molar mass by calibration in size-exclusion chromatography is subject to systematic error introduced in several ways. Even an ideally homogeneous polymer will elute over a range of elution volume, so that the apparent molar mass distributions inferred are in principle always too wide. There has been great interest[7] in applying digital corrections to remove the effect of dispersion by good experimental technique (slow flow rate, minimum dead volume) and to ignore that remaining. The effect is, in any case, minor for samples of polydispersity greater than 2. If a refractometer is used as a concentration monitor (Figure 3.)the molar mass dependence of specific rotation needs to be considered. In general, there is a critical molar mass below which that depenence is significant, but no relevant investigation of water soluble polymers seems to have been reported. The point that long-chain branching reduces molecular size was made above: in size-exclusion chromatography a molecule with long-chain branching behaves like a linear molecule of smaller molar mass. The importance of all these effects is difficult to evaluate for aqueous size-exclusion chromatography because of the prevalance of mechanisms other than size-exclusion. The most significant of these are adsorption on high-energy substrates and polymer-substrate charge effects: the latter can often be suppressed by using solvent containing an excess of simple electrolyte.

An attractive means of circumventing many of these difficulties is by the on-line measurement of molar mass (Figure 3.). Viscometry[8] and low-angle light-scattering photometry[9] have been applied. Each method infers molar mass from measurements extrapolated to infinite dilution, so that on-line use requires ancillary determination of concentration and, also, empirical constants to guide the extrapolation. On-line viscometry suffers from poor sensitivity at low molar mass and, for non-Newtonian polymer, the high shear-rate necessary for rapid on-line measurement. Poor sensitivity at low molar mass is a problem for on-line light-scattering photometry as well, and the very high sensitivity at high molar mass often means that the light-scattering measurement corresponds to a concentration below the limit of measurement by the ancillary detector.

CHARACTERIZATION OF POLYACRYLAMIDE

To place the above general discussion into a more practical perspective, a brief review of recent work in the characterization of a polymer of particular interest, will, in conclusion, be given. Polyacrylamide (see, especially, Chapters 3 and 19) is of interest from its use in the field of enhanced oil recovery, for which the distribution of molecular size is of central importance in determining solution viscosity and viscoelasticity, mechanical degradation and pore plugging. A traditional charactization by solution viscosity is quite inadequate in interpreting the behaviour in porous media.

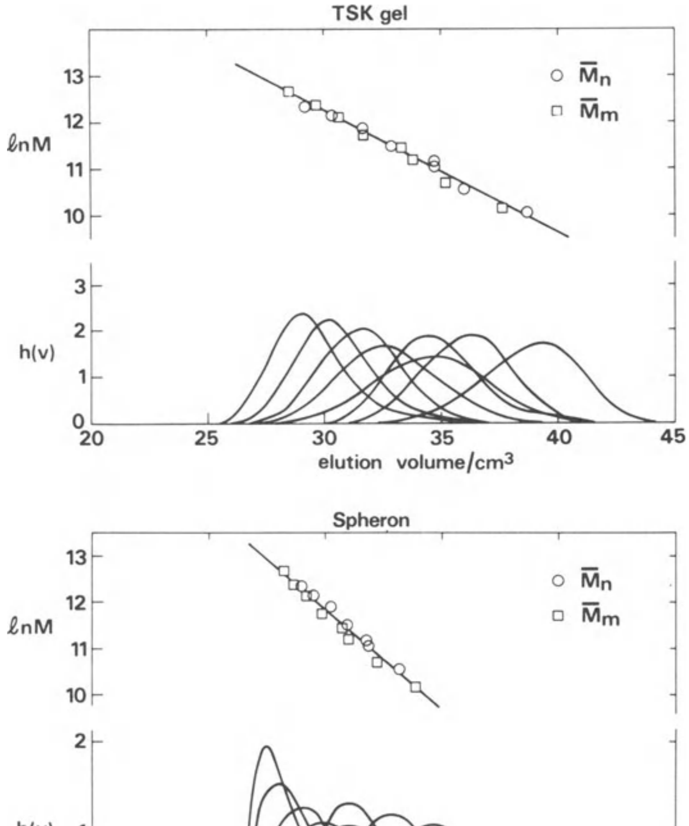


Figure 4. Calibration in SEC for poly(vinyl alcohol) (Reproduced from reference 5 by permission of the publishers, IPC Business Press Ltd.)

Each of the techniques discussed for polymer characterization figures in recent work with polyacrylamide. There are descriptions of fractionation by phase separation[10], of light-scattering photometry[10,11,12], osmometry[12] and ultracentrifugation[13,14]. Mark-Houwink parameters have been compared[13] critically. Mechanical degradation has been studied[14] by ultracentrifugation of fluorescently labelled polymer: the course of degradation could be modelled simply by relating the probability of rupture to molar mass. Much effort has been devoted to the development of size-exclusion chromatography. For unhydrolyzed polymer the use of controlled-pore glass in aqueous Na_2SO_4 appears successful[15], but many have tried and failed to repeat similar work in an earlier report[16]. Anionic polymer (20 - 30 % hydrolyzed) presents an even greater challenge.

This flurry of activity testifies to the importance of characterization of water soluble polymers. The more efficient use of the materials depends upon an understanding of the relation of properties to structure.

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WATER SOLUBILITY AND SENSITIVITY - HYDRATION EFFECTS

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1. SCOPE AND CLASSIFICATION

Chapter 7 outlines currently accepted polymer solution theories in terms of the properties of the macromolecule, polymer-solvent interactions and other variables, e.g. molecular weight, concentration, and temperature, which affect these interactions. In such theories the solvent is treated as a continuum, the contribution of which is expressed in terms of macroscopic properties such as viscosity or dielectric permittivity. This chapter attempts to show that the validity of such treatments is questionable when the solvent is water, because of the unique contributions of hydration effects to the measured quantities, and because of the entropic origin of some of the free energy effects.

The systems under discussion can be classified in three distinct ways: by the chemical nature of the polymers, by the degree of miscibility with water, and, phenomenologically, by the dominance of enthalpic or entropic factors in rendering the polymers soluble. Table 1 provides a chemical classification of the polymers discussed in this chapter. Emphasis is placed on non-electrolytes, because the behaviour of polyelectrolyte solutions is mainly determined by electrostatic effects, and these effects are treated in Chapter 10 .The list is by no means exhaustive, especially as regards the chemically modified carbohydrates, where only glucose derivatives are included. For the sake of brevity, microbial, sea weed, and plant derived polysaccharides have been omitted for the purposes of this discussion. Nevertheless, the arguments advanced in this chapter apply equally to solutions and gels of carrageenans, alginates, pectins, agar, xanthans, furcellarans, etc.

Table 1. Chemical classification of water soluble (sensitive) polymers.

<u>Vinyl derivatives</u>		
alcohol	PV-OH	Prepared by the hydrolysis of polyvinyl acetate, and contains a proportion of residual acetate groups
pyrrolidone	PVP	
methyloxazolidone	PVMO	
methyl ether	PVME	
<u>Polyethers</u>		
polyethylene glycol	PEO	
polypropylene glycol	PPO	
<u>Acrylic derivatives</u>		
acrylic acid	PAA	
acrylamide	PAAm	
methacrylic acid	PMAA	
methacrylamide	PMAAm	Also various N-alkyl derivatives
<u>Modified carbohydrates</u>		
methyl cellulose	MC	β 1→4 linked glucose
hydroxyethyl cellulose	HEC	
hydroxypropyl cellulose	HPC	
hydroxyethyl starch	HES	α 1→4 linked glucose
dextran	D	50 - 100 % 1→6 linked glucose

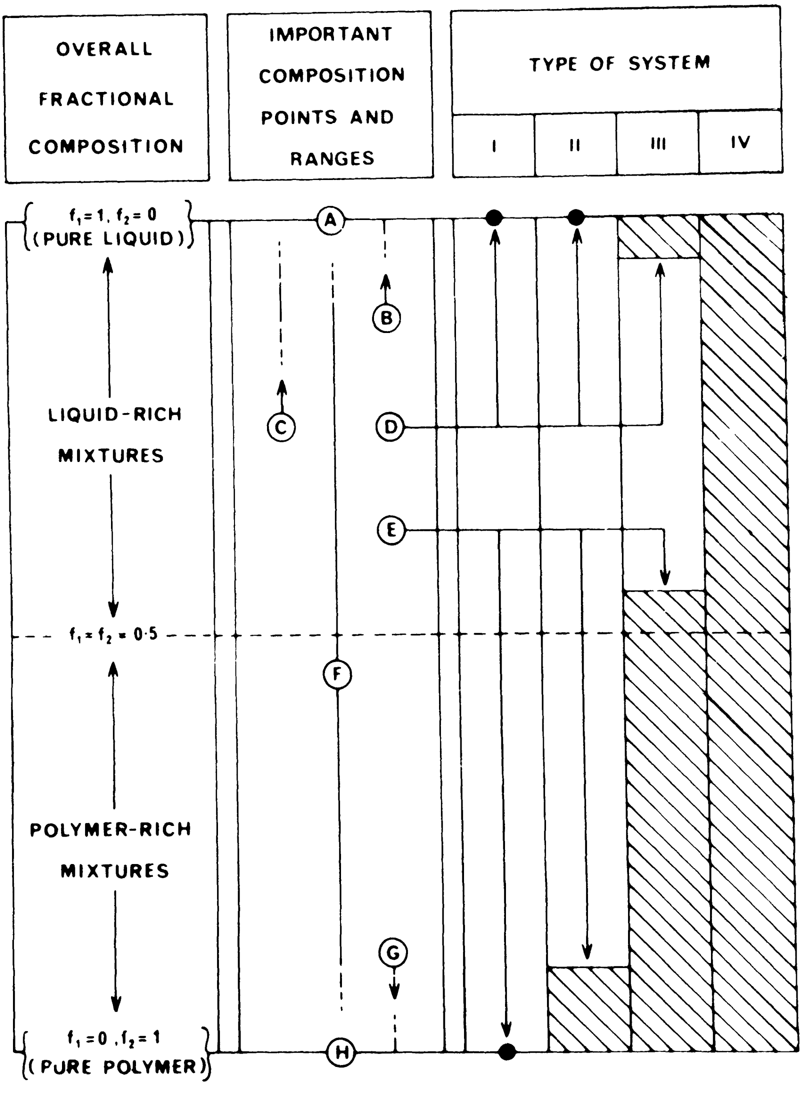

Figure 1. Classification of polymer-water systems according to their miscibility.
Reproduced, with permission, from Ref.[1].

The classification according to the degree of water miscibility is presented in Fig. 1, which has been taken from Molyneux[1]. Systems of type I, in which the components do not interact, hardly exist in practice. Some interaction is detectable, even in the polystyrene/water system, since water vapour is able to reduce the glass transition temperature of the polymer. Type II behaviour is common: here, the polymer sorbs a certain amount of water but does not actually dissolve. Water therefore acts as plasticiser. In systems of type III there is a marked degree of interaction, with the hydrated swollen polymer phase coexisting with an aqueous solution. Type IV systems exhibit complete miscibility. The classification in Fig. 1 refers to a given temperature. Thus, a drop in the temperature may change the behaviour of a given system from type IV to type III, or even II, and vice versa.

We can distinguish several important composition ranges, denoted by capital letters in Fig. 1. Thus, A corresponds to the infinitely dilute solution, where the polymer chain is unperturbed and interacts with the solvent only (unless intramolecular effects are significant). Formally, any measurements to determine the shape of the polymer chain in solution must be extrapolated to this point. At B ($f_2 \simeq 0.01$) we have the region of the dilute solution which is of importance in the determination of polymer-polymer interaction through the second virial coefficient. Region C is not precisely defined, but it corresponds to the beginning of chain overlap and entanglement; it is sometimes identified by $f_2 = \{\eta\}$, where $\{\eta\}$ is the intrinsic viscosity. D corresponds to the saturation solubility of the polymer, and E to that of water in the polymer. F is the region of practical importance; It extends from the dilute solution to gels of polymer, plasticised by water. G is the concentration of water in the polymer at which deviations from Henry's law are first observed, i.e. where water-water interactions become measureable in sorption experiments. Finally, H corresponds to an infinitely dilute solution of water in the polymer, as $f_1 \to 0$, and is obtained experimentally from the initial, linear, section of the sorption isotherm.

2. THERMODYNAMIC FORMALISM

The classification in Fig. 1 must now be placed on a more formal and quantitative basis, designed to rationalise the various types of phase behaviour observed in polymer/water systems. The Flory-Huggins (FH) theory provides the most popular framework for such rationalization, and it is outlined in Chapter 7 of this volume. It is the purpose of this chapter to discuss the shortcomings of the FH theory, as applied to aqueous solutions. Basically, the shortcomings arise from the fundamental assumptions that the cell model provides an adequate representation of an aqueous solution, that the ideal entropy of mixing can be used, that there is zero volume change on mixing, that deviations from ideal solution behaviour can be simply accounted for in terms of χ, the (enthalpic) solute/solvent interaction parameter and that the polymer chains are fully flexible. For heterodisperse solutions of finite volume fraction ϕ_2 it has been established that

$$\chi = \chi (M_n, \phi_2 , T) \qquad (1)$$

where M_n is the number average molecular weight, and T is the temperature. The complete expressions for χ are discussed in Chapter 7 . Here, it need only be emphasised that the classical FH theory cannot account for solutions with exothermic heats of dilution. Following from Eqn. 12 of Chapter 7 , we can write

$$\chi = \chi_H + \chi_S = - T (\partial\chi/\partial T) + \partial(\chi T)/\partial T \qquad (2)$$

$$= \Delta h_{12}/ RT - \Delta s_{12}/R$$

where Δh_{12} and Δs_{12} are the enthalpy and entropy changes resulting from water/polymer segment contacts for a lattice coordiniation number z = 1. Allowing for the concentration dependence, we can write

$$\left.\begin{aligned} \Delta h_{12} &= - RT^2 \phi_2^2 \, \partial\chi/\partial T \\ \text{and} \quad \Delta s_{12} &= \Delta s_{12}^{id} - R\phi_2^2 \, \partial(T\chi/\partial T \end{aligned}\right) \qquad (3)$$

where Δs_{12}^{id} is the ideal mixing entropy.

Experimentally, the temperature and concentration dependence of χ can be studied by the colligative properties and light scattering in the low T and $\phi_2 \to 0$ range, by sorption isotherms in the low T and $\phi_2 \to 1$ range, and by vapour phase chromatography at high T in the $\phi_2 \to 1$ range.

In FH theory and its subsequent extensions χ is assumed to be due almost exclusively to van der Waals type interactions and is therefore expressed in terms of polarisabilities of the polymer segment and water. leads to the results that $\chi > 0$. if ϕ_2 is small, then ΔG^M, the free energy of mixing, again, as above, following from Eqtn. 12 of Chapter 7, can be expanded to yield

$$\frac{\Delta G^M}{RT} = \frac{\phi_2}{N} \ln \phi_2 + \tfrac{1}{2} \phi_2^2 (1 - 2\chi) + \frac{1}{6} \phi_2^3 \qquad (4)$$

A more general form of Eqtn. (4) is[2]

$$\frac{\Delta G^M}{RT} = \frac{c}{N} \ln c + \tfrac{1}{2} v c^2 + \frac{1}{6} v^2 c^3 + \dots \qquad (4a)$$

where c is the monomer concentration per unit volume, and v is the where c is the monomer concentration per unit volume, and v is the so-called excluded volume parameter. Putting $\phi_2 = ca^3$, where a is the length of the monomer segment in the chain, we obtain

$$v = a^3 (1 - 2\chi)$$

The excluded volume can be regarded as the volume fromwhich a given polymer molecule effectively excludes all others. Clearly, this depends on the volume of the polymer molecule itself, and this in turn depends on the nature of the polymer/solvent interactions. Four special cases of Eqn. (4) are of particular significance:

(1) $\chi = 0$. Mixing is entirely entropic and is temperature independent: the solvent is a "good" solvent, and $v = a^3$.

(2) $\chi = \frac{1}{2}$. Attractive and repulsive forces cancel exactly; this is referred to as the 'theta' (θ) condition and can be achieved by the choice of a particular solvent at a given temperature or, where the solvent is given, by an adjustment of the temperature. In other words, for any solvent, there is at least one temperature, the 'theta'-temperature, at which $\chi = \frac{1}{2}$. In this case, $v = 0$ and the chains are ideal, with the root mean square end-to-end distance given by

$$\bar{r} = aN^{\frac{1}{2}}$$

where N is the degree of polymerisation.

(3) $\chi > \frac{1}{2}$. Polymer-polymer interactions exceed polymer-solvent interactions, so that phase separation may take place. In dilute solution the polymer chains collapse, giving more compact structures than in the ideal case (2); the solvent is a "poor" solvent.

(4) $0 < \chi < \frac{1}{2}$. This is the region where the solvent is a "good" solvent. The polymer chains therefore tend to swell, and the excluded volume effect becomes significant.

The above four cases have been discussed in terms of dilute solutions (low ϕ_2). However, since χ changes with ϕ_2, the dimensions of, and interactions between, polymer chains are also influenced by changes in concentration. Such effects are of particular importance in influencing the rheological properties of polymer solutions and their propensity for gel formation.

From Eqn. (2) it is apparent that 'theta' conditions can be achieved by one of two mechanisms:

$$\begin{array}{ll} (1) & \chi_H > 0, \quad \chi_S < 0.5 \\ \text{or} \quad (2) & \chi_H < 0, \quad \chi_S > 0.5 \text{ with } |\chi_S| > |\chi_H| \end{array} \qquad (5)$$

The first case shows the "normal" type of behaviour, termed θ_- behaviour, accounted for by FH theory. However, the second case, θ_+ behaviour, is commonly found with aqueous solutions, where phase separation occurs on heating (lower critical demixing).

Since one of the fundamental assumptions of the FH treatment is that χ is a measure of the energetic (enthalpic) solute-solvent interactions, lower critical demixing cannot be accounted for. Various attempts have been made to rationalise its occurrence within the confines of FH theory, but such treatments are hardly realistic, nor do they take into account the physical peculiarities of liquid water.

3. EXPERIMENTAL DATA

Figure 2 provides a summary of cloud point results for a number of aqueous polymer solutions, and Table 2 lists some extrapolated ($\phi_2 \rightarrow 0)\chi$ values. The direction of the arrow heads in Fugure 2 indicates the type of θ behaviour - i.e.:

→ indicates normal,
θ_- indicates demixing, and
← indicates demixing on heating (θ_+).

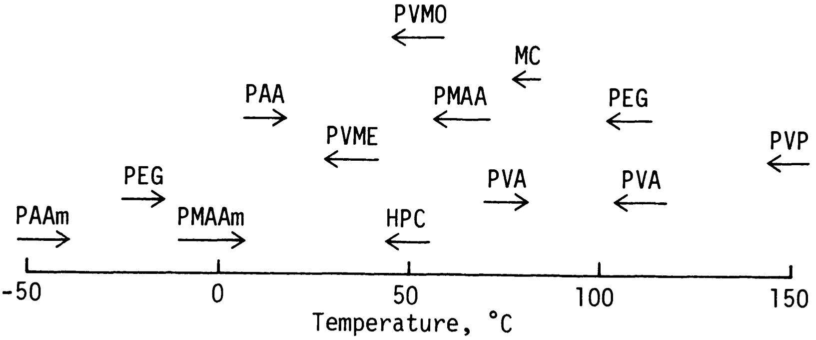

Figure 2. Cloud points of water-soluble polymers at 25°C.
θ_- behaviour is shown as →
θ_+ behaviour is shown as ←

Table 2. Flory-Huggins interaction parameters (χ) extrapolated to $\phi_2 = 0$ at 25°C.

Polymer	(χ)
PAAm	0.44, 0.49 (?)
PMAAm	0.490
PAA	0.498
HPC	0.482
PMAA	0.499
PV-OH	0.8
PVP	0.48
PEO	0.45

Several points need emphasizing: an increase in the polarity of the polymer (e.g., by replacing -COOH with $-CONH_2$) lowers the θ temperature. Similarly, the replacement of a hydrogen atom by an alkyl group raises the θ temperature (compare PAA with PMAA, or PAAm with PMAAm).[3] Several polymers exhibit both θ_- and θ_+ behaviour (e.g. PEG), and this leads to a closed miscibility loop. It is to be expected that all polymers should have an upper critical solution temperature, although it may not be experimentally accessible. On the other hand, lower critical demixing is confined to certain types of solute molecules (see below).

The results in Table 2 are remarkable in the sense that they cluster around $\chi = 0.5$, so that, at room temperature, water cannot be regarded as a good solvent for any of the polymers. For non-aqueous solutions, χ values span a much wider range, e.g. polymethyl methacrylate/chloroform (0.38), polystyrene/ethyl benzene (0.40), polymethyl methacrylate/isopropyl ketone (0.51)[4].

From osmotic pressure measurements at several temperatures it is possible to derive Δh_{12} and Δs_{12}; The former can also be obtained directly from heat of dilution measurements. Figure 3 shows some of the available data, as derived from osmotic pressure determinations[5]. Whilst all the polymers shown have exothermic heats of dilution,

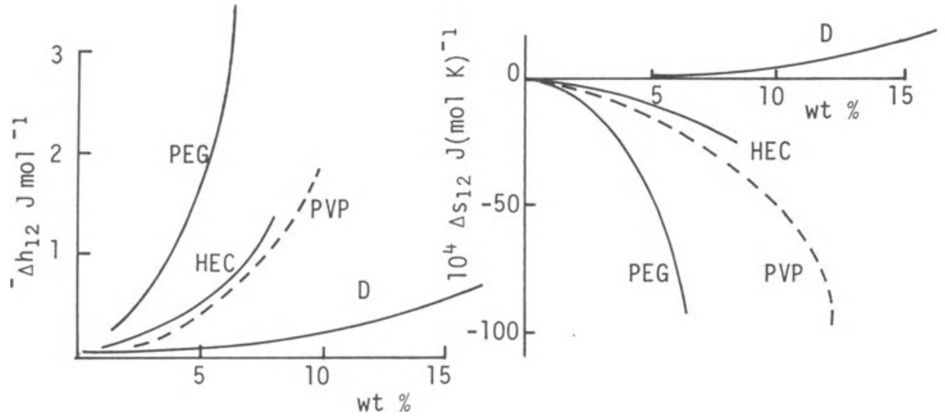

Figure 3. Enthalpies and entropies of water-polymer contacts, obtained from the temperature dependence of the osmotic pressure; adapted from Ref.[5]. For details, see text.

they also exhibit negative entropies; only dextran demonstrates a behaviour approaching normality (even with D, $\Delta h_{12} < 0$). According to the criteria of Eqtn.(5), PEG, HEC, and PVP should exhibit θ_+ demixing, and this has been established experimentally. The actual θ_- is more difficult to estimate, because it requires a knowledge of the manner in which Δh_{12} and Δs_{12} vary with temperature, i.e. a knowledge of the heat capacity of solute-water interactions. For instance, despite the observation that PVP is completely miscible with water, the thermodynamic properties of aqueous PVP solutions suggest a θ_+ behaviour: measurements on ternary systems PVP/water/salt, when extrapolated to zero salt concentrations indicate such behaviour in the vicinity of 150° C.

Recent direct measurements of the heat of dilution of aqueous solutions of a variety of polymers have highlighted the eccentric behaviour of such systems. Figure 4 summarizes some of these data[6]. The heat of dilution is given by

$$\Delta h_{dil} = RT\phi_2 \, \phi_2^1 \, \Delta n_1 \, \chi_H \qquad (6)$$

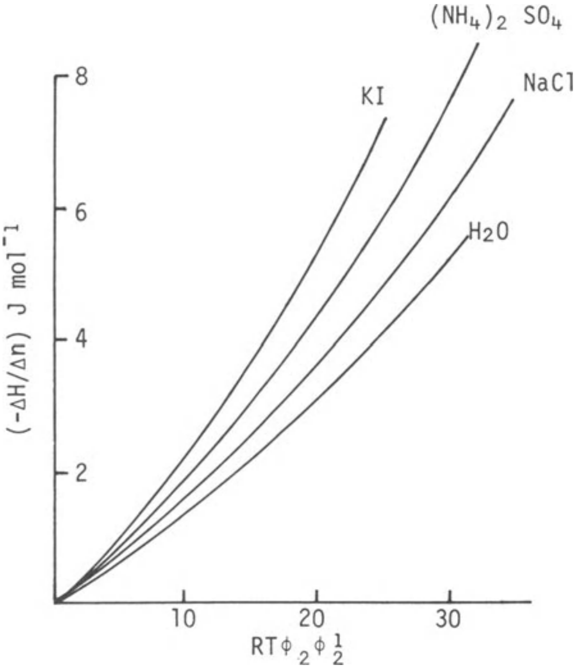

Figure 4. Heat of dilution of PVP in different aqueous solvent media; electrolyte concentrations: 0.5 $mol.dm^{-3}$. Redrawn from Ref.[6]

where Δn_1 is the number of mols. of water which have to be added to the mixture to change the polymer volume fraction from ϕ_2 to ϕ_2^1 The slopes of the plots in Figure 4 yield χ_H. The limiting values χ_H^o, of some aqueous solutions are summarized in Table 3. It is seen that only PAAm exhibits normal (endothermic) mixing. Phase separation in all the other systems is dominated by entropic effects. Indeed, the dilution of PVP is even more exothermic in the presence of electrolytes, and yet salts lower the θ_+ - temperature. $(NH_4)_2SO_4$ precipitates PVP even at room temperature, indicating a large unfavourable entropy effect[6].

Table 3. Limiting ($\phi_2 \to 0$) enthalpic interaction parameters, χ_H^o, of aqueous polymer solutions at 25°C.

Polymer	Solvent	χ_H^o
PVP	Water	- 0.036
PVP	0.5 -M. NaCl	- 0.06
PVP	0.5 -M. KI	- 0.1
PVP	0.5 -M.$(NH_4)_2SO_4$	- 0.11
PAAm	Water	0.075
P(N-Me)AAm	Water	- 0.06
P(N-diMe)AAm	Water	- 0.05
PEO (Mol. wt.6000)	Water	- 0.192

4. HYDROPHOBIC EFFECTS

The peculiar thermodynamic behaviour discussed above is not unique to solutions of macromolecules, but it is unique to aqueous solutions of certain classes of solutes, sometimes referred to as hydrophobic solutes. These include apolar molecules (rare gases and hydrocarbons) and alkyl and aryl derivatives with only one functional group (alkanols, ethers, amines, ketones). Indeed, the monomers or monomeric analogues of some water-soluble polymers, such as ethyl pyrrolidone and ethylene oxide, exhibit solution properties which closely resemble those of the polymers (PVP, PEG). These properties can be summarized as follows:

Consider the transfer of the solutes from some defined standard state (ideal gas or pure liquid) to an infinitely dilute aqueous solution, (X_2 = mol fraction),

$$S \text{ (standard state)} \rightarrow S \text{ (aq., } X_2 \rightarrow 0\text{)}$$

The excess thermodynamic functions characterizing this transfer, say at 25°C, have the following features in common:

$$\Delta G^E > 0 \;;\; \Delta S^E < 0 \;;\; \Delta V^E < 0 \;;\; \Delta H^E \gtrless 0 \;;\; \Delta C_p^E > 0 \;;\; \kappa_T^E \lesssim 0 \;;\; \alpha^E < 0,$$

where κ_T^E and α^E are the excess coefficients of isothermal compressibility and expansion respectively. The positive free energy is seen to arise from the negative excess entropy of mixing and not from an enthalpic repulsion term. This type of solute-water interaction is known as hydrophobic hydration, and is now believed to be due primarily to the loss of configurational degrees of freedom of the water molecules upon the introduction of the nonpolar molecule or nonpolar residue in an otherwise polar molecule[7]. For a homologous series the magnitude of ΔG^E increases with the number of methylene groups in the solute molecule. On the other hand, a substitution of CH_2 by, say, CHOH, reduces ΔG^E . Thus, the observed thermodynamic properties of the solution depend sensitively on the ratio of apolar groups to those residues capable of interacting with water by means of hydrogen bonding.

Consider now the transfer of a solute molecule to an aqueous solution of a finite, but low, concentration. The measured thermodynamic properties now also include a term due to solute-solute effects; in dilute solutions only molecular pair interactions need be considered - these are expressed as second virial coefficients, e.g. g_{22}, in the power expansion of the excess thermodynamic properties in terms of concentration; e.g.

$$\Delta G^E = g_{22}x_2^2 + g_{222}x_2^3 + ----$$

The classical theory of hydrophobic interactions predicted that such virial coefficients would have the opposite sign of the corresponding thermodynamic property characterizing hydrophobic hydration (solute-water effects)[8,9]. This was based on the premise that hydrophobic aggregation of alkyl chains must correspond to a partial reversal of the effects caused by hydrophobic hydration. As a first approximation this appears to be true, especially in more concentrated solutions. However, careful experiments on dilute solutions have shown that several of the excess thermodynamic properties pass through extrema at concentrations which critically depend on the number of methylene groups in the solute molecule[7]. This implies a fundamental change in the nature of the solute-solute interactions at some critical concentration.

Whilst the details of the pair hydrophobic interaction are not yet fully elucidated, several generalizations can be made, which also apply to interactions within and between polymer chains in aqueous solutions:-

1. The driving force for the solute-solute interaction is not an intrinsic attraction between solute molecules, but a reduction in the configurational constraints imposed on the water molecules by the solute[10]. The driving force is therefore of an entropic origin.

2. The hydrophobic interaction thus increases in magnitude with rise in temperature, and it therefore promotes lower critical phase demixing, characterized by θ_+ behaviour. Any theory which expresses solute-solvent and solute-solute interactions only in terms of van der Waals (enthalpic) effects, cannot therefore correctly predict the sign, let alone the magnitude of the temperature dependence of such interactions.

3. Lattice models applied to solutions in which the interactions are dominated by hydrophobic effects can at best be regarded as exercises in curve fitting[12].

4. The net solution interactions, as reflected in the osmotic second virial coefficient, are the resultant of normal, polar effects, and hydrophobic effects. Thus, polymers which, according to their chemical behaviour, appear to be polar, e.g. PV-OH, may nevertheless behave in solution as typically hydrophobic solutes. Even the introduction of a CH_3 group into a polar residue (e.g. PAA), can tip the balance towards hydrophobic behaviour (see Figure 2.), as can also the esterification of one of the -OH groups in glucose[13].

5. Hydrophobic interactions (and hydration) are characterized by large heat capacity effects and therefore change markedly with temperature. At some high temperature, the condition for hydrophobic behaviour,

$$T\,|\,\Delta S^E\,| > |\Delta H^E|$$

will no longer exist, and aqueous solutions can then be expected to behave 'normally' - e.g., to exhibit θ_- type behaviour, as do PEG and PV-OH (see Figure 2.).

6. Attempts to rationalize θ_+ behaviour in terms of the dissimilarity between the properties of the large solute molecule and the small solvent molecule (e.g. differences in thermal expansion coefficients[14]) must be discounted, because θ_+ behaviour (lower critical demixing) is also commonly observed in aqueous solutions of the monomer, e.g. with ethylene oxide and PEG, where such marked differences in physical properties do not exist.

The general conclusion must be that hydrophobic interactions which play a predominant note in determining the structure and aggregation behaviour of natural macromolecules are also of great importance in determining the solution behaviour of synthetic polymers. The observed free energy of solution of such substances is determined mainly by the negative entropy of mixing and cannot, therefore, be represented by a potential energy function of the usual van der Waals type[11]; in other words, $\Delta G^E \neq \Delta H^E$: a closer approximation would be $\Delta G^E \simeq -T\Delta S^E$.

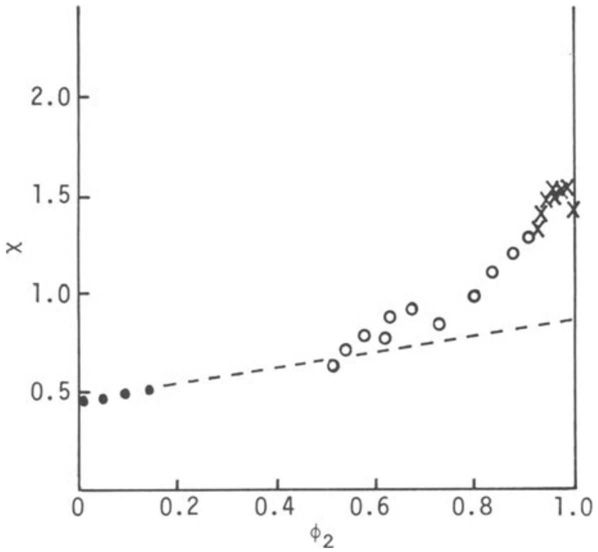

Figure 5. Concentration dependence of hydroxypropyl cellulose forn the system HPC/water at 25°C:
osmotic pressure ●
sorption isotherms o
vapour phase chromatography ×
Redrawn from Ref.[17].

5. CONCENTRATED SOLUTIONS

Where the polymer is completely miscible with water, or even where a hydrated polymer phase coexists with an aqueous solution (systems II,III, and IV in Figure 1.), a better understanding of solute-water interactions in the composition range $\phi_2 \to 1$ is of importance. For a polymer with $M_n \to \infty$, again following Eqtn. (12) in Chapter 7,

$$\mu_1 = (1 - X_n^{-1})\phi_2 + \chi\phi_2^2 \simeq 1 + \chi \qquad (7)$$

Bearing in mind that χ is a function of ϕ_2, its concentration dependence is often expressed as[16]

$$\chi = \chi_1 + \chi_2\phi_2 \qquad (8)$$

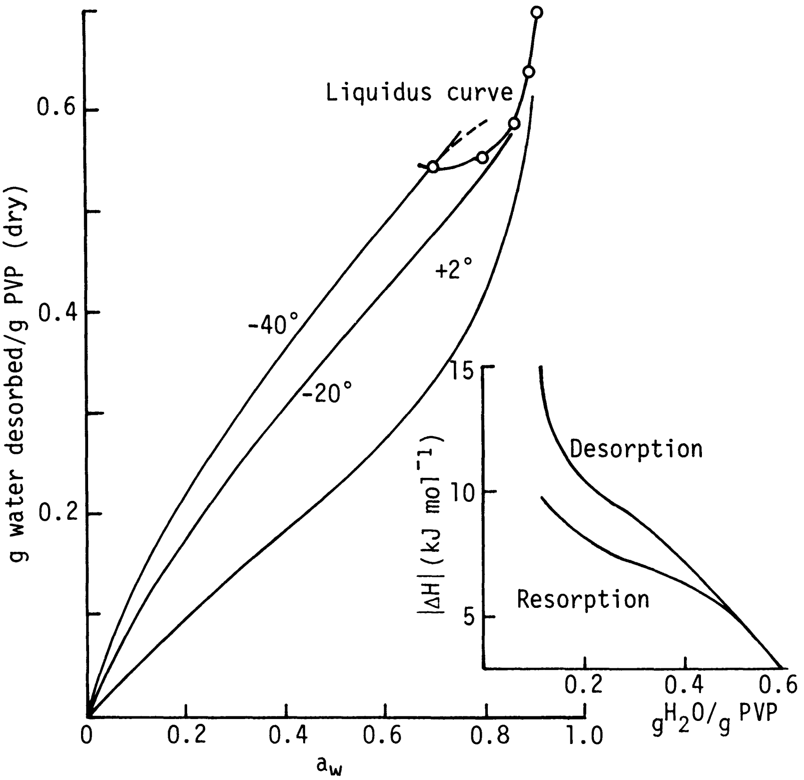

Figure 6. Desorption isotherms for water on PVP; Inset: isosteric heat of sorption. Redrawn from data in Ref.[20]

Osmotic pressure measurements on dilute solutions of HPC at different temperatures indicate that χ_1 = 0.500 at 40°C.[16] Extrapolation of the dilute solution data yields χ_2 = 0.371 in Eqtn. (8). This is equivalent to χ = 0.83 for ϕ_2 = 1. However, direct measurements by vapour phase chromatography suggest a value of 1.35 at $\phi_2 \rightarrow 1$ and 25°C.[17] Figure 5 shows the available data for HPC at 25°C. Apart from the marked deviation from the linear (ϕ_2) behaviour predicted by Eqtn. (8), there is also an indication of a maximum at low water contents which cannot easily be reconciled with FH theory. Similar maxima have been established for aqueous solutions of polyvinylmethoxyacetal,[1,18] and there is a suggestion of a shallow maximum for PVP near $\phi_2 \simeq 0.4$.[19]

6. NON-EQUILIBRIUM BEHAVIOUR: BOUND AND UNFREEZABLE WATER

There must be some doubt about the thermodynamic significance of experimental data for concentrated polymer solutions, especially at low temperatures. Water sorption isotherms are characterized by hysteresis effects which are quite reproducible - i.e.,the hysteresis loop does not diminish in area with repeated cycling or by allowing more time for a stationary state to be achieved. Figure 6 shows some of the available sorption isotherm data for the PVP/water system; the inset shows the heat of sorption, as obtained from adsorption and desorption isotherms[20]. It is apparent that at low water contents desorption is associated with larger energy changes than resorption. The other remarkable feature of the PVP isotherms is that, as $a_1 \to 0$, they do not pass through the origin but some water is retained by the polymer. This water, usually referred to as 'bound' water, is therefore osmotically inactive. The existence of bound water in concentrated polymer solutions can be demonstrated most strikingly by reference to the liquidus curves. Figure 7. represents the freezing point curves of PVP and HES solutions[20,21]: the molecular weights of the polymers are 44,000 and 450,000 respectively. On the basis of equilibrium thermodynamics, the freezing point depression should be minimal, but at weight fractions $w_2 \simeq 0.5$ marked freezing point depressions are observed and the curves come vertical at some finite value of w_2, indicating that at even higher concentrations the water in the system does not freeze, although it is in the presence of ice. Actually, the glass transition curve intersects the liquidus curve near - 40°C, so that the freezing could not take place below this temperature in any case, at least, not within a reasonable time. The liquidus curve does not exhibit a eutectic temperature, because the polymers in question do not crystallize: the solutions therefore tend to supersaturation and metastability. Although bound water must on no account be regarded as a stoichiometric hydrate, it is possible to assign notional hydration numbers (mol water/basemol). For PVP, PV-OH and HES, these are respectively 3.3, 4, and 5[22].

The significance of bound water is particularly well illustrated in ternary systems water/polymer/salt, where a binary salt/water eutectic exists. Such a system is described in Figure 8[23]. The binary system water/NaCl exhibits the well known eutectic at - 21.2°C and 22 % w/w NaCl If the polymer (HES) is now added to the eutectic mixture, it is found that the composition follows the solid line and not the broken line - i.e., it is impossible to obtain anhydrous HES. In addition, the eutectic temperature of the ternary mixture is invariant at - 21.2°C. The extrapolated concentration of the binary HES/water mixture corresponds to $w_{H_2O} = 0.35$, in good agreement with the limiting value of the extrapolated liquidus curve, shown in Figure 7.

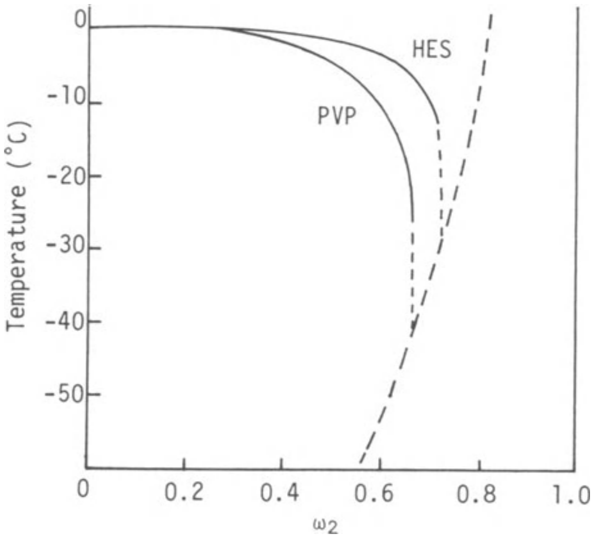

Figure 7. Liquidus curves for aqueous PVP and HES. The broken line denotes the glass transition curve. Redrawn from data in Refs.[20] and [21].

