DEVELOPMENTS IN IONIC POLYMERS—2

ALAN D. WILSON

HAVARD J. PROSSER

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and

HAVARD J. PROSSER

Laboratory of the Government Chemist, Department of Trade and Industry, London, UK

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PREFACE

Ionic polymers, like elephants, are easier to recognise than to define. Several methods of classification have been attempted but none is wholly satisfactory because of the extreme diversity of ionic polymers, which range from the organic, water-soluble polyelectrolytes, through hydrogels and ionomer carboxylate rubbers, to the almost infusible inorganic silicate minerals. For this reason, a general classification is not only difficult, but has minimal utility.

However, there are some characteristics of these materials that should be highlighted. The role of counterions is the significant one. These ions, either singly or as clusters, take part in the formation of ionic bonds which have a varying structural role. Often they act as crosslinks, but in the halato-polymers the ionic bonds form an integral part of the polymer backbone itself. Conversely, in polymers containing covalent crosslinks, such as the ion-exchange resins, the counterions have virtually no structural role to play, since they dwell in cage-like structures without affecting the crosslinking, and are readily exchanged. They are, perhaps, best described as ion-containing polymers rather than structural ionic polymers.

Another crucial factor is the role of water in ionic polymers. The presence of ionic bonds means that there is a tendency for these materials to interact with water. Where the ionic polymer contains a high proportion of ionic units, it acts as a hydrogel and may be highly soluble. Such interactions with water decrease sharply as the ionic content is reduced, though even then water can act as a plasticiser.

This book is the second volume in the *Developments in Ionic Polymers* series, the basis of which may be regarded as Holliday's *Ionic Polymers*, published in 1975. Since then certain areas have remained static and require no further treatment, while others have advanced dramatically. The two volumes in the Developments Series are together concerned totally with the latter areas.

This volume commences with a very comprehensive review of preparative methods for ionic polymers, both anionic and cationic (Chapter 1). Chapters following describe various ionic polymer types in terms of constitution and properties.

Hybrid silicate–organic structures are recognised as being potentially of great importance—indeed, one hypothesis of the origin of life assigns that essential role to them—but they have tended to be neglected as ionic polymers until now. This situation is remedied in Chapter 2.

The review of carboxylated rubbers which appeared in *Ionic Polymers* is now updated in Chapter 3.

The majority of ionic polymers consist of an anionic polymer and a small cationic counterion. However, not all ionic polymers conform to this pattern. Ionenes, conversely, consist of a small anion and a polymeric cation. They have tended to be neglected in the past but recently they have excited much interest. They are the subject of Chapter 4, which is perhaps one of the most comprehensive reviews to have appeared in recent years.

Another class of ionic polymers comprises the so-called polyelectrolyte complexes, where both the cation and the anion are polymeric, and encompasses some very useful advanced materials; one may cite, for example, electrically conducting polymers which are at the forefront of developments in high technology. Since polyelectrolyte complexes are important biopolymers of the living cell, interpolymer complexes prepared in the laboratory have been used as models to aid elucidation of complex biopolymer functions in their native environment in the living cell. A comprehensive review of their properties is presented in Chapter 5.

The applications of ionic polymers have not been neglected in this volume. One of their most important applications is as membranes. Certain members of this class are characterised by a high chemical resistance and find particular application in production of materials, involving corrosive intermediates, by electrolytic techniques. This topic is fully covered in Chapter 6.

Polyelectrolytes have found increasing use in medicine, pharmacy and biology in the last decade or so. Some possess intrinsic biological activity while others which are inert are used as carriers for the sustained release of drugs. The subject of biomedical applications is treated in Chapter 7.

Another interesting field is the formation of ionic polymers by

electrodeposition, a technique which is based on their fundamental characteristic. This technology finds application in the electrodeposition of coating systems and is described in Chapter 8.

