I

INTRODUCTION

I. INTRODUCTION

I.1 General

An ionic polymer is a polymer, either inorganic or organic, which contains both covalent and ionic bonds in its chain or network structure. A typical example is an ionomer, a du Pont name for a metal salt of a carboxylated polyethylene, but often used in a wider sense of ionic polymers. Ionic polymers are therefore a class of materials which fall between the formal divisions of chemicals, between covalent solids like diamond and polyethylene on one hand, and ionic solids like sodium chloride or sodium benzoate on the other (1).

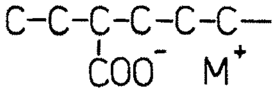
Since glass which can be regarded as an ionic polymer has a history of several thousand years, it means that ionic polymers have a respectable ancestry. It would be reasonable to say, however, that systematic work on these materials began with the works of Brown on rubbers (2) and of Fitzgerald and Nielsen on polyacrylates (3).

Ionic polymers exist in the salt or ionised form, i.e. the counterion - say a cation for a poly-anion is not hydrogen. Thus a metal polyacrylate is an ionic polymer, but polyacrylic acid is not. By definition, the range of ionic polymers is very wide, since it includes materials as dissimilar as glass, ionomers, carboxylated rubbers, alignate gels, soluble polyelectrolytes, etc. The formulae of some of them are shown in Fig.I.1.

The effect of inserting ionic bonds into covalent solids was explored and it involved covering a wide range of materials. The ionic bond is a strong bond, like the covalent bond; however, it can, under certain circumstances, be thermally labile and this can be a useful property. It can also show the property of ion exchange in aqueous or molten systems. In some instances it may be convenient to produce a more rigid product by adding ionic bonds rather than covalent bonds. In this connection, the fact that the ionic bond can be readily formed is a great advantage.

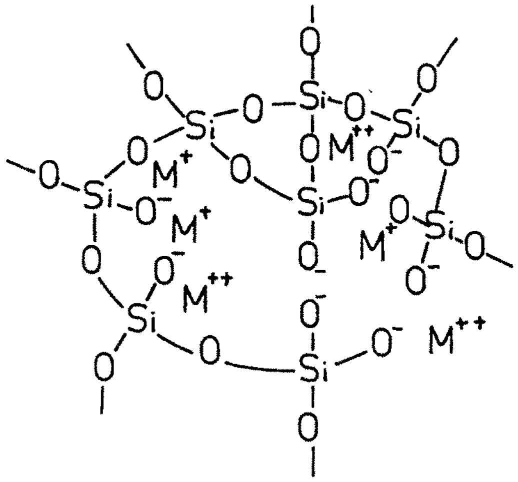
In the two structures shown in fig.I.2, structure in (a) represents the backbone of a vinyl polymer like polyethylene or PVC, whilst structure in (b) represents a polyether like polyethylene oxide. The bonds in the chain are called network bonds, and they connect the network atoms e.g. C and C or C and O. The two parameters, connectivity of network atoms (CN) and the relative number of covalent network bonds per unit volume (Ncr) have been discussed by Holliday and Holmes-walker (4).

Since the ionic bond is non-directional there is no network in the polymer sense, and the ions tend to cluster

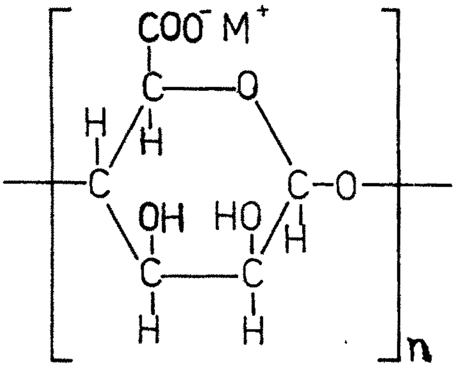


$$C-C-\underset{COO^-\ M^+}{C}-C-C-C-$$

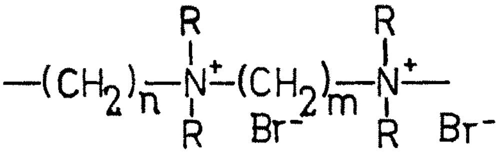
(a) Skeleton of ionomer or carboxylated rubber with univalent cation



(b) Partial 2—D representation of 3—D glass structure with silicate anion groups and univalent and divalent cations



(c) Repeat unit of metal salt of alginic acid



$$-(CH_2)_n-\overset{R}{\underset{R}{N^+}}-(CH_2)_m-\overset{R}{\underset{R}{N^+}}-\quad Br^- \quad Br^-$$