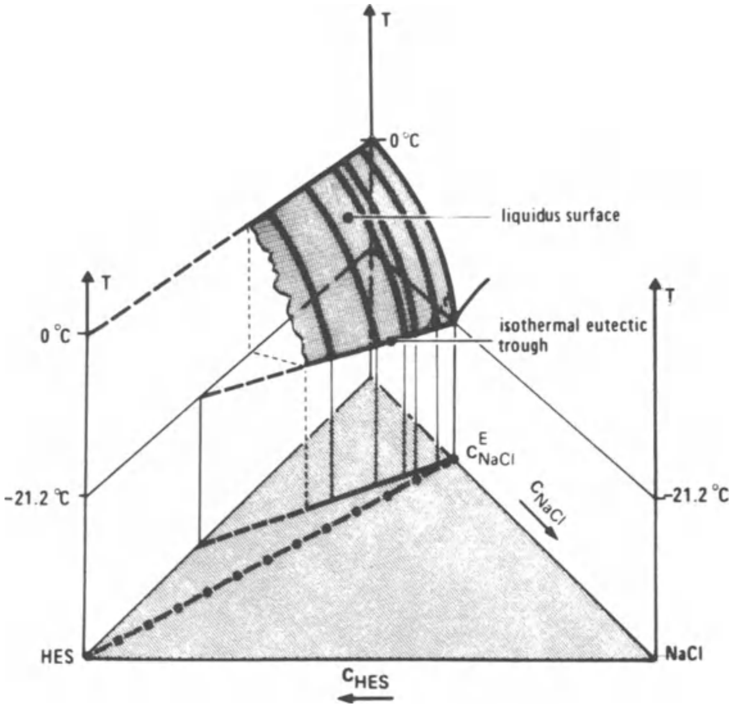

Figure 8. Ternary phase diagram for the system water/NaCl/HES, showing the pseudo-hydrate of HES and the invariant eutectic trough: reproduced, with permission, from Ref.[23].

The representation of the temperature/composition behaviour of the ternary system by a conventional phase diagram tends to conceal the fact, emphasized above, that the indication of a hydrated HES phase does not mean that such a stoichiometric compound exists in the sense of the Phase Rule, but is evidence of a highly supersaturated solution. It can hardly be stressed sufficiently that bound, or, as it is also known, unfreezable water, although an experimental fact, does not correspond to an equilibrium state, but results from diffucional barriers and 'frozen-in' metastable states. The phenomenon is of great physiological importance, because it is instrumental in rendering living organisms resistant to stress conditions, such as drought or freezing[24].

The electron microscopic examination of quenched and vitrified polymer solutions to below their glass transitions has revealed peculiar aggregation patterns. Aqueous solutions (PVP, PEG, HES, and PV-OH) appear to exist in the form of hydrated spherical aggregates of mean diameters $\lesssim$ 100 nm, even at the lowest concentrations at which complete vitrification could be achieved, $w_2 \simeq 0.15$, but at which apparently normal freezing behaviour is observed[21,22]. This makes it questionable whether such solutions can ever be regarded as dilute, in the sense that a truly infinitely dilute state can be achieved in which individual macromolecules exist in the predictable equilibrium configuration. It seems, rather, that when the solid polymer is dissolved in water, aggregates persist, even though the stoichiometric polymer concentration may be very low indeed. In this connection, it has already been mentioned that most of the polymers listed in Table 1 have χ values close to 0.5,which means that such solutions are always close to demixing. It is, of course, ineffective to heat such solutions in order to promote deaggregation, because most water-soluble polymers exhibit θ_+- behaviour, so that heating from below the theta-temperature would promote further aggregation.

7. TIME DEPENDENT PROPERTIES

Fluctuations in density, concentration, energy, etc., are natural features of all molecular ensembles, but when the life times of such fluctuations reach the orders of hours, days, or years, then it becomes difficult to distinguish such fluctuations from true heterogeneity, in the sense of the Phase Rule. This a glass can be regarded as a 'phase' frozen into a system when the cooling rate exceeds the diffusion rate of the molecular species. In a binary polymer/solvent mixture a phase might be defined as an inhomogeneity in excess of two surface molecular layers, a distance of the order of 1 nm. It should be noted that by this criterion, bound water is to be regarded as a distinct phase. Operationally, this may be useful, but thermodynamically it is, of course, incorrect.

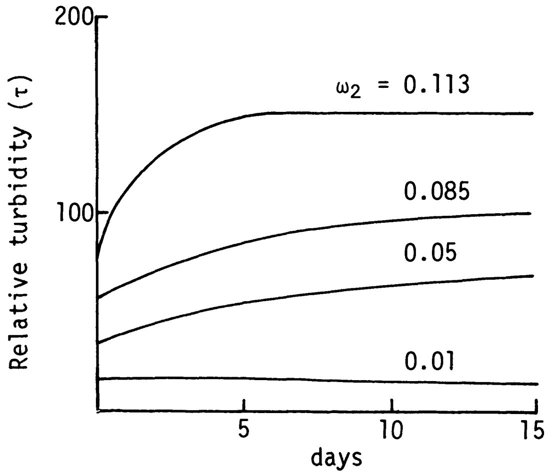

Figure 9. Effect of PV-OH on the increase in turbidity of solutions rapidly quenched from 90° to 20°C. Redrawn from Ref.[25]

The physical properties, e.g. viscosity, of many aqueous polymer solutions have long been known to be time variant - an extreme example of such time dependence is the eventual formation of gels. Although such time effects can be of great technological importance, few fundamental studies are on record, which might be able to provide the required basic information.

The time dependence of physical properties is particularly marked for solutions of PV-OH. Thus, it was found from light scattering studies that, at temperatures above 75°C, the turbidity (τ) of PV-OH solutions is constant, and given by

$$\tau = K_c/R_o \simeq M^{-1} + 2\,Bc \qquad (9)$$

where K is a constant, R_o is the Rayleigh scattering ratio (see Chapter 7), and B is the second virial coefficient[25]. Equation (9) appears to conform to the thermodynamic requirements for a dilute solution. However, the question arises whether the solution is truly homogeneous, or whether the turbidity just appears to be time invariant. At high concentrations and low temperatures, $\tau = \tau(c,t,T)$. Figure 9 describes the kinetics of the increase in scattering for solutions rapidly quenched from 90° to 20°C. It is found that $d\tau/dt = f(c)$. The temperature dependence of such time effects is shown in Figure 10 for solutions at constant concentration

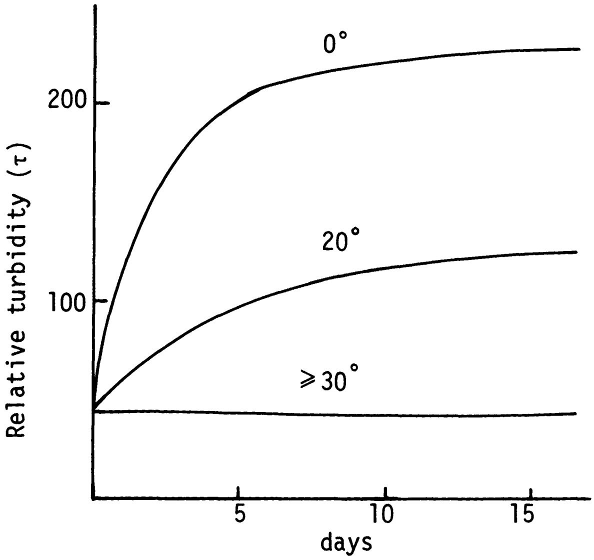

Figure 10. Effect of PV-OH concentration on the increase in turbidity of solutions rapidly quenched from 90^o to 20^{o}C. Redrawn from Ref.[25].

(w_2 = 0.086). Solutions quenched from 90^o to $\gtrsim$ 30^{o}C do not exhibit time dependent scattering (at least, not on a time scale measured in days). However, the limiting turbidity is considerably lower than that observed for lower temperatures.

The evidence from Figures 9 and 10 suggests that a new,metastable hydrated phase forms at low temperatures and/or high concentrations. This phase (or fluctuation with a long life time) must be of an amorphous nature because τ reaches a limiting value and there appears to be no induction period, such as would be expected for the nucleation of a crystalline phase. Depending on the molecular shape of the polymer, such a metastable phase can take the form of a gel. The time dependent effects described in this section give rise to the types of behaviour discussed in the previous section, where it was implicitly assumed that the metastable states were achieved instantaneously and could therefore be regarded as quasi-phases.

8. CONCLUSIONS

1. The behaviour of aqueous solutions of non-electrolytes (including polymers) is characterized by a balance of two effects - intercomponent hydrogen bonding and hydrophobic hydration. The latter effect arises from spatial and orientational changes in water, resulting from the introduction of an apolar molecule or residue. The hydrophobic interaction between two such residues cannot be modelled by a conventional potential energy equation.

2. Many concentrated aqueous solutions tend to supersaturation and must therefore be regarded as thermodynamically metastable. A fraction of the water appears to be osmotically inactive, but the phenomenon of bound/unfreezable water has its origin in diffusional barriers rather than in equilibrium binding of water molecules to various polar functional groups.

3. Frequently, the physical properties of aqueous polymer solutions are characterized by a time dependence, and it is by no means certain whether the eventual value measured corresponds to an equilibrium property or is indicative of a 'frozen-in' fluctuation.

4. It is unrealistic and unprofitable to attempt to fit the properties of aqueous solutions of hydrophobic molecules by a single set of parameters, covering the whole composition range. The properties of liquid water in the bulk and in dilute solutions bear little resemblance to those of discrete water molecules, such as are of importance in sorption isotherms, or in problems involving water acting as plasticizer.

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AQUEOUS SOLUTIONS OF POLYELECTROLYTES

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Polyelectrolytes are macromolecules which, in a suitable polar solvent, usually water, carry a large number of ionized or ionizable groups, often one per monomer unit. Under well defined conditions the macromolecules will bear a considerable charge distributed along the chain (the 'fixed charges') accompanied by an equivalent number of small ions of opposite sign (the 'counterions') in solution. The charge-bearing groups may all be identical or not, but we shall here treat only homopolyelectolytes, or polyelectrolytes behaving as such. Polyelectrolytes can be of natural origin (nucleic acids, many polysaccharides, etc.) or synthetically prepared (e.g. polyacrylic acid, polyvinyl pyridinium bromide, poly(maleic acid-vinylethylether)-copolymer, etc.).

Aqueous solutions of polyelectrolytes have been shown to exhibit certain specific properties, particularly in the absence of a large excess of simple (low molar mass) electrolyte[1]. The problems arising in the quantitative understanding of these specific effects are, however, very difficult, as they find their origin in a non-additive combination of macromolecular and electrolyte behaviour. Theoretical approaches mainly apply to highly simplified models. From an experimental point of view, polyelectrolyte solutions are often more difficult to handle than either solutions of ordinary macromolecules or of ordinary electrolytes, and proper care must be given to the appropriate experimental conditions necessary to determine certain characteristic quantities for those systems. For instance, the molar mass can only be obtained from classical Rayleigh light-scattering measurements, provided the polyelectrolyte solutior contains a sufficiently large excess of low molar mass electrolyte, and the refractive index increment of the macromolecule has been determined from measurements on a series of solutions of different macromolecular concentration (C_M), in which both water and the low molar mass electrolyte have constant chemical potential[1e].

1. THE PHENOMENOLOGICAL APPROACH

It is easy to understand qualitatively that the accumulation of identical charges on a macromolecular chain may have a far reaching influence on the average conformation of the polyelectrolyte or the properties derived from it. The electrostatic repulsions between the fixed charges on the same macromolecule will increase the local stiffness of the chain (short-range interactions) and the excluded-volume effect (long-range interactions), both tending to increase the average shape of the macromolecule as compared to a charge-free polymer. These repulsive interactions may be partially screened off by the presence of small ions and by interactions between the polyions themselves. It is thus expected that, in a very dilute polyelectrolyte solution, increase of the linear charge density

$$|\beta| \equiv Zq/L$$

(where Z = number of elementary charges, q, fixed on a chain with countour-length, L)

will generally be accompanied by an increase of the average dimensions of the macromolecule, which will tend to become rodlike in the limit of infinite dilution and absence of low molar mass electrolyte. When the concentration of the latter (C_S) is increased, this charge effect will be opposed , and additional screening may appear at higher polymer concentrations where the chains have a tendency to become intertwined. Unfortunately, there is no simple experimental means to demonstrate directly the charge- and concentration effects in polyelectrolyte solutions at low C_S. The classic way of measuring radii of gyration of macromolecules (Rayleigh scattering) is not applicable under these conditions. However, this light scattering technique can be applied when there is an excess of 1-1 electrolyte ($C_S >> ZC_M$) and both the charge effect and the salt effect on the dimensions of the polyion can be demonstrated[2] (Figure 1). When the salt content is rather low, the change in the average dimensions with increasing charge density can be shown indirectly through a viscometric titration experiment with a weak poly-acid: at constant C_M and C_S the reduced viscosity $\eta_{red} \equiv (\eta - \eta_o)/\eta_o C_M$ (where η and η_o are the viscosity

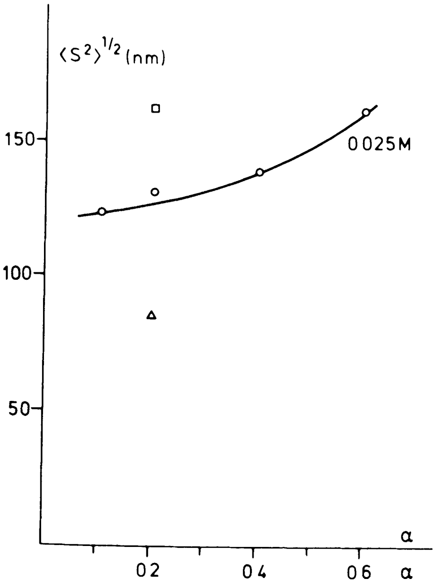

Figure 1. R.m.s. radius of gyration $<S>^{\frac{1}{2}}$ at infinite dilution of polyacrylic acid ($M \simeq 10^6$ g mol^{-1}) in aqueous NaBr solutions, as a function of degree of ionization α and salt concentrations: C_s = 0.01 M (□); 0.025 M (○); and 0.5 M (△).
Data from Kitano et al. Ref.[2].

of the solution and the viscosity of the solvent, respectively) increases steadily with increasing degree of neutralization α' (and thus also $|\beta|$) until it levels off at high values of α'. This rise can be considerably reduced by increasing the salt concentration[3] (Figure 2.). The polyion concentration effect can also quantitatively be illustrated by viscosity measurements. At constant high charge density $|\beta|$ and very low salt concentration $C_s \rightarrow 0$ the reduced viscosity of polyelectrolyte solutions is very small at high C_M but increases with decreasing polymer concentration. Very careful measurements even indicate a maximum at rather low values of C_M followed by a more conventional decreasing η_{red} with decreasing C_M[4]. This very specific concentration effect is also opposed by the salt effect as increasing C_s greatly affect the dependance of η_{red} on C_M, leading eventually, at very high C_s, to a linear increase of η_{red} with C_M. Although viscosity data remain difficult to interpret, they demonstrate qualitatively the different effects mentioned, and also, the possibility of using polyelectrolyte

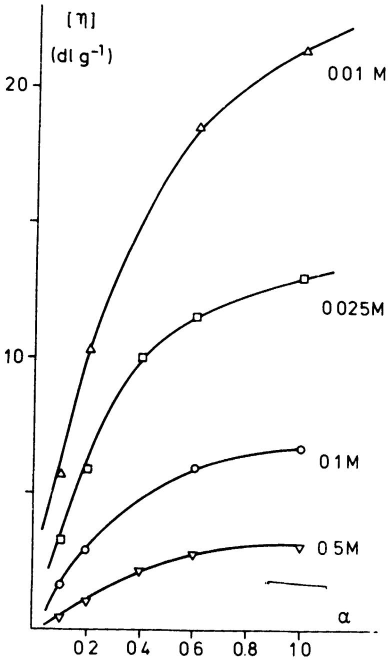

Figure 2. Intrinsic viscosity $|\eta| = \lim_{C_M \to 0} \eta_{red}$ of polyacrylic acid in aqueous NaBr solutions, as a function of α and salt concentration.
Data from Noda _et al_. Ref.[3].

solutions as a method of varying the viscosity over a wide range by easily controllable conditions.

The charge interactions described above do not only affect the macromolecular properties of polyelectrolytes, as described above. More typical electrolyte properties are also strongly influenced by the fundamental dissimilarity between 'fixed' charges, and the charges on the small ions. The former, in so far as they are fixed on the same chain, can only move through the solution in a highly cooperative way, with the severe restriction that the maximum separation between any two of these charges is that corresponding to a maximum extension of the chain between them. The latter do not have these limitations and can move more or less freely through the solution. As a consequence, the electrolyte properties seem to be dominated by the charge interactions between the fixed charges, and the charge interactions between the fixed charges and the small ions,

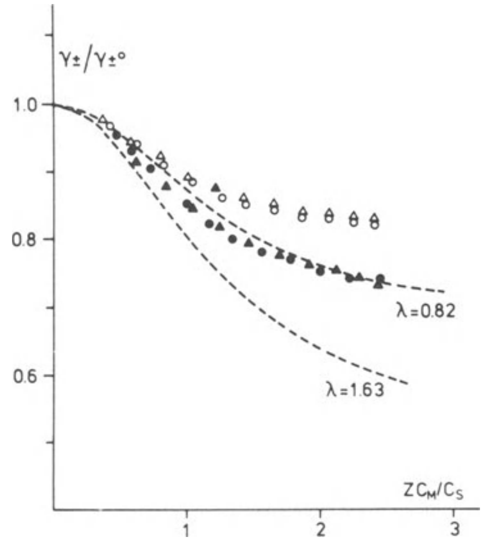

Figure 3. Ratio of the measured activity coefficient ($\gamma_{\pm}$) of NaCl in aqueous NaCl-pectinate solutions to the mean activity coefficient of NaCl in water ($\gamma^{o}_{\pm}$), for two pectinate samples, corresponding to $\lambda = 0.82$ (open symbols and $\lambda = 1.63$ (filled symbols) respectively. Circles refer to solutions with a polyelectrolyte equivalent molality of 0.01 and triangles to 0.025. Dotted curves represent the theoretical ratio according to Manning's theory. Data from Joshi et al. Ref.[5].

at least if the latter are not highly in excess. For instance, in a polyelectrolyte solution with only two species of small ions present, the mean activity coefficient of low molar mass salt will strongly decrease with increasing ratio ZC_M/C_s[5] (Figure 3.).

The strong interaction between polyion and the small ions, in particular the counterions, can be pictured by the simple model in which a certain fraction of the counterions remains remains, on the average, 'associated' (sometimes also called 'condensed' or 'bound') to each polyion, thus effectively reducing the number of charges on the chain from Z to Z†. In its simplest form, this model assumes that all the counterions are distributed over two phases: 1) the associated counterions in a (not necessarily well defined) macromolecular phase, and 2) the 'free' counterions in the bulk phase.

The latter are without any appreciable interaction with the polyions, as are also the co-ions, if present. Thus, the low value of the osmotic coefficient ϕ_M of a salt-free polyelectrolyte solution may be related to the fact that the associated counterions do not contribute to the osmotic pressure[6]. At sufficiently low C_M, we have

$$\Pi = \phi_M Z C_M RT = Z^{\dagger} C_M RT \qquad Z >> 1 \qquad (1)$$

Here, the interactions between the free counterions with the polyions or with themselves have been completely neglected. Of course, more sophisticated models for describing association can be used than the two-phase model. The interest of this concept lies in the fact that the value of $Z^{\dagger}$ derived for a given system from different experimental quantities, including transport properties, is always of the same magnitude.

Another specific electrolyte effect is revealed through the titration behaviour of a macromolecular chain bearing a large number of (identical) moderately weak acidic or basic groups. For such systems, the typical buffering effect observed with low molar mass analogues is almost completely missing, particularly at low C_s. Considering a weak poly-acid which becomes progressively charged upon neutralization (e.g., a poly-carboxylic acid), this absence of buffering may be ascribed to s decrease of the dissociation constant K with increasing degree of dissociation α or linear charge density $|\beta|$. This may be expressed in the following way[7]:

$$pH - \log(\alpha/1 - \alpha) \equiv pK = pK_o + (0.434 \, \Delta F_e/RT) \qquad (2)$$

Here K_o represents the intrinsic dissociation constant of the acidic group $K_o = (K)_{\alpha=0}$ and ΔF_e is related to the extra amount of free energy per acidic group necessary to remove a proton from the polyion to the bulk against the electrostatic attraction of the negatively charged polyacid. Obviously, ΔF_e will increase with increasing α and so will also the apparent association constant K^{-1}. Empirically, the titration curve may be represented analytically by the extended Henderson-Hasselbach equation[8], valid around $\alpha = 0.5$

$$pH = pK_a + n \log(\alpha/1 - \alpha) \qquad (3)$$

where pK_a and $n \neq 1$ are constants for a given titration but depend on the nature of the polyacid and C_s, or by the equation based on a polynomial expansion of pK and valid over the complete titration domain[9] (Figure 4.):

$$pH = pK_o + \log(\alpha/1 - \alpha) + b_1\alpha + b_2\alpha^2 + \ldots \qquad (4)$$

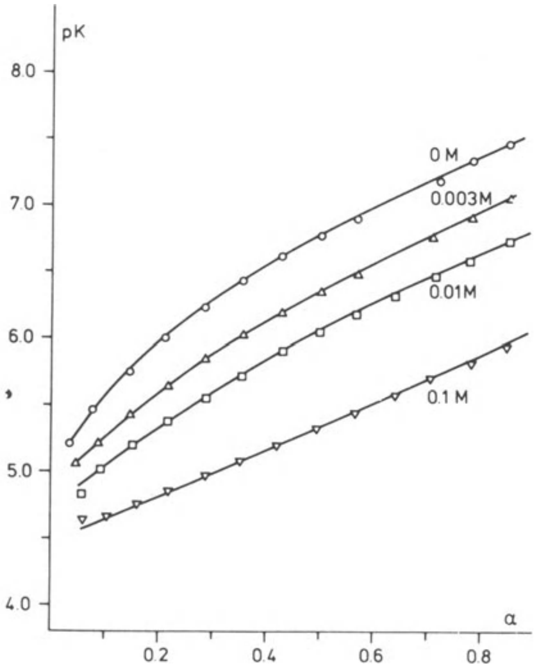

Figure 4. Change of pK with α at different salt concentrations for poly-acrylic acid in aqueous mono-monovalent (Na) salts. Drawn curves correspond to least-squares second degree polynomials.
Data from Mandel. Ref.[9].

where the different parameters also depend on the nature of the macromolecule and of C_s.

In some cases, the change of pK with increasing α is characterized by the appearance of maxima and minima which are attributed to more-or-less discontinuous changes in the average conformation of the macromolecule in the course of the charging. Simple examples are poly-methacrylic acid (Figure 5) and poly-glutamic acid, where there are apparently stabilized conformations at low values of α (corresponding to a hypercoiled and an α-helix state, respectively), which disappears with increasing α[10]. Such discontinuous changes in the average conformation may be related to charge induced conformational transitions.

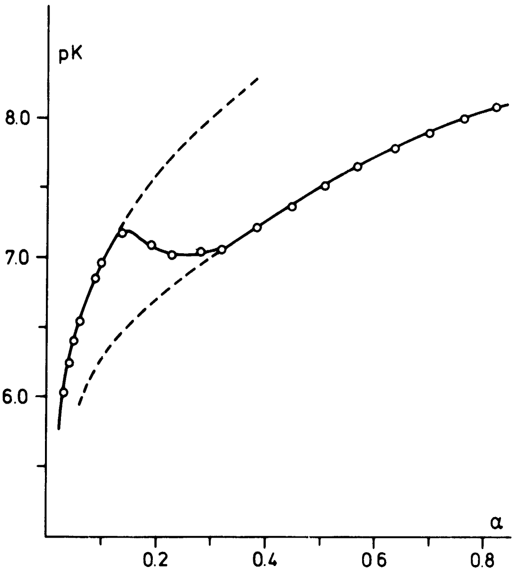

Figure 5. Change of pK as a function of α for poly-methacrylic acid in water (5^{o}C) showing a conformational transition in the range 0.15 < α < 0.30.
Data from Mandel, Leyte and Stadhouder, J.phys.Chem., 1967,71,603.

The binding or dissociation of protons in the case of moderately weak polyacids is a particular case of the more general one which corresponds to specific binding (i.e., binding to well defined groups on the macromolecular chain) of low molar mass to polyions. In such binding studies, analogous effects to those observed in the titration can be expected.

Within the space available, it is impossible to discuss even briefly the interesting effects observed with less classical techniques such as dielectric measurements, NMR investigations, quasi-elastic light scattering, electro-optics, etc. Results obtained by these methods are qualitatively in agreement with the general ideas outlined so far, but often necessitate additional concepts specific for the quantities measured.

2. THE THEORETICAL APPROACH

It is not surprising that most theoretical attempts at a more quantitative approach to the interactions between fixed charges and small ions have been inspired by the Debye-Hückel treatment of ordinary electrolyte solutions. The classic method, recently revived, starts with a Poission-Boltzmann equation which defines an average potential ψ around a charged macromolecule fixed in a given (average) conformation characteristic for the distribution of the fixed charges. Generally, the macromolecule is represented as a rigid rod with a uniform distribution of fixed charges along its axis and impermeable to solvent and small ions. Although for $C_s \to 0$ and $C_m \to 0$ the average conformation of a highly charged polyion will tend to become rodlike, under other conditions this is not necessarily the case. As far as properties independent of the length of the macromolecular chain are concerned (e.g.colligative properties) the rod-like approximation may be reasonable as long as the screening length of the electrostatic forces between the like fixed charges is much larger than $A \equiv L/Z$, the average countour distance between two successive fixed charges along the chain. The macromolecule is then sufficiently stiff in local regions to justify the use of a cylindrical model on that scale. Assuming that interactions between fixed charges on different chains and end effects may be neglected, the Poisson-Boltzmann equation then reads, for the case of one species of monovalent cations and one species of monovalent anions

$$\frac{d^2\phi}{dr^2} + \frac{1}{r}\frac{d\phi}{dr} = 4\pi Q \{C_c(r_o)e^{-\phi} - C_a(r_o)e^{+\phi}\} \qquad r > a \qquad (5)$$

Here, the reduced potential, $\phi \equiv q\psi/kT$, has been used. $Q \equiv q^2/4\pi\varepsilon_o\varepsilon kT$ stands for the Bjerrum length (with ε_o the permittivity of free space and ε the relative permittivity of the solvent), $C_c(r_o)$ and $C_a(r_o)$ for the concentration (in ions per unit volume) of cations and anions respectively at the position r_o with respect to the axis of the cylinder where $\psi(r_o) = 0$ and, finally, a for the radius of the cylinder. In the case of a salt-free polyelectrolyte solution Eqtn.(5) can be simplified as one of the terms on the r.h.s. of the Equation is zero. The differential equation can then be solved analytically[11,6], and the potential expressed in terms of known parameters if suitable boundary conditions are used. A remarkable result is that a given position $r \neq r_o$ the potential $|\phi|$ increases with increasing charge density $|\beta|$ or the related charge parameter λ

$$\lambda \equiv q|\beta|/4\pi\varepsilon\varepsilon_o kT = Q/A \qquad (6)$$

but reaches a limiting value which remains constant upon further increase of λ. In fact, for $C_M \to 0$ the value of the potential does not alter for $\lambda > 1$. This behaviour has been called 'condensation' of the counterions, and seems to be verified, at least quantitatively, by experiment. It indicates that there is a limit to stable charge densities on the chain.

In cases where there is a large excess of salt, $C_s \gg ZC_M$, the Poisson-Boltzmann equation reduces to

$$\frac{d^2\phi}{dr^2} + \frac{1}{r}\frac{d\phi}{dr} = 8\pi QC_s \sinh\phi = \kappa^2\sinh\phi \qquad r > a \qquad (7)$$

where κ^{-1} is the Debye screening length and the concentration C_s of the salt is expressed in molecules per unit volume. No analytical solution exists, but Eqtn.(7) may be integrated numerically with a solution put into the following form[12]

$$\phi(r) = G(r;\lambda,\kappa)\phi_L(r) = G(r;\lambda,\kappa)\ 2\lambda\ K_o(\kappa r)/\kappa a\ K_1(\kappa a) \qquad (8)$$

where ϕ_L is the solution of the linearized Poisson-Boltzmann equation - i.e., the solution in the approximation $\kappa^2\sinh\phi \simeq \kappa^2\phi$ if the radial electric field at the surface of the cylinder $(r = a)$ is fixed, and $K_n(x)$ represent modified Bessel functions of the second kind of order n. It is found that for $\lambda < 1$, $G(r) \simeq 1$; but for $\lambda > 1$, on the contrary, $G(r) < 1$ and with increasing λ $G(r)\lambda$ tends rapidly to a limiting value which depends on κa or C_s. Therefore, here again 'condensation' seems to be predicted.

Another theoretical approach which does not start explicitly from the Poisson-Boltzmann equation is easily applicable to a variety of different situations and leads to relatively simple expressions, although, strictly speaking, it is only valid at infinite dilution. In this approach[13], the polyion is represented as an (infinitely long) line charge of uniform linear charge density $|\beta|$, each elementary charge of which gives rise to a screened coulomb potential which, by analogy with the Debye-Hückel potential, is proportional to $e^{-\kappa r}/r$. Here, the screening constant κ may containcontributions from the counterions provided by the dissociation of the polyelectrolyte in so far as they are not 'condensed'. In fact, condensation plays an essential role, as λ is limited to a maximum value of 1, and the number of condensed counterions per polyion is given by $Z(1 - \lambda^{-1})$ for $\lambda > 1$. The reduced potential around the charged macromolecule is given by

$$\phi_M = 2\lambda\, K_o(\kappa r) \qquad \lambda < 1 \tag{9a}$$

$$\phi_M = 2\, K_o(\kappa r) \qquad \lambda > 1 \tag{9b}$$

(note that for $\lambda < 1$ the expression of ϕ_M is identical to that of ϕ_L for $a \to 0$).

Once the potential around the macromolecule has been derived the Helmholtz energy of interaction between the polyion and the small ions, ΔF_e, may be evaluated by a procedure analogous to that followed in the Debye-Hückel theory of ordinary electrolyte solutions. Therefore, non-ideal contributions to thermodynamic quantities may be evaluated which turn out to be qualitatively, or, sometimes, even semi-quantitively, in agreement with experimental data (Figure 3).

Obviously, the theoretical approach, based on a cylindrical model for the charged macromolecule cannot be used to predict the dependence of the average dimensions on λ and C_s, even at low polymer concentrations. Only recently, some promising developments for treating this difficult problem have taken place, based on the use of the wormlike chain model[14,15]. In the absence of excluded volume effects, the average dimensions of a wormlike chain depend on the value of two parameters only, the countour length L, and the persistence length ℓ. The latter is a measure for the countour distance over which orientational correlation between the chain segments is maintained, and is related to the Helmholtz energy of curvature of the macromolecule pictured as a continuous space curve. In the case of a charged polyelectrolyte this Helmholtz energy may be assumed to consist of two parts, one connected to the intrinsic properties of the uncharged chain itself, the other resulting from the electrostatic repulsion between the fixed charges. Consequently, the persistence length may also be split up into independent contributions, the intrinsic or bare persistence length ℓ_p and the electrostatic contribution ℓ_e. Expressions for ℓ_e can be derived for conditions where $\ell \gg \kappa^{-1}$ and $A \ll \kappa^{-1}$ by assuming that the fixed charges on the chain interact through the Debye-Hückel potential.

$$\ell = \ell_p + \ell_e = \ell_p + \frac{Q}{4\pi^2 A^2} \tag{10}$$

Eventually, 'condensation' may be introduced into this combined picture of a wormlike chain with Debye-Hückel interactions by replacing, in (10), A by A_{eff}, where the effective A will equal the true A below the condensation threshold and its minimum value above (e.g., according to the simple condensation approach[13] $A_{eff} = A$ for $\lambda < 1$ and $A_{eff} = Q$ for $\lambda > 1$). Note that it has been shown[16] that the condensation of counterions as formulated by Manning is not affected if the flexibility of the polyelectrolyte is taken into account.

With the help of Eqtn.(10), unperturbed average dimensions of a charged macromolecule may be evaluated under the appropriate conditions, e.g. using the classic formula for the square radius of gyration of the wormlike chain. Outside Θ-conditions, and if $L > \ell$, excluded volume effects have to be taken into account. For polyelectrolyte solutions, where the wormlike chains may be assumed to be rather coiled up than stretched ($L \gg \ell$, high salt concentration), the average dimensions may be estimated[17] yielding the following expressions for the mean square radius of gyration, as far as its dependence on contour length, persistence length, and ionic strength is concerned.

$$\langle S^2 \rangle \sim L^{6/5} \, \ell^{2/5} \, \kappa^{-2/5} \qquad (11)$$

These theoretical predictions seem to be consistent with experimental data[18,19] which are,however, scarce. Note that they apply only to very dilute conditions. In fact, recent theoretical work[20,21] suggests that in polyelectrolyte solutions concentration effects may already appear at low values of C_M, depending, however, on C_s, considerably affecting many properties of those solutions, and also the average dimensions of the polyions. Some experimental evidence for crossing from the dilute into the semi-dilute regime has been forwarded by the rather spectacular increase of the apparent translational diffusions coefficient with increasing polyelectrolyte concentration[22] (Figure 6.)

Of course, we are still far from a good quantitative understanding of the physical-chemical behaviour of aqueous polyelectrolyte solutions which are highly complicated systems. With the help of simplified models it is possible to gain some insight into that behaviour and even to predict at least the correct order of magnitude of the effect observed. Further experimental and theoretical work is needed to progress along these lines.

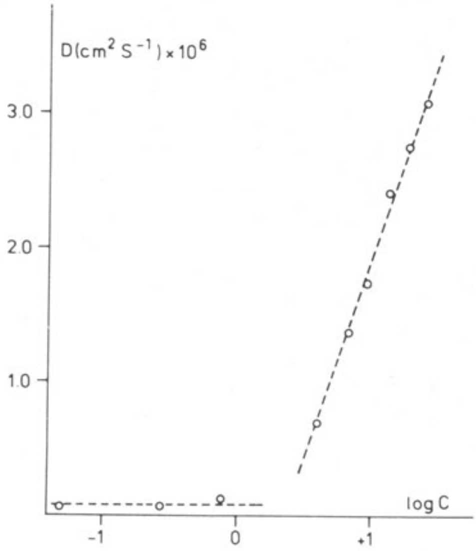

Figure 6. Variation with concentration C (in g.l^{-1}) of the diffusion coefficient (as measured by quasi-elastic light scattering) of polystyrene sulphonate ion in aqueous 0.01 M NaCl solutions. Note that according to theory, the critical concentration separating the dilute from the semi-dilute regime is $C^* \simeq 1$ g.l^{-1}.
Data from Koene *et al.*, Ref.[22].

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POLYMER-SMALL MOLECULE INTERACTIONS

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INTRODUCTION

The solubility and behaviour of polymers in solution is controlled by the balance of all the interactions between the solvent molecules and the polymer segments. In non aqueous systems, the solvent-solvent interaction is often weak, whilst in aqueous systems it is strong and can dominate the solution behaviour of polymers. When solid polymers are dissolved in relatively non-polar solvents, the main energy contribution to their dissolution comes from the entropy arising from the increased volume available to the solvent molecules[1]. For polar polymers dissolving in polar solvents, there are important additional contributions from the interactions between dipoles or charges. Water can be regarded as an extreme example of a polar liquid having, in addition to these simple elctrical interactions, an important three dimensional structure, disruption of which can produce large entropy changes. When polar molecules or ions dissolve in water, there must be sufficient energy from the solvent-water interaction to overcome any decrease in entropy, arising from the change in ordering of the water molecules.

For non-polar solutes, there is little energy to be obtained from their interaction with water molecules so that the strong water-water interactions prevent solutes from achieving high solubility. This effect has been extensively studied and discussed[2,3,4] under the heading of 'hydrophobic interactions'. In contrast, the interaction of water with hydrophilic groups of polymers has been much less studied, and has often been considered to be simple a means of providing sufficient energy to take non-polar parts of the polymer into aqueous solution. There is an increasing amount of evidence, though none of it is conclusive, that the ordering of water around hydrophilic groups may extend beyond the first one or two layers. This long range ordering may well influence the closeness approach of other hydrated species in solution, such as ions, and thus the phase behaviour of polymers in salt solution.

A. INTERACTION OF POLYMERS WITH WATER

(i) Hydrophobic interactions

As outlined above, the strength of the interaction between water molecules causes hydrophobic (usually hydrocarbon) groups to aggregate and it requires other charged or polar entities to provide the energy necessary for solubility in water. This manifests itself in the solubility behaviour of poly(vinyl alcohol), a copolymer containing both acetate and hydroxyl side groups. When the acetate content exceeds about 30 %, the polymers are difficult to dissolve in water, due to the association between these blocks of acetate groups and gels or swollen solids often result. Pure poly(vinyl alcohol) (without acetate groups) also gels, but for different reasons discussed in the next section. Similarly, copolymers of vinyl acetate and vinyl pyrrolidone are readily soluble in water, only when the content of the pyrrolidone is $> \sim 50$ %. Poly(propylene oxide) is also insoluble in water (except for low molecular weight materials where the hydroxyl groups allow solubility), whilst poly(ethylene oxide) (with H instead of CH_3 side groups) of all molecular weights is readily soluble.

(ii) Hydrophilic interactions

The two important aspects of the interaction of water with polar or charged groups on polymers are (a) the energy involved, and (b) the ordering of water around these groups, extending beyond the first hydration layer. For most water-soluble polymers, the heats of dilution are exothermic[5,6,7], as a results of the net heat of formation between the polar polymer segments and water molecules. Only for polyacrylamide[8] is the heat of dilution in water endothermic, and this may be a result of the very strong interaction between the amide group and water, forming 'complexes at low water contents[8]. It should be noted that polyacrylamide has a projected upper critical solution temperature (UCST) below 0°C, unlike most other water-soluble polymers.

While the heats of formation of bonds between water and polymer segments follow largely that expected from small molecule interactions, the ordering of water around polar groups is more difficult to quantify. Thhere are now a number of experiments on forces between surfaces separated by aqueous solutions showing an additional force to that expected from electrostatic or van der Waals interactions. Several measurements of the forces between lipid layers, separated by aqueous solutions, have been made, and the results reviewed recently by Rand[9]. They show that at close lipid layer separations (< ~ 2 nm) a force, attributed to hydration can dominate the electrical and van der Waals contributions. This hydration force decayed approximately exponentially, with a characteristic length of about .25 nm. Israelachvili[10,11] and Pashley[12] have shown that the force between charged, molecularly smooth mica surfaces separated by electrolyte solutions had a contribution at close separations (~ 3 nm) that was attributed to the hydration of ions adsorbed on to the mica surface. The enhanced stability of bubbles in electrolyte solutions, compared to that in pure water, also indicates that this hydration forces extends past the first water layer. Thus, although not conclusively proven, there are indications that the structure of water around charged or polar groups is different from pure water over a distance approaching 2 nm. Charged and polar groups on macromolecules, through their strong interaction with water, not only provide the enthalpy needed for the dissolution of the macromolecule in water, but, by altering the structure of the neighbouring water molecules, may influence the distribution of other cosolute molecules around the macromolecule.The consequences of this are discussed below. In addition, the hydration of specific hydrophilic groups of a macromolecule can alter its bond angle, as shown by calculations on hydrated peptides[13].