Finally, it must be emphasised that the volume is not meant to provide an encyclopaedic coverage of the subject, nor does it even aim to cover all the latest developments. Rather, the object has been to present a selection of the most interesting contemporary developments. As such, it is essentially complementary to Volume 1 of the series and together the two volumes represent an updating of Holliday's earlier work on ionic polymers. For topics that have remained essentially unchanged, recourse should be made to Holliday's earlier work.

A. D. WILSON
H. J. PROSSER

LIST OF CONTRIBUTORS

KOJI ABE

Department of Functional Polymer Sciences, Shinshu University, Ueda 386, Japan.

FRITZ BECK

Fachbereich 6—Elektrochemie, Universität Duisburg, (Gesamthochschule), Lotharstrasse 65, D-4100 Duisburg, Federal Republic of Germany.

PAULINE J. BROOKMAN

Laboratory of the Government Chemist, Department of Trade and Industry, Cornwall House, Waterloo Road, London SE1 8XY, UK.

F. G. HUTCHINSON

Imperial Chemical Industries plc, Pharmaceuticals Division, Mereside, Alderley Park, Macclesfield, Cheshire SK10 4TG, UK.

GERHARD LAGALY

Institut für anorganische Chemie der Universität Kiel, Olshausenstrasse 40, D-2300 Kiel, Federal Republic of Germany.

JOHN W. NICHOLSON

Laboratory of the Government Chemist, Department of Trade and Industry, Cornwall House, Waterloo Road, London SE1 8XY, UK.

M. PINERI

Commissariat à l'Energie Atomique, Institut de Recherches Fondamentales, Centre d'Etudes Nucléaires de Grenoble, Avenue des Martyrs, 85X 38041, Grenoble Cedex, France.

The late R. A. M. THOMSON

Department of Chemical and Physical Sciences, The Polytechnic, Queensgate, Huddersfield, West Yorkshire HD1 3DH, UK.

EISHUN TSUCHIDA

Department of Polymer Chemistry, Waseda University, Tokyo 160, Japan.

TETSUO TSUTSUI

Graduate School of Engineering Sciences, Kyushu University, 39, Kasuga-shi, Fukuoka 816, Japan.

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Chapter 1

PREPARATION OF IONIC POLYMERS

The late R. A. M. Thomson

Department of Chemical and Physical Sciences, The Polytechnic, Huddersfield, UK

1 INTRODUCTION

Ionic polymers have been defined[1] as organic or inorganic materials which contain both ionic and covalent bonds in their chain or network structure.

Methods of classification of such materials are generally based on the degree of ionic character and the degree of crosslinking of the polymer.[2,3] Increase in the former is associated with increase in electrolytic behaviour, although the counterion is of great importance in determining the nature of the material. Increase in extent of crosslinking is associated with reduction in solubility· and in swelling character.

The present chapter will be restricted to a discussion of organic polymers displaying little, if any crosslinking, but a wide range of ionic character resulting from the presence of a range of numbers of charged or potentially charged sites per repeat unit. In most cases, the polymers under discussion are those which consist of water-soluble chains with charged groups pendent to the backbone, and associated with small counterions. Such materials are normally termed poly-electrolytes, and although they are of considerable commercial impor-tance, relatively few comprehensive reviews of their formation have appeared in the literature.[4-15]

Organic polyelectrolytes may be subdivided into anionics, cationics and ampholytics, according to the sign of the charges carried, and each

class may be further subdivided according to the variability of the charge concentration with change in environment, particular pH.

The usual routes to such materials are:

(i) polymerization or copolymerization of charged monomers with suitable charged or uncharged comonomers either by addition or step-reaction,

(ii) suitable modification of uncharged preformed or other functionalized polymer or copolymer.