(d) Simple ionene

fig. I.1

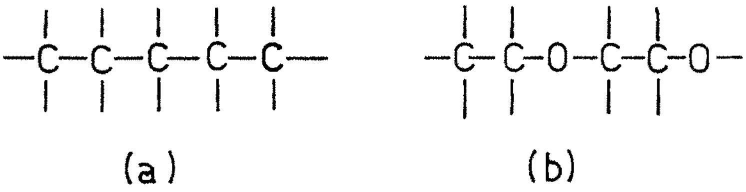


fig. I. 2

or pack as closely as possible. Because of this, there is no degree of freedom of atomic arrangement in a purely ionic material like sodium chloride, as there is in a covalently bonded solid. In fact, compared with covalent solids, ionic solids are always tightly packed aggregates of matter. Though ionic solids may contain covalent bonds within the cation or anion, as in sodium benzoate or a quaternary ammonium salt, the same comments about close packing of cations and anions apply as with simpler materials like sodium chloride. This unhampered close packing of ionic solids partly explains the ease with which they crystallize compared with covalent solids.

Ionic polymers contain both covalent and ionic bonds, which together form chains, branches and networks. In the vast majority of cases, the covalent bonds themselves already exist along the chain, sheet or network characteristic of the polymer. The ionic bonds are additional to this structure, and modify the properties. In certain cases, as yet unimportant but which may become of greater significance, the covalently bonded moiety is too small to be considered a polymer (e.g. sebacic acid) but it acquires polymer-like properties in the salt form, i.e. when ionic bonds are introduced into the structure.

I.2 Classification of ionic polymers

A homopolymer polyelectrolyte would contain a homopolymeric polyanion or polycation. A copolyelectrolyte has isolated salt groups as in a carboxylated rubber. A polysalt is a complex formed between oppositely charged polyelectrolytes. Holliday (5) drew a distinction between those materials with a continuous covalent backbone or network and those with a discontinuous backbone.

The classification shown in table I.1 was proposed based partly on the arrangement of the covalencies, and partly on the type of ionic bond. The diagrammatic representations act as a visual aid to distinquishing the various types of ionic polymers, and carry no particular implications as to the spatial arrangement of the ionic bonds. As shown in the table, ionic polymers are divided into three groups. In the first, the covalent network is continuous in three (or two) dimensions; in the second, continuous covalent chains exist (i.e. they are continuous in one dimension); while in the third group the covalent segments are relatively short. Within these groups, there is a further important distinction between organic and inorganic ionic polymers.

Organic ionic polymers

The covalent skeletal structure can be derived virtually from any normal polymer. The chain atoms are carbon, but may include other atoms such as oxygen or nitrogen. In addition,the covalent skeletal structure may be made up of relatively short segments, as in the

TABLE I.1

Types of ionic polymers

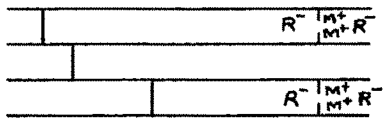
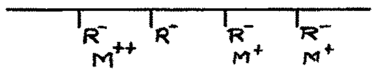
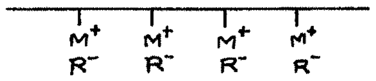
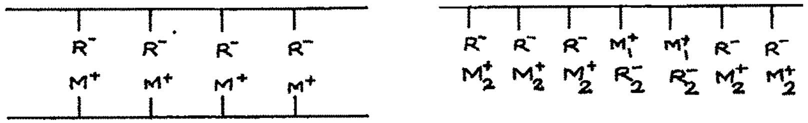
Chain or network type	Diagrammatic representation (full lines are covalent bonds)	Ion type	Examples	Ref
I Covalent network + ionic bonds		Polyanion	(a) Glass (b) Sheet silicates (c) Cement (d) Clay products (e) Cation exchange resins	
		Polycation	(a) Anion exchange resins (b) Rubbers with quaternary N cross-links	
		Mixed	(a) Amphoteric ion exchangers	
II Long covalent chains + ionic bonds		Polyanion	(a) Linear silicates (b) Polyphosphates (c) Ionomers (d) Metal salts of polyacrylic acid (e) Salts of carboxylated rubber (f) Anionic polyelectrolytes (g) Polysaccharide gels	 2
		Polycation	(a) Cationic polyelectrolytes (b) Ionenes (N^+ in main chain)	 12

TABLE I.1(Contd)

Chain or network type	Diagrammatic representation (full lines are covalent bonds)	Ion type	Examples	Refs.
		Mixed	(a) Polysalts (b) Charge mosaic complexes (c) Snake cage polyelectrolytes (d) Amphoteric ion exchangers	16
III Short covalent chains +ionic bonds	$R^- — R^-M^{++}R^- — R^-M^{++}R^- — R^-M^{++}$	Dianion	(a) Metal salts of dicarboxylic acids (b) Invert glasses (c) Polysulphides	21 22
	$M^+ — M^+R^{--}M^+ — M^+R^{--}M^+ — M^+R^{--}$	Dication		

metal salts of α,ω-dicarboxylic acids. Although there is virtually no limit to the types of structures which can be envisaged, in practice relatively few types of ionic polymers have been commerciallized, based mostly on a few vinyl monomers or diolefins.