Finally, in this section, the hydrophilic interactions between polymers themselves are considered. Cellulose, a polymer of sugar residues, is quite insoluble in water, as shown by the insolubility of cotton fabrics. In contrast, the individual sugar groups are readily soluble in water. The polymer is insoluble in water because there is a regular hydrogen bonding between the hydroxyl groups of adjacent polymer chains. The co-operative nature of the interaction (resembling a zipper-action) leads to the insolubility of the polymer. Solubility can only be achieved by disrupting this regular array with, e.g. methyl or ethoxy groups. Thus, in this special case, solubility in water can be enhanced by the introduction of hydrophobic groups. Methyl cellulose is soluble, provided it has a moderate degree of substitution, but is insoluble if it is extensively methylated. Similar considerations apply to poly(vinyl alcohol), where the equilibrium water solubility of the pure alcohol is enhanced by the addition of disrupting side chains, such as acetate groups.

B. INTERACTION WITH IONS

The effect of ions on the solution behaviour of polymers depends largely on whether the polymer itself is charges. Polyelectrolytes have already been discussed by Mandel (Chapter 10): the only additional comment to be made is that large changes in solution properties (e.g. viscosity) cane be observed in the electrolyte concentration range of 10^{-3} to 10^{-1} mol dm^{-3}, the effects being dependent on the ionic strength, but often largely independent of the nature of the electrolyte. For uncharged polymers, significant effects are usually observed only at concentrations $> 10^{-1}$ mol dm^{-3} and depend markedly on the type of polymer and electrolyte[14]. The effect of different ions on the phase separation of an uncharged polymer, poly(ethylene oxide) is shown in Figure 2. The wider differences occur within the series of anions, rather than cations, the largest effects being with PO_4^{---} and SO_4^{--}, and the smallest with I^-. This effect on the phase behaviour of water soluble polymers is observed with many non-ionic polymers. In addition, transitions (such as helix-coil) in polypeptides can be induced to different extenst by various electrolytes, as shown in Table 1. The order of the effectiveness of the anions in causing the phase separations or transitions is known as the Hofmeister or Lyotropic series. However, addition of SO_4^{--} does not induce all water soluble polymers to phase separate[15]; polyacrylamide and dextran are both essentially unaffected by addition of electrolytes, at least at 298°K. Thermodynamics requires[16] that in the salting-out of a polymer by a second solvent component (e.g., ions or other non-solvent), this component must be negatively adsorbed from the polymer. This can be expressed mathematically as

Table 1. Influence of anions on polymer configuration or phase separation.

	Helix Native Salting-out	Coil Denatured Salting-in
Collagen gelation	$SO_4^{--} < CH_3COO^- < Cl^- < Br^- < NO_3^- < ClO_4^- < I^- < CNS^-$	
Ribonuclease	$SO_4^{--} < CH_3COO^- < Cl^- < Br^- < ClO_4^- < CNS^-$	
Poly(vinyl-methyloxazolidinone) or Poly(ethylene oxide)	$PO_4^{---} < SO_4^{--} \sim CO_3^{--} < OH^- < F^- < Cl^- < ClO_4^- < CNS^-$.	

Some data taken from Ref 14.

$$d\mu_s^\theta = \sum_{i=1}^{c} N^*_{si}\, d\mu_i$$

where μ_s^θ is the standard chemical potential of a non-electrolyte in a solution of different solvent components, i ; N^*_{si} is the difference in concentration of the ith component in volume elements near to and far from the non-electrolyte. For $d\mu_s^\theta$ to increase (salting-out) N^*_{si} must be negative, indicating a depletion of the elctrolyte from regions immediately adjacent to the polymer. What causes this depletion is not certain, though it is possible that the water structure around the polymer and certain ions is not compatible, giving rise to repulsion between the ions and the polymer (in a manner similar to that observed between two surfaces, as mentioned above). This treatment of phase separation does not apply to cases where a new species is precipitated, e.g. Ca^{--} addition to sodium polyacrylate, producing a precipitate of calcium polyacrylate. It should be noted that theories of 'salting-out' based on (a) internal pressure or free volume by the ions in water, (b) dehydration of the polymer due to the elctrolyte lowering the water activity, or

Table 2. Interaction between polymer and surfactant

Polymer	Surfactant		
	Anionic	Cationic	Non-ionic
Uncharged	Strong interactions Weaker with more hydrophilic polymers	Weaker interaction than with Anionic surfactants	Usually no interaction
Anionic Polyelectrolyte	Usually no interaction; Polymer can phase separate	Precipitation of polymer--surfactant complex	No interaction
Cationic polyelectrolyte	Precipitation of polymer-surfactant complex, followed by redissolution with excess surfactant	No interaction	No interaction

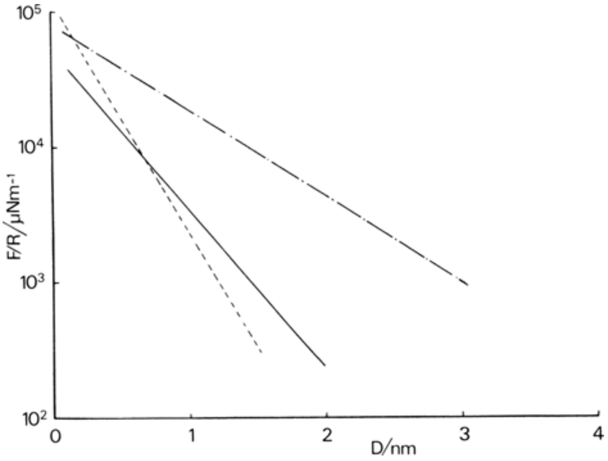

Figure 1. Net hydration force (F) between two curved mica surfaces, (radius R), separated by aqueous solutions of

a) -------------- 10^{-3} mol dm^{-3} CsCl, pH 5.8

b) __.___.___.___ 2.8×10^{-4} mol dm^{-3} KCl. pH 5.6

c) ______________ 1.1×10^{-3} mol dm^{-3} KCl, pH 5.6

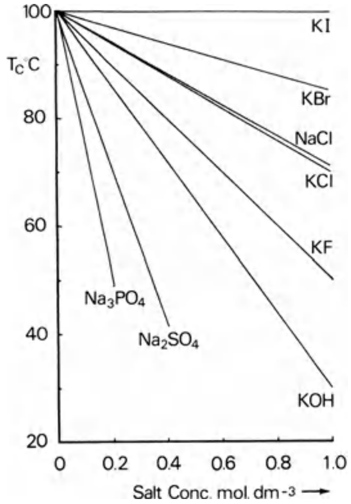

Figure 2. Temperature, T_c, for the phase separation of poly(ethylene oxide) in salt solutions. Data from F.E.Bailey and R.W.Callard,J.appl.polymer Sci.,1959,<u>1</u>,56.

(c) association between the macromolecules, are incorrect. If (a) were the case, then all polymers would be salted out by, e.g. Na_2SO_4, which is not the case. That (b) is not so, is obvious from the fact that the same water activities can be achieved using salting-in and salting-out ions, though phase separation can only be achieved with the latter. Both (b) and (c) require the distribution of ions to be the reverse of that demanded by simple thermodynamic principles.

C. INTERACTION WITH SURFACTANTS

The interaction between polymers and surfactants is more complex than with ions, as surfactants can form aggregates or micelles, that play a large part in their association with polymers. The interaction between polymers and surfactants has been comprehensively reviewed elsewhere[17] and can be generally summarized as shown in Table 2. Anionic surfactants with uncharged polymers have been the main category studied: the results show that the more hydrophobic the polymer, the stronger the interaction. The strength of interaction increases[18-21]: PAM < PV-OH < PEG < PV-OAc <∼ PPG < PVP. Likewise, the interaction decreases if the head group of the surfactant is more hydrophilic[22]. The binding isotherms of anionic surfactants on to polymers are unusual, as binding does not begin at the lowest surfactant concentration (Figure 3.). The isotherm can be represented by

$$\frac{dN}{d\mu_2} = \frac{\overline{N^2} - \bar{N}^2}{kT}$$

where N = number of surfactants on a polymer,
μ_2 = chemical potential of surfactant.

Thus, the sudden onset of binding implies $\overline{N^2} - \bar{N}^2$, meaning binding is a co-operative process and that surfactants do not bind individually. The mechanism for the interaction thus appears to be that the polymer, by being attached to the micelle near the head groups, is able to reduce the electrostatic repulsion between these head groups (Figure 4.). This allows the micelles to form at lower surfactant concentrations and hence they condense on the polymer, the free surfactant activity rising until micelles form freely in solution. Interaction between uncharged polymers and cationic surfactants is often weaker than with anionic surfactants, though it is not clear why this should be. Nonionic surfactants have an even weaker interaction with polymers, probably because of the small repulsion between the ethylene oxide head group.

Polyelectrolytes interact with oppositely charged surfactants, the electrostatic attraction being the added force which allows binding to occur at the lowest surfactant concentration (Figure 5).

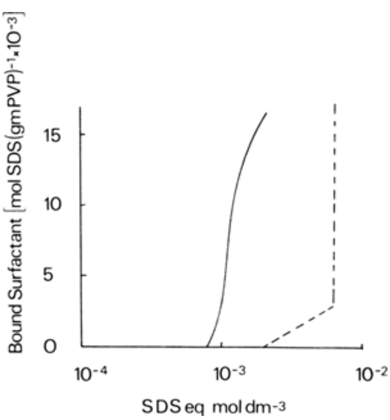

Figure 3. Binding isotherm for sodium dodecyl sulphate(SDS) on to poly(vinyl pyrrolidone)(PVP). SDS is the concentration of free SDS at equilibrium·

-------- PVP (9.9 to 8.1 x 10^{-3} mol dm^{-3}); from M.L. Fishman and F.R.Eirich,J.phys.Chem.,1975,75,3135

________ PVP (0.1 % + o.1 N.-NaCl); from M.Murata and H.Arai,J.coll.Interface Sci.,1973,44,475.

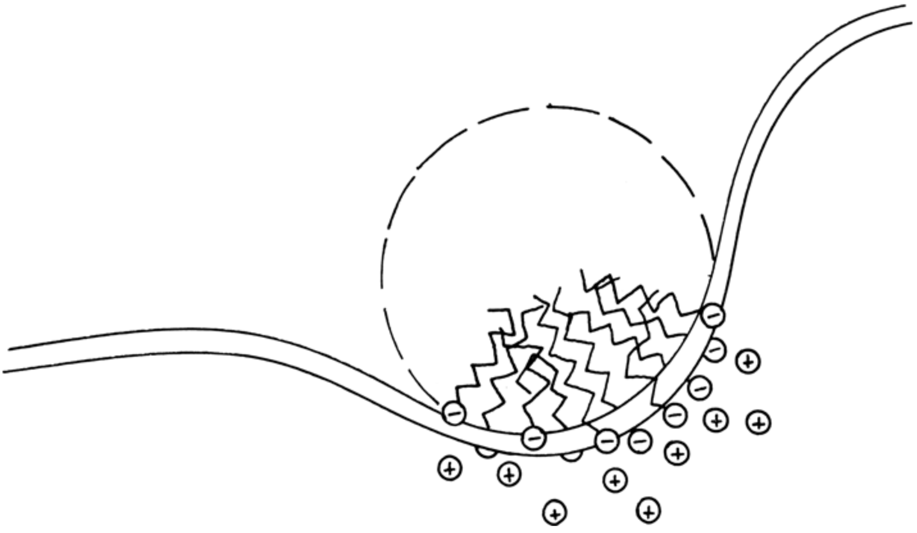

Figure 4. Schematic representation of cluster formation of anionic surfactant on uncharged polymer.

As the charges on the polyelectrolyte are progressively neutralized by the surfactant, the solubility of the complex decreases, and precipitation is often observed. The precipitate can be regarded as a neutral polymer which will further interact with surfactant and be resolubilized. The net charge on the polymer is then reversed from its original charge. Cationic polyelectrolytes precipitated with anionic surfactants are more readily solubilized than when the charges are reversed (i.e., anionic polymers and cationic surfactants). This is probably due to the stronger interaction of anionics with neutral polymers as surfactants.

The precipitation of polyelectrolytes by surfactants leads to the formation of a new compound - i.e., the complex - and, therefore, the thermdynamic considerations outlined in the case of the salting-out of polymers by electrolytes do not apply.

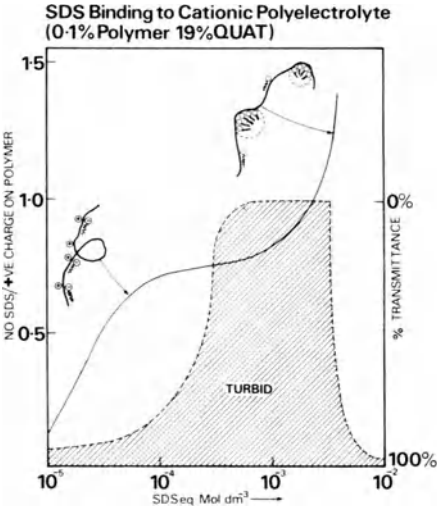

Figure 5. Binding isotherm of sodium dodecylsulphate (SDS) to cationic polyacrylamide showing individual and co-operative binding at different surfactant concentrations. Data from Dr.S.Barnes, this laboratory.

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EXCLUDED-VOLUME INTERACTIONS OF NEUTRAL POLYMERS IN SOLUTION

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INTRODUCTION

In this article, based in part upon notes prepared for a tutorial seminar, I have attempted a rather simple account of the nature and consequences of excluded-volume interactions between neutral macromolecules. In spite of some quite gross approximations (to which I draw attention) this treatment has provided at least qualitative, often quite good quantitative, agreements with experiment.

1. GENERAL THERMODYNAMIC RELATIONSHIPS

G is the Gibbs Free Energy of a system containing n_i moles of components i, relative to pure components in defined standard states. Chemical potentials are defined by

$$\mu_i = (\partial G/\partial n_i)_{\text{all other } n} \qquad (1)$$

Since any quantity of the system can be created by successive transfers to it of δn_i, each proportional to n_i, from the standard states,

$$G = \sum n_i \mu_i \qquad (2)$$

If the system is in internal equilbrium, $\delta G = 0$ for any small transfers of components within; therefore, by Eqn. (1)

$$\sum \mu_i \delta n_i = 0 \qquad (3)$$

Comparing this with the complete differential of Eqn.(2), we obtain the Gibbs-Duhem equation

$$\sum n_i \delta\mu_i = 0 \qquad (4)$$

which states the relationship between changes of composition and changes of chemical potentials. In addition, from Eqn.(1)

$$\begin{aligned}\mu_{ij} &= (\partial\mu_i/\partial n_j)_{\text{all other } n}\\ &= \partial/\partial n_j(\partial G/\partial n_i)\\ &= \partial/\partial n_i(\partial G/\partial n_j)\\ &= (\partial\mu_j/\partial n_i)_{\text{all other } n} = \mu_{ji} \qquad (5)\end{aligned}$$

For a system internally stable, $\delta G \geqslant 0$ for any or all small internal transfers of components, which requires

$$\sum_i \sum_j \mu_{ij}\delta n_i \delta n_j = 0 \qquad (6)$$

that is, that the determinant

$$\begin{vmatrix} \mu_{11} & & \\ & \ddots & \\ & & \mu_{kk} \end{vmatrix} \geqslant 0 \qquad (7)$$

and that all its principal minors $\geqslant$ 0 (Note 1). (8)

2. EXPRESSION OF CHEMICAL POTENTIALS IN TERMS OF COMPOSITION

If any molecule of i can, irrespectively to the distribution of other molecules, be placed with equal probability anywhere within the volume of the solution, statistical considerations lead to the 'ideal'

$$\mu_i = \mu_i^o + RT \ln c_i \qquad (9)$$

where c_i is the molar concentration. Deviations from this, due molecular interactions are expressed by

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Note 1. For more extensive and exact treatments, see: L.Prigogine and R.Defay, 'Chemical Thermodynamics' (ed.D.H.Everett) 1954:Longmans, Ch.XVI, and H.Tompa, 'Polymer Solutions' 1956:Butterworth, Ch.7.

$$\mu_i = \mu_i^o + RT \ln c_i y_i \tag{10}$$

For uncharged molecules, the dependence of the activity coefficient y_i on composition can be generally expressed by

$$\ln y_i = a_{ii} c_i + \sum_j a_{ij} c_j + \text{higher order terms in } c_i, c_j \tag{11}$$

where a_{ii} etc. are constant coefficients. We must note, however, that putting Eqn. (11) into Eqn. (10) and differentiating according to Eqn. (5) does not lead to

$$\text{all } a_{ij} = a_{ji} \tag{12}$$

If we wish (see Section 6) Eqn. (12) to hold, we must, as an approximation, replace molar c_i by <u>molal</u> m_i in Eqns. (10) and (11).

3. BINARY (ONE-SOLUTE)AND TERNARY (TWO-SOLUTE) SYSTEMS

Putting Eqn. (11) into Eqn. (10), both in molal form, neglecting terms of higher that first order, and taking notice of Eqn. (5)

$$\mu_2 = \mu_2^o + RT (\ln m_2 + a_{22} m_2 + a_{23} m_3) \tag{13a}$$

$$\mu_3 = \mu_3^o + RT (\ln m_3 + a_{33} m_3 + a_{32} m_2); \tag{13b}$$

$$a_{23} = a_{32}$$

By putting the differentials of equations (13) into Eqn.(4) and integrating, remebering that m_1(solvent) = $1/M_1$, we obtain for the solvent

$$\mu_1^o - \mu_1 = \pi V_1 = RTM_1 (m_2 + a_{22} m_2^2/2 + m_3 + a_{33} m_3^2/2 + a_{23} m_2 m_3) \tag{14}$$

where π is the osmotic pressure and V_1 is the molar volume of solvent.

The conditions for internal stability of the solution (Eqns. (7) and (8)) become

$$\mu_{22} = RT\left(\frac{1}{m_2} + a_{22}\right) \geqslant 0 \qquad (15a)$$

$$\mu_{33} = RT\left(\frac{1}{m_3} + a_{33}\right) \geqslant 0 \qquad (15b)$$

$$\mu_{22}\mu_{33} - \mu_{23}^2 = (RT)^2\left\{\left(\frac{1}{m_2} + a_{22}\right)\left(\frac{1}{m_3} + a_{33}\right) - a_{23}^2\right\} \geqslant 0 \qquad (15c)$$

We note, without enquiring in detail into causes, that the *a* coefficients may have any values, negative or positive. Negative values imply that the relevant molecules are, on average, more closely associated, positive values that they are less closely associated in space, than would accord with the 'ideal' statistical distribution. There is always a region of composition within which Eqns. (15a) and (15b) are satisfied, but Eqn. (15c) can be satisfied only if a_{22} and a_{33} have the same sign, irrespective of the sign of a_{23}.

4. CONSEQUENCES OF NON-IDEALITY

(i) The *solubility* of, say, component 2 is reached when μ_2 in solution equals that of the solid state. Eqn. (13a) shows that the addition of component 3 increases or decreases the solubility of 2 as a_{23} is negative or positive.

(ii) *Partition* of 2 between solvent and solution containing 3 is in favour of the former if a_{23} is positive, the latter if it is negative.

(iii) A *conformation* of 2, (2'), is favoured in the presence of 3 if $a_{2,3}$ is less positive than a_{23}.

(iv) *Aggregation* of 2, with itself or with another component, is promoted by 3 if the *a* coefficient of the aggregate is less positive than the mass-action combination of *a* coefficients of the aggregating molecules.

(v) Eqn. (14) shows that non-ideal variations of the *osmotic pressure* occur in solutions of 2 or 3 alone, or in mixed solutions positive or negative according to the signs and magnitudes of a_{22}, a_{33} and a_{23}.

(vi) *Separation* into liquid phase of differing composition occurs if Eqns. (15) are not satisfied, in ways depending on the signs of a_{22}, a_{33} and a_{23}. I shall confine attention to the case where all *a* values are positive (see Note 1). Here

Eqns.(15a) and (15b) are always satisfied, but, provided that

$$a_{22}a_{33} - a_{23}^2 \geqslant 0 \qquad (16)$$

there will be a region of composition, reached as m_2 and m_3 increase, within which Eqn.(15c) is not satisfied. Separation will occur into solvent-rich phases containing respectively excess of 2 and of 3. Eqn. (15c) describes the 'spinodal' curve which bounds the region of composition of absolute instability. The 'binodal' curve upon which co-existent compositions lie, connected by the 'tie-lines', is tangential to the spinodal at the 'critical-' or 'plait' point: elsewhere it lies between the spinodal and the m_2, m_3 axes (Fig.1). The compositions of

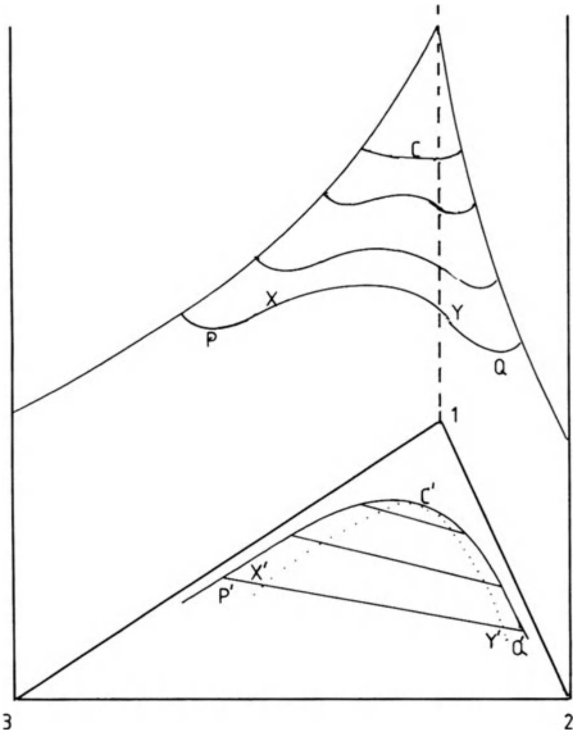

Figure 1. Illustrative plot of mean free energy ($\sum \mu_i n_i / \sum n_i$) (ordinate) against composition for a two-solute system (solvent = 1) exhibiting incompatible phase-separation. Inflexion points of the surface, X,Y (projecting to X',Y' on the base) represent the limits of absolute instability, defining the spinodal curve. P,Q (projecting to P',Q') are points of tangential contact of the surface with common planes; they represent cO-existent compositions, connected by the tie-lines, and define the binodal curve. The curves are tangential at the critical point C (projecting to C').

co-existent solutions can, however, be obtained only by numerical solution of Eqns. (14), (13a), and (13b) for the condition that all three of μ_1, μ_2 and μ_3 are equal in both. The position of the critical point is given by:

$$(\partial\mu_2/\partial n_2)_{\mu_1,n_3} = 0 \tag{17a}$$

$$(\partial^2\mu_2/\partial n_2^2)_{\mu_1,n_3} = 0 \tag{17b}$$

which, with Eqns. (13) gives:

$$\left(\frac{1}{m_2}c + a_{22}\right) = a_{23}\left(m_3^2 / m_2^c\right)^{\frac{2}{3}} \tag{18}$$

where m_2^c, m_3^c are the critical-point values. Given these values and any one of a_{22}, a_{33}, a_{23} the other two <u>a</u> values can be calculated and used to compute the binodal curve[1].

5. EXCLUDED-VOLUME INTERACTION OF POLYMERS

A readily soluble polymer is so because of favourable short-range associative interactions with solvent, as compared with its self-interaction in the solid state. Once dissolved in considerable excess of solvent, interactions of polymer molecules with each other closely resemble those with solvent, and the thermodynamic properties of the solution are dominated by the entropy of dilution: that is, by the statistics of distribution of the molecules with the available volume. For neutral macromolecular solutes, a simple approach to this is based upon Flory's (1953) 'dilute solution' treatment[2]; in this, the solvent is regarded as a continuum, a space between which solute molecules are distributed. Their distribution is modified by the inability of the centre of any given molecule to occupy a position within the volume of the solution such that any part of it overlaps a part of any other molecule. A given molecule will therefore have only a fraction E of the total volume available to it; its <u>effective</u> concentration is 1/E times higher than its concentration (c_i) expressed per total volume; and in Eqn. (10)

$$y_i = 1/E \tag{19}$$

6. APPROXIMATE EXPRESSION OF AVAILABLE VOLUME

a. Spherical molecules: a solution contains c_2 and c_3 moles/ml. of molecules 2 and 3 having molecular radii r_2 and r_3. The fraction of volume available to 2 is the probability that a given molecule of 2 can be placed anywhere in the solution without overlapping any other molecule. With respect to other molecules of 2, we may consider the given molecule as having effective radius $2r_2$, the remaining 2 molecules being points, randomly distributed (Poisson distribution) (Note 2). The fraction of volume available to the given molecule is then limited by other 2 molecules to:

$$E_{22} = \exp -\left(\frac{4\pi N}{3} (2r_2)^3 c_2\right) = \exp -(U_{22}c_2) \qquad (20)$$

where U_{22} is the molar co-volume of 2 with 2.

Similarly, with respect to molecules of 3, we regard the given molecule of 2 as having effective radius $(r_2 + r_3)$ and the 3 molecules as being points. The fraction of volume available to 2, due to the presence of 3, is limited to:

$$E_{23} = \exp -\left(\frac{4\pi N}{3} (r_2 + r_3)^3 c_3\right) = \exp - (U_{23}c_3) \qquad (21)$$

The fraction of volume available to 2 is therefore $E_{22}E_{23}$. Consequently, by Eqn. (19)

$$\ln y_2 = U_{22}c_2 + U_{23}c_3$$

and, by Eqn.(10)

$$\mu_2 = \mu_2^o + RT(\ln c_2 + U_{22}c_2 + U_{23}c_3) \qquad (22a)$$

and, similarly

$$\mu_3 = \mu_3^o + RT(\ln c_3 + U_{33}c_3 + U_{32}c_2) \qquad (22b)$$

From this argument, U_{23} must equal U_{32}, but, as has been pointed out in Section 2., above, differentiation of Eqns. (22),according to Eqn.(5) does not yield this identity: it would do so, if c

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Note 2. This assumption neglects the mutual effects of 'other' molecules upon each others' distribution; this amounts to considering only nearest-neighbour,neglecting higher order interactions, which become increasingly important at higher concentrations. A more rigorous treatment of interactions between chain-polymeric and compact spherical molecules is give by Hermans[3], accounting for discrepancies found by Atha and Ingham[4].

in Eqns. (22) were replaced by m, but then the products Uc would not be (as they should be) dimensionless. Use of Eqns. (22) in either form therefore involves an approximation.

b. Other molecular forms. For molecules other than spheres more subtle geometrical argument is needed to evaluate co-volumes in terms of molecular dimensions, and to demonstrate that U_{23} always equals U_{32}. For example, the centre of a sphere 2 is totally excluded by an envelope distant r_2 from the surface of a rod or ellipsoid 3, but the reciprocal relationship requires consideration[5,6] of the limitation (therefore partial exclusion) of orientation of 3 if the centre of the latter lies at less than its greatest radial dimension from the surface of 2. Flory[2] has calculated co-volumes of random-coil molecules on the basis of local mutual exclusion by their segments. Non-spherical molecules can be approximately treated as equivalent spheres[1,7].

7. EFFECT OF CONCENTRATION ON THE CONFIGURATION OF CHAIN-POLYMERS

It was pointed out in Section 4. that in the presence of polymer 3, a change of conformation which lowers a_{23}, i.e. which lowers U_{23} by contraction of the domain of 2 to lower equivalent r_2, is favoured. Increase of concentration of 2 itself will have the same effect. According to Flory[2] a chain-polymeric molecule has an 'unperturbed' configuration in which the intrinsic entropy of distribution of its segments is maximal; departure from this produces an 'elastic' force in the direction of restoring the unperturbed state. In a good solvent and additional positive change of entropy results from dilution of the segments of the molecule with solvent (i.e., from expansion from the unperturbed state). Therefore, in a good solvent, the molecule is expanded by a linear factor α to a configuration in which changes of elastic and dilution entropies balance.

An equivalent statement is that there is an internal osmotic pressure (tending to expansion of the molecule) balanced by an internal elastic force. The difference of osmotic pressure between the inside of the molecule and the solution external to it is maximal at zero concentration of the solution, so that the molecule is then maximally extended (α is maximal). As the concentration of the solution increases, the internal-external osmotic pressure difference falls and the domain of the molecule shrinks to achieve a new balance.

So long as α remains > 1, overlapping of molecular domains (by interpenetration of the chains)cannot occur, since this would require either increase of segment concentration in the region of overlap, or extension of the chains (increase of α)

in that region. Either, or any combination of them, would lead to local decrease of entropy. However, when the osmotic pressure of the whole solution (or, through fluctuations, any local part of it) reaches a value at which α would be less than 1, a positive entropy charge becomes available,by expansion to $\alpha = 0$, to balance the decrease of solution entropy resulting from interpenetration. Therefore, above the concentration of the solution at which $\alpha = 0$, individual molecules are in their unperturbed configuration, interpenetrating increasingly as the concentration increases. It follows that the concentration of segments within the domain of any molecule cannot, on average, be less than in the solution as a whole, and that the condition $\alpha = 0$ is reached at the overall concentration (usually denoted c^*) at which the solution is completely occupied by molecular domains (Note 3).

8. SOME EXPERIMENTAL EXAMPLES

Solubility. Laurent[8] showed that the solubilities of a number of proteins are effected by the presence of dextran in reasonable quantitative agreement with theory. Hellsing[9] measured effects of dextran on the solubility of immune complexes. Atha and Ingham[4] found general agreement in measurements of the effects of polyethylene oxides (PEO) on the solubilities of proteins, but demonstrated some important quantitative discrepancies (Note 2).

Partition. Ogston and Phelps[10] demonstrated the effect of hyaluronic acid on the partition of several proteins. Comper and Laurent[11] have related the partitions of mannitol and PEO in animal tissues in vivo to their polysaccharide contents. Laurent and Killander[12], and Ogston and Silpananta[13] interpreted partitions of solutes in gel chromatography on the basis of excluded-volume. Ogston and Preston[14] used light-scattering to demonstrate the exclusion of protein by individual molecules of hyaluronic acid. Atha and Ingham[4] demonstrated the exclusion of PEO by protein.

Osmotic Pressure. Laurent and Ogston[15], snd Preston, Davies, and Ogston[16] showed that excess osmotic pressures of mixed solutions of protein and hyaluronic acid are accounted for by excluded-volume.

Note 3. See Ogston & Preston[17] for quantitative treatment; more rigorous treatments are given by de Gennes[23] and by Graessley[24].

Conformation. Ogston and Preston[17] demonstrated the shrinkage of molecules of several dextran fractions with increase of concentration. Lerman[18] showed that DNA takes up a more compact configuration in the presence of high concentration of polyethylene oxide.

Aggregation. Laurent[19] showed the effect of dextran on lowering the K_ms of enzyme-substrate complexes. Laurent, Preston and Carlsson showed[20] the effects of dextran and of polyethylene oxide on increases of the melting-temperatures of poly-AG. Nichol, Ogston and Wills[21] accounted for the effect of polyethylene oxide on stabilizing a pyruvate dehydrogenase complex.

Phase separation. Edmond and Ogston[1,22] studied the incompatible phase-separations in mixed solutions of protein or dextran fractions and polyethylene oxides, showing that these can be reasonably accounted for on the basis of excluded-volume. Ogston and Silpananta[13] demonstrated phase separation in a Sephadex-polyethylene oxide system.

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POLYMER ADSORPTION

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INTRODUCTION

The adsorption of macromolecules at solid/solution interfaces differs in several respects from that of small molecules. Some of these differences are reflected in the adsorption isotherm (Figure 1). Region A corresponds to isolated adsorbed macromolecules, adsorbed in a tail/loop/train configuration (Figure 2). This minimum free energy situation depends on the balance between the net changes in potential energy (ΔU) and entropy (ΔS) associated with the adsorption process. ΔU reflects changes in the number of segment/surface, solvent/surface and segment/solvent contacts; ΔS reflects not only changes in the configurational entropy of the adsorbed polymer concerned, but also changes in the thermal entropy of the adsorbed polymer and desorbed (or released) solvent molecules.

With increasing coverage, lateral interaction between adsorbed polymer molecules become important. Polymer molecules arriving from solution will be prevented, to increasing extents, from adopting the 'isolated' configuration mentioned above. This results in a lower area per molecule (a), a lower fraction (p) of sgements in trains, and a greater 'thickness' (δ)[+] of the adsorbed polymer, over region B. In region C (the plateau region), further adsorption is precluded - i.e., no more polymer molecules are able to contact the surface. Here, a and p attain their minimum values, and δ its maximum value.

[+] 'Thickness here is difficult to define absolutely; it is some measure of the extent of the loops and tails normal to the surface.

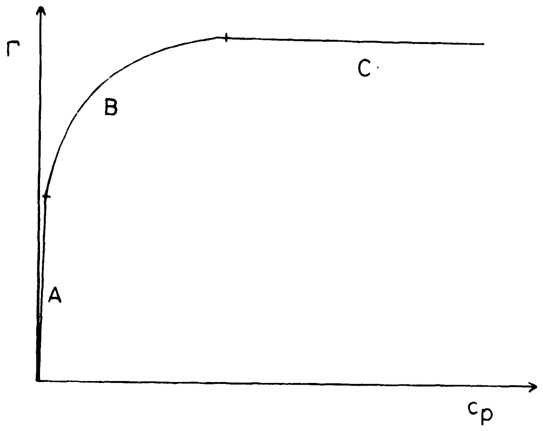

Figure 1. Typical polymer adsorption isotherm.

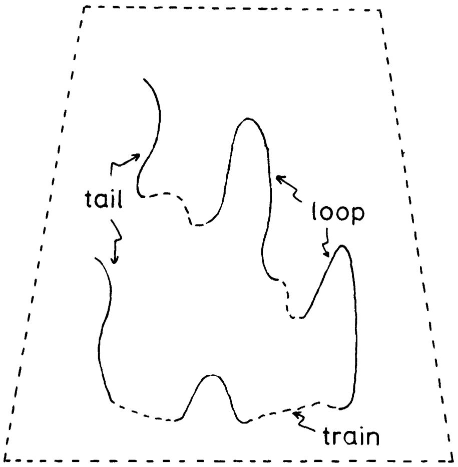

Figure 2. Typical conformation of an adsorbed polymer.

It is implicit in the above discussion that the adsorption of high molecular weight polymers is generally considered to be irreversible; more strictly, the rate of desorption tends to be zero. The adsorption of individual segments is, however, reversible. This implies a dynamic situation so that configuration properties such as a, p, and δ are time or ensemble averages - i.e. $\langle a \rangle$,$\langle p \rangle$and $\langle \delta \rangle$. The kinetics of adsorption involve two stages: (i) the rate of arrival of random coils at the surface, which is a function of the concentration and diffusion coefficients of the molecules; and (ii) the rate of conformational rearrangement at the surface.

In practice, most polymers are polydisperse in molecular weight and one is, therefore, strictly dealing with multicomponent ststems. This complicates both the kinetic and the equilibrium situation. For example, the time for equilibration may be considerably longer than for a similar monodisperse system, because of the gradual displacement of lower molecular weight fractions by those of higher molecular weight.

THEORETICAL PREDICTIONS

Considerable attention has been given in recent years to statistical, mechanical, and computer simulation analyses of polymer adsorption. These have recently been reviewed elsewhere[1], so will not be discussed in detail. Only a summary of the main theoretical predictions will be given.

The objectives of any theory in this area must be to predict the main thermodynamic properties of the system (the adsorption isotherm, the enthalpy of adsorption, etc.) and/or the main conformational properties of the adsorbed molecules (e.g. p and δ, mentioned above, and, if possible, the segment density distribution, $\rho(z)$, normal to the surface).

Models for both theta and good solvent regimes in general predict that p is a decreasing function of coverage. At low coverages (region A, Figure 1.) and fixed, low molecular weight (M), p is an increasing function of the net adsorption energy $(\Delta\varepsilon^{\sigma})^{+}$. In the limit of high molecular weight ($M \rightarrow \infty$), p is zero for $\Delta\varepsilon^{\sigma} < \Delta\varepsilon^{\sigma}_{crit}$ (i.e., some critical value of $\Delta\varepsilon^{\sigma}$) and an increasing function of $\Delta\varepsilon^{\sigma}$ for $\Delta\varepsilon^{\sigma} > \Delta\varepsilon^{\sigma}_{crit}$. For fixed small $\Delta\varepsilon^{\sigma}$,

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[+] i.e., the difference in the surface/segment and surface/solvent interaction energies.

$p \propto M^{-1}$ whilst for fixed, large $\Delta\varepsilon^{\sigma}$, p is a weakly decreasing function of M. In addition,it is generally predicted that p decreases as the quality of the solvent is increased.

At low coverages, large $\Delta\varepsilon^{\sigma}$ and large M, δ is predicted to be independent of M, but a decreasing function of $\Delta\varepsilon^{\sigma}$, whilst for low coverages, small $\Delta\varepsilon^{\sigma}$ and large M, $\delta \propto M^{\frac{1}{2}}$ for theta solvents ($\chi < 0.5$).

Predictions concerning p and δ at high coverages (regions B and C of Figure 1.) are less general since early theories were restricted to isolated adsorbed polymers. However, one of the most recent comprehensive, statistical mechanical theories of polymer adsorption which deals with high coverages is that of Scheutjens and Fleer[2,3] . A lattice model is used: the main variables are the lattice type, the chain length, the net polymer/surface - surface/solvent interaction parameter ($\Delta\varepsilon^{\sigma}$), the polymer-solvent interaction parameter (χ) and the bulk polymer concentration. The first paper[2] predicts adsorption isotherms and segment density profiles: in the second paper[3] the authors predict loop,tail, and train size distributions. Perhaps the major novel theoretical insight emerging from this work concerns the form of $\rho(z)$ for adsorbed homopolymers. Previous theories had, in the main, suggested an exponential decrease in segment concentration normal to the surface. Scheutjens and Fleer show that, close to surface, ρ decreases approximately exponentially, but at larger distances the decay is much slower. They attribute this to the fact that a considerable fraction of the adsorbed segments is present in the form of long dangling tails.

Other typical predictions of the Scheutjens-Fleer theory concern the molecular weight dependence of the various adsorption parameters: Γ is shown to reach alimiting value with increasing M in an athermal solvent ($\chi = 0$) , but increases uniformly with M in a theta solvent ($\chi = \frac{1}{2}$) ; p decreases slightly with increasing M; and δ (r.m.s. value) increases as $M^{\frac{1}{2}}$ (for both $\chi = 0$ and $\chi = 0.5$).

EXPERIMENTAL METHODS

Three types of parameters may be established for adsorbed polymer films:-

(i) thermodynamic: e.g., the excess amounts of material, or the excess energies and entropies, of the interfacial region, with respect to the bulk solution (or solutions, in the case of the liquid/liquid interface);

(ii) structural: e.g., the effective thickness of the inerfacial region, molecular conformation, and molecular(segmental) concentration profiles, parallel and normal to the interface.