Route (i) may prove impracticable because of inability of the monomers to undergo suitable polymerization by virtue of charge or reactivity factors, or alternatively, the inability to copolymerize in the correct proportions. If the method is practical, however, it will normally yield consistent, well-defined products. Problems associated with polymer modification, route (ii), include difficulties in ensuring good mixing, temperature control and constant reaction conditions, particularly if the reacting system is viscous or heterogeneous—a common situation. Differences in the nature of reactant and product polymers in solubility, may pose problems and side reactions, such as chain degradation and crosslinking, may deleteriously affect the product. Neighbouring-group effects may also exert a significant influence.

The main types of polyelectrolyte discussed in this chapter will be:

(i) anionics, e.g. ions derived from carboxylic ($-COOH$), sulphonic ($-SO_3H$), phosphate ($-O \cdot P(O)(OH)_2$) and phosphonate ($-PH(O)(OH)$) groups;

(ii) cationics, e.g. protonated amines ($-\overset{+}{N}H_3X^-$); $-\overset{+}{N}RH_2X^-$ or $-\overset{+}{N}R_2HX^-$), quaternary ammonium compounds ($-\overset{+}{N}R_3X^-$), sulphonium ($-\overset{+}{S}R_3X^-$) and phosphonium salts, ($-\overset{+}{P}R_3X^-$), the latter two being relatively unimportant;

(iii) ampholytics, e.g. polyelectrolytes containing each of the above types of group.

In the above list, carboxylic and amino groups behave as 'weak' electrolytes; the remainder are effectively completely ionized at all pH values and behave as 'strong' electrolytes. In general, the former class displays complicated ionization behaviour. The polymer has a greater pK_a value than that of the corresponding monomer and it increases with increase in degree of ionization as explained later, i.e. with increase in pH in the case of the polyacids and decrease in pH in the

case of the polybases. It also increases with the decrease in ionic strength of the system and the increase in base counterion radius.[16]

Polymerization and post-polymerization modification techniques for the formation of these classes of polymer will be discussed.

2 ANIONIC POLYELECTROLYTES

2.1 Carboxylic-based Polymers

2.1.1 Polymerization of Acrylic Acid (AA), Methacrylic Acid (MAA) and Their Salts

AA and MAA are both potentially hazardous in the pure, anhydrous state, since they are liable to polymerize spontaneously and explosively. Thus, they should be kept in that state as briefly as possible, and certainly stored above their melting points (~13°C). Use of a copper-gauze filled fractionation column is recommended in the reduced-pressure distillation of the inhibited monomers, together with other safety procedures.[17] Both polymers are insoluble in their monomers and in a wide range of organic solvents, from which they normally precipitate during preparation as fine powders. Solubility in water increases with temperature in the case of poly(acrylic acid), PAA, but decreases in the case of poly(methacrylic acid), PMAA. The monomers are soluble in a wide range of solvents.

Several reviews of the polymerization and copolymerization of AA and MAA have appeared in recent years.[18-24] Polymerization may be carried out under homogeneous or heterogeneous conditions in either aqueous or non-aqueous media. Free-radical initiation is the usual route employed. Conventional initiators, such as organic azo compounds[25] (often water-soluble),[26] inorganic and organic peroxides and related compounds, alone[27] or coupled with suitable reducing agents or catalytic ions, are usually effective.[28,29]

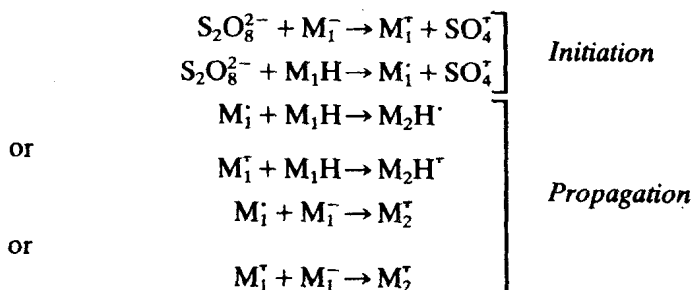#### 2.1.2 Solution Polymerization

Initiator systems have been reviewed recently by several authors[24,30,31] and although these are not specific to the polymerization of AA and MAA, there is little doubt that they will usually be effective.