Inorganic ionic polymers

In case of inorganic ionic polymers, the commonest chain atoms are silicon or phosphorous, arranged alternatively with oxygen as

$$- Si - O - Si - O -$$
$$- P - O - P - O -$$

These structures form the backbones of the mineral silicates, inorganic glasses, polyphosphates, etc. In addition to Si, P and O, many other atoms such as B, Al, Zr, N, etc. may act as chain atoms.

I.3 Brief Survey

3(a) Covalent networks and sheets containing ionic bonds

These systems are examplified by (i) polyanions (ii) polycations and (iii) ampholytes.

(i) Polyanions

Ionic polymers based on silicate ions are important on account of their occurrence and variety, such as inorganic glass, sheet or network silicates, cement, clay products, etc.

The three dimensional silica lattice may be modified by the introduction of other network forming atoms such as aluminium or boron. The materials formed in this way may be crystalline or amorphous, but in general they share certain properties, such as rigidity, strength, high melting temperature, etc. As they are cheap, they have been of immense importance in industry.

The relationship of silica with other silicate products is seen in terms of the O:Si ratio, which varies from 2 in quartz and its polymorphs to 4 in the orthosilicates. Fig.I.3 illustrates this point (6).

Ionic polymers based on organic anions are the commercially useful cation exchange resins containing the polyanions such as sulphonate, carboxylate, phosphonate, etc. The covalent cross-links preserve the structural integrity of the materials, whilst the fixed ions provide the ion-exchange sites. A cation exchanger is an anionic polyelectrolyte, consisting of immobilised anions fixed to the structure and mobile cations as counter ions. It can also be regarded to have a sponge-like structure, with counter ions floating in the pores.

The examples of cation exchange resins are (i) styrene copolymerized with divinyl benzene and sulphonated and (ii) methyl methacrylate copolymerized with divinyl benzene and hydrolysed after polymerization.