(iii) dynamic: e.g., what are the characteristic modes and frequencies of molecular (or segmental) motion in the interfacial region ? Dynamic parameters of this type (e.g. segmental rotational correlation times) govern the rate of conformational rearrangement involved in the adsorption process.

Discussion will centre here on how one may determine some of these parameters for adsorbed polymers in two main types of system:-

(a) those involving macroscopic interfaces, i.e. separating two semi-bulk phases (in particular, solid/liquid and liquid/liquid interfaces);

(b) those involving colloidal dispersions (in particular, particulate dispersions and emulsions).

This review cannot be too detailed or completely comprehensive, and only the more well-established or promising techniques will be outlined, with brief mention of other methods. For general reviews, see Refs.[1,4-6].

(a) Macroscopic interfaces

The adsorbed amount,Γ, of polymer (i.e., the excess number of moles of polymer per unit area of interface) is given by

$$\Gamma = \frac{V\Delta c}{A} \qquad (1)$$

where V is the total volume of the bulk solution, A is the surface area of the adsorbent, and Δc is the change in the polymer concentration resulting from adsorption. The relatively small values for A in the case of macroscopic interfaces normally correspond to very small values for Δc. Hence, methods which involve determining concentration differences in bulk solution are not generally suitable. Unfortunately, indirect methods based on interfacial tension measurements, coupled with the use of the Gibbs' equation, cannot be used either,since one cannot assume, unambiguously, that adsorption equilibrium has been achieved. Indeed, as shown by Lankveld and Lyklema[7]in the case of the adsorption of polyvinyl alcohol at the oil/water interface, anomalous results for the adsorbed amount are obtained if the Gibbs' equation is used.

Direct studies of the polymer film are therefore required. Radioactive labelling of the polymer (e.g. tritium labelling of polystyrene[8]) coupled with the use of a Geiger counter offers one possibility. Optical studies, in particular ellipsometry, have proved more useful. This method involves monitoring the relative changes in the amplitude and the pase of the normal and parallel acid in free aqueous films. Sonntag et al.[15] have measured the thickness of aqueous PV-OH films between two compressed oil droplets, and Andrews et al.[16] have studied 'inverted' systems - i.e. water/oil/water. With regard to SLS films, Ottewill et al.[17,18] have developed a technique in which a thin liquid film is formed between two smooth spherical caps of transparent (silicone) rubber that deform to give a parallel film, the thickness of which may be measured either using light reflectance or multiple beam interferometry. Israelachvili[19] and Klein[20] have used a related technique in which a thin film is formed between two cylindrical mica (molecularly smooth) surfaces on which polymer has been adsorbed. The thin mica sheets are glued to polished glass cylinders. The upper glass cylinder is rigidly attached to a piezoelectric crystal tube and the lower (crossed) cylinder is mounted on a weak cantilever spring of known force constant. By using (i) a differential spring mechanism to control the position of the lower disc, (ii) the piezoelectric crystal, the distances between the surfaces can be monitored to ± 1 Å. This technique, in which these distances are measured using multiple beam interference fringes, must represent one of the most accurate ways of determining polymer layer thickness for a molecularly smooth substrate.

(b) Particulate Dispersions

With particulate systems, the relatively higher values of A (Eqtn.1) make direct determination of Γ through measurement of Δc much more tractable. However, sensitive techniques are still normally required to measure equilibrium polymer concentrations, particularly those corresponding to the steeply rising part of the adsorption isotherm (Figure 1.). Radioactive tracers are excellent in this regard: Ash and Clayfield[21] were able, for example, to detect very low concentrations (~ p.p.m.) of poly(ethylene oxide) in this way. However, this does require preparation of labelled polymer. A more general technique is differential interferometry, particularly for the concentration range 100 → 1000 p.p.m. In addition, specific turbidometric analytical techniques have been developed for given polymers in aqueous solutions (usually involving complex formations): e.g., polyvinyl alcohol plus boric acid and potassium iodide[22], and polyethylene oxide plus tannic acid[23].

The determination of Δc invariably involves the separation, usually by centrifugation, of the particles (plus their adsorbed layers) from the equilibrium solution. However, n.m.r. offers one possible means of monitoring the free polymer concentration *in situ*. The n.m.r. spectral linewidths of polymers in solution are generally broader than those of small molecules, but are still detectable. Due to their greater restricted motion the spectral linewidths of *adsorbed* polymers (as for polymers in the *solid* state) are so broad, that using conventional n.m.r. spectrometers the spectrum is usually inseparable from the background noise. Thus, changes in n.m.r. peak height reflect removal of polymer from the solution.

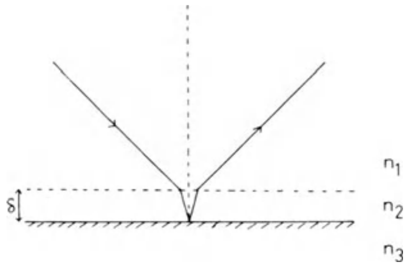

Figure 3. Ellipsometry: principles.

reflection coefficients for polarized light incident on the polymer film (Figure 3.). If the refractive indices of the substrate and the solution (n_1 and n_3 respectively) are known, then it is possible to calculate n_2 and δ, i.e., the average refractive index and thickness of the film,respectively. Details of the methods and the analysis are set out in Ref.[4]. The method requires optically flat surfaces (e.g., metals or polished surfaces) and reasonable increments between n_1, n_2 and n_3. The polymer concentration (and hence Γ) may be calculated from n_2 if the relationship between polymer concentration and refractive index is determined independently.

A further groups of techniques which has been used to estimate the thickness of adsorbed polymer films are based on capillary flow[9-11]. Effectively, one measures the rate of flow of solvent ($\dot{V}$) through the capillary, before and after adsorption of the polymer on the walls; the change in the effective radius (a) of the capillary may then be calculated using the Poiseuille equation:

$$\dot{V} = \frac{\pi p a^4}{8L\eta} \qquad (2)$$

where p is the viscosity difference across the capillary of length L, and η is the viscosity of the solution.

A direct measure of the thickness of adsorbed polymer films may be obtained using methods devised for estimating the forces acting across thin liquid films (for reviews of this topic, see Refs.[1,12,13]). Vapour/liquid/vapour, liquid/liquid/liquid and solid/liquid/solid films may all be studied in this way. An example of the first is the study by Lyklema and van Vliet[14] of polyvinyl alcohol (PV-OH) and partially esterfied polymethacrylic

A number of techniques have been used to determine the hydrodynamic thickness (δ_h) of the adsorbed layer. Viscosity, although, in general, less accurate than other techniques in this group, does have several advantages: the measurements are reasonably straightforward, are not restricted to spherical particles, and a reasonable level of polydispersity may be tolerated. Thus, for example, Fleer et al.[24] were able to estimate the thickness of adsorbed layers of polyvinyl alcohol for aqueous dispersions of polycrystalline, polydisperse silver iodide particles (average radius 50 nm) using capillary viscometers. the establishment of shear stress-shear rate curves for the system is advantageous, since one is then able to detect whether any particle aggregation is present and to use the high shear limiting value of the viscosity if it is present[25].

A generalized form of the Einstein relationship is normally used in the analysis, i.e.

$$\eta_{sp}/\phi = K_E + k' K_E^2 \phi \qquad (3)$$

where η_{sp} is the specific viscosity of the dispersion having particle volume fraction, ϕ; k' is the Huggins constant and K_E the Einstein coefficient. The presence of the adsorbed layer increases the effective volume fraction of the particles (i.e., $\phi' = f\phi$). Assuming that k' and K_E are unchanged when adsorbed polymer is present on the particles, then

$$\eta'_{sp}/\phi = K_E f + k' K_E f^2 \phi \qquad (4)$$

where η'_{sp} is the specific viscosity of the system in the presence of adsorbed polymer. Hence f may be determined from the intercept of a plot of η'_{sp}/ϕ against ϕ. Knowing the particle geometry, δ_h may then be evaluated - e.g., for equivalent spheres of radius $\bar{a}$,

$$\delta_h = \bar{a} (f^{1/3} - 1) \qquad (5)$$

Because one is making use of the intercept at $\phi = 0$, the effect of interparticulate interactions is minimized, but the possible effects from the primary electroviscous effect should be considered: the presence of the adsorbed layer may modify these effects and lead to changes in K_E. The addition of electrolyte reduces the primary electroviscous effect.

When sedimentation coefficients, diffusion coefficients or electrophoretic mobilities are similarly used to evaluate δ_h, one should also restrict measurements to <u>dilute</u> systems (or better still, take the extrapolated value for $\phi \rightarrow 0$) in order to minimize effects from interparticle interactions. Garvey et al.[26] have described the use of an ultracentrifugal technique for determining the adsorbed layer thickness of polyvinyl alcohol on polystyrene latices, based on monitoring the changes in the sedimentation coefficients arising from the adsorption on the particles. Although this is an accurate technique, which places less stringent demands on the system (with regard to purity and monodispersity) than, say, light scattering techniques, it is time-consuming and requires independent knowledge of the adsorption isotherm[26].

Photon correlation light scattering is a quick,accurate technique for determining particle diffusion coefficients and, hence, hydrodynamic adsorbed layer thicknesses[27]. However, it is necessary to remove all impurities and to use monodisperse spherical particles. The principle of the method, in outline, is closely related to the analogous so-called quasi-elastic light scattering technique, in which one monitors the broadening of the scattered (laser) light frequency due to a Doppler shift effect resulting from interactions between the moving particle and incident photons. The half-width (at half-height), $\Delta\nu$, of the spectrum of the scattered light is given by[28]

$$\Delta\nu = K^2D \qquad (6)$$

where K is the scattering vector ($K = (4\pi/\lambda)\sin\theta/2)$; D is the particle diffusion coefficient, which is related to the particle radius, a (for particles obeying Stokesian hydrodynamics) by the relationship

$$D = \frac{kT}{6\pi\eta a} \qquad (7)$$

where η is the viscosity of the medium. In the presence of the adsorbed polymer layer, equation (6) becomes

$$D' = \frac{kT}{6\pi\eta(a + \delta_h)} \qquad (8)$$

Hence, δ_h may be calculated.

Homola and Robertson[29] have described a mass transport electrophoresis method for determining polymer adsorbed layer hydrodynamic thicknesses.

As mentioned above, methods described primarily to monitor steric interactions can be used to measure δ. This is also true for particulate systems. Thus, one may use compressional techniques, e.g. in two-dimensions using a surface balance as described first by Doroszkowski and Lambourne[30] and, more recently, by Garvey et al.[31], or in three-dimensions using a compression cell of the type described by Cairns et al.[32] Garvey et al.[27] have described a slow-speed centrifugation technique for assessing adsorbed polymer layer thickness. This involves packing the stable particles into a (hexagonal) close-packed array in a capillary tube. δ is then calculated from the known geometry of the system.

As with macroscopic surfaces, methods for determining p, the fraction of bound segments, have been devised for particulate systems. Microcalorimetry offers one possibility here, and a recent comparison[33] of this technique with the i.r. technique has shown good agreement between the two methods for polyethylene oxide adsorbed on to silica particles from non-aqueous solvents.

Unfortunately, the infra-red technique, which monitors changes in the vibrational frequency of segments in contact with the surface (compared to free solution), cannot readily be used with aqueous systems, but has been applied to non-aqueous systems with some success. It may be possible to use laser Raman spectroscopy for this purpose.

Two related spectroscopic techniques which are finding increasing application in the evaluation of p, for aqueous as well as non-aqueous systems, are e.s.r. and n.m.r. Both methods rely on the assumption that, for an adsorbed homopolymer the segments in trains have a lower mobility (i.e., longer rotational correlation time) than those in loops or tails. This implies, therefore, a 'two-state' situation for the segments: the reality of the proposition is, of course, open to question. Nevertheless, differences in magnetic relaxation times have been observed for unpaired electrons (e.s.r.) or nuclei having a magnetic moment (n.m.r.), contained in segments in trains compared to those in loops or tails. If the signals from the two components can be separated, then their relative intensities, and hence p, can be calculated.

The e.s.r. technique[34] involves incorporating a spin label (e.g., a nitroxide group) into the polymer and a simulation procedure for the spectrum of the adsorbed polymer from similar spectra for the polymer in solution under different conditions - i.e., under low solution viscosity conditions reflecting motion in trains. The pulsed n.m.r. technique[35,36], although less sensitive, is an absolute method, the theory of which has been explained in detail elsewhere[35]. It involves separation of the two spin-components (i.e., protons in loops/tails and those in trains) using a sequence of 90° and 180° pulses. The presence of trace H_2O in the D_2O solvent used can normally cause serious problems, but the H_2O signal can be eliminated using a further pulse sequence, in this method.

The n.m.r. studies have indicated that the rotational correlation times for segments in trains are comparable to those for the equivalent solid state polymer, whilst those for loops and tails are somewhat shorter, as might be expected. These observations underlie the use of conventional high resolution (frequency domain) n.m.r. methods in the determination of polymer adsorption isotherms, as described above.

The use of small angle neutron scattering in the area of polymer adsorption is still in its infancy[37-39], but it offers great potential for determining both structural and dynamic information. Indeed, neutron scattering is the only scattering technique in which both the energy and momentum transfers are simultaneously of the right order of magnitude for probing the segments in a polymer chain. Since there are no selection rules,as in photon spectroscopy, the equivalents of both i.r. and Raman spectroscopy can be carried out with inelastic neutron scattering measurements, leading to vibrational information. Similarly, quasi-elastic neutron scattering should lead to information concerning the diffusion (rotational and translational) motion of segments.

EXPERIMENTAL RESULTS

By way of illustration, experimental data will be presented for one system which may be regarded as being typical for polymers adsorbed from aqueous solution: polyvinyl alcohol adsorbed on to polystyrene latex particles. However, in many respects, aqueous systems are not ideal for comparison with theoretical predictions, because of the complex nature of water as a solvent and the presence of free charge (ions). Nor is PV-OH the ideal adsorbate to study, although it is widely used commercially as a dispersion stabilizer (see Chs. 15 and 17) . PV-OH is, in fact, normally a copolymer containg residual acetate as well as alcohol groups. The primary interaction, controlling $\Delta\varepsilon^{\sigma}$, is though to be the hydrophobic interaction between these acetate groups and the (largely) hydrophobic polystyrene surface. Polyethylene oxide (PEO) on the other hand is a true homopolymer and its absorption onto polystyrene(PS) particles has been extensively studied[37], but it is much less strongly adsorbed than PV-OH. The interactions contributing to $\Delta\varepsilon^{\sigma}$ for PEO on PS particles are not well-defined. Studies by Rubio and Kitchener[40] on the adsorption of PEO from water onto silica particles have been given some consideration here. By controlling the temperature to which silica particles are pre-heated (in vacuo), one may vary the relative surface concentrations of (hydrophilic) -OH groups and (hydrophobic) -O- groups. The adsorbed amount of PEO from water was found to be a maximum at ~ 700°C pretreatment temperature. In this state the spacing between isolated surface-OH groups is such that the -CH_2-CH_2- groups of a PEO chain can 'sit' on the hydrophobic regions of the silica surface with alternate ether oxygens H-bonded to surface -OH groups[41,42], but the primary interaction could well be a hydrophobic one similar to that occurring with the silica particles, mentioned above.

Typical adsorption isotherms are shown for PV-OH (88 % vinyl alcohol, 12 % vinyl acetate) on to PS latex particles in Figure 4(a)[26]. It can be seen that the extent of the region B (of Figure 1.) increases with $M^{\frac{1}{2}}$. The values were obtained from sedimentation coefficients - i.e., they are strictly δ_h (hydrodynamic) values. The apparent agreement with the Scheutjens-Fleer theoretical predictions, with regard to the dependence of δ on $M^{\frac{1}{2}}$, has, howver, to be regarded with caution. In a later paper by Garbey et al.[27], it was found that measured δ values (but not Γ values) are dependent on particle radius: the effect is illustrated in Figure 5. The effect was explained in terms of the 'coning' effect on the volume space available to coils adsorbed on surfaces of increasing curvature. It was suggested that, for comparison purposes, it is better to use δ_{eff}, where δ_{eff} refers to the value of the thickness on an equivalent flat surface. It was shown in that case that $\delta_{eff} \sim M^{\sim 1}$, rather than $M^{\frac{1}{2}}$. It was also found[27] that good agreement resulted for δ_{eff} values obtained using different techniques - i.e., from sedimentation coefficients, diffusion coefficients, and from slow-speed centrifugation, as shown in Table 1.

Table 1. Comparison of δ_{eff} values (nm) for polyvinyl alcohol fractions adsorbed on to polystyrene latex particles.

$\bar{M}_w$	Ultracentrifuge$^+$	Photon correlation	Slow-speed centrifugation
67,000	38.0 ± 5.0	38.2 ± 3.0	39.3 ± 2.0
43,000	27.5 ± 3.5	28.9 ± 3.0	34.9 ± 2.0
28,000	18.0 ± 3.0	22.0 ± 3.0	19.3 ± 2.0
17,000	12.0 ± 3.0	19.4 ± 3.0	15.2 ± 2.0
8,000	3.5 ± 2.5	7.1 ± 3.0	9.0 ± 2.0

$^+$ values corrected for size effect.

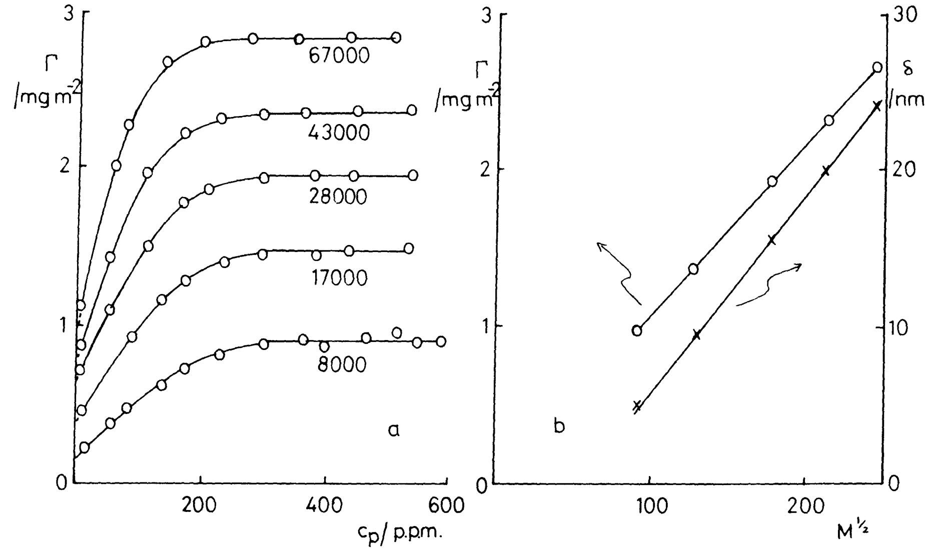

Figure 4. Adsorption of polyvinyl alcohol onto polystyrene latex from water[26]:

(a) adsorption isotherms (numbers indicate molecular weight);
(b) plateau levels of Γ and δ plotted against $M^{\frac{1}{2}}$.

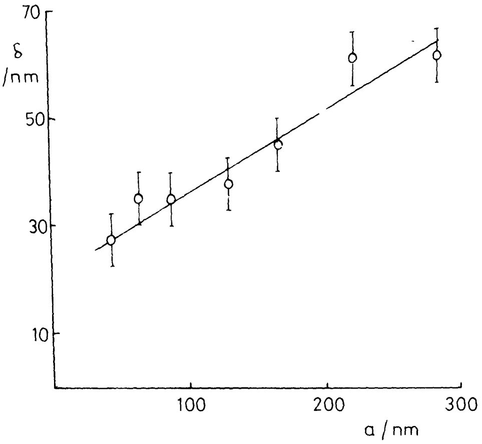

Figure 5. Dependence of δ on particle radius, a. Ref.[27]

The effect of solvency on both Γ and δ was reported for the PS-latex/PV-OH/water system in subsequent papers[43,44]. Water becomes an increasingly poor solvent for polyvinyl alcohol with increasing temperature, or with increasing electrolyte concentration. Over the temperature range 5 to 50°C, Γ was found to increase and δ to decrease[43]. Similarly, in the presence of increasing concentrations of various elctrolytes (in particular, Na_2SO_4) Γ increased and δ decreased[44]. This effect of solvency is, in general, in agreement with theoretical predictions.

Barnett et al.[38] have recently obtained values for the fraction of segments in trains (p) and the second moment of the segment density distribution (σ) for polyvinyl alcohol adsorbed onto PS latex particles from water. Typical values for polyvinyl alcohol (M = 11,500; 88 % vinyl alcohol, 12 % vinyl acetate) are shown in Table 2., as a function of coverage, θ ($\theta = \Gamma/\Gamma_{max}$)[38]. Also[43] shown is the corresponding value for δ_h for θ = 1. p values were obtained using a pulsed n.m.r. technique. The decrease in p with increasing coverage is in line with other experimental data using this technique[35]. For example, in Figure 6., values of p for polyvinylpyrrolidone adsorbed on to silica from water (D_2O) are shown[36], together with data for a similar system obtained using an e.s.r. technique[45]. Both the n.m.r. and e.s.r. techniques reflect local segmental rotational correlation times: the generally higher values obtained by e.s.r. may result from the fact that the spin-label introduced into the polymer could contribute to the adsorption process. However, the very high values of p obtained by both techniques for this system indicate that $\Delta\varepsilon^{\sigma}$ is much stronger for the PVP/silica/water system than for the polyvinyl alcohol/polystyrene/water system.

The second moment of the segment density distribution (σ), obtained from small angle neutron scattering studies (contrast match technique), clearly increases with increasing coverage over the range θ = 0.1 → 1.0. This indicates that the chains adopt a more extended configuration normal to the surface with increasing coverage (essential over the region B of Figure 1.): this finding is in line with the decrease in p values over this region

Table 2. Values of p, σ, δ_h as a function of coverage, θ. Ref.[38]

θ	p	σ/nm	δ_h/nm
0.1	0.1 ± 0.05	0.35	-
0.5	-	1.3	-
1.0	0.06 ± 0.01	1.6	5 ± 2

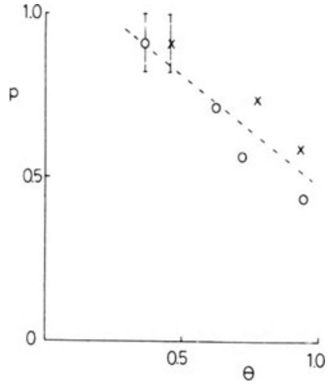

Figure 6. p values as a function of coverage (θ) for polyvinyl pyrrolidone adsorbed on to silica from D_2O:
o = n.m.r. results[36] × = e.s.r. results[45]
(M = 40,000)

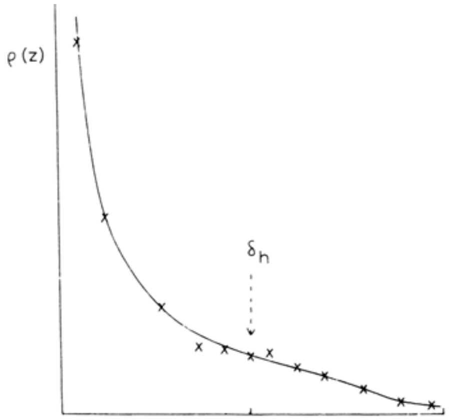

Figure 7. Polyvinyl alcohol segment density as a function of distance normal to the polystyrene surface.[38]
($\bar{M}_{PV\text{-}OH}$ = 11,500; θ = 1.0).

σ is defined by Equation 9, i.e.

$$\sigma^2 = \int_0^\infty \rho(z)\, z^2\, dz - \left[\int_0^\infty \rho(z)\, z\, dz\right]^2 \qquad (9)$$

The value of σ, therefore, depends explicitly on the form of $\rho(z)$. For example, for a rectangular distribution of $\delta = \sqrt{12}\,\sigma$. The values quoted for σ and δ (for $\theta = 1.0$) in Table 1. are not, therefore, incompatible. However, the value of σ does not uniquely define the form of $\rho(z)$. Small angle neutron scattering also offers the possibility of obtaining $\rho(z)$ directly. Theoretical details are given elsewhere[38,39] ; it is, however, desirable to point out that it is necessary to carry out a sine transform of the neutron density, as a function of acattering angle data, in a manner analogous to Fourier transform from reciprocal to real space in X-ray crystallography. Figure 7. shows the transform representing $\rho(z)$ (unnormalized) against z for polyvinyl alcohol (molecular weight = 11,500) adsorbed on to polystyrene latex particles at $\theta = 1.0$[38]. The arrow indicates the corresponding value of δ_h (i.e. 5 nm, in Table 2.). The conclusion is that there is a high concentration of segments close to the surface, but a slow decay in segment density away from the surface (probably due to long tails), as predicted by Scheutjens and Fleer[2].

It has not been possible here to mention the adsorption of polyelectrolytes or biopolymers. Clearly, an understanding of these topic is relevant to a great many industrial and biological problems. Other parameters come into consideration in these areas: for simple polyelectrolytes, e.g. polymethacrylic acid[46], one has to consider the degree of ionization of the polyelectrolyte molecule and the surface charge density of the solid: in addition, for biopolymers, the conformational rearrangements which may arise are of primary importance[47].

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THE ROLE OF POLYMERS IN THE STABILIZATION OF DISPERSE SYSTEMS

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INTRODUCTION

Nonionic polymers can impart stability to a colloidal dispersion in at least two different ways:

(i) if attached to the colloidal particles, they can generate *steric* stabilization;

(ii) if free in solution, they may generate *depletion* stabilization.

Steric stabilization has been exploited continuously for some five millennia since the production in Ancient Egypt of 'instant' inks for writing on papyrus. Nowadays, it is exploited in paints, inks, foods, pharmaceuticals, etc., and is evident in biological systems (e.g. milk, blood, etc.). There are at least three advantages that steric stabilisation possesses over electrostatic stabilization:

(i) its relative insensitivity to high concentrations of electrolytes;

(ii) the fact that high solids dispersions display relatively low viscosities;

(iii) it is equally effective in both aqueous and nonaqueous dispersion media.

THE ATTRACTIVE INTERACTION

It is a matter of common observation that a dispersion of naked uncharged colloidal particles undergo very rapid coagulation.

This is a consequence of the strong long-range London dispersion attraction between the particles. London dispersion forces have a quantum mechanical origin and are responsible for the liquefaction of rare gases at low temperatures.

GENERAL METHODS FOR IMPARTING COLLOID STABILITY

In order to generate stable dispersions, it is necessary to provide repulsive interactions which outweigh the London interaction. Currently, there really exist only the general methods by which colloid stability can be usefully imparted:

(i) electrostatic stabilization;

(ii) polymeric stabilization.

At the present time, stabilization by what are termed 'solvation forces' does not seem to be sufficiently long range or sufficiently well-understood to be exploited.

STERIC STABILIZATION

The best steric stabilizers which have been prepared to date are amphipathic block or graft copolymers. These are composed of a nominally insoluble 'anchor' polymer, and soluble stabilizing moieties. Whilst homopolymers can impart stability, they are comparatively ineffectual. Homopolymers impose conflicting requirements on the dispersion medium: on the one hand, it must be a good solvent for effective stabilization, whereas on the other, it must be a poor solvent for effective adsorption.

Optimum stability is usually achieved if (i) the 'anchor' polymer is about one-third by weight of the amphipathic copolymer, and (ii) the particles are fully coated. Condition (i) ensures that the stabilizing chains do not desorb under the stress generated by a Brownian collision, whilst condition (ii) ensures that the chains cannot undergo lateral motion away from the stress zone. Colloidal dispersions stabilised by homopolymers, or poorly anchored stabilizers, often exhibit instability arising from the lateral movement and/or desorption of the stabilizing chains.

A third criterion for optimum stability is the need for reasonably high molecular weight stabilizing moieties to ensure that the van der Waals' forces of attraction between the core particles is rendered negligible.

THE PHENOMENOLOGY OF FLOCCULATION

Providing that the anchoring is adequate, the particle size is not too large, and the stabilizer molecular weight is reasonably high, thermodynamic factors are found to limit stability. This limit is independent of the nature of the anchor polymer and, in many systems, the nature ans size of the latex particles. The thermodynamic factors that limit stability are governed primarily by the chemical nature of the stabilizing moieties and the dispersion medium.

Instability can usually be induced by decreasing the solvency of the dispersion medium for the stabilising moieties. This can be accomplished by (i) changing the temperature, (ii) changing the pressure, and (iii) adding a non-solvent for the stabilizing moieties to the dispersion medium.

The transformation from long-term stability to catastrophic flocculation occurs abruptly at the critical flocculation point (cfpt), as shown in Fig 1. This critical flocculation point may be a critical flocculation temperature (cft), a critical flocculation pressure (cfp), or a critical flocculation volume (cfv) (for a nonsolvent that induces flocculation).

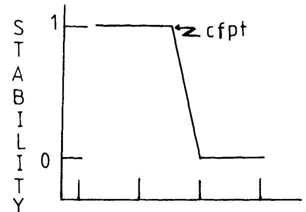

Figure 1. Transformation from long-term stability to catastrophic flocculation for poly(oxyethylene) stabilized latices in 0.39 M $MgSO_4$.

Table 1. Comparison of Theta-temperature with Critical Flocculation Temperature

Stabilizers	Molecular weight	Dispersion medium	cfpt/K	U/L	θ/K
Poly(ethylene oxide)	10,000	0.39 M $MgSO_4$	318 ± 2	U	315 ± 3
Poly(ethylene oxide)	96,000	0.39 M $MgSO_4$	316 ± 2	U	315 ± 3
Poly(ethylene oxide)	1,000,000	0.39 M $MgSO_4$	317 ± 2	U	315 ± 3
Poly(acrylic acid)	9,800	0.2 M HCl	287 ± 2	L	287 ± 5
Poly(acrylic acid)	51,900	0.2 M HCl	283 ± 2	L	287 ± 2
Poly(acrylic acid)	89,700	0.2 M HCl	281 ± 1	L	287 ± 5
Poly(vinyl alcohol)	26,000	2 M NaCl	302 ± 3	U	300 ± 3
Poly(vinyl alcohol)	57,000	2 M NaCl	301 ± 3	U	300 ± 3
Poly(vinyl alcohol)	270,000	2 M NaCl	312 ± 3	U	300 ± 3
Polyacrylamide	18,000	2.1 M $(NH_4)_2SO_4$	292 ± 3	L	-
Polyacrylamide	60,000	2.1 M $(NH_4)_2SO_4$	295 ± 5	L	-
Polyacrylamide	180,000	2.1 M $(NH_4)_2SO_4$	280 ± 7	L	-
Polyisobutene	23,000	2-methylbutane	325 ± 1	U	325 ± 2
Polyisobutene	150,000	2-methylbutane	325 ± 1	U	325 ± 2
Polyisobutene	760,000	2-methylbutane	327	U	318
Polyisobutene	760,000	2-methylpentane	381	U	376
Polyisobutene	760,000	2-methylhexane	423	U	426
Polyisobutene	760,000	3-ethylpentane	463	U	458
Polyisobutene	760,000	cyclopentane	455	U	461

cont.....

Table 1 (cont.)

Stabilizers	Molecular weight	Dispersion medium	cfpt/K	U/L	θ/K
Poly(α-methyl styrene)	9,400	n-butyl chloride	254 ± 1	L	263
	9,400	n-butyl chloride	403 ± 1	U	412
Polystyrene	110,000	cyclopentane	410	U	427
Polystyrene	110,000	cyclopentane	280	L	293
PDMS	3,200	n-heptane/ethanol (51:49 v/v)	340	L	340 ± 2
PDMS	11,200		340	L	340 ± 2
PDMS	23,000		341	L	340 ± 2
PDMS	48,000		338	L	340 ± 2

IDENTIFICATION OF THE CRITICAL FLOCCULATION POINT

As shown in Table 1, which is a compilation of results from three different research groups, there is a strong correlation between the cfpt and the θ-temperature (or Flory temperature) for the stabilizing moieties in free solution. Similar results have been obtained for cfps and cfvs. A further check on this correlation, also evident from Table 1, is the insensitivity of the cft to the molecular weight of the stabilising moieties (at least for molecular weights $\geqslant$ 5,000).

NOTES ON THE THETA-POINT

Macromolecules in free solution do not, in general, obey the ideal van't Hoff equation for minimolecules:

$$\pi/c_2 \quad = \quad RT/M$$

where π = osmotic pressure, and c_2 = polymer concentration. They display positive deviations in a good solvent and negative deviations in a poor solvent. The θ-solvent corresponds to the situation where the ideal van't Hoff equation for minimolecules is obeyed, by macromolecules, at least up to several per cent concentration. There is a far reaching analogy between the Boyle point for non-ideal gases and the θ-point for polymer chains. The θ-point can be established by osmometry, light scattering, phase separation and cloud point titration studies. It is found to be insensitive to the molecular weight of the polymer.

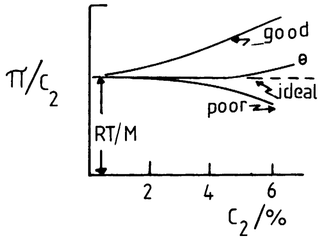

Figure 2. Reduced osmotic pressure for polymer solutions in different solvents.

CLASSIFICATION OF STERICALLY STABILIZED DISPERSIONS

The temperature dependence of stability gives a clue to the thermodynamic factors controlling the stability near to the cfpt. In principle, all sterically stabilized dispersions can be flocculated both by heating and by cooling. It is, however, not always possible to observes both critical flocculation points. Hence, many dispersions flocculate either on cooling or on heating. If flocculation occurs on heating, it is termed an upper critical flocculation point; if on cooling, it is termed a lower critical flocculation point.

The temperature dependence can be understood from

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

where ΔG_T = free energy of close approach of sterically stabilized particles and ΔH_T and ΔS_T are the corresponding enthalpy and entropy terms. This leads to the following possible combination of signs near to the cfpt:

ΔH_T	ΔS_T	$\lvert\Delta H_T\rvert/\lvert\Delta S_T\rvert$	type	flocculation
+	+	$\geqslant 1$	enthalpic	on heating
-	-	$\leqslant 1$	entropic	on cooling
+	-	$\gtrless 1$	combined	inaccessible

Some typical examples of how different dispersions may be classified near to their cfpt are shown in Table 2.

Table 2. Classification of some sterically stabilized dispersions near to room temperature and pressure

Stabilizer	Dispersion medium		
	Type	Example	Stabilization
Poly(ethylene oxide)	aqueous	0.48 M $MgSO_4$	enthalpic
Poly(vinylalcohol)	aqueous	2 M NaCl	enthalpic
Poly(methacrylic acid)	aqueous	0.02 M HCl	enthalpic
Poly(acrylic acid)	aqueous	0.2 M HCl	entropic
Polyacrylamide	aqueous	2.1 M $(NH_4)_2SO_4$	entropic
Polystyrene	non-aqueous	cyclopentane	entropic
Polyisobutene	non-aqueous	2-methyl-butane	enthalpic

It should be noted that enthalpic stabilization is more common in aqueous systems under ambient conditions, whilst entropic stabilization is more common in non-aqueous systems. Furthermore, both enthalpic and entropic stabilization occur in both aqueous and non-aqueous media; indeed, every dispersion should, in principle, display both types of stabilization under different conditions of temperature and pressure.

THE UNIMPORTANCE OF DISPERSION FORCES IN INCIPIENT FLOCCULATION

For many sterically stabilized systems, the dispersion forces are too small to be responsible for flocculation near to the θ-point.. Rather, flocculation results from the attraction between the 'stabilizing' chains in slightly worse than θ-solvents. It follows that the ensheathing chains are thus responsible for repulsion, in better than θ-solvents and for attraction in worse than θ-solvents.

A quite different pattern of behaviour is observed if the stabilizing moieties are relatively low in molecular weight, or if the van der Waals' forces of attraction between the core particles is abnormally high. This would be the case with metal sols. Flocculation is then apparent in better than θ-solvents.

QUALITATIVE DISCUSSION OF THE ORIGINS OF STERIC STABILIZATION

Many phenomena give rise to the interactional forces in steric stabilization:

(i) Combination effects arising from entropy of mixing of polymer segments with molecules of the dispersion medium. These always oppose flocculation, and increase with increasing temperature, as they are purely an entropy effect ($-T\Delta S_{comb}$);

(ii) Free volume (equation-of-state) contributions arising from the dissimilarities in the free volumes of the articulated macromolecules and the minimolecules of the dispersion medium. These may contain both entropic and enthalpic contributions, although in non-aqueous dispersion media the entopic contributions are usually dominant and promote flocculation (i.e., are attractive). Such effects normally increase in absolute magnitude with increasing temperature;

(iii) Contact dissimilarity contributions may be enthalpic and/or entropic in character. In non-aqueous media, the entropic effect is small or non-existent and the larger enthalpic effect usually promotes flocculation. Dissimilarity effects may be relatively insensitive to temperature over small temperature changes, but would be expected to decrease in absolute magnitude with increasing temperature. In aqueous media, specific interactions between the water molecules and the stabilizing moieties may lead to enthalpic interactions that oppose flocculation, the concomitant entropic contributions promoting flocculation (e.g. poly(ethylene oxide) and poly(vinyl alcohol). This behaviour is not universal, however, and is unlikely to apply to polyacrylamide and poly(acrylic acid) (see below).

The free energy of interpenetration of these steric barriers may thus be resolved into at least three components:

$$\Delta G_{\text{inter}} = \Delta G_{\text{comb}} + \Delta G_{\text{free vol}} + \Delta G_{\text{contact}}$$

Whilst some non-aqueous systems are understood qualitatively by free volume theory, there is no corresponding ab initio theory for aqueous systems because of the strong interactions between the polymer segments and water. Some of the following terms are speculative in relation to aqueous systems:

Non-Aqueous (and some aqueous) dispersions

	combinatorial		free volume		contact	
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
	o	-ve	+ve(small)	+ve	-ve	$\sim$o
ΔG	+ve		-ve		-ve	
Promotes	stabilization		flocculation		flocculation	
$\frac{\partial \Delta G}{\partial T}$	+ve		-ve		+ve(small)	

This table shows that on heating non-aqueous dispersions, the free volume dissimilarity contribution changes faster than the combinatorial term, resulting in flocculation, Just below the upper criticalflocculation temperature (UCFT), $\Delta H_{\text{free vol}}$ gives rise to enthalpic stabilization. We further observe that, on cooling, the combinatorial term decreases and the contact dissimilarity term becomes more important; both the free volume and contact terms may contribute to flocculation on cooling. Just above the lower critical flocculation temperature (LCFT), ΔS_{comb} gives rise to entropic stabilization.

Aqueous dispersions

	combinatorial		free volume		contact	
	ΔH	ΔS	ΔH	ΔS	ΔH	ΔS
	o	-ve	+ve	+ve	+ve	+ve
ΔG	+ve		-ve		+ve	
Promotes	stabilization		flocculation		stabilization	
$\frac{\partial \Delta G}{\partial T}$	+ve		-ve		-ve	

Just below the upper critical flocculation temperature, $\Delta H_{contact}$ gives rise to enthalpic stabilization. On further heating, the free volume contribution becomes more negative and the contact term less positive, resulting in flocculation. The lower critical flocculation temperature is usually inaccessible, but if it was observed, ΔS_{comb} would give rise to entropic stabilization.