The following are among systems recently reported for the initiation of polymerization of AA and MAA.
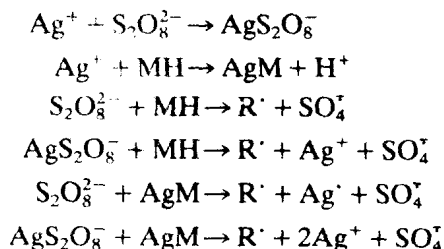
The use of potassium persulphate as initiator[32] for the polymerization of concentrated sodium methacrylate $(3 \cdot 15 - 4 \cdot 67 \, \text{mol dm}^{-3})$ solutions has indicated second-order termination with an initiator exponent of $0 \cdot 5$ but the rate of polymerization (R_p) was zero order in monomer. The overall activation energy appeared rather high $(91 \cdot 5 \, \text{kJ mol}^{-1})$.

A study of AA and MAA polymerization using the same initiator was reported by Venkatarao et al.[33] These workers deduced that initiation involves interaction between persulphate ions and monomer, which could be in either the ionized or un-ionized form, depending upon the solution pH:

$$\left.\begin{array}{l} S_2O_8^{2-} + M_1^- \rightarrow M_1^\tau + SO_4^{\cdot -} \\ S_2O_8^{2-} + M_1H \rightarrow M_1^\cdot + SO_4^{\cdot -} \end{array}\right\} \quad \textit{Initiation}$$

or

$$\left.\begin{array}{l} M_1^\cdot + M_1H \rightarrow M_2H^\cdot \\ M_1^\tau + M_1H \rightarrow M_2H^\tau \\ M_1^\cdot + M_1^- \rightarrow M_2^\tau \end{array}\right\} \quad \textit{Propagation}$$

or

$$M_1^\tau + M_1^- \rightarrow M_2^\tau$$

The values of $[M_1^-]$ and $[M_1H]$ thus control the overall rate of initiation and therefore R_p would be expected to display a dependence upon the pH of the system.

Ag^+ ions were found to catalyze the persulphate initiation, an effect ascribed to reactions of the type:

$$Ag^+ + S_2O_8^{2-} \rightarrow AgS_2O_8^-$$
$$Ag^+ + MH \rightarrow AgM + H^+$$
$$S_2O_8^{2-} + MH \rightarrow R^\cdot + SO_4^{\cdot -}$$
$$AgS_2O_8^- + MH \rightarrow R^\cdot + Ag^+ + SO_4^{\cdot -}$$
$$S_2O_8^{2-} + AgM \rightarrow R^\cdot + Ag^\cdot + SO_4^{\cdot -}$$
$$AgS_2O_8^- + AgM \rightarrow R^\cdot + 2Ag^+ + SO_4^{\cdot -}$$

This mechanism explains the relatively minor salt effects observed. For example, Cu^{2+} ions were found to retard the rate of polymerization. This effect was ascribed to oxidative transfer with the growing radicals, leading to reduced rate and degree of polymerization:

$$\sim\!\!\sim\!\!CH_2 - \dot{C}HR + M_{(aq)}^{n+} \rightarrow \sim\!\!\sim\!\!CH=\!\!=CHR + M^{(n-1)+} + H^+$$

The catalytic effect of Ag^+ ions was also observed[34] in the polymerization of MAA by potassium peroxodiphosphate in aqueous H_2SO_4, reducing the overall energy of activation from the already low value of $34.5 \, \text{kJ mol}^{-1}$ to $19.3 \, \text{kJ mol}^{-1}$.

An interesting procedure was reported[35] for controlling product degree of polymerization in systems using redox initiators in the presence of multivalent metal ions. Addition of a powerful ion-chelating agent such as EDTA was found to cause the cessation of polymerization, whereupon the monomer concentration could be increased before addition of further metal ions to re-start the initiation process.