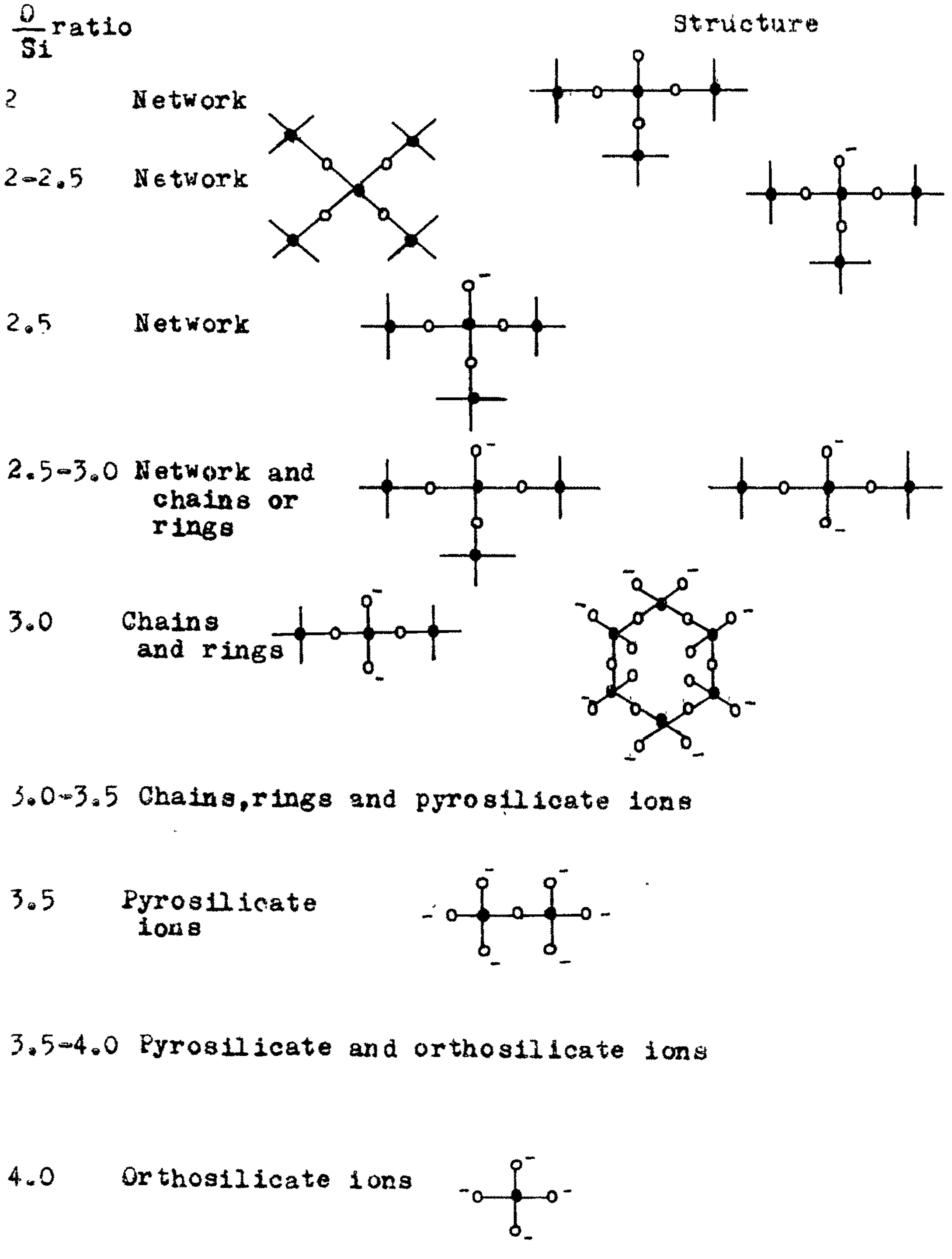


fig. I. 3 Effect of oxygen-silicate ratio on silicate network structure

Si ○ O

Anionic polyelectrolytes have also been prepared from copolymers of styrene by sulphonation (7). Tough, coherent films can be made from these materials.

(ii) Polycations

The ionic polymers carrying fixed cations are the anion exchange resins. The example is styrene copolymerized with divinylbenzene, followed by chloromethylation and quaternization.

(iii) Ampholytes

Ionic polymers carrying both bound anion and cation sites in the network are the amphoteric ion exchange resins.

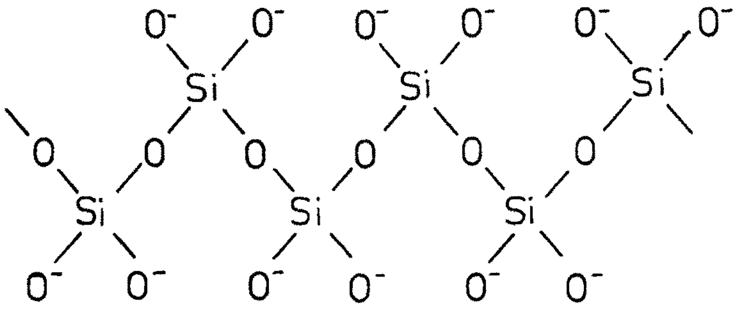
3(b) Long covalent chains containing ionic bonds

Examples of these systems are (i) polyanions, (ii) polycations and (iii) polysalts.

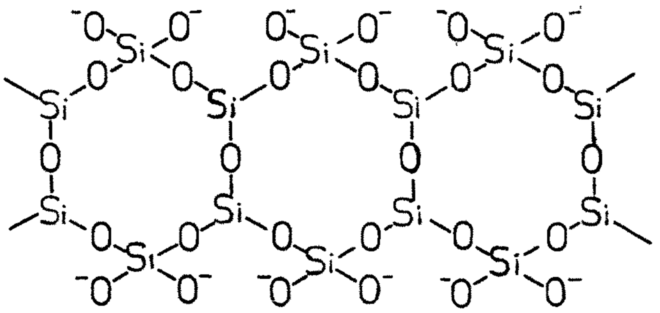
(i) Polyanions

These are exemplified by linear silicates, linear phosphates, ionomers, metal salts of polyacrylic acid and carboxylated rubbers, anionic polyelectrolytes, polysaccharide gels, etc.

Linear silicates, based on single and double strands (fig.I.4) of the type of O-Si-O-Si-, are of widespread natural occurrence.