QUANTITATIVE CALCULATION OF REPULSIVE POTENTIAL ENERGY

It is not yet possible to predict the magnitude of the repulsion precisely, Clearly, no interaction is possible if the minimum distance between the particles exceeds 2L, where L = thickness of the stabilizing moieties. If, however, this minimum distance lies between 2L and L, the stabilizing layers can interpenetrate, leading to repulsion in a good solvent and attraction in a worse than θ-solvent. In this interpenetrational domain, the interaction free energy ΔG_T arises primarily from the mixing of polymer segments and molecules of dispersion medium:

$$\Delta G_T = \Delta G_{mix}$$

If the distance is less than L, not only does interpenetration occur, but also the stabilising layers on one particle are compressed by the impenetrable surface of the other particle. This generates an elastic contribution to stabilization which always opposes flocculation:

$$\Delta G_T = \Delta G_{mix} + \Delta G_{elastic}$$

If the segment density distribution function is known, the Flory-Huggins theory can be exploited to calculate ΔG_{mix}. For example, for a (non-physical) constant segment density in the interpenetrational domain:

$$\Delta G_{mix} \sim 2\pi N_A \omega^2 (\bar{v}_2{}^2/V_1) (1/2 - \chi_1) aSkT$$

where ω = weight of stabilizing moieties per unit area,
$\bar{v}_2$ = partial specific volume of moieties,
χ_1 = interaction parameter,
a = particle radius,
N_A = Avogadro's constant, and
$S = 2(1 - d_o/2L)^2$.
Here L = barrier layer thickness ($L << a$), and
d_o = minimum distance between particle surfaces.

Expressions can also be derived in the interpenetrational and compressional domain. These lead to potential energy diagrams of the type shown in Fig. 3

It should be noted that there is no primary minimum as there is for electrostatic stabilization. Sterically stabilized dispersions may therefore be thermodynamically stable (in contrast to electrostatically stabilized dispersions which are metastable). Flocculation occurs in a pseudosecondary minimum close to the

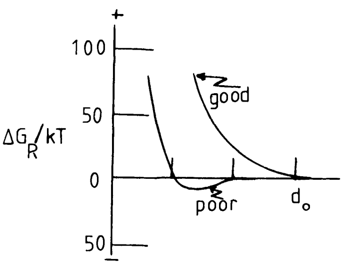

Figure 3. Potential energy diagrams for sterically stabilized dispersions in different solvents.

θ-point because in a slightly worse than θ-solvent the stabilizing segments become 'sticky'.

ENHANCED STERIC STABILIZATION

The correlation between the θ-point and the cfpt is lost if the anchoring is poor. Flocculation occurs in better than θ-solvents, as it does if the stabilizer undergoes crystallization, or the van der Waals' attraction between the core particles is important. The correlation is also, lost if the chain is attached at a large number of points (multipoint anchoring). Stability is observed in significantly worse than θ-solvents - this is termed 'enhanced' steric stabilization (see Fig. 4).

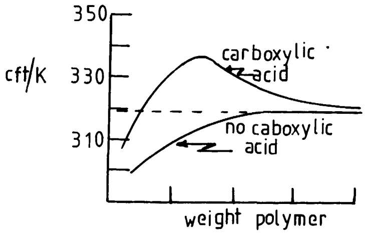

Figure 4. Enhanced steric stabilization for poly(oxyethylene) chains attached to polystyrene latex particles containing surface carboxylic acid groups.

Enhanced steric stabilization may arise in part from the low segment densities in the peripheral regions of the steric barrier, changed thermodynamic parameters, etc. It may be expected that random copolymers would impart enhanced steric stabilization if one of the copolymers is soluble in the dispersion medium and the other is insoluble (e.g., partially hydrolysed poly(vinyl alcohol).

ELASTIC STERIC STABILIZATION IN POLYMER MELTS

It has been demonstrated experimentally that stable dispersions can be prepared in polymer melts (e.g. poly(ethylene oxide) of molecular weight = 6,000). In this instance, the stability limit is dependent upon the particle size and molecular weight of the stabilizer (in contrast to the independence of cfpt for instability near to the θ-point). This suggests that the origins of stability and instability are different from that outlined above. Elastic (not mixing) effects are probably responsible for stability.

HETEROSTERIC STABILIZATION

Dispersed particles stabilized by different types of polymers may exhibit heteroflocculation or heterosteric stabilization on mixing. Stability is normally observed on mixing particles stabilized by incompatible polymers. Particles stabilized by compatible polymers, especially those that coprecipitate or coacervate, often undergo heterocoagulation. Selective flocculation of one type of sterically stabilized particle in a mixture of particles is also possible.

DEPLETION STABILIZATION

It is found experimentally that free polymer, when added at lower concentrations to the dispersion medium can induce flocculation of some dispersions whilst at higher concentrations no flocculation occurs (see Fig. 5).

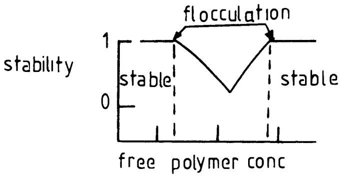

Figure 5. Schematic representation of the effects of free polymer.

Depletion flocculation arises whenever the particles are so close as to exclude polymer chains from the interparticle zone. Closer approach is favoured by the lowering in free energy resulting from the mixing of (almost) neat solvent with the bulk polymer solution (see Fig. 6).

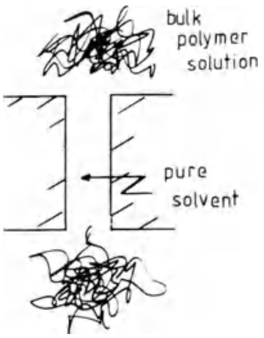

Figure 6. Origin of depletion flocculation

It is not possible, however, in a good solvent, to obtain the depletion zones depicted above between the particles except by 'unmixing' polymer chains and solvent. This requires work - i.e., it results in a repulsive force at larger distances of separation. The potential energy diagram for the two colloidal particles immersed in a polymer solution is shown in Fig. 7.

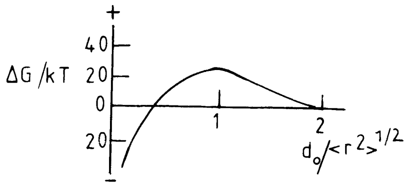

Figure 7. Potential energy diagram for depletion stabilization.

Depletion stabilization represents a thermodynamically metastable state resembling electrostatic stabilization. It contrasts with steric stabilization, which usually corresponds with thermodynamic stability rather than metastability. It would be expected that the effects of free polymer would depend on:

(i) polymer composition and molecular weight;
(ii) nature of solvent;
(iii) particle size;
(iv) any adsorbed/attached polymer.

It should be noted that the free polymer may be different from any attached/adsorbed polymer, and still generate depletion flocculation and stabilization.

SCHEMATIC REPRESENTATION OF THE EFFECTS OF IDEALIZED HIGH MOLECULAR WEIGHT POLYMER

Fleet has proposed that the effects of polymer on colloid stability may be represented schematically as shown in Fig. 8.

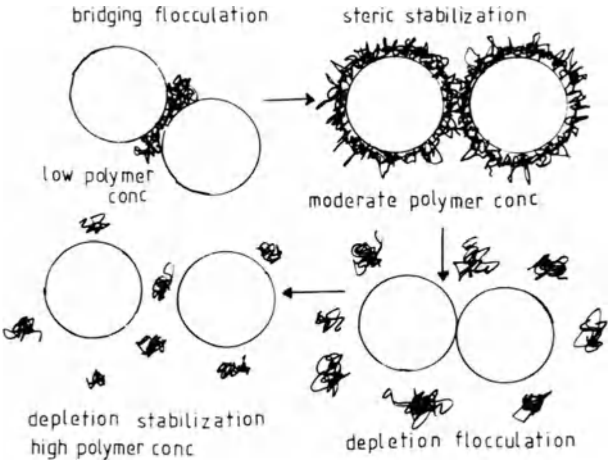

Figure 8. Effects of polymer on colloid stability.

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WATER-SOLUBLE POLYMERS IN THE STABILIZATION OF DISPERSIONS, INCLUDING POLYMERIZING SYSTEMS

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INTRODUCTION

Many recipes for stable dispersions have been developed in several spheres of activity but these have been, and still are, the result mainly of trial-and-error experiments. The technologists who formulate dispersions build up their formulating knowledge by correlating the properties of the dispersions with their recipes.

The term 'stabilization' is indefinite in this context, and must be interpreted in terms of the effect desired - i.e., by defining the physical and chemical conditions to which a given dispersion is to be subjected, and the period of time for which it must remain substantially unchanged under those conditions. Practical dispersions are frequently complex and few water-soluble polymers (WSPs) have been studied in depth even in simple systems, although a vast range of natural, semisynthetic and synthetic WSPs may be found in examples of dispersion formulations in patents, trade literature, and formularies.

'Emulsion' paint is an example of a dispersion which is required to remain stable for long periods when subjected to widely varying conditions on storage: it may contain:

- A polymer 'emulsion' - i.e., a latex dispersion which is itself complex - see Section 4;
- A dispersed pigment - e.g. titanium dioxide, coloured inorganic or organic pigments;
- An extender - e.g. talc; china clay; calcium carbonate;

- A pigment dispersant - e.g. a surfactant; a poly(meth)-acrylic salt; sodium tripolyphosphate;
- A 'thickener'(the water-soluble polymer) - e.g. hydroxyethylcellulose;
- A 'coalescent' (a fugitive plasticiser for the polymer) - e.g. 2-(2-butoxyethoxy)ethyl acetate;
- A preservative (to prevent microbial attack);
- A corrosion inhibitor - e.g. sodium benzoate;
- An alkali to adjust pH - e.g. sodium hydroxide, ammonia solution, amines.

The term 'thickener' is often used for the WSP in the mixture, thus emphasising the importance of the effect of the WSP on rheological properties. The term 'protective colloid', also fairly frequently encountered, appears to place more emphasis on stability.

Studies in stabilization are often specific to the system under examination and the results can be used only as a general guide in other dispersions. In polymerizing systems, the WSP may frequently be modified chemically during the polymerization reaction: the results of measurements of the interfacial properties of WSPs, found by experiments with non-reacting dispersions, must therefore be used with great caution when attempting to explain stability phenomena in polymer dispersions.

The following brief review attempts to point out various aspects of the behaviour of WSPs relevant to the stabilization of aqueous dispersions, and to help those wishing to make a deeper study to locate relevant literature.

1. ADSORPTION BEHAVIOUR OF WATER-SOLUBLE POLYMERS

a. Adsorption on 'model' polymer dispersions

The favoured model disperse phase is 'cleaned' polystyrene latex. The method of preparation influences the surface $-SO_3H$, -COOH, and -OH groups, which probably affects results[1,38]. The usual type of isotherm is of the form shown in Figure 1[2,3]. The effect of the polymer in dispersion should be noted: polyvinyl acetate (PV-OAc) vs. polystyrene (PS). Polystyrene (much the more hydrophobic) shows a 'high affinity' type isotherm with polyvinyl alcohol - PV(-OH/-OAc) : 88/12 . The effect of the dispersed polymer[4] is also shown in the adsorption of bovine serum albumin on PS and polymethyl methacrylate (PMMA) in Figure 2. The importance of polymer polarity is also shown in adsorption studies with surfactants[39].

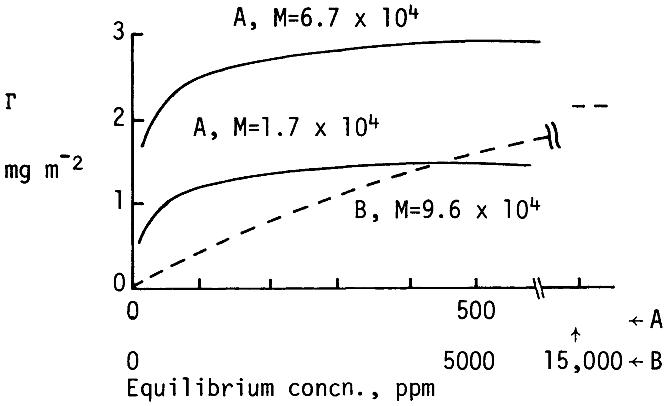

Figure 1. Adsorption of partly hydrolyzed polyvinyl alcohol (PV(-OH/-OAc): 88/12) on
A : polystyrene (PS) particles (Ref. 2), and
B : polyvinyl acetate (PV-OAc) (Ref. 3).

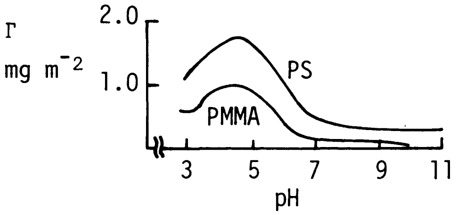

Figure 2. Effect of pH variation on the adsorption of bovine serum albumin on polystyrene (PS) and polymethyl methacrylate (PMMA) particles (From Ref. 4).

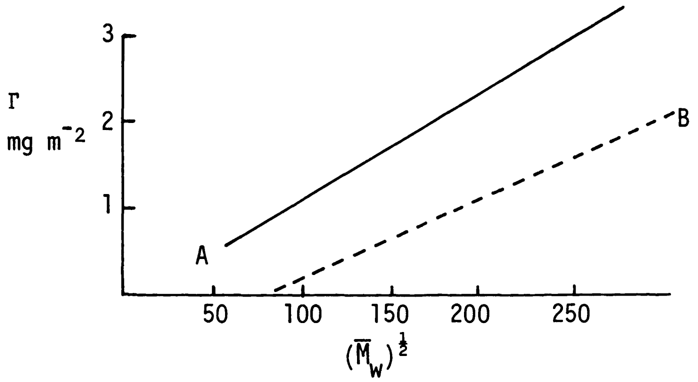

Figure 3. Plateau adsorption of partly hydrolyzed polyvinyl alcohol (PV(-OH/-OAc) : 88/12) on polystyrene and polyvinyl acetate particles, against molecular weight of polyvinyl alcohol.
A : polystyrene (PS) particles (Ref. 2)
B : polyvinyl acetate (PV-OAc) particles (Ref. 3).

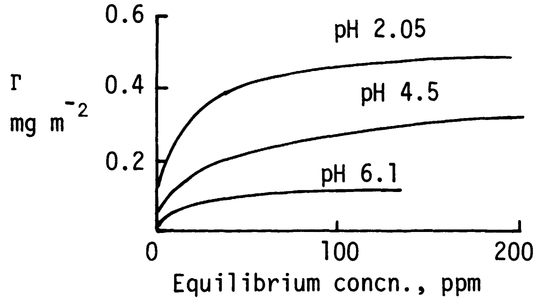

Figure 4. Adsorption isotherms of fully hydrolyzed polyvinyl alcohol (PV(-OH/-OAc) : 99/1) on 'Cabosil' at different pH values (from Ref. 5).

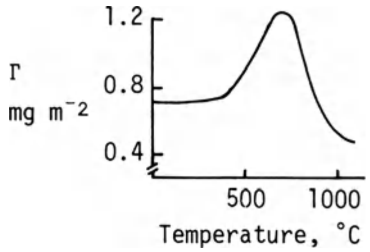

Figure 5. Effect of heat treatment of 'Cabosil' on partly hydrolyzed polyvinyl alcohol (PV(-OH/-OAc) : 88/12) plateau adsorption (from Ref. 5).

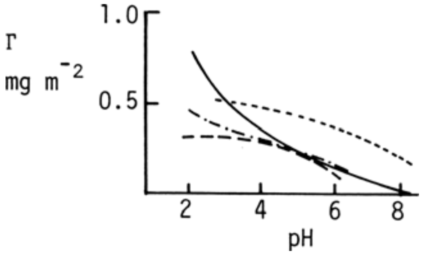

Figure 6. Plateau adsorption of polyvinyl alcohols on different silicas at various pH values (from Ref. 5).

———————————— 'Cabosil'/(PV(-OH/-OAc) : 88/12)
.... precipitated silica/(PV(-OH/OAc) : 98/2)
-.-.-.-.-.-.-.-.-.-.- 'Cabosil'/(PV(-OH/-OAc) : 99/1)
- - - - - - - - - - - - 'Ludox'/(PV(-OH/-OAc) : 88/12)

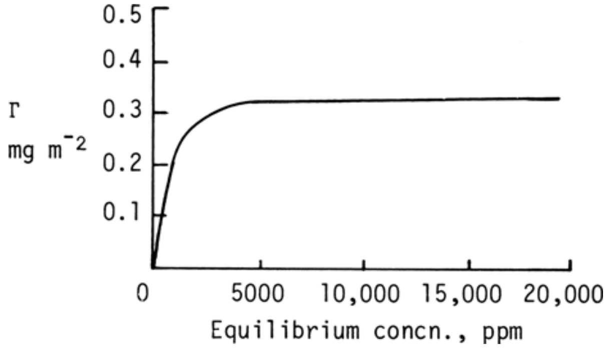

Figure 7. Adsorption of hydroxyethylcellulose (mol.wt. = 4.65×10^5) on r-titania (conventionally coated), specific surface (BET) = 8.36 m^2 g^{-1}. (from Ref. 7).

The molecular weight of the WSP affects the amount of polymer adsorbed[2,3].

b. Adsorption on inorganic dispersions

The adsorption of polyvinyl alcohol on silica is affected by the condition of the silica surface, and by the effect of pH on that surface[5], as shown in Figures 4,5, and 6, where it is notable that 'high affinity' type isotherms are observed at low pH. Adsorption isotherms of several WSPs on coated a- and r-titanium dioxide pigment have been published[6,7], e.g. as in Figure 7, which illustrates a 'low affinity' type isotherm. Polymeric carboxylic acids at pH 6.5 (polyacrylic acid NH_4^+ salt ?) on coated r-titanium dioxide pigment also show low affinity isotherms, although they are unusual in shape, and contrast with the adsorption of polyvinyl alcohol on to polystyrene illustrated in Fig. 1, which shows a decrease of adsorption with increasing molecular weight. These adsorption isotherms of polycarboxylic acids are shown[8] for two different types of coated r-titania in Figures 8a and 8b.

c. Effect of low molecular weight surfactants on adsorption

The adsorption of methylcellulose on PS in the presence of varying amounts of sodium dodecyl sulphate (SDS) has been determined. From the data shown[9] it does not appear that adsorption takes place is complete surface coverage with SDS has first been obtained.

The adsorption of hydroxyethylcellulose on poly(n-butyl acrylate) and poly(n-butyl methacrylate) latices prepared in the presence of SDS indicated a strong influence of the polymer, with no adsorption with poly(n-butyl acrylate) and a strong adsorption with the corresponding methacrylate polymer. Adsorption is prevented by the presence of sodium octylphenol polyoxyethylene ether sulphate, but polyacrylic acid adsorbed strongly on the latex particles under all conditions investigated[10].

Rheological measurements on emulsion paints have been used to investigate the effect of added surfactants - the results obtained were interpreted in terms of the interactions of the surfactants with the WSPs (HEC and MC) at the interface[11].

2. INTERACTIONS OF WATER-SOLUBLE POLYMERS WITH SURFACTANTS

Surfactants are frequently used with water-soluble polymers in preparing stable dispersions. The two types of stabilizer may interact to form associated complexes which may be more, or less, soluble in water than either alone. A review of the topic appeared in 1972[12].

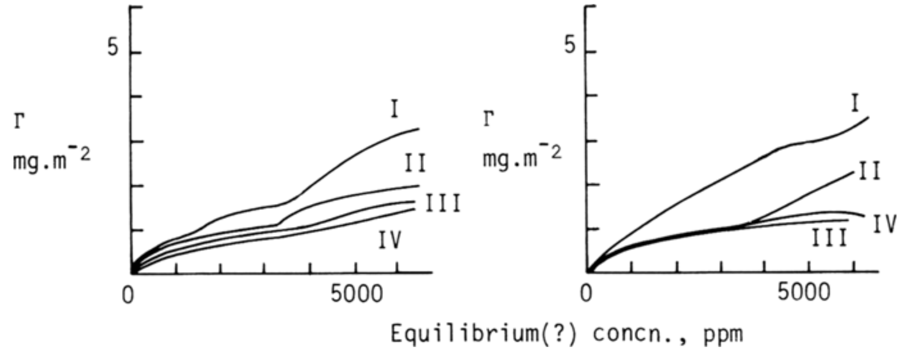

Figure 8. Adsorption of -COOH polymer (polyacrylic acid ?) on to two types of r-titania (Al$_2$O$_3$, SiO$_2$, ZnO coated), specific surface (BET) = 17.35 m.^{2} g.$^{-1}$(from Ref. 8). Mol.wt. × 10^{-4}: I = 0.87 ; II = 2.34; III = 5.38; IV = 8.26.

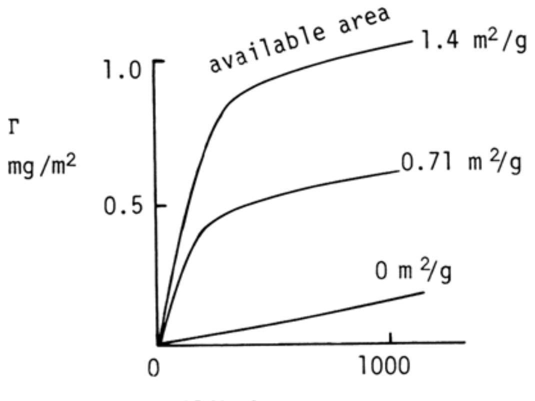

Figure 9. Adsorption of methyl cellulose on PS particles in the presence of sodium dodecyl sulphate (SDS) (from Ref. 9).

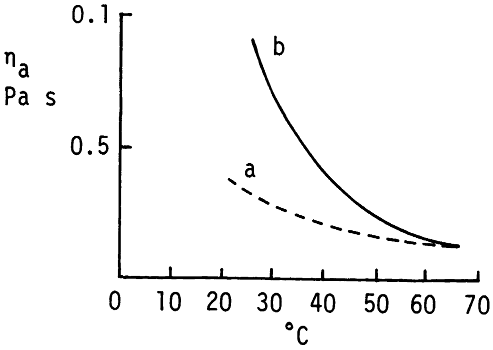

Figure 10. Viscosity change with temperature of 4 % aqueous solution of polyvinyl alcohol (PV(-OH/-OAc) : 88/12) (from Ref. 13)
a. alone b. with 1% SDS.

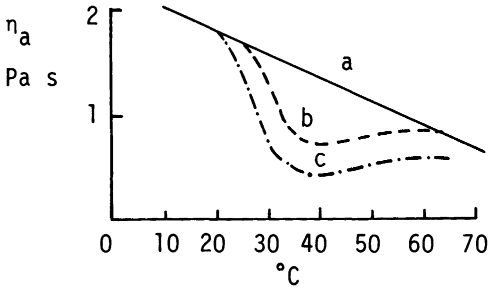

Figure 11. Viscosity change with temperature of 2 % aqueous solution of hydroxyethyl cellulose (HEC) with nonylphenolethoxylate-(9) (NP9EO) (from Ref.13)
a = 0; b = 1 %; c = 2%.

Generally, non-ionic WSPs with hydrophobic segments will adsorb molecules of surfactants which have large hydrophobic groups. With addition of anionic surfactants, e.g. SDS, the viscosity of the WSP solution will often increase. The relative increase in viscosity is less as the temperature is increased (Figure 10). The effect of an anionic surfactant on partly hydrolyzed polyvinyl alcohol solutions depends on the molecular weight, and on the degree of hydrolysis, as expressed as the OH/OAc ratio[13], as shown in Table 1. With non-ionic surfactants which have a low cloud point,

Table 1. Ratio of apparent viscosity of 4 % aqueous polyvinyl alcohol solutions containing 1 % sodium dodecyl sulphate (SDS) to apparent viscosity of similar solutions without SDS

Molecular wt. $\bar{M}_w$	OH/OAc Ratio 99.5/0.5	97.5/2.5	88/12	80/20
29×10^3			2.7	
84×10^3			12.8	
97×10^3	1.1	1.8	13.9	9.9
140×10^3			13.1	
176×10^3			15.0	

e.g. NP9EO (nonylphenolethoxylate-(9)), with a cloud point of 51°C, the effect may be to form a complex of reduced water solubility which has a lower cloud point than either component:'solution' viscosity is reduced , as shown in Figure 11[13].

3. EFFECTS OF WATER-SOLUBLE POLYMERS ADDED TO DISPERSIONS

A WSP is often used to modify rheological behaviour, although its effect on the dispersion, where stability is usually increased, is recognized, and employed, especially where extreme physical stress is applied to the dispersion - e.g. high shear, freezing, or high temperature.

Colour strength of pigments is linked to the degree of dispersion, as shown in Figure 12. A wide variation in colour strength with change of WSP has been noted[14], as in Figures 13 and 14.

When a WSP is not adsorbed, flocculation may occur by depletion of the free volume of dispersion medium between particles of the disperse phase[40].

Rheological effects[11,15,16,17] are frequently the topic of publications concerned with flow of paints during and after brushing, and the rate of recovery of 'structure', as shown in Figures 15, 16 and 17.

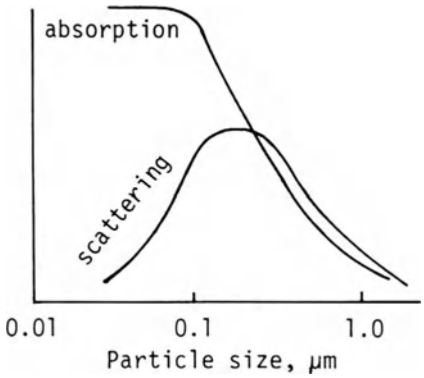

Figure 12. Effect of particle size on pigment strength (from Ref.14)

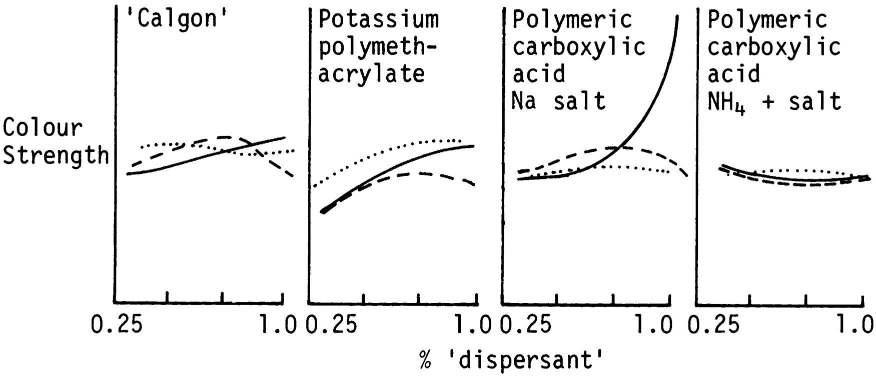

Figure 13. Effect of dispersant on colour strength for three organic pigments (from Ref. 14).

——————— Red 2G, --------- Yellow G, ... Blue G.

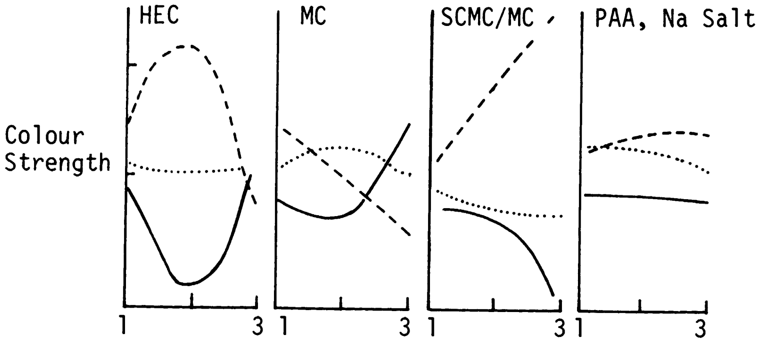

Figure 14. Effect of WSP on colour strength for three organic pigments (from Ref. 14)

——————— Red 2G, -------- Yellow G, ... Blue G.

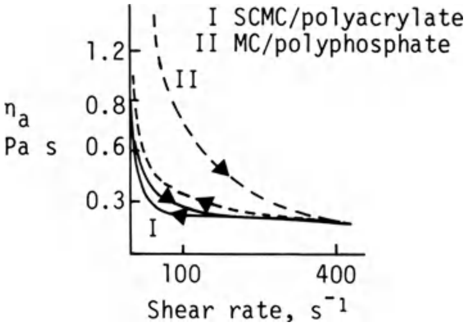

Figure 15. Viscosity of emulsion paints with increasing and decreasing shear (from Ref. 15).

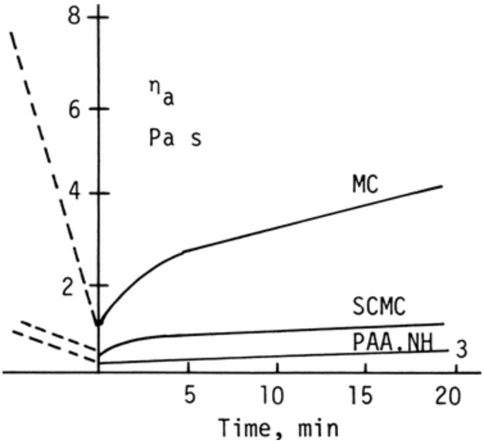

Figure 16. Viscosity recovery of 'emulsion' paints after high shear (from Ref. 16).

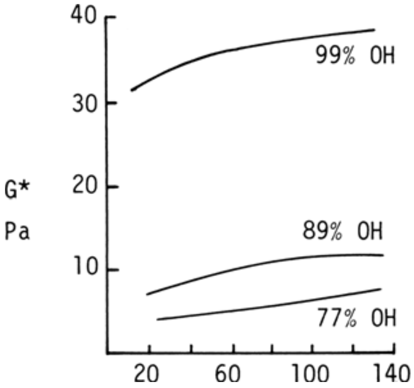

Figure 17. Polyvinyl alcohol-thickened emulsion paints. Time dependence of complex modulus recovery (from Ref. 17).

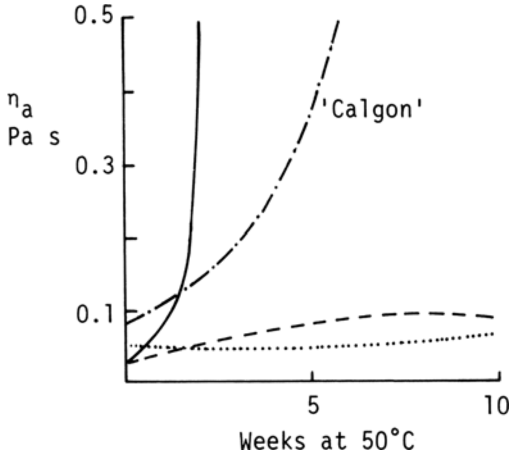

Figure 18. Viscosity of 'emulsion' paints on storage (from Ref. 18).

―――――――――――― 'PVA' with 'Calgon'
-------------- 'PVA' with polyacrylic acid, NH_4^+ salt.
-.-.-.-.-.-.-. 'Acrylic' with 'Calgon'.
.... 'Acrylic' with polyacrylic acid, NH_4^+ salt.

The stability to ageing at elevated temperature is also important. One WSP (believed to be an ammonium polyacrylate salt) is claimed to give good results in this respect[18] (see Figure 18), although an earlier publication[19] indicated a very powerful flocculating action (at ambient temperature) by the sodium salt of polyacrylic acid, giving a hard dispersible sediment, with flocs of $\leqslant$ 20 µm.

The sodium salt of polyacrylic acid[19] was compared with the effects of SCMC and MC. SCMC flocculated the pigment particles, but the paint lost 'structure' permanently on shearing: the flocs dispersed on brushing. MC produced large,loose pigment flocs and the paint did not lose 'structure' on shearing. References[7,10] above also discuss the phenomena of stability.

Other benefits accrue from the inclusion of WSPs in dispersions - e.g. 'water retention', which is a reduced rate of penetration of the aqueous suspension medium into porous substrates, permitting a uniform coating to be applied easily to paints, paper coating slurries, plaster, and cement pastes.

4. WATER-SOLUBLE POLYMERS AS STABILIZERS IN DISPERSION POLYMERIZATION

a. Technological aspects

Dispersion or 'emulsion' polymerization is of great importance in the manufacture of addition polymers of ethylenically unsaturated monomers. Heterogeneous polymerization of this type has been reviewed[20]. WSPs (especially special grades of partly hydrolyzed polyvinyl alcohol, and MC) are widely used for polyvinyl chloride (PVC) production: the amounts of WSP used are usually low, and the dispersion is maintained only during polymerization in an agitated vessel. Other polymers are also made by a closely related technique (e.g. styrene bead polymers). Many recipes using WSPs are to be found in patents. Stable fine particle size ($\leqslant$ c. 1 µm diameter) polymer dispersions ('emulsions') at high concentration are made in large quantity, for paints, adhesives, textiles and paper coatings from vinyl acetate (VA) and other vinyl esters, styrene (S), acrylic esters, and other monomers, frequently as copolymers, often as copolymers of two or more monomers.

Many WSPs have been quoted as stabilizers for PVA dispersions[21]. Those most often mentioned are partly hydrolyzed polyvinyl alcohol (usually the 88/12 type - a comprehensive review was published in 1973[22]) and low-medium viscosity grades of HEC[11].

A generalized recipe for the production of polymer dispersions is:

Monomer	100 parts by weight	
WSP	0 - 10	totalling rarely 10, often less.
Anionic surfactant	0 - 5	
nonionic surfactant	0 - 5	
Initiator	0.1 - 1.0	
Water	to give 40 - 65 % non-volatile after polymerization.	

Actual recipes may be more complex since:

i. The monomer may consist of 1 - 4 (or more) copolymerizable compounds;

ii. The WSP may be a mixture[21] of WSPs;

iii. The initiators are per-compounds (e.g. H_2O_2) or, occasionally) azo-compounds generating free radicals thermally or through addition of promoter ions and reducing agents (redox initiators);

iv. Buffers, radical transfer agents, etc., may also be included.

Many recipes for stable fine particle size dispersions are to be found in patents and technical sales literature published by manufacturers of monomers, WSPs and surfactants; each is designed to give specific technical effects in the intended end use.

The technique of polymerization may be to charge all ingredients to the reactor, and to heat under reflux (cooling once the polymerization commences, to maintain polymerization and steady reaction conditions) or (more often) to charge a portion of the ingredients initially, and to feed in the remainder gradually. Continuous emulsion polymerization has also been described. Partly hydrolyzed polyvinyl alcohol is often used when the polymer dispersion is intended for use as an adhesive: no surfactant need be employed if sufficient polyvinyl alcohol is used. The rheology of the dispersion produced varies with the type and quantity of polyvinyl alcohol - this is indicated by the results shown in Figures 19 and 20.

Variations are found in the behaviour of PV(-OH/-OAc) made by different techniques. These differences arise from variations in the molecular structure[23,24,25,26,27] originating in both stages (polymerization; hydrolysis) of manufacture. HEC is normally found only in recipes with other surfactants, usually giving a less viscous dispersion than PV(-OH/-OAc). Other types of WSPs, such as meth(acrylic acid) (co)polymers[28] and a number of special polyelectrolytes (e.g.[29,30,31]) have been described. Polyelectrolytes are used more often for styrene and acrylic ester (co)polymerization than for other monomers.

b. The function of WSPs in polymerizing dispersions

With bead dispersions, a simple mechanism in which the WSP stabilizes monomer droplets by adsorption at the interface whilst the droplets are polymerized may operate. However, chemical modification of the WSP is postulated for a PVC slurry polymerization.

The mechanism of formation of dispersions ('emulsion') is still the subject of much investigation. The consensus seems to be that using water-soluble initiators, the polymer grows in aqueous solution to a point where it becomes insoluble, when agglomeration takes place. The agglomerates are stabilized by adsorption of surface active materials from the dispersion medium and polymerization continues in the particles. Further adsorption takes place as particles grow. At the agglomeration point, association 'complexes' (cf. surfactants and WSPs) may be formed. However, due to the high concentration of free radicals the environment is highly reactive.

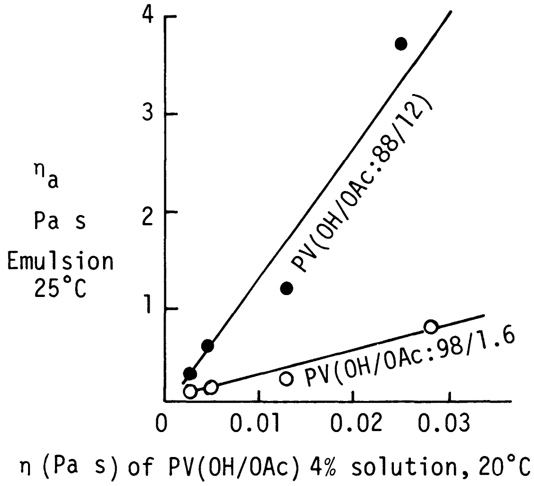

Figure 19. Viscosity of polyvinyl acetate emulsions in relation to the solution viscosity of partly hydrolyzed polyvinyl alcohol (PV(-OH/-OAc))(from Ref. 22)

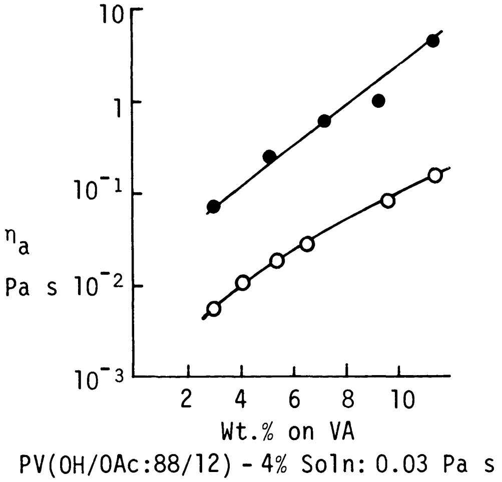

Figure 20. Solution viscosity of polyvinyl alcohol (PV(-OH/-OAc)) -o-o- and the resulting polymer emulsion viscosity -•-•- (from Ref.22).

In many cases, the WSP may participate in the polymerization reaction, with the production of graft polymers which stabilize the particles by means of the water-soluble portion at the interface. Grafting with PV(-OH/-OAc), HEC, and polyoxypropylene-polyethylene block copolymers in VA polymerization has been demonstrated[32,33,34]. When HEC is used, it is rapidly degraded in the free radical environment and the fragments may be the grafting entity. With growing radicals of high reactivity (such as S or acrylic esters), the WSP may become too greatly modified to be effective: recipes for stable acrylic and styrene polymer dispersions include radical transfer agents[35,36,37], which possibly inhibit the grafting reaction. Other influences on the stabilizing property of a WSP may result from surface groups derived from initiator - e.g. $-SO_3^-$ from $-S_2O_8^{--}$ (References[1,38]).

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MEDICAL AND PHARMACEUTICAL APPLICATIONS OF WATER SOLUBLE POLYMERS

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INTRODUCTION

The use of hydrophilic polymers in medicine and pharmacy cannot be regarded as of recent origin, but it is only in the last 30 years or so that the potential of custom made synthetic products has begun to be realized. Applications of water soluble in biology, medicine and pharmacy are diverse, but can be classified under three general headings:-

1. Therapeutic - polymers having some intrinsic biological activity or effect and used as remedial agents;
2. Biomedical/prosthetic - polymers having minimal biological activity or good biocompatibility, used to replace or augment natural tissue;
3. Pharmaceutical - polymers having no biological activity, used in drug formulation/dosage design.

The boundary between these separate classifications may be indistinct and the use of a hydrophilic polymer may encompass elements of all three effects.

1. POLYMERS USED THERAPEUTICALLY/PROPHYLACTICALLY

Both natural and synthetic polymers may be used as remedial agents - these may be further differentiated between those which have pharmacological activity, and those which are inert and do not affect cell viability.