Aldehydes such as butanal, pentanal and hexanal in dioxane[36] and benzil dimethyl ketal (I) in aqueous solution at high pH[37] were

I
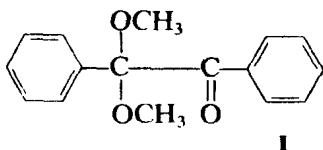
reported to be effective initiators. Photochemical decomposition of the latter in a mixture of acrylamide (ACM) and AA was claimed to give a more rapidly dissolving copolymer, which was considerably richer in AA units, than did II.

II
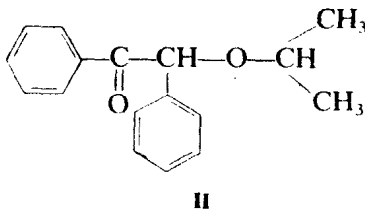
Nitrogen dioxide in tetrahydrofuran (THF) or 1,4-dioxane has been shown[38] to be an effective free-radical initiator (overall energy of activation $68 \, \text{kJ mol}^{-1}$). Peroxysilanes of the general structure III,

$$(CH_3)_{(4-n)}Si((CH_3)_3COO)_n$$

III
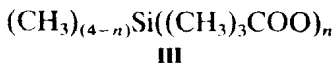
where $n = 1 - 3$, were used as initiators.[39] For $n = 3$, initiation with primary radicals formed by induced decomposition of the initiator yielded polymers containing peroxy groups. Poly(γ-

mercaptopropylsiloxane–lanthanide) complexes were also shown to initiate polymerization of AA by a radical mechanism.[40]

Manganese(III) has proved to be an efficient constituent of polymerization initiators. Manganese(III) benzenesulphonatobis(acetylacetonate), **IV**, where $C_5H_7O_2$ = ligand, R = H, Me, CH=CH$_2$, OH,

$$(C_5H_7O_2)_2MnSO_3-\!\!\left<\!\!\bigcirc\!\!\right>\!\!-R$$
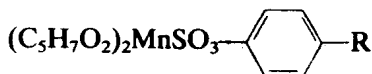
IV

COOH or $C_{10-14}H_{21-29}$, was found[41] to be an efficient initiator at 10–20°C in the presence of atmospheric oxygen. Initiation with manganese(III) acetate in aqueous H_2SO_4 displayed[42] a decrease in R_p with increase in ionic strength and [H$^+$]. Mn(OH)$^{2+}$ was postulated as the initiating species and manganese(III) as the terminating species.

Comparison[43] of the manganese system (**IV**) and persulphate/ascorbic acid initiating systems in the polymerization of AA showed that in the former case the rate of polymerization and degree of polymerization were greater by factors of about 80 and 2 respectively. It was also shown that a small quantity of ethanol acted as a chain transfer agent and controlled the rate of chelate decomposition and therefore polymerization.

Several redox systems involving manganese(III) have been used for the polymerization of AA. Mn(CH$_3$CO$_2$)$_3$/diglycolic acid[44] and Mn(CH$_3$CO$_2$)$_3$/isobutyric acid[45] in aqueous media both function by oxidation of the organic acid via complex mechanisms to yield reactive free radicals. Termination was ascribed to the interaction of growing chains with manganese(III) and manganese(III)–acid complexes, leading to regeneration of manganese(II).

Other systems have also been studied. These include the hydrogen peroxide/ascorbic acid system,[46] which gave overall energies of activation of 75·7 and 62·6 kJ mol^{-1} for AA polymerization in the pH range 7–9·4; these energies correspond to ionized monomer reacting with virtually un-ionized and completely ionized chains respectively. In the absence of monomer, the main product is oxalic acid. Sodium hypophosphite/2,2'-azobis(2-amidinopropane)/HCl is claimed to yield high molecular weight products.[47] Presumably, the initiator is redox in the early stages, after which thermal decomposition of the azo compound becomes the main initiation process.