The most obvious class of high molecular weight materials with pharmacological activity are the naturally occurring enzymes and polypeptides. Polypeptides are based on about 20 different α-amino-acids, but only the lower molecular weight peptides are amenable to total chemical synthesis. Advances in microbiology and gene manipulation have made possible the synthesis of high molecular weight proteins by genetic engineering. These high molecular weight pharmaceuticals include such compounds as insulin and the emergence of new types -e.g., interferons - which gives this class of drugs enormous potential.

Synthetic polymers, other than those based on poly(α-amino acids), can also exhibit biological activity. These polymers possess structural features which enable the polymer, or segments of it, to interact at the cellular level. Many of these polymers are polyelectrolytes and the synthesis, structure, and biological activity of polyanions has been recently reviewed[1,2]. Although by no means comprehensive, a variety of synthetic polymers with biological activity is listed in Table 1.

The most intensively studied copolymer is that obtained from the copolymerization of divinyl ether and maleic anhydride[3,16]. Its exact mode of action is uncertain, but its antiviral activity is thought to be due to interferon-stimulating effects These types of polymers also have antibacterial, antifungal, and anticoagulant properties. This last property may be explained in part by the surface active properties of the polyanion which leads to its adsorption onto platelets and other blood elements. Adsorption onto cell membranes may also help to explain the antibacterial activity.

A second class of active polymers are those in which the biologically active agent is covalently bound to, or complexed with, the water soluble polymer. The use of a water soluble polymer as a drug carrier can provide a useful method for controlling the administration of a drug substance, or its duration of activity or metabolism[12,17,18].

Low molecular weight polymers having amphipathic properties can affect cell viability. For example, the non-ionic ethoxylated alkyl phenols often are the active ingredients in topical vaginal contraceptives[19]. When adsorbed onto sperm, they alter membrane permeability, allowing intracellular fluids to escape into the extracellular medium, thus killing the sperm. Polyoxyethylene polymers have also been claimed to show anti-tuberculous effects[20].

Table 1. Synthetic polymers with biological activity

Maleic anhydride (co)polymers[3-10]	Antiviral, antitumour Anticoagulant
Acrylic acid (co)polymers[11]	Antimicrobial
Acrylamide (co)polymers[12]	Antiviral, anticoagulant
Bisguanidines[13]	Antibacterial
Sulphonamide polymers[14]	Antibacterial
Thiosemicarbazide polymers[15]	Antimicrobial,antiparasitic

In contrast to these active polymers, a number of water soluble resins have been shown to be inert in biological systems, and, for this reason, have found widespread application as plasma expanders to maintain or expand blood volume in cases of trauma. Clinically, the plasma expander should maintain a satisfactory osmotic pressure in increased blood volume by remaining in circulation for several hours. A molecular weight ($\bar{M}_w$) of 30,000 or more is required. The kidney threshold for clearance of water soluble polymers is about 50,000, so, in considering the use of a water soluble polymer, it is more important to consider the molecular weight distribution than the average molecular weight figure alone. The presence of very large molecules is undesirable, since they may cause erythrocyte aggregation. The plasma expander should have good biorheological properties and, when used, should impart to the blood volume flow properties which are not too dissimilar to those of blood. Following administration, the expander should not be retained by the body for periods longer than required. Polymers which have been evaluated as plasma expanders include polyvinyl pyrrolidone[21], dextran[22] and gelatin[23]. Other polymers considered for this application include polyaspartamide[24], and other polyacrylamide types[25].

Dextran is now the most widely used plasma expander. At molecular weights of 40,000 or less, the polymer is completely excreted in the urine within 48 hours, whereas with a molecular weight of 110,000 it can remain in the circulation for 2 - 3 days. High molecular weight dextrans (> 50,000) are removed from the circulation by the reticuloendothelial system, but, as dextranases are present in these tissues, they are ultimately degraded and excreted via the kidney.

Modified natural polymers, which are inert, are used in a variety of applications. Use of cellulose polymers are often dictated by their physicochemical properties such as clarity, viscosity, and swellability. Hypromellose is used as artificial tears and other cellulose derivatives - e.g. methyl cellulose - have found occasional use in the treatment of constipation as the water swellability of the polymer contributes to the bulk of the faeces and promotes peristalsis.

2. BIOMEDICAL/PROSTHETIC USES

Polymeric materials used in biomedical applications often have properties greatly different from the tissue with which they are interfaced or are replacing. In the field of biomaterials, considerable interest has focused on the utilization of the bulk or surface properties of hydrogels for biomedical applications[26,27]. In their physical characteristics, these materials resemble living tissue more than any other class of synthetic biomaterial (see Chapter 4). By definition, a hydrogel is a three-dimensional cross-linked network which swells, but does not dissolve in an aqueous environment. The cross-linking is usually covalent or ionic, but hydrogels may also be generated by linear amphipathic block copolymers[28], or block graft copolymers[29]. In general, as the water content of hydrogels increases, the physical properties (modulus, strength) tend to decrease, and consequently, these materials are usually designed to have water contents of ~ 40 - 80 %[27] (e.g., for soft contact lens applications). Hydrogels are usually prepared by the copolymerization of hydrophilic monomers, notably hydroxyethyl methacrylate (HEMA), in the presence of a cross-linking agent. An alternative synthetic approach is the conversion of existing polymers to a hydrophilic but water insoluble product[26].

The hydrogels most commonly considered are:-

(i) polyhydroxyalkyl methacrylates;
(ii) polyacrylamide and derivatives;
(iii) polymethacrylamide and derivatives;
(iv) poly(N-vinyl pyrrolidone);
(v) anionic and cationic hydrogels and polyelectrolyte complexes;
(vi) polyvinyl alcohol.

There are major differences for each type of material with respect to synthesis, properties and biocompatibility. For this reason, it is more appropriate to outline the advantages of hydrogels generally and to described their applications.

The principal clinical use for hydrogels is in soft contact lenses, which are usually based on polyhydroxyalkyl methacrylates. The equilibrium water content of the swollen matrix affects oxygen permeability, mechanical properties, and biocompatibility of the hydrated product[30]. The degree of hydration of the hydrophilic polymer is determined by such factors as the monomers used in the preparation, the nature and the density of the cross-linking agents, and the temperaturepH and ionic strength of the hydrating medium. Poly(hydroxyethylmethacrylate) is a neutral hydrogel and is largely unaffected by these factors unlike hydrogels based on polyelectrolytes or their complexes.

At equilibrium swelling, hydrogels are relatively soft elastic products and their non-abrasive character contributes to the bio-compatibility by reducing frictional irritation with surrounding tissues. Hydrogels are also permeable to body fluids and thus do not present an impermeable barrier to normal physiological processes. For these various reasons, they have been evaluated as soft and hard tissue prostheses, in duct and canal replacement, ocular surgery, as artificial organs and for sustained drug delivery[26,27].

As the surface and interfacial properties of hydrogels are somewhat similar to those of natural tissue, hydrogels have been used to improve the biocompatibility of hydrophobic biomedical materials[26]. When the hydrophobic material is coated with the hydrogel, a low interfacial tension may be exhibited at the interface of the coated product and tissue, reducing the tendency of proteins in body fluid to be adsorbed and so giving better biocompatibility. (When proteins are adsorbed on to surfaces they tend to undergo changes in chain conformation which can lead to their denaturation. This can lead to the initiation of adverse biological responses, including thrombosis and rejection of the prosthesis).

Various techniques are available for depositing hydrogel coatings , including:-

1. Dip coating - using a solution of hydrogel polymer. The hydrogel is not bonded to the surface;
2. Surface activation - activation of the surface to be coated, either chemically, or by high energy radiation, followed by polymerization of hydrophilic monomer, to give a surface grafted hydrogel[26].

Surface coating of a hydrogel on to a hydrophobic surface modifies polymer/tissue interaction and leads to materials with improved biocompatibility. Radiation grafted poly(hydroxyethyl methacrylate) hydrogels on cellulose acetate, for example, have a lower thrombo adherence than untreated cellulose acetate[31].

Hydrogels have been evaluated as coating materials in a number of applications involving sutures, IUD's, catheters, and vascular grafts. Although hydrogels do not have the mechanical properties required for use as surgical sutures, the have been examined as suture coatings. The differences in cell growth action between coated and uncoated sutures has been attributed to the hydrophilicity of the hydrogel in the coated suture[32,33].

A further example of the biomedical use of water soluble polymers is the development of dental cements for the permanent restoration of teeth. These applications utilize polymers with reactive functional groups, such as polyacrylic acid, which can be cross-linked in situ[34]. These systems are broadly classified as glass ionomer cements. Using certain types of ion-leachable glasses and solutions of polyacrylic acid, a hard insoluble gel is obtained when polyvalent cations are leached from the glass, and which then cross link the polyanionic chains.

3. PHARMACEUTICAL APPLICATIONS

The use of water soluble polymers in therapeutic systems is dominated by their pharmaceutical applications. Although widely used as processing aids, more importantly, they offer the formulator the opportunity to design and manufacture the most effective and practical dosage forms for drug delivery.

The most common forms of administration are oral and parenteral (subcutaneous and intramuscular) and as these (and other routes of administration) are often far removed from the site of action, the effect of the drug is dependent on the drug being released into some aqueous absorption pool and then entering the systemic circulation (Figure 1.). The absorption of the compound from the absorption pool is determined by such factors as its aqueous solubility, its concentration in solution , and rate of release into the absorption pool. These parameters are dependent on the nature and release properties of the dosage form.

The dosage form is a drug delivery system and drug formulations may be solids, suspensions or solutions. Their design has three component parts:-

(i) getting the drug to the target tissue;

(ii) supplying the drug at an adequately high level for a sufficient time for optimal therapeutic effect;

(iii) fabricating a delivery system to meet the needs of (i) and (ii).

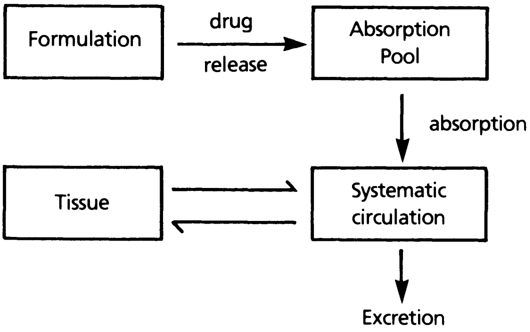


Figure 1. Absorption of drug into systemic circulation.

The use of water soluble polymers in the fabrication and design of dosage forms includes:-

Processing aids - granulating or binding agents;

Formulation aids - tablet coatings;

Tablet disintegrants - for rapid release of drug;

Controlled release agents - enteric coatings;

Capsules - hard and soft forms, based on gelatin;

Microcapsules - sustained release/repeat action dosage forms;

Sustained drug delivery - to extend duration of release and give sustained pharmacological effect;

Drug complexing agent - to increase bioavailability of poorly soluble drugs;

Drug carriers - to control administration, metabolism of a drug substance;

Dispersing agent - to maintain stability of suspensions;

Flocculating agent - to easily dispersed sediments;

Solubilizing agent - to maintain clarity of syrups and elixirs;

Stabilizing agent - to inhibit crystal growth in suspensions.

3.1 Processing and formulation aids; disintegrants

The oral route is the most common route of administration and the compressed tablet is the most frequently employed dosage form throughout most areas of the world. The compressed tablet offers both precision of dosage and convenience of administration but the maker also has to ensure that the medicament can be released in a predictable manner. Water soluble polymers often have a useful role to play in both facilitating the manufacturing process and assuring reproducibility of release from the finished tablet.

Materials for compression into a tablet must possess good flow characteristics and compressibility. Good flow characteristics are required in order that the tabletting die is filled reproducibly and easily prior to compaction. Improved flow properties are often achieved by granulation, which is the conversion of the powdered materials into aggregates or granules[35]. Both natural and synthetic polymers are used as binders or granulating agents and include gelatin, starch, and alginic acid, as well as modified cellulose polymers. Synthetic polymers, such as poly(vinyl pyrrolidone), which are soluble in organic solvents, are also used, particularly when water sensitive drugs are involved in the granulation process.

High drug concentrations in the absorption pool usually give rise to optimal bioavailability of drug and rapid disintegration of the table generates such high concentrations. Consequently, hydrophilic polymeric agents are incorporated, whose function is to overcome the binding forces in the tablet which have been generated under compression. Many disintegrants are polymeric species that swell or expand when exposed to gastric fluids. When hydrated, disintegrants exert sufficient mechanical pressures within the tablet to disrupt the binding forces or, alternatively, the disintegrant facilitates transport of water into the tablet, dissolving the binding agent and generating a hydrostatic pressure. Both synthetic (cross-linked and un-cross-linked) and natural polymers have been used as disintegrants, including alginates, cellulose derivatives, and poly(vinyl pyrrolidone).

3.2 Tablet coating

There are a number of advantages of using film coating, as polymer films provide only a small increase in tablet weight, whilst giving a durable protective coating which is resistant to cracking and can act as a protective barrier to light and air. Tablet coating can also mask taste and odour and minimise loss of active agent due to sublimation. Modified celluloses are most commonly used - e.g. hydroxypropyl cellulose, hydroxypropyl methyl cellulose, but other polymers including polyethylene glycol and poly(vinyl pyrrolidone) offer advantages for coating of water sensitive drugs.

These non-enteric coatings are soluble in all regions of the alimentary tract, in contrast to enteric coatings. The solubility of these is pH dependent, so they can be used for targetting release in the gastrointestinal tract. Enteric coatings include cellulose acetate phthalate and hydroxypropyl methyl cellulose phthalate. Other synthetic polymers which have been evaluated include maleic anhydride copolymers and copolymers of methyl methacrylate and methacrylic acid. Enteric coating polymers are not soluble in gastric fluid at $pH < 5$, such as that in the stomach, but are solubilized at $pH > 6 - 7$ in the upper part of the small intestine. Such coatings are used as:-

1. protection from nausea/distress when drugs capable of irritating the stomach are used;
2. protection of acid sensitive drugs from gastric fluids;
3. delivery of drugs for local action - e.g. intestinal antiseptics;
4. sustained release formulations.

3.3 Microencapsulation

In contrast to coating of tablets and the use of gelatin capsules, microencapsulation is a relatively new and expanding technology. Various techniques can be utilized to apply relatively thin coatings to small particles of solids or droplets of liquids in suspensions or dispersions. The unique feature of microencapsulation is the small size of the coated particles: uses of these coated products in dosage forms include protective coatings, sustained release formulations, and taste masking. Methods of microencapsulation include air suspensions, spray drying, interfacial polymerization, and coacervation phase separation[36-40]. The coating materials comprise a wide range of polymers and amongst the water soluble materials employed are gelatin, starch, poly(vinyl pyrrolidone) and cellulose derivatives.

3.4 Sustained drug delivery

The applications of sustained drug delivery is a large and expanding field: Its rationale and scope is discussed at length elsewhere[41-43]. The stimulus for this technology is the need to provide safer and more efficient means of drug delivery. Classical dosage forms can be inefficient in their utilization of medicament, as the active ingredient is not delivered to the target site of action at the precise time, in the quantities required for safe and effective therapeutic effect. This is illustrated in Figure 2. by comparing a typical drug concentration with the time profile for a conventional oral dosage form and one which has some element of sustained release in its design.

The most effective use of drug is shown in case B, as the drug persists in the circulation at an effective level for a longer period of time than in case A. The possibility of toxic side effects is also reduced, as very high blood levels are less likely to be achieved.

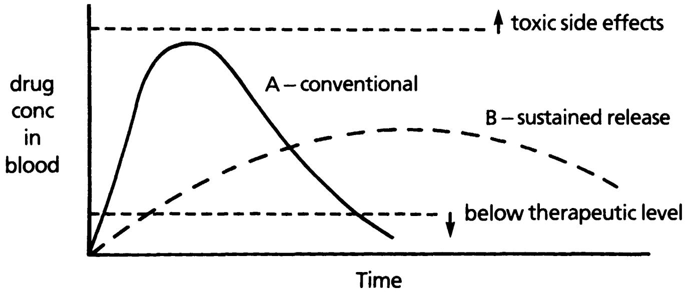


Figure 2. Drug concentration in blood for conventional and sustained release formulation.

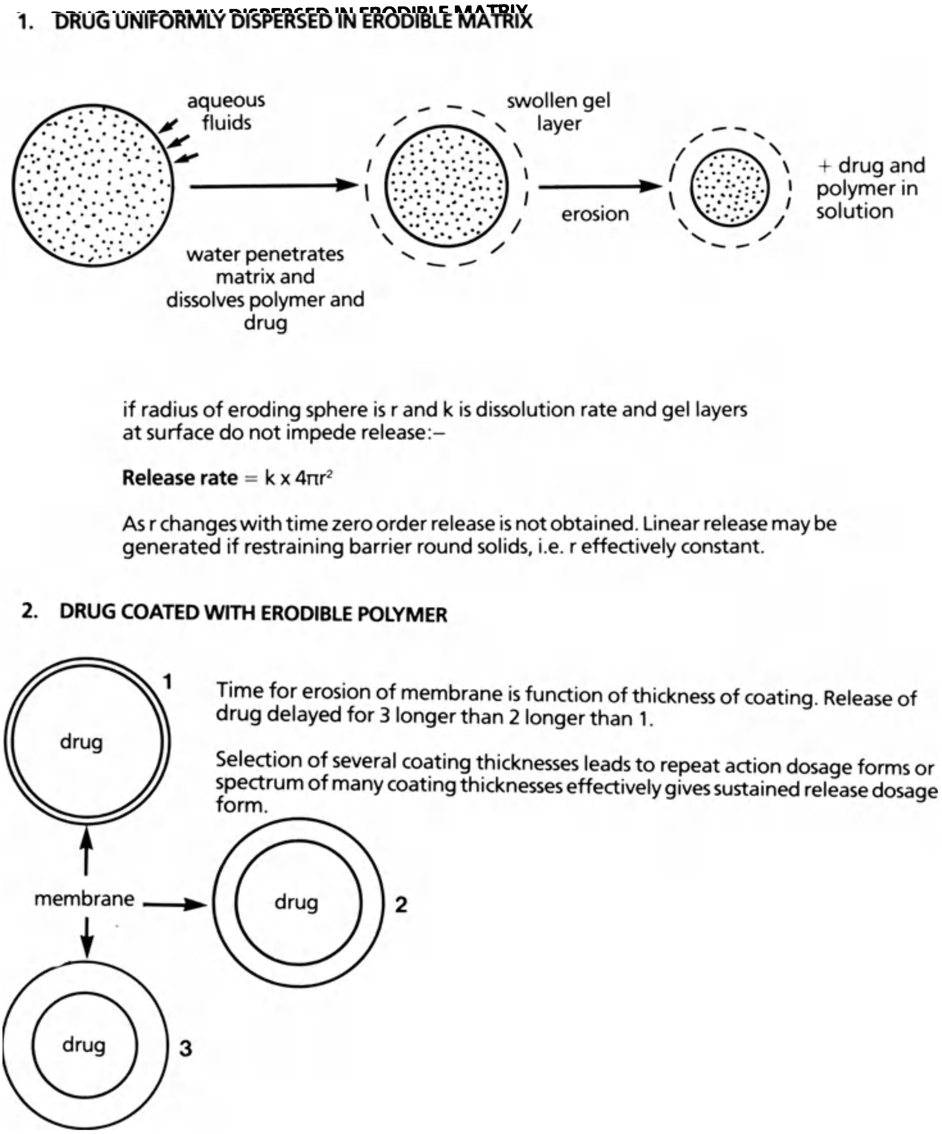
A basic assumption in formulating a sustained release product is that, whatever the route of administration, the delivery and maintenance of drug at the receptor site can be achieved by controlling the rate at which the drug moves from the dosage form to the absorption pool (Figure 1.). There are four basic physicochemical processes which give rise to transport of drug from the dosage form:-

1. Degradation;
2. Disintegration;
3. Dissolution;
4. Diffusion.

Degradation

Release consequent upon degradation can be achieved using water swellable, but insoluble polymers. Such materials can be generated by cross-linking hydrophilic polymers - e.g. gelatin: degradation or dissolution of this and other water soluble polymers have been shown to be enzyme mediated[44]. Alternatively, co-monomer units may be incorporated into hydrophilic polymers sufficient to render the high molecular weight species insoluble. Examples are synthetic polypeptides, which may be used for sustained drug delivery[45]. These biodegradable products allow drug release by both diffusional and degradation mechanisms.

The theoretical treatment for release of active agent from biodegradable products has been evaluated[40] for erodible materials with constant erosion rate. This predicts that, if degradation alone were the rate limiting step of release, then zero order release would be generated by a slab.



if radius of eroding sphere is r and k is dissolution rate and gel layers at surface do not impede release:–

Release rate = $k \times 4\pi r^2$

As r changes with time zero order release is not obtained. Linear release may be generated if restraining barrier round solids, i.e. r effectively constant.

Time for erosion of membrane is function of thickness of coating. Release of drug delayed for 3 longer than 2 longer than 1.

Selection of several coating thicknesses leads to repeat action dosage forms or spectrum of many coating thicknesses effectively gives sustained release dosage form.

Figure 3

Disintegration and dissolution of polymers

The disintegration and dissolution of pharmaceutical dose forms have long been of primary concern to the pharmaceutical researcher[47]. The rate of release of drug is intimately associated with the rate of decay of the dosage form in an aqueous environment.

Sustained release oral products employing dissolution as the rate limiting step are, in principle, the easiest to prepare. A drug with a slow dissolution rate is inherently sustained and even if a drug has a rapid rate of dissolution it is possible to incorporate it into a tablet with a carrier with a slow rate of dissolution. This effectively reduces or limits the rate of appearance of drug in the absorption pool. the two types of dosage form which release drug by dissolution of the matrix are the drug impregnated matrix, and encapsulated diffusion control[48] (Figure 3.).

When the drug is incorporated uniformly into a slowly soluble polymeric matrix its release is only constant if the surface area remains constant. For a slowly eroding delivery system, surface area changes, and, so, zero order release, only occurs if some restraining diffusion barrier is placed round the eroding solid. A wide variety of water soluble polymers may be used in this type of dissolution control, including polyethylene oxides, poly(vinyl pyrrolidone) and modified cellulose polymers.

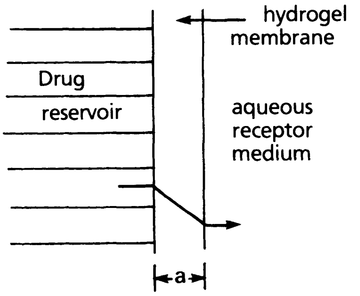
In practice, it is found that release of agent may be critically dependent on the molecular weight of the eroding polymer. Not only does this affect the rate of penetration of aqueous fluids and rate of dissolution, but molecular weight determines the magnitude and extent of aqueous swollen gel layers at the surface of the eroding tablet. These may act as a restraining diffusion barrier. This has been shown to be the case for simple water soluble salts in tablets based on poly(vinyl pyrrolidone) of varied molecular weight[49]. It is often the combination of slow solution rate and formation of viscous surface layers which makes water soluble polymers useful for controlling the release of drugs.

Encapsulated dissolution control in sustained release preparations refers to coating individual particles or granules of drug with varying thickness of slowly dissolving water soluble coating materials. The time required for dissolution of the coating is a function of both coating thickness and dissolution rate. Sustained release of agent can be achieved by using a mixture of particles with different thickness coatings. Coated particles may be compressed into a tablet or placed in gelatin capsules to give an easily administered and convenient dosage form.

Diffusion

In the absence of internal energy changes, the transport of matter is controlled by the difference in chemical potential between one region in space and another. Transport always takes place from a region of high concentration to a region of low concentration, If the initially high concentration resides within a polymer or a polymer membrane system, transport of the drug will be modified by the physical nature of the barrier polymer[50].

(a) Diffusion control by hydrogel membrane

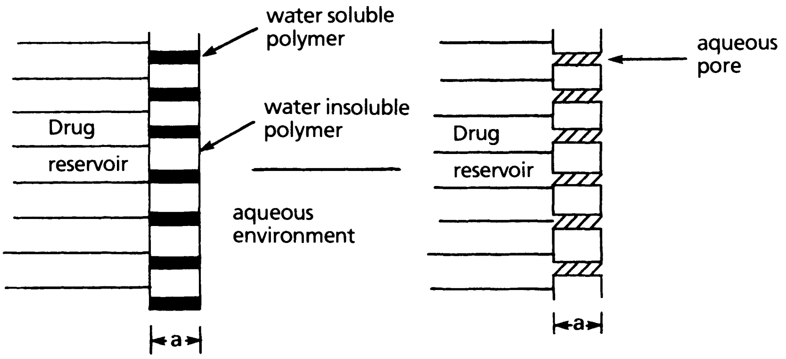


Amount of drug released (M) at steady state:

$$M = \frac{A.D.K.\Delta C.t.}{a}$$

where D is diffusion coefficient
A is surface area
K is partition coefficient
a is thickness of membrane
ΔC is concentration difference across membrane
t is time

(b) Diffusion control by partially erodible membrane, e.g. polyblend of water soluble and water insoluble polymers



When aqueous pores generated, release of drug is given by:

$$\text{Release rate} = \frac{A.D.\Delta C}{a}$$

where A is surface area
D is diffusion coefficient
ΔC is concentration difference across membrane
a is membrane thickness

Figure 4. Transport across membranes.

Two types of diffusional release are commonly encountered:-

1. Transport across membranes (Figure 4.)

In these, the active agent forms a core or reservoir surrounded by an inert diffusion barrier. The rate controlling membrane may be either a hydrogel, such as those based on polyhydroxyethyl methacrylate, or a polymer blend of a water insoluble species with a water-soluble one. In the former type of membrane, release of the drug is achieved by partition from the reservoir into the membrane and transport through it to the receptor medium. In the second type of membrane the water soluble component is leached out, generating aqueous pores through which the agent can diffuse - e.g., ethyl cellulose with methyl cellulose[48] or with polyethylene glycol[51]. In both cases, the release of drug is linear with respect to time over a major part of the period of release if the thermodynamic activity of the drug in the reservoir is constant - i.e., the drug exists as either a solid or a saturated solution in equilibrium with the solid. The use of polyhydroxyethyl methacrylate has been evaluated as the rate controlling membrane for the sustained delivery of narcotic antagonists[52], antitumour drugs[53], hormone and steroids[54], and macromolecules[55].

2. Matrix controlled diffusion

Two types of matrix controlled diffusion can be noted[50]:-

(a) the drug is insoluble in the matrix, but is uniformly dispersed;
(b) the drug is soluble in the matrix.

Hydrogels based on polyhydroxyalkyl methacrylates, polyacrylamides, and polyethylene oxides have been evaluated as the rate controlling elements for the release of low molecular weight drugs (prostaglandins[28], pilocarpine[56]) and high molecular weight drugs such as insulin[57,58]. In contrast to reservoir devices, where the release of the drug is of zero order, the desorption of the drug for matrix controlled diffusion follows a $(\text{time})^{\frac{1}{2}}$ dependency in the initial period of release[50]. The simultaneous release of drugs and swelling of a hydrogel/drug matrix has also been evaluated[59]. (In these delivery systems, the active agent is reversibly entrapped, but hydrogels have been used for immobilization of proteins and enzymes for a range of biomedical applications[26,60]).

3.5 Drug complexing agents

Certain drugs, for example digitoxin[61], reserpine[62], and griseofulvin[63], have poor bioavalability not because they have poor intrinsic absorption, but because they have low solubility and a low rate of dissolution in gastric juices. Increased bioavailability can be achieved by using specific interactions which occur between these drugs and polymers such as polyvinyl pyrrolidone and polyethylene oxide. These drug-polymer complexes may assume various forms, ranging from solid solutions to co-precipitates[61-63]. In an aqueous environment, these may dissolve to generate high concentrations of drugs and although these solutions are intrinsically metastable, absorption of the compound occurs prior to precipitation of active agent.

Water soluble polymers such as polyvinyl alcohol and poly(vinyl pyrrolidone) form stable complexes with iodine[64,65] which have excellent antibacterial activity and find use as antiseptics.

3.6 Stabilization of dispersions/controlled flocculation

Water soluble polymers are widely used in liquid pharmaceutical preparations as stabilizers or to induce controlled flocculation. The bulk viscosity of a polymer solution determines its effectiveness as a suspending agent for solids. The high viscosity of the medium decreases the sedimentation rate of suspended particles and, in liquid dispersions, inhibits coalescence of particles. In addition, adsorption of polymer on to the surface of the particle results in the modification of surface properties and gives rise to steric stabilization[35,66] (Figure 5a.).

Conversely, the same polymers which may provide steric protection when effectively coating the particle may promote flocculation when adsorbed a low surface coverage by bridging between particles, generating a structure in the dispersion. As pharmaceutical suspensions usually involve particles of > 1 μ, almost all these suspensions separate on standing, if given sufficient time to sediment. In consequence, the major concern of the formulator is not to eliminate separation, but to decrease sedimentation rate and ensure resuspendability. Resuspendability of sediment resulting from a completely deflocculated system is difficult, as the sediment tends to form a compact cake. Water soluble polymers are therefore used at low surface coverage to achieve loose dispersible sediments. The high molecular weight polymer forms bridges between adjacent particles and compact sedimentation is prevented because the steric stabilization factor effectively lowers the coordination number of a particle with respect to its nearest neighbours[67,68] (Figure 5b).

Water soluble polymers have also been used to maintain the stability of aqueous solutions of crystalline materials. Particles in these suspensions tend to undergo dissolution and recrystallization with the result that particle size distribution changes with time. Mant steroids which have low solubility in water do not give stable suspension when the particle size is < 1 μ if crystal growth inhibitors are absent.

Growth rates of crystals may be inhibited by many water soluble polymers which are adsorbed at the crystal/water interface, thus preventing and inhibiting dissolution of drug molecules. Nonionic surfactants at very low concentrations can stabilize suspensions of steroids and gelatin and poly(vinyl pyrrolidone) retard the crystal growth of sulphathiazole in water[67].

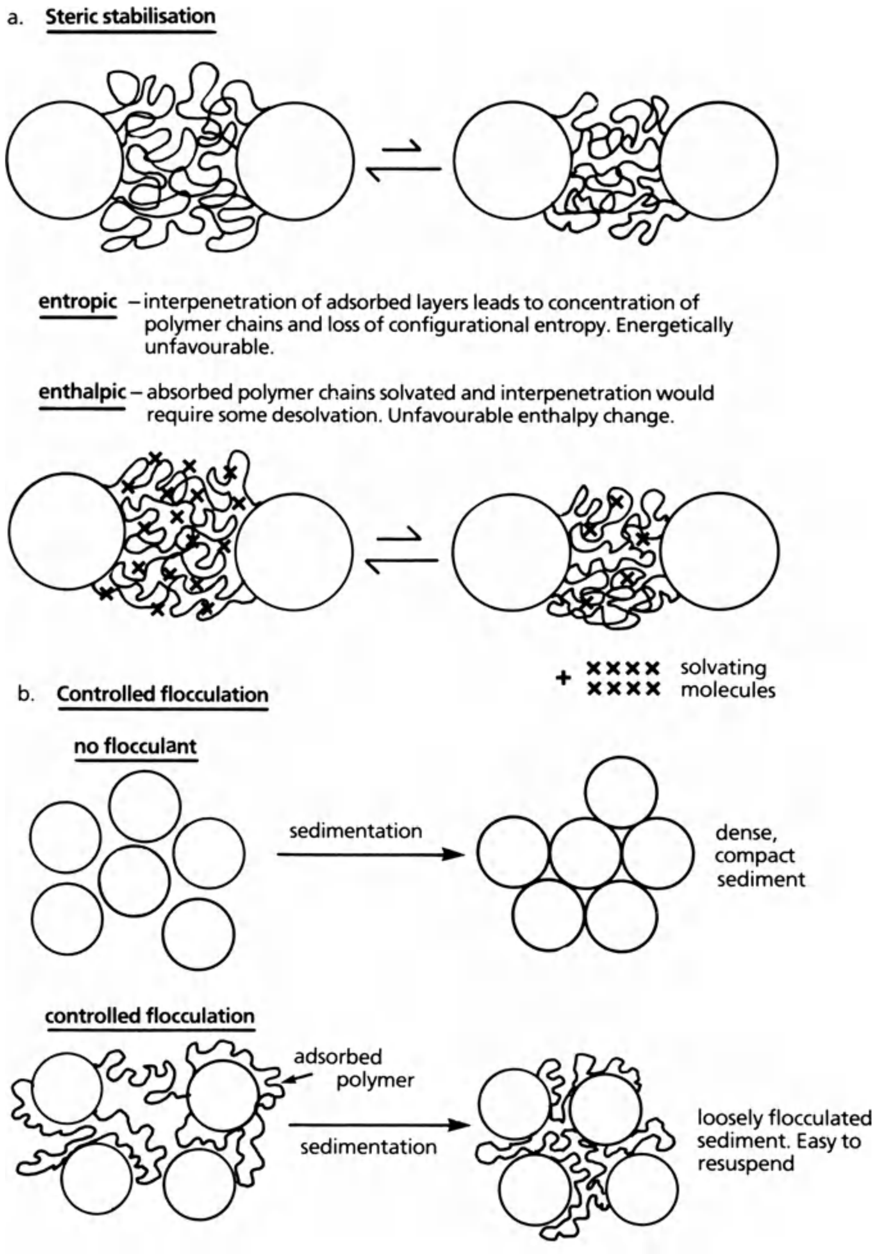


Figure 5. Mechanisms of steric stabilization and controlled flocculation.

4. CONCLUSION

The most important applications of water soluble polymers in medicine and pharmacy are dependent on whether the polymer is inert or interacts with body tissues and also upon the bulk, surface, and solution properties. At present, the most practical and general use of water soluble polymers lies in the systemic formulation of pharmaceuticals.

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SOME PROPERTIES OF POLYVINYL ALCOHOL AND THEIR POSSIBLE APPLICATIONS

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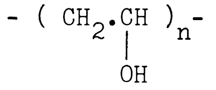
1. INTRODUCTION

Some of the more specialized properties of polyvinyl alcohol are considered, in relation to the apparent structure of the polymer. These properties include the water solubility of polyvinyl alcohol in relation to its molecular structure, the diffusion properties of polyvinyl alcohol film, compared with those of other polymer films, and the relation between heat treatment (and the consequent increased crystalinity) on the density of the polymer.

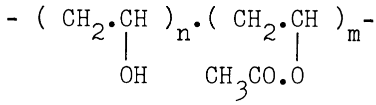
2. GENERAL

Although the term 'polyvinyl alcohol' is widely used to indicate a polymer of the general structure



$$-(CH_2.\underset{OH}{\underset{|}{C}H})_n-$$

it is realized that this terminology is, at best, incomplete, and, in fact, misleading, since there are many variables within the general structure[1]. A more satisfactory general representation is given by



$$-(CH_2.\underset{OH}{\underset{|}{C}H})_n.(CH_2.\underset{CH_3CO.O}{\underset{|}{C}H})_m-$$

although this does not indicate the features of non-random acetate side-group distribution, and of the presence of side-chains, both of which are of significance in relation to the physical properties, especially the solution properties, of the polymer. The principal structural variations in the polymer are:-

a. chain length;

b. chain length distribution.

As with other vinyl polymers, there are also the variables of:-

c. chain branching;

d. chain branching distribution;

e. side-chain stereoregularity.

More specific to 'polyvinyl alcohol' is:-

f. the degree of hydrolysis, or, alternatively, the degree of acetylation.

All these structure features affect the solution and solid properties of the polymer, but are rarely, if ever, defined satisfactorily in polymers used for industrial purposes. The nominal description of grades of commercial 'polyvinyl alcohol' provides only a limited guide (Table 1). The 'degree of hydrolysis'(f.) (usually expressed as the molecular %) is, essentially, based on a determination of the amount of added alkali solution under standard conditions. Alternatively, the proportion of non-substituted acetate groups can be expressed by the 'Ester Index', which is, by definition, the number of mg of KOH needed to saponify 1 gm of polyvinyl alcohol completely.

The viscosity (of a 4 % aqueous solution at 20°C) which is a measure of the size and shape of the molecule in solution, and an indication, more or less direct, of all the other structural features (a.) - (e.) above. It is well known[2] that the nature of several, if not all, of these features is related to the methods and condiitions of polymerization of the polyvinyl acetate from which the polyvinyl alcohol is prepared. Since these conditions are rarely, if ever, published for commercial polymers, the quoted properties of such polymers should be viewed with some suspicion, even if the viscosities and degrees of hydrolysis are nominally similar. It should also be realized that commercial polyvinyl alcohols may be prepared to a particular 'specification' by blending separate polymers of possibly different origins and properties: this process will tend to broaden the range of the variables (b.), (d.), and possibly (e.) above.

The effect of this considerable uncertainty is that it is difficult, if not impossible, to make detailed comparisons of the 'secondary'properties of polyvinyl alcohols of nominally similar specifications, in terms of viscosity and degree of hydrolysis. An outline comparison of commercial polyvinyl alcohols is given in Table 1, which shows only approximate equivalents, which are likely to differ in solubility, surface activity, and other properties of industrial importance. The typical solubility behaviour of a range of Poval grades in water, is relation to the degree of hydrolysis of polymers of viscosity 24 - 30 Pa s at 20°C (nominal degree of polymerization = 1750; approx. molecular weight 75,000 - 80,000) is shown in Figure 1. The presence of a small number of residual acetate groups can cause significant changes in the solubility at 40 - 60°C, as shown in Figure 2.

2. FILM SOLUBILITY AND SWELLING IN WATER

The solubility of polyvinyl alcohol films - such as those which are deposited on synthetic fibres during warp sizing - varies to a significant extent with the heat treatment during which the film is dried, and can be of considerable economic importance in the de-sizing process. Heat treatment causes the crystallinity of fully hydrolyzed polyvinyl alcohol to increase, so reducing their solubility in water (Figure 3). In practice, films of fully hydrolyzed grades do not lose their solubility if the heat treatment temperature is kept below 100°C. Partly hydrolyzed grades (87 - 89 % hydrolysis), however, maintain almost the same water solubility (at 40°C) unless they are subjected to the relatively severe treatment of 180°C for 1 hour. In recent years, problems of insolubility , in the de-sizing of fibres treated with polyvinyl alcohol-based sizes (notably polyester fibres), have been reduced by the introduction of small amounts of acidic groups into the sizing polymer, either by copolymerization or by grafting.

The crystallinity of polyvinyl alcohol is related to(density)$^{-1}$, as shown, for an experimental series of fully hydrolyzed polymers (Figure 3). It has been suggested that the marked decrease in solubility observed with more severe heat treatment is due to the impedment of the water solubility by an increase in the rigid junction points formed in the amorphous regions of the polymer[3]. Solubility, therefore, depends on the degree of crystallinity and on the structure of the amorphous regions. As indicated above, the nature of these regions, especially, are likely to depend on the randomness (or otherwise) of residual acetate groups, and of branching, of the polymer chain. Both properties are affected by the conditions of polymerization to polyvinyl acetate, and its subsequent hydrolysis.

In practice, polyvinyl alcohol films are dired at about 100°C when deposited from aqueous solution: this does not significantly reduce solubility. Heat treatment at 180°C can be used to impart

Table 1. Some typical commercial grades of polyvinyl alcohol.

Viscosity cP (Pa s) (4 % aqueous soln. at 20°C)	Degree of hydrolysis (mol. %)	Degree of polymerization (Note 1.)	Grade (Note 2.)
A. Low hydrolysis grades			
4 - 6	73 - 74	-	Rhodoviol 5/270P
20 - 30	74.5 - 79	1600	Polyviol W25/240
-	78 - 81	2100 - 2150	Poval PVA-420
32 - 38	78.5 - 81.5	< 1500	Gohsenol KH 17
44 - 52	78.5 - 81.5	< 1500	Gohsenol KH 20
4 - 6	80 - 82	-	Rhodoviol 4/200P
20 - 30	81 - 84	1600	Polyviol W25/190
20 - 30	81.5	-	Rhodoviol 25/200M
8 - 12	83 - 87	-	Shin-Etsu L 11
B. Medium hydrolysis grades (86 - 89 % hydrolyzed)			
4 - 6		300 - 600	Denka B-05
			Gelvatol 20 - 30
			Gohsenol GL 05
			Mowiol 8 - 88
			Polyviol V.03/140
			Poval PVA-204
			Rhodoviol 4/125P
			Shin-Etsu P 05
10 - 20		800 - 1400	Gohsenol GM 14L
			Mowiol 18 - 88
			Polyviol M13/140
			Rhodoviol 14/135 P
20 - 30		1700 - 2100	Gelvatol 20 - 60
			Gohsenol GM 14
			Gohsenol GH 17
			Polyviol W25/140
			Poval PVA-217
			Poval PVA-220
			Rhodoviol 30/20M
			Shin-Etsu P 18
			Vinol 523

Viscosity cP (Pa s)	Degree of hydrolysis	Degree of polymerization	Grade	
40 - 60		2200 - 2600	Denka	D 24
			Gelvatol	20 - 90
			Gohsenol	GH 20 GH 23
			Mowiol	40 - 88
			Polyviol	W40/140
			Poval	PVA-224
			Rhodoviol	50/125M
C. High hydrolysis grades (97 - 99 % hydrolyzed)				
4 - 6		300 - 600	Denka	K 05
			Elvanol	70-05
			Gelvatol	1 - 30
			Mowiol	4 - 98
			Polyviol	V.03/20 M.05/20
			Poval	PVA-105
			Rhodoviol	4/20P
10 - 20		800 - 1200	Mowiol	10 - 98
			Polyviol	M.13/20
			Rhodoviol	16/20P
20 - 30		1700 - 2000	Denka	K 17
			Elvanol	71-24
			Elvanol	71-30
			Gelvatol	3 - 60
			Gohsenol	AH 17
			Mowiol	20 - 98
			Polyviol	W.28/20
			Rhodoviol	30/20M
			Shin-Etsu	M 17
			Vinol	125
40 - 60		2400 - 2500	Denka	K 24
			Elvanol	72-51
			Elvanol	72-60
			Gelvatol	1 - 90
			Gelvatol	3 - 90
			Mowiol	42 - 98
			Mowiol	56 - 98
			Polyviol	W.48/20
			Poval	PVA-124
			Rhodoviol	60/20M
			Vinol	325
			Vinol	350

Table 1.(Cont.)

Viscosity cP (Pa s)	Degree of hydrolysis	Degree of polymerization	Grade
D. Completely hydrolyzed grades (99 - 100 % hydrolyzed)			
10 - 20			Gohsenol NM 11
25 - 35		1600	Elvanol 100-30 Gohsenol NH 17 Poval PVA-117H Polyviol W.28/10 Shin-Etsu A
35 - 45			Denka K 20E Gohsenol NH 20
55 - 65			Denka K 24 Elvanol 100-60 Poval PVA-124H

Notes: 1. Calculated from viscosity data: approximate data only, since the assumptions made concerning polymer shape in solution are of uncertain validity.

2. Trade names.

Denka	Denka Kagaku Kogyo K.K., Tokyo, Japan.
Elvanol	E.I.Du Pont de Nemours & Co., Inc., Wilmington, U.S.A.
Gelvatol	Monsanto Inc., St.Louis, U.S.A.
Gohsenol	Nippon Synthetic Chemical Industry Co.Ltd., Osaka, Japan.
Mowiol	Hoechst A.G., Frankfurt, Germany.
Polyviol	Wacker-chemie G.m.b.H., Munich, Germany.
Poval	Kuraray Co. Ltd., Osaka, Japan.
Rhodoviol	Rhone-Poulenc S.A., Paris, France.
Shin-Etsu	Shin-Etsu Chemical Industry Co. Ltd., Tokyo, Japan.
Vinol	Airco Inc., Allentown, PA., U.S.A.

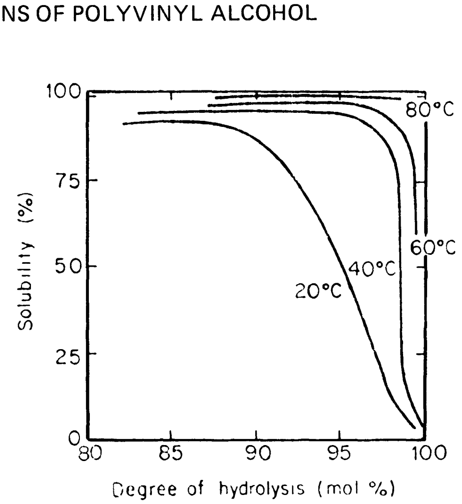


Figure 1. Relation between solubility in water and degree of hydrolysis of polyvinyl alcohol of nominal degree of polymerization = 1750

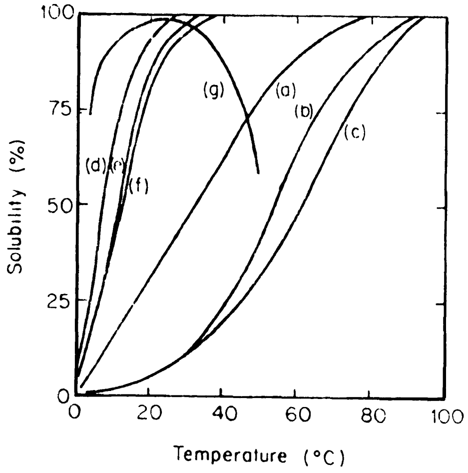


Figure 2. Relation between solubility in water and solution temperature for polyvinyl alcohol of different degrees of hydrolysis and nominal degrees of polymerization

	Hydrolysis (mol %)	degree of polymerization
(a)	98 - 99	500 - 600
(b)	98 - 99	1700 - 1800
(c)	98 - 99	2400 - 2500
(d)	87 - 89	500 - 600
(e)	87 - 89	1700 - 1800
(f)	87 - 89	2400 - 2500
(g)	78 - 81	2000 - 2100

water resistance , but this temperature should not be exceeded, since thermal decomposition begins to occur above 200°C.

Swelling of films of the polymer shows a roughly similar pattern of behaviour to that of solubility, as may be expected. When conditions of film formation are identical, the degree of swelling has a direct relation to the degree of crystallinity, irrespective of the degree of polymerization. Water swelling is governed not only by the degree of crystallinity (measured by X-ray) and by the average chain length of the amorphous regions, but also by the presence of residual acetate groups, which tend to decrease crystallinity, thus causing an increase of the swelling in water.

4. SOLUBILITY IN ORGANIC SOLVENTS

Polyvinyl alcohol films are highly resistant to organic solvents and oils. The resistance tends to increase with increasing degree of hydrolysis, but there appears to be no significant difference in the solvent resistance of low, medium and high viscosity grades, within the same degree of hydrolysis range. Swelling behaviour, which is generally similar, is indicated in Table 2. However, polyvinyl alcohols with a degree of hydrolysis less than about 73 % are insoluble in water or ethanol alone, but are soluble in ethanol-water mixtures containing up to about 70 % ethanol: signifcant amounts of methanol, ethanol, and isopropanol can be added to aqueous solutions of medium hydrolysis polyvinyl alcohols. On rather limited evidence[4], based on the observed interaction parameters, χ, for a small number of solvents, including acetamide, dimethyl formamide, glycerol, and ethanediol, it has been suggested that the value of χ tends to decrease with the solvent with the greatest tendency to form intramolecular hydrogen bonds.

In practical terms, with changing economic climates, there appears to be an interesting area for development of alcohol-water based systems, replacing organic-solvent systems, notably in surface coating and other film-forming applications, using, as the film forming polymers, polyvinyl alcohols with a very low degree of hydrolysis, as indicated above. Unfortunately, these polymers, although produced some years ago, have had only limited commercial availability in recent years.

5. PROPERTIES OF POLYVINYL ALCOHOL FILMS

Unsupported film cast from aqueous solutions of polyvinyl alcohol containing a plasticiser, such as glycerol, is transparent, tough, tear and puncture resistant, with good gas barrier properties, and good solvent and oil resistance, if the fully hydrolyzed polymer

Table 2. Swelling resistance of films of polyvinyl alcohol (viscosity of 4 % aqueous solution at 20^{o}C = 20 - 25 Pa.s) (nominal degree of polymerization = 1700) to organic solvents.

	Degree of hydrolysis(%)	Benzene	Isooctane	Monochloro-benzene	CCl_4	Soya oil	Light hydrocarbon oil
Swelling (% by weight)	98 - 99	- 0.6	- 0.5	- 0.8	- 0.5	-0.4	- 0.2
	87 - 89	- 1.3	- 1.1	- 1.4	- 1.1	-0.6	- 0.9
Swelling (% by area)	98 - 99	- 1.6	- 2.6	- 2.4	- 2.0	-1.2	- 0.3
	87 - 89	- 2.4	- 2.3	-1.4	- 0.9	-1.0	- 1.3

Source: Modified from Ref. 1, p.377.

is employed, whilst those made from partly hydrolyzed polymer are hydrophilic. The property of water resistance can be further enhanced by cross-linking with borax or glyoxal, or with formaldehyde-releasing agents, such as urea or melamine resins (see also Chapter 5). Water resistance, as indicated above, can also be obtained by promotion of crystallinity by controlled heat treatment (see Figure 3.). The tensile strength of polyvinyl alcohol films is markedly increased by orienting by stretching - typically, stretching by five times increases the tensile strength by a similar factor.

The hygroscopicity and the solubility of water vapour in films increase with lower degrees of hydrolysis, so that the water-vapour permeability coefficient is also increased, together with the solubility and degree of swelling. Heat treatment reduces hygroscopicity and water vapour permeability. The permeability of polyvinyl alcohol films to different gases, under various conditions, are compared in Tables 3 - 9, calculated from available data. Unfortunately, in some cases, the original sources do not provide details of the polymers under test, so comparisons can only be relative, and no absolute conclusions can be drawn. However, the following points can be indicated from the data available:-

- Polyvinyl alcohol films have a high degree of impermeability to many gases, especially oxygen, compared with other polymers commonly used for packaging applications (Tables 3 and 4);
- The permeability to water vapour (and also to ammonia, although no detailed data is available), especially of plasticized films, is considerably higher(Tables 6 and 9);
- The permeability of polyvinyl alcohol films to oxygen is also dependent on the level of plasticizer (normally glycerol) present in the polymer , in a roughly linear pattern (Tables 5 and 6);
- The rate of permeability increases with the relative humidity of the atmosphere at the faces of the polymer film, for both water vapour (Tables 6,8 and 9) and oxygen (Table 7);
- The rate of vapour permeability increases with temperature (Table 7).

The results of a simple test of the practical application of polyvinyl alcohol film, in comparison with other polymers used in packaging, are shown in Table 10, where the time to the first observation of odour passing through the films gave an indication of the practical value of the film.

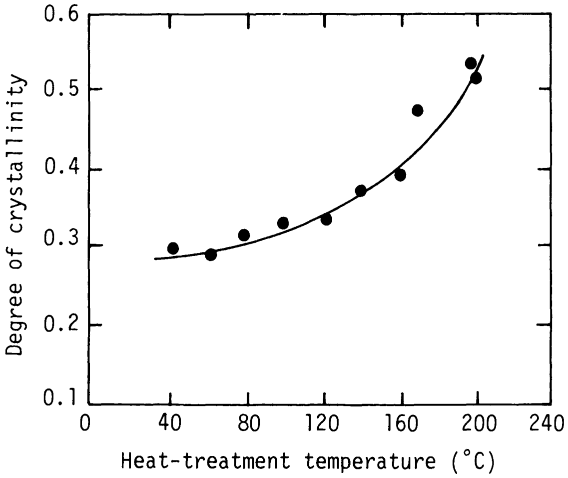


Figure 3. Effect of heat treatment on crystallinity of polyvinyl alcohol.

Table 3. Comparative oxygen permeability of polymer films (Ref.6)

	P_{O_2} (ml cm/cm^2 s cm Hg)
Polyvinyl alcohol	6.24×10^{-17}
Cellulose	8.94×10^{-14}
Polyvinylidene chloride	2.76×10^{-13}
Nylon 6	6.17×10^{-13}
Polyethylene terephthalate	2.45×10^{-12}
High density polyethylene	6.13×10^{-11}
Polypropylene	1.37×10^{-10}
Low density polyethylene	3.07×10^{-10}

Table 4. Vapour permeability coefficients for carbon dioxide, P_{CO_2}, and for 'Freon', P_F. (Ref. 7)

	$P_{CO_2} \times 10^{11}$ (ml cm/cm^2 s cm Hg)	$P_F \times 10^{11}$ (ml cm/cm^2 s cm Hg)
Polyvinyl chloride	2.0	0.18
Natural rubber	1030	109
High density polyethylene	20	4.6
Low density polyethylene	120	10.8
Polyethylene terephthalate	1.6	0.4
Polyvinyl alcohol	0.01	< 0.01

Table 5. Oxygen permeability through polyvinyl alcohol (viscosity 28 - 32 Pa s ; 99 -99.8 % hydrolyzed) containing 16 % glycerol at 3°C.

Relative humidity	P_{O_2} (ml cm/cm^2 s cm Hg)
60	$< 1.6 \times 10^{-7}$
60 - 80	$< 8.0 \times 10^{-7}$
100	$< 2.1 \times 10^{-9}$

(Source: Du Pont)

Table 6. Water vapour transmission rates of plasticized polyvinyl alcohol films (98 - 99 % hydrolyzed; viscosity 25 - 31 Pa s) in relation to plasticizer content.

Film thickness: 0.02 mm
Temperature : 40°C
Relative humidity (%) of film faces: 0/90

Glycerol content (%) (based on polymer)	$P_{H_2O} \times 10^8$ (g $H_2O/m^2/s$)
0	2
5	7
10	13
15	19
17	21

(Source: Kuraray)

Table 7. Vapour permeability coefficient of oxygen, P_{O_2}, of polyvinyl alcohol film (99.9 % hydrolyzed; viscosity 20 - 26 Pa s) against relative humidity at different temperatures.(Ref.8).

Relative humidity (%)	$P_{O_2} \times 10^{14}$ (ml cm/cm^2 s cm Hg)		
	26°C	35°C	45°C
0	3	4	7
40	3.2	4.5	7.5
50			8.0
55		5.0	
58	3.5		
60			11
68	5.0		
70		6.5	14
80	6.5		
85		11	

Table 8. Vapour permeability coefficients of carbon dioxide, P_{CO_2}, and nitrogen, P_{N_2}, through polyvinyl alcohol film at 15°C at different relative humidities (Ref. 7)

Relative humidity (%)	$P_{CO_2} \times 10^{11}$ (ml cm/cm^2 s cm Hg)	$P_{N_2} \times 10^{11}$
10	0.01	0.01
48	1	0.05
77	7	0.5
85	15	1.5
92	32	3.5
95	58	6.4

Table 9. Water vapour transmission rate of unplasticized polyvinyl alcohol film (3 mm thick) (99 - 99.8 % hydrolyzed; viscosity 28 - 32 Pa s).

Relative humidity (%) at film faces	$P_{H_2O} \times 10^9$ (g H_2O/cm^2/s)
0/50	8.1
50/72	170

Method: ASTM E 96-53T (Source: Du Pont)

6. GELLING AND PRECIPITATION OF POLYVINYL ALCOHOL

Many inorganic compounds, mainly salts, are able to precipitate polyvinyl alcohol from aqueous solutions. A selection of these is shown in Table 11. Most compounds are only effective in this respect with fully hydrolyzed grades. The coagulating power of the anions is in the order:-

$$SO_4^{2-} > CO_3^{2-} > PO_4^{3-}$$

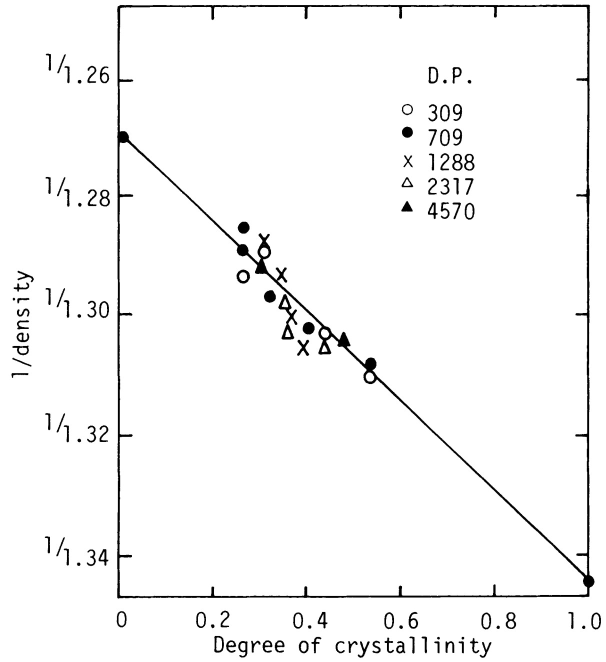


Figure 4. Relation between crystallinity and density for polyvinyl alcohols of different nominal degrees of polymerization.

Table 10. Odour test on packaging films (Ref.8)

Film	Thickness (µm)	Time of first observation of odour (days) vanilla	heliotrope	peppermint	camphor
Polyvinyl alcohol	20	100	107	160	165
Polyethylene	20	0	0	0	0
Polyvinylidene chloride (PVDC)	20	1	1	1	1
PVDC-coated viscose ('Cellophane')	26	9	8	108	92
'Moisture-proof' viscose	24	31	52	163	114
Normal viscose	21	65	71	157	78

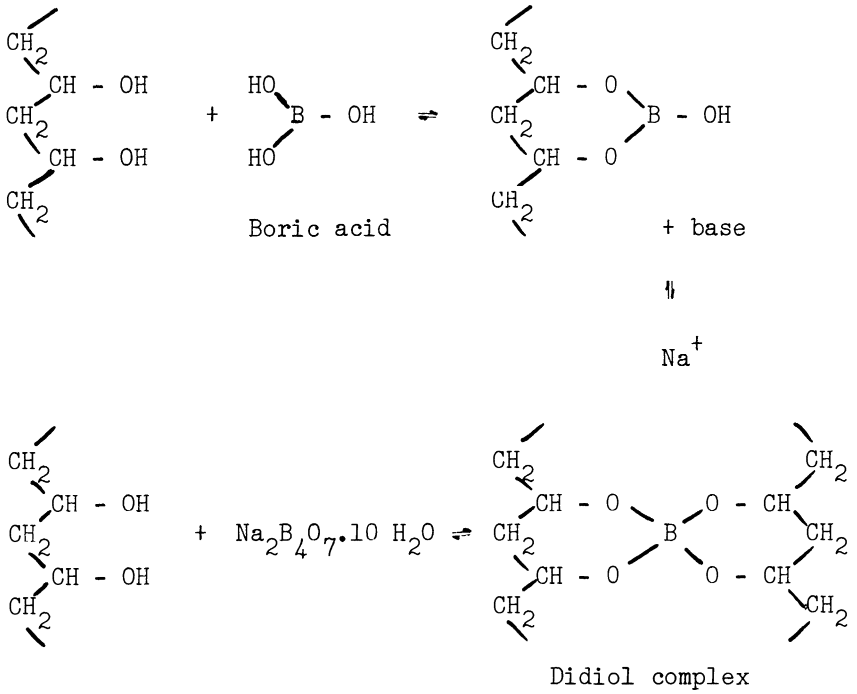
Method: 1 gm of sample was sealed in a 5 cm x 5 cm film package and placed in a 250 ml bottle. The time elapsed before odour was observed in the bottle was noted.

The coagulating power of Cl^- and NO_3^- is very weak. With cations, coagulation is in the rough order:-

$$K^+ > Na^+ > NH_4^+$$

This is in approximate agreement with ionisation potentials. Strong bases and acids have weak coagulating power. In practice, sulphates, such as Na_2SO_4 and $(NH_4)_2SO_4$ are used as coagulants in the spin-bath during the production of polyvinyl alcohol fibres by wet spinning.

Boric acid and borax cause thickening and gelation of polyvinyl alcohol by chemical bonding (see Table 12, and also Chapter 5). The reactions involved are: -



Didiol complex
(gel)

The behaviour of aqueous solutions of fully hydrolyzed polyvinyl alcohol of different degrees of polymerization with borax and boric acid, at 20° and 60°C are shown in Table 12, which indicates the point at which gelation occurs. The effects of the change in residual acetyl group content, with boric acid and with borax, causing precipitation and/or gelation are shown[5] in Figure 5. From both these groups of data, it can be seen that the difunctional borax is more effective as a gelling agent than the monofunctional boric acid, as may be expected. It is also notable that the larger molecules, of polymer with a higher degree of polymerization,

Table 11. Minimum salt concentration to precipitate a 5 % solution of polyvinyl alcohol (98 - 99 % hydrolyzed; viscosity 25 - 31 Pa s)

Salt	Minimum salting-out concentration		Salting-out effect
	(N)	(gm/l)	(1/N)
$(NH_4)_2SO_4$	1.0	66	1.00
Na_2SO_4	0.7	50	1.43
$ZnSO_4$	1.4	113	0.71
$FeSO_4$	1.4	105	0.71
$MgSO_4$	1.0	60	1.00
$Al_2(SO_4)_3$	1.0	57	1.00
$KAl(SO_4)_2$	0.9	58	1.11
NH_4NO_3	6.1	490	0.16
$NaNO_3$	3.6	324	0.28
KNO_3	2.6	264	0.38
$Al(NO_3)_3$	3.6	255	0.28
NaCl	3.1	210	0.32
KCl	2.6	194	0.38
Na_3PO_4	1.4	77	0.71
K_2CrO_4	1.4	136	0.71
H_3BO_3	0.8	165	1.25

Table 12. Effect of degree of polymerization, concentration and temperature on the gelling of polyvinyl alcohol solutions by boric acid or borax.

Concentration of polyvinyl alcohol solution (% by wt.)		10		8		5		3	
Nominal degree of polymerization	Temperature (^{o}C)	Boric acid	Borax	Boric acid	Borax	Boric acid	Borax	Boric acid	Borax
2010	20	2.7	0.1	3.1	0.2	4.0	0.5	4.0	1.2
2010	60	> 12	0.6	> 12	3.1	> 12	7.3	>12	18
1470	20	4.0	0.3	4.5	0.5	5.0	1.0	> 5	1.5
1470	60	> 12	4.6	> 12	7.6	> 12	15	> 12	> 20
980	20	4.5	0.8	4.5	0.9	5.0	1.2	5	1.7
980	60	> 12	1.3	> 12	14	> 12	18	> 12	> 20
300	20	5	1.0	5	1.3	1.5	1.5	5	2.0
300	60	> 12	1.5	> 12	> 20	> 12	20	> 12	> 20

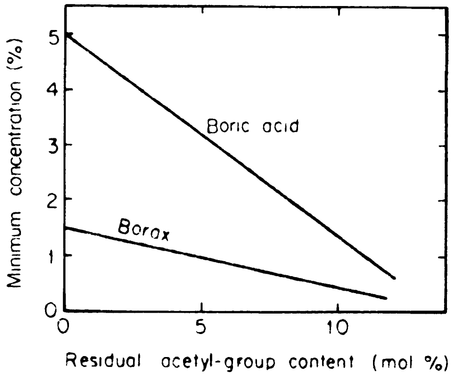


Figure 5. Minimum concentrations of boric acid and borax solutions causing precipitation of a 5 % aqueous solution of polyvinyl alcohols (nominal degree of polymerization = 500) of different degrees of hydrolysis.

more readily form gels at lower concentrations of the borax/boric acid additive.

In practical terms, the polyvinyl alcohol-borax reaction may be used as the active component in low-cost, heavily-filled, gellable water-based systems for adhesives and paper sizes. Since gelation occurs immediately on contact, and is not reversible on heating, two-stage sizing processes can be developed, where the polymer and the borax are applied separately and complex formation occurs on the substrate. In another system, boric acid may be added to the polyvinyl alcohol solution, to form a soluble complex, which converts to the gel form on contact with alkali. These systems are sensitive to relatively small variations in pH. An aqueous solution of polyvinyl alcohol thickened with boric acid can combine a high wet tack with low substrate penetration, which can be of interest in high speed paper converting applications. Increasing the temperature of polyvinyl alcohol solutions increases the salt coagulation action, but weakens the gelation, so that the solutions behave as thermally reversible gels.

7. CONCLUSION

In each of the above phenomena, where the physical chemistry concerned is worthy of further investigation, there is the possibility of continuing development of many interesting, and cost-effective, systems, especially in the fields of paper and other surface coating, and of fibre treatment.

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POLYMERIC FLOCCULANTS

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INTRODUCTION

Dispersions of particles are either stable or unstable, depending on whether the particles remain dispersed or have a tendency to form aggregates. The stability or otherwise of colloidal particles can often be described in terms of a balance between electrical repulsion and van der Waals attraction, an approach which was pioneered by Deryagin and Landau[1]and Verwey and Overbeek[2], and is now usually referred to as 'DLVO theory' . The electrical repulsion between charged particles in dilute electrolyte solutions can be sufficient to prevent very close approach of the particles so that van der Waals attraction is not significant. By reducing the charge on the particles, or by increasing the ionic strength of the solution, the electrical repulsion can be reduced, which allows particles to approach close enough for van der Waals attraction to operate, and for aggregation to occur. The aggregation of colloidal particles is known either as 'coagulation' or 'flocculation'. These terms are sometimes used interchangeably, but some authors use the different terms to imply different mechanisms of aggregation. We shall return to this question below.

It is well known that the adsorption of polymers on to colloidal particles can cause profound changes in colloid stability, and that DLVO theory does not always apply in such cases. Stability may be either increased or decreased by adsorbed polymer, and, in the former case, the effect is known as 'steric stabilization' (see Chapter 14). The opposite effect, where stability is decreased, was known as 'sensitization' in the older colloid literature[3] and may have a number of different causes. Some of these, such as effects on van der Waals attraction[4] and electrical repulsion[5] are of some fundamental interest, but of no great practical concern. Furthermore, these effects are not greatly dependent on the polymeric nature of the adsorbing species and can be observed with quite small molecules such as surfactants.

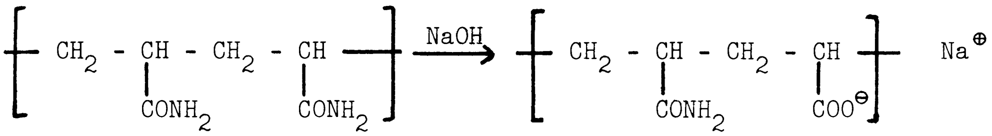
Destabilization of particles by polymers can occur by mechanisms which depend crucially on the log-chain nature of the molecules and leads to flocculation of suspensions, which is exploited in many industrial applications. In some texts, the term 'flocculation' is restricted to aggregation produced by long-chain polymers, whilst 'coagulation' is used to describe effects due to a reduced electrical repulsion between particles (e.g. by the addition of salts). Flocculation of polymers may be a result of bridging between particles by adsorbed polymer chains or, if particles and polymer have charges of opposite sign, charge neutralization may play a significant part. A third possibility which has recently come to light is flocculation by free (i.e. unadsorbed) polymer[6] as a results of the exclusion of large polymer chains from the solution between approaching particles. Although this effect may be important in certain cases, especially with concentrated dispersions, it is probably of only limited significance in practical flocculation processes and will not be further considered here. We shall consider only the bridging and charge neutralization mechanisms, after a brief account of the nature of polymeric flocculants.

NATURE OF POLYMERIC FLOCCULANTS

Effective flocculants are nearly always linear homopolymers, which may be nonionic in character but more often have a number of ionizable groups distributed along the chain, either anionic or cationic. Molar masses (molecular weights) of available flocculants range from a few thousand to several million. The most important characteristics of polymeric flocculants are the molar mass and the charge density. These and other properties need to be determined if the mechanism of flocculation is to be fully understood[7]. Unfortunately, most reported work on polymer flocculation has been with poorly-characterized materials of commercial origin, and intrepretation of the results can be very difficult. A major problem is the fact that quoted molar masses are invariably average values (usually from viscosity data) and there may be a very broad distribution of chain lengths within a given sample.

Early examples of polymeric flocculants were based on natural products such as isinglass, gelatin , alginates, and starch, and many of these are still used in certain applications such as the clarification of beer and wine. In India, crushed nuts or seeds of the Nirmali tree have been used for centuries to clarify turbid waters and the extract has been shown to be a very effective flocculant[8].

Since the 1950's, synthetic flocculants have become available and these are now more widely used than the natural materials. The most common ones are based on polyacrylamide, which can be conventiently prepared by polymerization of acrylamide monomer in aqueous solution or in organic solvents[9] (see Chapter 3), to give products of different molar mass. Although polyacrylamide is nominally nonionic in character, hydrolysis of amide groups usually occurs to some extent giving a number of carboxylic groups, which ionize in neutral or alkaline solutions. Anionic polyacrylamides are prepared by controlled alkaline hydrolysis:



$$\left[CH_2 - \underset{CONH_2}{CH} - CH_2 - \underset{CONH_2}{CH} \right] \xrightarrow{NaOH} \left[CH_2 - \underset{CONH_2}{CH} - CH_2 - \underset{COO^{\ominus}}{CH} \right] \quad Na^{\oplus}$$

Complete hydrolysis could give sodium polyacrylate.

The vast majority of commercial anionic polymers are based on partially-hydrolyzed polyacrylamide. Cationic polymers based on polyacrylamide can also be prepared, for example by copolymerization of acrylamide with a suitable cationic monomer. Other examples of synthetic polymeric flocculants are:

Nonionic:	Polyvinyl alcohol; polyethylene oxide.
Anionic:	Sodium polystyrene sulphonate.
Cationic:	Polyethyleneimine; polydiallyldimethylammonium chloride ('Catfloc').

Polyelectrolytes with weakly-ionic groups such as carboxylic acid or tertiary amine have charge densities which depend on solution pH. With strongly ionized groups, such as sulphate and quaternary ammonium, the charge density is practically independent of pH.

BRIDGING FLOCCULATION

Adsorption Mechanisms

Essentially, bridging flocculation arises because of the adsorption of segments of a polymer chain on more than one particle, thus linking the particles together. For adsorption to occur, there must be some favourable interaction between polymer segments and the particle surface: this can arise in a number of ways.

If the particles and polymer have opposite charges (e.g. negative particles and cationic polymer), then ionic interaction will give strong interaction and complete adsorption of the polymer. This case is considered in the next section.

For nonionic polymers, or where particles and polymer have the same sign of charge, there must be some specific interaction responsible for the binding of polymer segments to the particle surfaces. Some postulated types of interaction are:

a) Hydrophobic bonding.
This may be responsible for the adsorption of non-polar segments on to hydrophobic surfaces. An example is the adsorption of polyvinyl alcohol on silver iodide[10].

b) Hydrogen bonding.
When the particle surface and the polymer molecules have suitable H-bonding sites, this may be sufficient to cause adsorption of an appreciable fraction of the polymer segments. Most oxide particles acquire a surface layer of hydroxyl groups in aqueous suspensions and these probably provide an opportunity for H-bonding with, for instance, the amide group of polyacrylamide. Such a mechanism has been demonstrated for the adsorption of polyacrylamide[11] and polyethylene oxide[12] on silica.

c) Dipole-crystal field effects.
Another possibility with ionic crystals is the interaction of polar groups on the polymer with the electrostatic field at the crystal surface. Such a mechanism was postulated for the adsorption of polyacrylamide on fluorite particles[13].

All of the above interactions are of very short range and could not operate if there were strong electrical repulsion between the particles and polymer chains, for example, with negative particles and anionic polyelectrolytes. In virtually all such cases, no adsorption occurs in the absence of added salt. Some critical concentration of electrolyte is necessary to promote adsorption[14]. There is convincing evidence[15] that this is not simply an ionic strength effect, but that ions such as Ca^{++} promote adsorption by binding anionic groups on the polymer chain to negative sites on the particle surface.

The adsorption mechanisms discussed above are rather specific, depending on the nature of the polymer and the particle surface. In a mixed suspension, polymer adsorption may occur on one type of particle but not on others. This leads to the very important possibility of the selective flocculation of mineral mixtures[16].

Flocculation by bridging

Ruehrwein and Ward[17] in 1952 were the first to suggest bridging as a flocculation mechanism. They pointed out that typical flocculant molecules might be comparable in dimension to many colloidal particles (0.1 - 1 μm), and that attachment of a polymer chain to many particles might occur. Effective bridging flocculation requires that adsorbed polymer extends far enough from the particle surface to attach to other particles, and that there is sufficient unoccupied surface available for adsorption of segments from these extended chains. If excess polymer is adsorbed on the particles, they can become restabilized simply because of surface saturation or, possibly, by steric stabilization. The concepts of bridging flocculation and restabilization are illustrated schematically in Fig. 1.

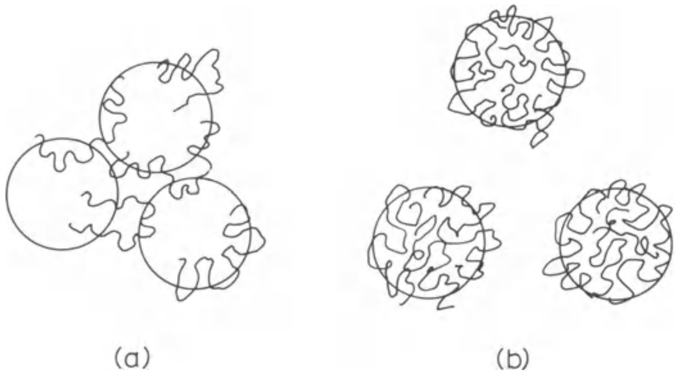


Figure 1. Schematic illustration of a) bridging flocculation and b) re-stabilization by adsorbed polymer.

Michaels[18] studied the flocculation of clay suspension by polyacrylamide and found that the effect became greater with increasing chain length of the polymer. He also showed that there was an optimum degree of hydrolysis (or anionic character) of about 30 % , which gave the best flocculation. This was explained in terms of an increasing expansion of the polymer chain, by mutual repulsion between charged segments, as the degree of hydrolysis increased and a decreasing tendency of the anionic polymer to adsorb on to negative particles. The expansion of the chain would give better flocculation whilst the reduced adsorption would give the opposite effect. The optimum degree of hydrolysis represents the best practical compromise between these two effects. A similar effect was found by La Mer[19],using starches as flocculants. A limited degree of anionic character (imparted by phosphate groups) was found to give improved flocculation.

In practice, the optimum degree of hydrolysis may differ significantly from 30 %, depending on the process conditions.

The effect of ionic strength can be important for a number of reasons. According to DLVO theory the repulsion between charged particles depends on ionic strength. At low electrolyte concentrations the electrical double layer around a charged particle can be quite extensive (of the order of 100 nm) and particles could not approach very close to each other. For bridging flocculation to occur, the adsorbed polymer must span the gap over which double layer repulsion operates and so at low ionic strength only high molar mass polymers should be effective. As the salt concentration is increased the range of double layer repulsion will fall to quite low values (e.g. about 1 nm in 1.-M NaCl) and bridging should occur with polymers of quite low molar mass. For nonionic polymers, this concept of bridging through a repulsion barrier seems to be confirmed by a number of experiments (see, e.g. Vincent[20]).

In the case of polyelectrolytes, the problem is more difficult since, as well as reducing the range of inter-particle repulsion, increasing ionic strength can cause the polymer chain to become less extensive by screening the repulsion between charged segments. There is the further effect that adsorption on to a similarly-charged particle will be enhanced as the ionic strength is increased.These effects might lead to an optimum ionic strength at which bridging flocculation by polyelectrolytes is most effective, although there is little experimental evidence on this point.

Very effective bridging flocculation can occur when sufficient salt is added to a suspension to cause a small degree of coagulation. Polymer chains can then bind small aggregates together to form large strong flocs[15]. The strength of flocs produced by polymer bridging is mentioned below.

KINETIC ASPECTS OF BRIDGING FLOCCULATION

In nearly all applications of polymeric flucculants in practice, the addition of polymer and the subsequent flocculation process are carried out under conditions where the suspension is agitated in some way, such as stirring. Such agitation is necessary initially to give thorough mixing of the polymer throughout the suspension and then to encourage collisions of particles to form aggregates. Other rate processes that need to be considered are the adsorption and re-conformation of polymer molecules on the particles and the possible break-up of flocs caused by agitation of the suspension.

The mixing process is very important, since an uneven distribution of polymer can lead to local overdosing and a restabilization of some of the particles. This may be the cause of haze formation and poor filtration properties in some flocculated suspensions[13]. However, we shall assume here that mixing is very rapid and not a rate-determining step. This leaves the following rate processes to be considered, which are illustrated schematically in Fig. 2.:

a) Adsorption of polymer molecules on the particles;

b) Re-arrangement (or re-conformation) of adsorbed chains;

c) Collisions between destabilized particles to form aggregates (flocs);

d) Break-up of flocs.

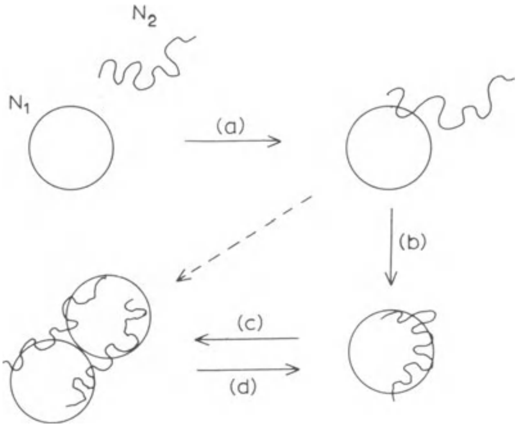


Figure 2. Kinetics of polymer adsorption and flocculation (see text).

Each of these steps depends on a number of factors and the rate would be difficult to predict, even in isolation. The fact that all four processes occur simultaneously makes the problem very much worse. All that can be attempted at this stage is a brief qualitative discussion of the relative rates.

The adsorption step (a) can be regarded as a second-order rate process depending on the number concentration of particles, N_1, and of polymer molecules, N_2. The rate of adsorption, J_A, can be written:-

$$J_A = K_A N_1 N_2$$

where K_A is a rate constant.

The collision or flocculation step (c) is also a second order process, but depends on the square of the particle concentration, so that the rate of flocculation, J_F, is:-

$$J_F = K_F N_1^2$$

Making realistic assumptions about the sizes of particles and polymer molecules, it can be shown that, in the absence of agitation (i.e., where adsorption and particle are entirely diffusion controlled) the adsorption process will usually be much faster than the collision rate[21]. However, in a sheared (agitated) suspension, both adsorption and collision rates become dependent on orthokinetic processes (induced by fluid motion) and polymer adsorption may be relatively low compared to the collision rate, especially for particles larger than about 2 µm. It is likely that several polymer bridges would need to be formed between particles to give aggregates capable of withstanding moderate shear (it has been estimated that a carbon-carbon bond in a polymer chain can be broken by a force of 1 - 10 nN, which is much smaller than typical hydrodyanamic forces between particles[22]). This means that a given particle may undergo several collisions with other particles before sufficient polymer chains have been adsorbed to allow bridging flocculation to occur.