A systematic study[48] of MAA polymerization initiated by perpropi-

onic acid/metal acetate in benzene showed that the reaction proceeds in the presence of oxygen and that the activity of the catalyst increases in the order:

$$Ce < Fe < Cu < Co < Mn$$

Finally, the hydrogen peroxide/3,4,5,6-tetrahydroxy-2-oxohexanoic acid lactone(V) was shown[49] to be very effective in the polymerization of AA in alkaline solution, a temperature rise of 2°C being observed over the first 30 s of reaction.

$$
\begin{array}{c}
\overset{O \quad O}{\overset{\|\quad\|}{C—C}} \\
O{\diagup}\quad{\diagdown}CHOH \\
CH—CHOH \\
CH_2OH
\end{array}
$$
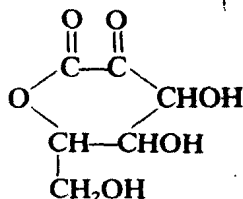
V

2.1.3 Emulsion Polymerization[50,51]

Homogeneous polymerization of AA and MAA in aqueous solution will normally yield a viscous solution or gel which may cause problems in handling. Use of water-miscible organic solvents often leads to precipitation of the polymer which, under suitable conditions, may yield an easily handled product. An alternative and widely practised technique is inverse emulsion or suspension (water-in-oil) polymerization.

This involves the production of submicroscopic water-swollen hydrophilic spheres by suitable mixing of aqueous monomer solution, hydrophobic phase, emulsifier, water-soluble or oil-soluble initiator and a wide range of other additives. These form the principal polymerization loci, but, in contrast to conventional oil-in-water emulsions, they are much more comparable in size with the aqueous monomer droplets which constitute the monomer reservoir; hence the situation is more complex. Inverse emulsions are also less stable and may tend to settle out over a period of days.

Dimonie et al.[52] compared inverse suspension with solution polymerization of ACM, and it is probable that their general conclusions can be extended to most water-soluble polymers. They examined the effect of method of aqueous phase addition, type and concentration of emulsifier, salt concentration, time intervals between mixing, and

other variables, on the rate of polymerization and polymer molecular weight and nature.

They found that polyacrylamides prepared in inverse suspension are of considerably lower molecular weight than those prepared using the same initiator concentration in solution. These workers also found that in the former case, product molecular weight is independent of initiator concentration whereas in the latter, the normal rate-dependence was observed.

It was also found that in suspension polymerization, product degree of polymerization decreases with increase in surfactant concentration.

Addition of inorganic salts was found to have little effect whereas even small amounts of carboxylic acid salts caused a marked increase in product molar mass. Neither the length of time elapsing between mixing the phases and commencement of polymerization nor the intensity of stirring has much effect on the product molar mass.

On commencement of polymerization, phase-inversion was found to occur, yielding a continuous aqueous phase of increased viscosity.

Table 1 gives brief details of a few of the many recipes that have been reported in the literature for the polymerization or copolymerization of AA and/or MAA. A vast patent literature exists for the emulsion polymerization of other water-soluble monomers and such recipes will probably be effective in the present case. Detailed discussion is outside the scope of this chapter.

2.1.4 Factors Affecting the Polymerization Process

(a) Aqueous solution. The nature of the solvent medium[64] has been shown to exert a considerable effect on the polymerization of AA, MAA and other inorganic monomers. This is most clearly understood in studies of homogeneous polymerization under a range of conditions. In particular, variation of pH, ionic strength, nature of counterion and choice of different solvent compositions has provided a valuable insight into polymerization mechanisms.

Kabanov et al.[65] studied the effect of pH on the aqueous-phase polymerization of AA and MAA and their results are shown in Fig. 1.

AA monomer is a typical weak acid which undergoes ionization with a pK_a of 4·2. Ionization of PAA is a more complicated process, since partial ionization imparts a negative charge to the polyion and increases the free energy of ionization, thereby hindering further release of hydrogen ions. This results in a pK_a value which is usually considerably higher than the single pH-independent value for the