There is very little information available concerning the re-conformation step (b), although for long chain polymers, times of the order of a second or more may be involved[23]. Furthermore, the reconformation rate should not depend directly on the particle concentration and it follows that,in fairly concentrated dispersions, particle collisions might occur before the adsorbed polymer chains had attained their equilibrium configuration. Intuitively, adsorbed chains in an extended, non-equilibrium state should be more capable of forming bridges by attachment to other particles than those in a flatter, equilibrium configuration. In very concentrated dispersions, where particles are already quite close together, it might be more reasonable to think in terms of near simultaneous adsorption of different segments of the same polymer chain on more than one particle. This effect should lead to more effective bridging flocculation as the particle concentration increases and may be of considerable significance in practical applications. However, very little fundamental attention seems to have been paid to this point.

In working with polymeric flocculants, it soon becomes apparent that the flocs can be very much stronger than the aggregates produced by the action of simples salts. The so-called 'pelleting flocculation'[24] is an extreme example, where very tough flocs are produced as a result of 'mechanical syneresis', brought about by uneven hydrodynamic forces. Despite many qualitative observations, quantitative measurements of floc strength are virtually non-existent. Usually, some empirical measure,such as the maximum floc size produced under given shear conditions, is quoted. Although flocs produced by polymers may be strong, they <u>can</u> be broken by the application of high shear. This disruption may be due to the detachment of polymer segments from adsorption sites, or by the breakage of links in the polymer chains. In view of the multi-point nature of polymer adsorption, the latter possibility is perhaps more likely. It is known that long chain polymers in free solution can be degraded into smaller units by the application of shear[25,26] and there are hydrodynamic reasons why breakage of polymer bridges between particles should be easier than the scission of free polymer chains.

When flocs are broken by shear, it has often been found that they do not readily re-form (see e.g. Pelton[27]). This could be explained by the breakage of polymer bridges, or by the detachment of segments from particle surfaces and subsequent reconformation. In both cases, there could be less particle surface available for bridge formation when the shear is reduced. For this reason, intense agitation should be avoided, or applied only briefly to ensure good mixing.

One final dynamic aspect of bridging flocculation is worth mentioning. There are some processes, notably paper-making, where small colloidal particles need to be deposited on much larger particles (such as cellulose fibres). In a sheared suspension, it can be shown [28] that the smaller particles orbit the larger ones at relatively large distances (up to 1 μm or more), well beyond the range of normal colloidal forces, so that deposition cannot occur. However, with adsorbed polymer chains, bridging may occur over distances comparable with the minimum separation between particle and fibre, allowing deposition to occur[22]. This might explain the effectiveness of polymeric 'retention aids' in the papermaking process.

CHARGE NEUTRALIZATION

In some applications, e.g., in water and effluent treatment, it is often found that the only effective flocculants are those of opposite charge to the particles. Since most natural particles are negatively charged, cationic polymers are widely used in such applications. Anionic polymers are effective when used in conjunction with hydrolyzing salts such as aluminium sulphate, but in this case it is likely that the precipitating hydrous oxide particles carry a slight positive charge and readily adsorb anionic polymers. (Pelleting flocculation' can be especially effective under these conditions[29]).

It is possible that the effectiveness of oppositely charged polymers in these applications is simply a result of the ease of adsorption, and that the bridging mechanism is still appropriate. However, with strong ionic interaction, polyelectrolytes are likely to adsorb in a rather flat configuration[30] which would reduce the likelihood of dridging. There is also the possibility that neutralization of the particle charge by the adsorption of polyelectrolyte may be largely responsible for the destabilization.

In view of the practical importance of the process, it would seem worthwhile to establish the relative importance of charge neutralization and bridging in the flocculation of particles by oppositely charges polymers. For instance, if charge neutralization is the predominant mechanism, then there should be no need for very high molar mass polymers, which are more expensive and inconvenient to use. It is also likely that polymers of high charge density should be most effective.

There is now an appreciable body of evidence suggesting that, for cationic polymers and negative particles, charge neutralization plays a large part in the flocculation process. The most direct evidence come from measurements of electrophoretic mobility of particles does with polyelectrolyte. With such different particles as clays[31], latex[32], cellulose fibres[33], silica[34]and bacteria[35], it has been found that the optimum flocculation dosage of cationic polymer corresponds quite closely with the amount required to give zero electrophoretic mobility (i.e., to neutralize the particle charge). It is likely that the kinetic effects discussed in the previous section would still be important and that bridging might occur at high particle concentration because of the relatively slow attainment of a 'flat' configuration of the adsorbed polyelectrolyte chains.

Although simple charge neutralization goes a long way towards explaining the observed behaviour, there are some effects of molecular weight and ionic strength [36] which do not fit the simple picture. These can be better explained by the 'electrostatic patch' model proposed independently by Kasper[30] and by Gregory[36]. Essentially, this model recognizes that many cationic polymers have a high charge density, whilst typical particles may have a rather low negative surface charge density. Consequently, when overall neutralization of the particle charge is achieved, there still remains areas of negative charge on the particle surface, together with patches of adsorbed polymer carrying excess positive charge, as shown in Fig. 3. During an encounter between particles with this 'mosaic' type of charge distribution, it is likely that positive and negative areas on different particles would come into contact, giving strong attachment. This could still be regarded as a form of 'bridging' by the adsorbed polymer. Aggregates formed in this way are not as strong as those formed by the usual bridging mechanism.

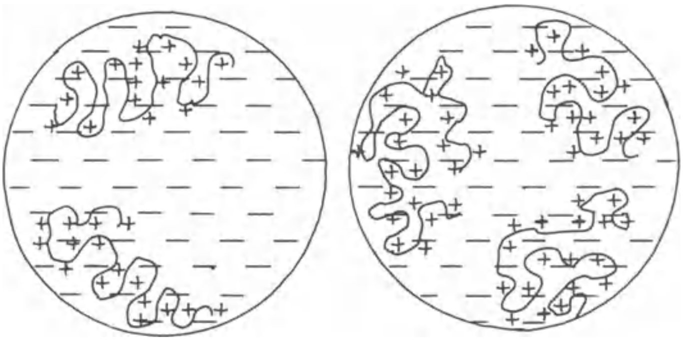


Figure 3. 'Electrostatic patch' model for the interaction of negatively charged particles with adsorbed cationic polymer.

One method of distinguishing between the polymer bridging and change neutralization mechanisms is to examine the effect of high shear on the aggregates. In the case of bridging, flocs do not readily reform, as mentioned above, whilst those produced by charge neutralization can be broken and re-formed very easily[37].

In certain applications, it is found that the addition of a fairly low molar mass cationic polymer followed by a much larger anionic polymer leads to especially good flocculation. This is most likely due to the attachement of anionic polymer to positive patches and bridging to similar patches on other particles. Because of the remaining negative areas on the particle surface, adsorption of the anionic polymer would be restricted to positive patches, which could result in extended loops and tails, and enhanced bridging opportunity.

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POLYMERS IN OIL RECOVERY AND PRODUCTION

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ABSTRACT

Polymers are used in a wide variety of oil field operations in recovering and producing crude oil. In the majority of cases their main function is to control the viscosity of aqueous fluids for a variety of different reasons. These reasons are highlighted for drilling, cementing, reservoir fracturing and reservoir mobility control fluids and also oil producing chemicals. The complex nature of each fluid is discussed and the difficulties in polymer flooding a multizonal reservoir are highlighted. The different chemicals are briefly discussed in terms of their advantages and limitations.

1. INTRODUCTION

1.1. Terminology

Polymers are used in a wide range of operations essential to oil recovery and production: their functions are many and varied. In technical terms, there is a small but significant difference between a polymer and a surfactant. For the purpose of this paper, the term 'polymer' will refer to a molecule consisting of many (sometimes repeat) units. By this definition, a 10 unit molecule may be considered a polymer, but, again for this paper, a distinction will be made between a lower molecular weight oligomer and a higher molecular weight (often having a molecular weight approaching or exceeding three orders of magnitude) polymer. This terminology will include different types of polymers, such as homopolymers, random and block copolymers, and natural polymers.

1.2. Scope for application

Polymers find many applications in oil recovery and production, including such areas as :-

(i) drilling fluids;
(ii) cementation of well bore;
(iii) reservoir fracturing;
(iv) controlling fluid flow in the reservoir;

and the multistage processes of

(v) oil production, and
(vi) refining (See Refs.[1,2]).

Here, consideration will be given principally to the areas (i) to (iv), with only a brief mention of (v) and (vi).

The chemical components which constitute the fluids used for each operational area are related to the specific role of the polymers in the fluids. The more widely used polymers , discussed in more detail, have structures which have been shown to be suitable for many of the environmental conditions to which the fluids are exposed. A brief description has been given of the complex topic of the use of polymers in controlling the flow mobility in oil field reservoirs as well as highlighting the difficulties facing petroleum engineers when injecting polymer solutions.

2. OPERATIONS EMPLOYING POLYMERS

2.1. Drilling Fluids

There are several different types of drilling fluids currently available, each designed for specific well conditions of rock type, temperature, depth, pH, etc. A typical variant is the production of a drilling fluid which consists of high solids content, and an alternative with low solids content. Although the overall fluid composition will change to accomodate the differences in specific well conditions, the overall functions of the fluid will remain unchanged.

The principal functions of drilling fluids are concerned with enabling the drilling of a bore hole into the reservoir with minimum damage to the drilling bit and the structure of the bore. Consequently, it is essential that the fluids which are pumped around the drilling bit are able:-

(i) to cool and lubricate the bit;
(ii) to clean the hole bottom of drilling debris and cuttings to minimise damage and heat;
(iii) to life the formation cutting to the surface;

(iv) to control the formation pressure during drilling; and
(v) to prevent fluid loss into the reservoir and well structure.

To achieve these functions, the essential physical properties of the drilling fluid is that it should be a thixotropic solution with a high strength at low shear but low strength at high shear. The latter property is very important forcooling and cleaning actions in the region of the drill bit, whilst the former property is important for fluid loss prevention, for controlling well pressure, and for lifting formation cuttings. The essential parameters for a typical drilling fluid are shown in Table 1. It should be stressed that the data in this Table are not exhaustive, but reflect the main types of ingredients added to drilling fluids. Suppliers of drilling fluids frequently modify fluids depending on the well location and their scope.

Table 1. Composition of a typical drilling fluid

Component	Chemicals	Functional role
1. Weighting agent	Barytes; Iron Oxide; Calcium carbonate	To ensure that fluids are heavier than up-flowing gas and oils
2. Prevent fluid loss	CMC; Starch;Resins; CMHEC; PAA (also possibly wood fibres, sawdust, cellulose, etc)	To prevent fluid loss into porous well structures fractures and caverns
3. Control fluid viscosity	Bentonite; Attapulgite; Xanthan; HEC;Guar Gum; Polyacrylamides; Locust Bean Gum	To prevent sands or cuttings from sedimenting into bottom hole; also to seal bore with temporary filter cake
4. Dispersants	Lignosulphonates; Lignite; Tannin	To thin fluid as control against clays and marls used to thicken fluids
5. Miscellaneous	Corrosion inhibitors; biocides;specialist products; NaCl; KCl; Caustic soda; Lime; Soda Ash	To support action of polymers in specific well locations and scope

CMC = carboxymethylcellulose
CMHEC = carboxymethylhydroxy-ethylcellulose
HEC = hydroxyethylcellulose
PAA = sodium salt of polyacrylic acid

The specific role of polymers can be readily observed as fluid loss preventatives, controlling fluid viscosity, and, indirectly, in the role of corrosion inhibition and biocidal action. It is clear, therefore, that polymers are added principally for their viscosifying action, to increase fluid viscosity, so preventing fluid flow into the porous well wall structures, and also preventing sands and well cuttings from sedimenting under gravity into the well bore bottom. However, it is not possible merely to increase the fluid viscosity per se because the fluid must flow freely around the drilling bit to keep it cool. In addition, preventative action against an increase in the fluid viscosity, due to the presence of clay and marl chippings, is often required, so another type of polymer may be added, classed as a dispersant. There is, therefore, the apparent paradox of a balance where , on the one hand, high density weighting agents are added to ensure that the fluid is heavier than the up-flowing potential of gas and oils, but these must be kept in suspension (along with the well cuttings) by, firstly, a viscosifying polymer, and, secondly, another polymer which prevents fluid loss into the well structure by forming a high viscosity filter cake. On the other hand, to enable this medium to cool and clean the drill bit, and flow in the well bore without undue viscosity/pressure build up, a polymeric dispersant is added. It is easy to recognize (in physical terms) the balance required to gain an optimum drilling fluid and to maintain a fluid likely to be operative under high temperatures and shear rates. As the bore well is drilled to greater depths, the uplift pressure from gases and oils in the permeable parts of the reservoir becomes greater, so that a more dense fluid is required: there is, in consequence, a higher viscosity fluid needed to keep the weighting material in suspension, but the fluid requires the same ability to maintain fluidity and cleaning power at the drill bit.

Examination of the polymers employed in drilling fluids shows that some are naturally occurring (e.g. starch, xanthan, lignosulphonates) and others are partially or wholly synthetic (e.g. carboxymethylcellulse (CMC), hydroxyethylecellulose (HEC), carboxymethylhydroxyethylcellulose (CMHEC). These are discussed more fully later.

2.2. Cementing fluids

Once the drilling has been completed in a well, a drill casing is installed between the producing zone of the oil reservoir and the surface. The casing is normally cemented into the well bore to provide mechanical support for the casing, to restrict fluid movement between reservoir formations (particularly to prevent pollution of fresh water reservoirs), to prevent casing corrosion, and to control high pressure zones, reducing the possibility of oil blowouts.

The cementing fluid is a water-based slurry mixed to produce a specific density depending on well depth and pressure. The cementing fluid is pumped down the casing until the appropriate volume has been added and then by using(usually) drilling muds, the cementing fluid is forced upwards between the casing and well bore wall, penetrating the superficial structures of the bore wall only, but completely filling the gap between the outside of the casing and the bore wall. This process is normally carried out in several stages if the well bore is very deep. The composition of the cementing fluids impart the scope for coping with fluctuating temperatures and pressure (when cementing rates may need to be accelerated or retarded), altered fluid density to improve pumpability, and for minimising penetration into the formation. The major components of cementing fluids are listed in Table 2.

Table 2. Composition of a typical cementing fluid.

Component	Chemicals	Functional role
1. Cement	Neat Cements(vary in composition with well depth and temperature)	Catalyst for cementation processes
2. Fluid extender	Bentonite;Diatomite; Gypsum;Attapulgite	To control fluid density and maintain correct water/cement ratio
3. Prevent fluid loss	CMC; Polyamines;HEC	To prevent fluid loss into porous well structures, fractures or caverns
4. Control fluid viscosity	Xanthan; HEC; Guar gum	To prevent sedimentation of weighting materials
5. Control cementing rates	Calcium and sodium chlorides; sodium silicate; lignosulphonates Glucoheptonates	To accelerate and retard cementing rates and give long term heat stability
6. Miscellaneous	Hydrochloric acid; KOH; KCl; NaCl; Iron oxide; Barytes	To control pH. To stabilize hydration of clays and prevent swelling. To control weighting of fluid.

CMC, HEC - as in Table 1.

From Table 2, it is notable that polymers are used in similar roles to those in drilling fluids (Table 1) - i.e., to control the fluid viscosity and to aid weighting agent suspension and to prevent fluid loss into the reservoir structures. Similar types of natural and partially wholly synthetic polymers are used. The advantages of each are discussed below.

2.3 Fracturing fluids

When reservoir permeabilities (of normally consolidated sandstone foundations) are very low to crude oil or gases, then reservoir fracturing can be considered. In this technique, fluids are pumped into the reservoir under high pressure to fracture the reservoir physically, so creating channels. To maintain the fractures, the fluid pumped into the reservoir will contain 'proppants' which will hold open reservoir fractures after the treating pressure has been released. To prevent the proppants from being withheld out of the reservoir fractures, the fracturing fluids are pumped as a polymer gel into the reservoir. This gel is created *in situ* by cross-linking agents - polymers typically employed are noted in Table 3. The gel structure must be broken, following reservoir fracturing, to create fluid pathways for the fluids to follow. The remaining chemical components, listed in Table 3, are very similar to those in Tables 1 and 2, with the exception of the surface tension controlling surfactant. Here, it is important that the fluid has a low interfacial tension against reservoir structure and fluids, to enable good penetration into the rock structure to occur. In addition, the surfactants will act to prevent both emulsions, and also foams, forming in the reservoir as the fluids are forced at such high pressures into the oil bearing rock, and into the reservoir gas cap.

2.4 Mobility control for water flood recovery

In order to demonstrate the concept of using polymers to control water mobility for improved oil recovery, it is necessary to discuss briefly the flow of fluids in a reservoir in terms of planar zonal and also of cross zonal flow regimes. The French engineer, Henry Darcy, developed an equation describing fluids flow in reservoirs which has since become a standard tool for petroleum engineers[3] In the simple case of a planar zone structure, the sweep of fluids through an oil field reservoir can be explained by the linearized form of Darcy's Law:

$$Q_i = \frac{k_i}{\mu_i} \frac{dp}{dl}$$

Table 3. Composition of a typical reservoir fracturing fluid

Component	Chemicals	Functional role
1. Gelling polymers	Guar gum, HEC, CMC, CMHEC, xanthan	To carry the proppants in the fluid flowing in the reservoir.
2. Cross-linking agents	Borates; polyvalent cations, e.g. Al, Ti	To control gel strength during fracturing.
3. Gel breakers	Enzymes, oxidizing agents, acids	To control gel strength following fracturing
4. Prevent fluid loss	CMC, starch, CMHEC	To control fluid loss into reservoir structures
5. Friction reducers	Guar gum, HEC, CMHEC	To reduce pressure loss by friction when pumping at high fluid rates
6. Control surface tension	Surfactants - nonionic (ethylene oxide adducts); anionic (petroleum sulphonates); cationic (quaternary amines)	To reduce surface tension for greater penetration into reservoir and prevent emulsion formation in oil bearing zone and foaming in gas cap.
7. Biocides	Commercial products	To inhibit microbiological growth and oil saving
8. Clay stabilizers	Potassium chloride	To stabilize clay structures
9. Proppants	Sand, glass beads	Inert material to act as fillers during fracturing to maintain fracture

CMC, HEC, CMHEC - as in Table 1.

where Q_i is the apparent flow velocity of fluid component i ($cm.s^{-1}$);

k_i is the permeability of the zone to fluid component i (darcies);

μ_i is the viscosity of fluid component i (poise); and

$\frac{dp}{dl}$ is the pressure gradient across the reservoir (atmospheres cm^{-1}).

The ratio k_i/μ_i is known as the mobility of the reservoir to fluid component i.

For the flow of both oil and water fluids in a given reservoir, the mobolity ratio M is defined as the mobility of the fluids (w, water and o, oil) ahead of the fron divided by the mobility of those fluids behind the front:-

$$M = \frac{\left. \frac{k}{\mu}_w + \frac{k}{\mu}_o \right|_{\text{ahead front}}}{\left. \frac{k}{\mu}_w + \frac{k}{\mu}_o \right|_{\text{behind front}}}$$

or, in a more idealized case, as:-

$$M = \frac{k_w \mu_o}{k_o \mu_w}$$

In an oil bearing reservoir where, typically, oil has a higher viscosity than the water phase and k_w and k_o have fixed values, in order to improve the flow of oil at the expense of water the value of M needs to be reduced. Since μ_o cannot easily be changed, μ_w must be increased and this is typically achieved by polymer bulk viscosity effects.

Water is injected into oil field reservoirs in a variety of patterns such as 'four-spot','five-spot', etc., or direct-line drive or staggered-line-drive displays. These arrays involve different spatial arrangements between the producing and injection wells and are characterized by slightly different sweep efficiencies; sweep efficiency is defined as'that fraction of the total area (of a two dimensional reservoir model) contacted by the displacing fluid at the time of the breakthrough of that fluid'.A detailed relationship between the area sweep efficiency, mobility ratio, and the displaceable volumes injected for given arrays of wells is beyond the scope of this paper, and is discussed in earlier technical publications[4], or in standard text books[1]. It has been calculated[4] that, for a five-spot well array, a mobility ratio of 0.5 will yield an area sweep efficiency of approximately 70 % at the breakthrough of the displacing(water) fluid, whilst at a mobility ratio of 7.5 the area sweep efficiencv approaches 100 %. The sweep efficiency improves as more pore volumes of displacing fluid (water) are injected into the reservoir - e.g., for a mobility ratio of 0.5, the sweep efficiency is ~ 96 % after two displaceable volumes of water.

For a water flood sweep in an idealized five-spot well array (Figure 1.) a theoretical representation of the water sweep pattern is given in three of the four sections, with an example of what

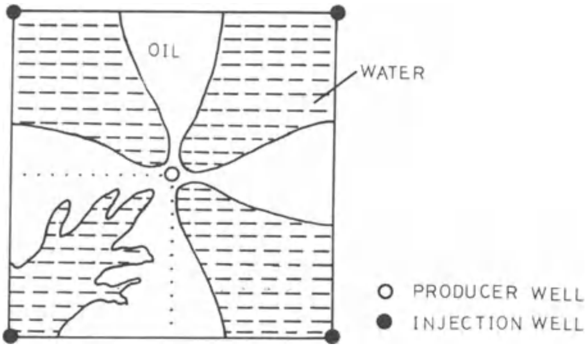


Figure 1. Schematic diagram of a water sweep for an oil zone using a 5-spot well array showing 3 idealized sweeps and 1 practical fingering sweep.

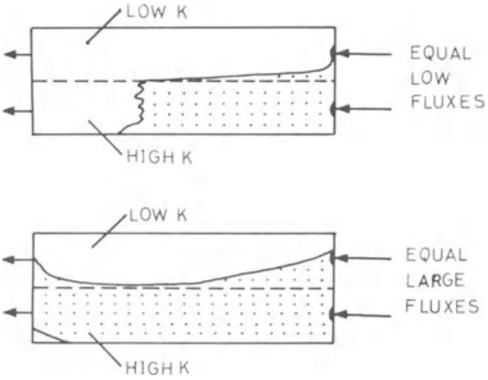


Figure 2. Schematic respresentation of crossflow sweep in two layer model.

of what could be experienced in practice in the fourth section. The section shows a fingering effect which is a consequence of zonal rock inhomogeneity - one factor over which petroleum engineers have no control.

In addition to this, and to complicate the water flood process further, zonal cross flow can often render whole zone areas untouched. Such zonal cross flow between different reservoir layers can be a dominant factor in determining the outflow ratio between the different layers. This is shown schematically in Figure 2. The cross flow of displacing fluid from the low permeability structure to the higher permeability structure is unswept by the fluid. A cross flow index has been defined according to separate flow regimes[5] and used to quantify cross flow in a model two layer water flood using a polymer solution[6]. Such data, as reported[6] are shown in Figure 3. Unfortunately, where there is good communication between the zonal layers, any polymer flowing into the lower permeability layer (which is a direct consequence of (negative) cross flow from the higher to the lower permeability layer) will tend to be bypassed during subsequent water flood sweeping polymer more effectively from the higher permeability layer. Injecting polymer solutions into correct reservoir heterogeneity is not a practical process unless it is possible to exclude the polymer from the lower permeability zones.

It is, perhaps, worth considering the environmental conditions that polymers, injected into oil field reservoirs, must be expected to withstand. It is also worth reflecting on the fact that any polymer used as a secondary or tertiary phase oil recovery aid must be expected to remain in the environment periods of weeks or months and perhaps (depending on the size of the field and its production rate) for several years. Such reservoir conditions for the Forties field for a crude oil of 37° API gravity are indicated in Table 4. Consequently, when selecting polymers for use in the reservoir, it is essential for the test to be carried out at suitable temperatures and pressures, with shearing conditions to simulate those expected in practice.

Table 4. Characteristics of Forties Field reservoir.

Depth (below sea level)	2100 m.
Initial temperature	96°C
Initial pressure	3215 p.s.i.(218.7 atm.)
Permeability	240 - 770 mDarcy
Porosity	27 %
Water saturation	19 %
Oil production rates	500,000 BPD (1981 ave.)
Injection water	Sea water
Injection rates	10 to 40 × 1000 BPD
Injection pressure	4300 p.s.i. (292.5 atm.)

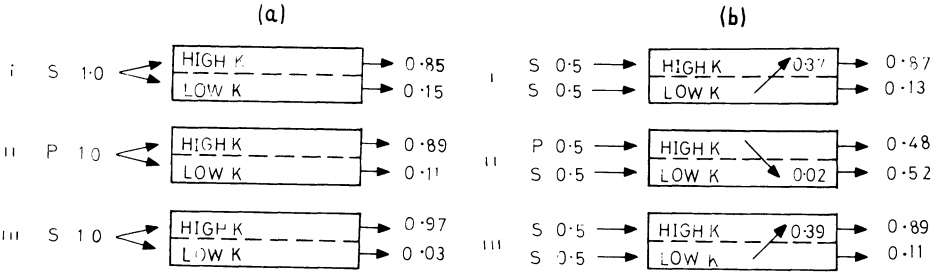


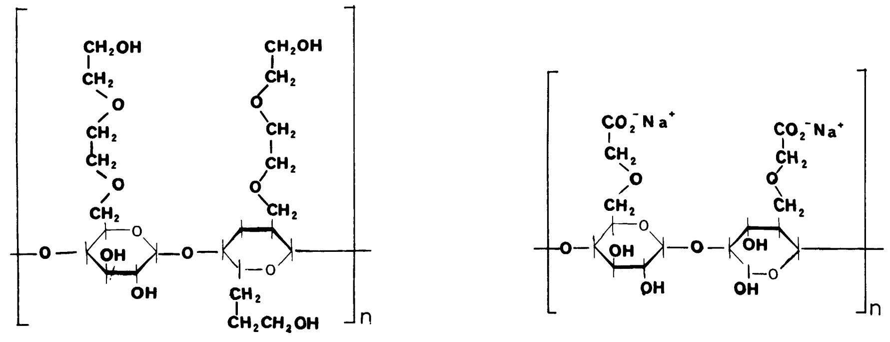
Figure 3. Schematic representation of polymer-modified water flood of a two layer porous bed model using (a) common feed, and (b) separate feeds; S represents sea water and P represents polymer solution. Data reproduced from Ref.[6] with kind permission.

In the foregoing sections, a brief attempt has been made to highlight four quite separate operations in which polymers are widely used[1,2] (i.e., drilling, completion and workover, and fluid mobility control) in preparing the oil field for oil production and enhancing such production. In all cases, the polymers are used primarily to maintain fluid viscosity or prevent fluid loss. It is perhaps important to highlight at this stage that, although polymers are used (and often the same polymers may be used) in all the above operations, the functional role in each area is often significantly different, and the overriding factor for specific polymer selection (setting aside technical suitability and effectiveness, which are essential) is cost effectiveness. The main chemicals employed are now considered in more detail.

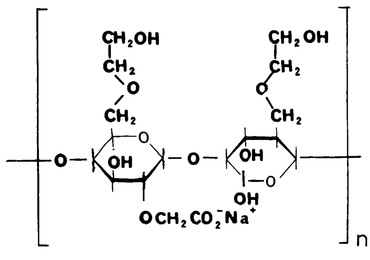
3. POLYMERS EMPLOYED IN RESERVOIR PREPARATION AND OIL RECOVERY

3.1. Cellulose derivatives

Cellulose is the most abundant natural polymer, and is therefore accepted as a readily available source of base units for modification to furnish derivatives suitable for oil production. Probably the most commonly used cellulose derivative is carboxymethylcellulose (CMC) (Figure 4.) which is prepared by reacting cellulose with monochloracetic acid in the presence of sodium hydroxide[7]. CMC is classified as a water soluble anionic polymer and can have a variable degree of substitution. Whilst CMC is generally compatible with monovalent salts, it is somewhat intolerant of divalent cations[7]. This has the distinct drawback of inducing aggregation by salting out effects and therefore reducing solution viscosity. The cellulose derivative hydroxyethylcellulose (HEC) (Figure 4.) is a nonionic species and is therefore more



(a) HYDROXYETHYLCELLULOSE (b) SODIUM CARBOXYMETHYLCELLULOSE

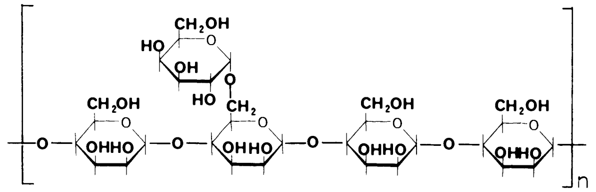


(c) SODIUM CARBOXYMETHYLHYDROXYETHYL-CELLULOSE

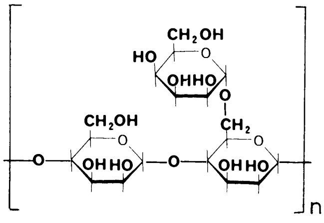
Figure 4. Structure of some modified cellulose derivatives

tolerant to divalent cations than CMC. HEC is prepared by reacting alkali cellulose with ethylene oxide . However, reacting sodium cellulose with ethylene oxide and then with monochloracetic acid produces sodium carboxymethylhydroxyethylcellulose (CMHEC) (Figure 4.)[7] which has both nonionic (HE) and anionic (CM) groups.

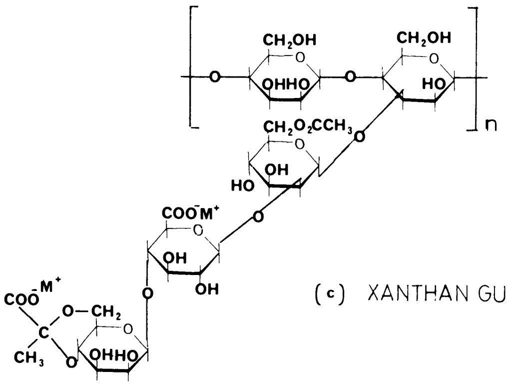
Although CMC is not a good viscosifying polymer under high saline solutions, it is satisfactory for low salinity solutions. Although HEC has improved salt tolerance, however it does not have such good viscosity. On the other hand, CMHEC combines the viscosity benefits of CMC with the salt tolerance of HEC, and is consequently finding favour as a viscosifying agent and as a fluid loss preventative chemical in drilling, cementing and fracturing operations. In addition, both HEC and CMHEC are semisynthetic, and therefore have fewer impurities than their natural polymer counterparts, and have less tendency for impurity aggregation and



(a) LOCUST BEAN GUM



(b) GUAR GUM



(c) XANTHAN GUM

Figure 5. Structures of some natural gums.

blocking of reservoir pores. HEC is often preferred over CMC and CMHEC for deep wells because of its better temperature stability profile. In addition, the potential for cross-linking of HEC and CMHEC by polyvalent cations (especially chromium and aluminium) is important in relation to their successful use in fracturing fluids.

It has been shown, on the laboratory scale, that CMC will not provide a sufficiently long term increase in solution viscosity at reservoir temperatures, and is likely to be ruled out as a mobility control polymer[6]. However, modified carboxymethylhydroxy-ethylcellulose has been proposed as a possible polymer in a cross linked structure[8]. In general, the cellulosic polymers do not find application in controlling fluid mobilities in reservoirs.

3.2. Naturally Occurring Gums and their derivatives

The three principal gums employed in drilling, cementing, and fracturing fluids are xanthan, guar, and locust bean gum. Xanthan and guar find a greater usage mainly because of their availability.

Xanthan, the structure of which[9] is shown in Figure 5, is obtained from the fermentation of sucrose by Xanthomonas campestris. Because of the specific association of xanthan polymer chains, it[10,11] has good potential for increasing fluid viscosity: in addition, it is to;arant of salts, and is therefore able to provide good efficiency in fresh as well as salt waters[12]. The polymer has the additional advantage of being sensitive to cross linking, notably with such agents as chromium cations. The rheological properties developed by polymer-polymer association are easily destroyed by shear forces, but are rapidly recovered on release of the shear[11]: these are ideal properties for drilling fluids. The rheological properties of xanthan are greater at high and low solution pH, in contrast to those of guar gum solutions. However, the long term (~ 500 days) storage of xanthan solutions at 90°C indicates only a slight reduction in viscosity, which is again in contrast to guar gum (at a considerably higher concentration) where a higher initial viscosity rapidly decreases with storage over a ~ 100 day period[6] (see Figure 6.). A recent potential improvement in xanthan via the fermentation route has been to modify the fermentation, so producing a structure devoid of the pyruvate side chain, and, consequently, a molecule with reduced ionic sensitivity to divalent cations[13]. This polymer raises its potential in oil recovery processes where compatibility with saline water is a problem; it does little, however, to improve the long term efficiency at elevated temperatures[6].

Guar gum, which is insoluble in organic solvents, but is soluble in water, is extracted from the ground endosperms of guar plants (typically Cyanopsis tetragonolobus L.) grown in India, Pakistan, and S.W. United States. The structure (see Figure 5.) is that of a nonionic polysaccharide molecule with a 'sugary' backbone of mannose units. The tolerance to saline water gives the polymer a general application particularly where polyvalent cations are anticipated, but the biodegradability and sensitivity to high temperatures make it of limited use for mobility control in oil recovery, although it is suitable for well preparative fluids. In particular, the fact that guar gums may be cross linked by selected transition metal ions under a wide range of pH conditions to give highly viscous solutions is an advantage[14]. It can be seen from Table 2. that guar gums are not used in cementing fluids - they are difficult to hydrate in alkaline conditions[15]. Several attempts have been made to overcome this hydration problem[16], with limited success.

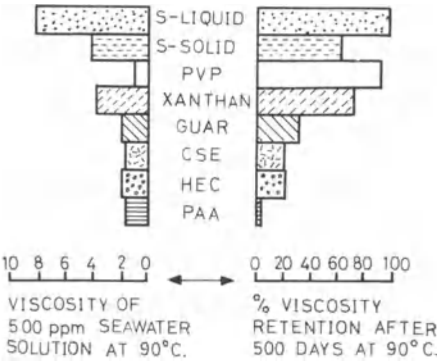


Figure 6. The viscosity of polymer-sea water solutions and the viscosity retention following high temperature storage. 10 units of viscosity represent 3 mPa.s. Abbreviations - see text. 'S' represents scleroglucan. Data reproduced from Ref.[6] with kind permission.

3.3. Starch and its derivatives

Starch, extracted from a variety of sources, including maize, potatoes, rice and wheat, in the form of granules, is arguably the most readily available of the natural polymers. However, the relatively poor viscosity increments (compared with other polymers such as cellulose,gums and polyacrylamides) have done as much to limit the use of starches in oil field preparative and recovery stages as its thermal instability[19,20]. Recently, starch derivatives have been prepared by grafting acrylamide on to starch[21] and by hydroxyalkylation of starch[22] to give increased viscosity effects. The latter material has found some application in drilling fluids, and the former in mobility control agents.

3.4. Acrylamide polymers

Polymers and copolymers of acrylamide are perhaps the largest group of synthetic polymers used in oil field preparation, recovery and production.Polyacrylamides(Figure 7.) are generally prepared as the partially hydrolyzed polymer, giving a degree of uncertainty of polymer solution viscosity, shear dependency and salt tolerance (especially with divalent and higher polyvalent cations). This partial hydrolysis has been related to the acrylamide-acrylic acid block copolymer where identical physical properties have been observed[23,24].

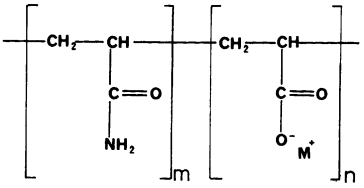


Figure 7. Structure of partially hydrolyzed polyacrylamide

Acrylamide polymers of various degrees of hydrolysis have been used extensively in low salinity waters where solution viscosities are high. They have also been used in fracturing operations to reduce friction losses[25], as fluid loss polymers in drilling fluids[26], and as mobility control agents in oil recovery processes[27,28]. However, recent data have indicated that the viscosity increase offered by PAM has a limited lifetime at high temperatures[6]. However, these laboratory data have been, to some extent, contradicted by the results of a full scale trial which has been successfully carried out in a North Sea operated field using 1000 ppm PAM: it should be remembered that the polymer had a short period in the field, which had previously been flooded with water, and was therefore somewhat cooler than the test conditions used in Ref.[6] PAM cross linking has been used to offer some potential to water mobility control where in situ cross linking by ions such as aluminium or chromium has been envisaged[29,30].

A significant development in the application of PAM has been the preparation of a so-called 'liquid polymer' - i.e., polymerizing the acrylamide monomer units in an emulsion[31,32]. Here an initial acrylamide (water-in-oil) emulsion is prepared and the polymerization is carried out in the emulsified water droplets. The result is to prepare a polymer already hydrated and dispersed within emulsified water droplets of an emulsion having a very low viscosity (10's of centipoise): the droplets can contain up to 60 % or more polymer by weight. This polymer is released to give a high solution viscosity by dilution with water, or on addition of an inverting surfactant. The liquid polymer system has also found significant use in providing a flocculating polymer for effluent treatment plants[31,32,33].

4. OIL PRODUCTION POLYMERS

Since water is used in secondary and tertiary stages of oil recovery, and oil zones are almost always associated in aqueous zones, it is not surprising that water is coproduced with crude oil. This coproduction gives rise to three main problem areas of oil production which utilize polymers in their resolution. These areas are scale formation and its inhibition, corrosion and its inhibition, and emulsions and their resolution. These are briefly discussed below.

4.1. Scale Formation

Scale is a mineral deposit which is formed as saline waters change temperature or pressure or are mixed with other waters. Most common scales associated with oilfield brines are calcium culphate, barium sulphate and calcium carbonate. The reasons for the precipitation of soluble salts is still much studied although it is generally recognized that scale inhibition can be obtained by the continuous chemical treatment of a phosphorus containing chemical acting as an efficient complexing agent, sequestering metal ions such as Ca^{++} or Ba^{++}.

4.2. Corrosion Inhibitors

Corrosion is an electrochemical phenomenon which invariably requires the presence of moisture. Chemicals which form an organic film between the moisture and the metal will reduce the corrosion. Polar molecules with long hydrophobic chains are typical, but the molecule must be oil soluble (or at least dispersible) and adsorb at the metal surface irreversibly. Inhibitors improve with increasing hydrophobic chain length and with a minimum of chain branching which creates a less permeable film. Most chemicals used in producing oil and gas wells are organic nitrogenous chemicals with long chain lengths. Fatty amines, monoamines, diamines, and ethoxylated amines based on fatty acids derived from natural tallow and coconut oils are primary chemicals used as inhibitors. Ethoxylated diamines are often preferred.

4.3. Demulsifiers

Crude oil contains naturally occurring surface active agents which stabilize water-in-oil emulsions. Heat, mechanical devices, electrical techniques and chemical demulsifiers are among the methods used to resolve the emulsions obtained. Such chemical demulsifiers are widely used in the oil industry, although each oilfield requires a different chemical system because of the many variables associated with each field, such as type of crude oil, emulsifying agents, mixing intensity, temperature and water content. Typical demulsifier chemicals include alkyl phenols, polyol esters and smaller ethoxylated alkyl phenols, such as butyl, nonyl or octyl phenols with 4,5, or 6 ethylene oxide units. Propylene oxide condensates of alkyl phenols are also used as an additional hydrophobe in the demulsifier molecule.

SUMMARY

The oil field operations in crude oil recovery and production where there is scope for polymers include well preparative and reservoir fracturing fluids, oil mobilization controlling fluids and production chemicals. In general, the polymers are used to control the fluid viscosity directly, but, in directly, are also used to hold buoyant the fluid weighting agents, chipping debris, proppant media, etc., as well as being used to hydrate clays and form gels or filter cakes to minimize fluid losses by fingering into reservoir structures. The clases of polymers which find wide acceptance in oil field operations are celluloses, starches, naturally occurring gums and acrylamides. In many cases, chemical derivatives have been identified which have improved salt tolerance and temperature stability, as well as the maintenance of suitable rheological properties.

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