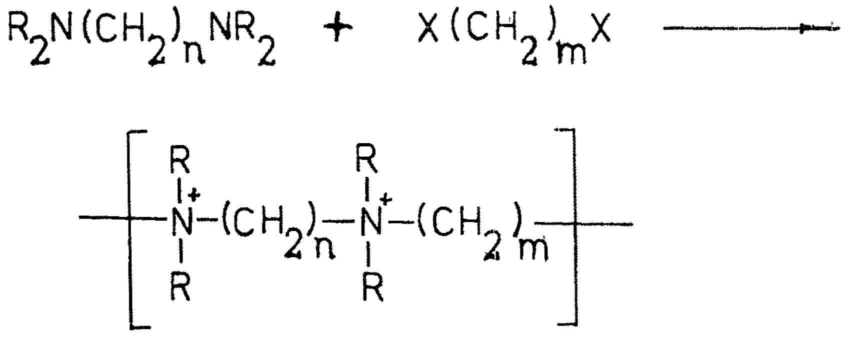


single strand



double strand

fig. I. 4



$$R_2N(CH_2)_nNR_2 + X(CH_2)_mX \longrightarrow \left[-\overset{R}{\underset{R}{\overset{|}{\underset{|}{N^+}}}}-(CH_2)_n-\overset{R}{\underset{R}{\overset{|}{\underset{|}{N^+}}}}-(CH_2)_m- \right]$$

fig. I. 5

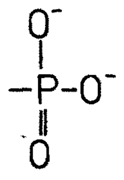
Examples of mineral silicates with single chain ions are the proxenes, such as enstatite ($MgSiO_3$), diopside ($CaMg(SiO_3)_2$), β-wollastonite ($CaSiO_3$), angite, jadeite and spodumene.

Examples of silicates with double stranded chain ions are the amphiboles, such as tremolite, actinolite, crocidolite; anthophyllite and amosite.

Eisenberg (8-10) examined the viscoelastic properties of solid silicates in the composition region $M_2O:SiO_2 \approx 1$, and compared them with the polyphosphates and other ionic polymers.

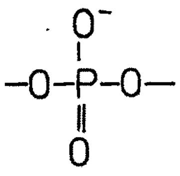
Condensed phosphates are made by the dehydration of orthophosphates at elevated temperatures or by the hydration of phosphorus pentoxide. They can be regarded as made up of three building blocks:

End unit



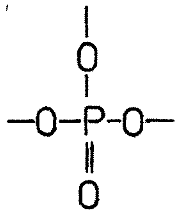
$-P(=O)(O^-)-O^-$

Middle unit



$-O-P(=O)(O^-)-O-$

Branching unit



$-O-P(=O)(-O-)-O-$

Since the branching unit is trifunctional, it might be expected that crosslinked polyphosphate would occur. Condensed polyphosphates are therefore normally encountered as rings and chains rather than sheets or networks. Condensed phosphates form soluble complexes with many metals. They are used industrially for this purpose, for example in water softening.

Compared with normal low density polyethylene, the ionomers are characterised by high strength, good clarity and improved oil resistance.

Metal salts of polyacrylic acid, and copolymers of acrylic acid and acrylates form another class of ionic polymers studied by Nielsen (3). A large number of composites were made with these materials, some with interesting mechanical properties. Maleic and Fumaric acids can lead to similar interesting products, with a slightly different disposition of carboxyl groups.

Miller and Reid (11) proposed the treatment of films of copolymers of butadiene and methacrylic acid with salts of polyvalent metals as a technique of hardening the film. Brown's invention (2) specifically concerns crosslinking rubbers using ionic bonds.

Anionic polyelectrolytes of importance contain carboxyl or sulphonic groups. They are used as ion exchange materials. Their mechanical properties depend upon the degree of crosslinking and the proportion of bound anions.

Non-cross-linked anionic polyelectrolytes are widely used industrially as solutions or gels. In their anhydrous state they tend to be brittle solids, and the question of whether they will dissolve or form a gel in water is largely controlled by the proportion of bound anions in the chain.

Because of the ready availability of acrylic and methacrylic acids, homopolymers and copolymers of these materials are widely prepared and used industrially. Solutions of the homopolymers are used in such applications as dispersing, thickening or suspending aqueous systems.

Many polysaccharide gels having carboxylate or Sulphonate groups can be regarded as ionic polymers. Examples of such materials are the alginate gels, much used in dentistry as impression materials.

(ii) Polycations

The quaternary ammonium polymers, can be divided into the following classes :

(i) Polymethacryloxyalkyl
(ii) Polymethacrylamidoalkyl
(iii) Polyalkenyl
(iv) Polyvinyloxy
(v) Polyvinylbenzyl
(vi) Polydiallyl
(vii) Polyvinyl pyridinium
(viii) Polyvinylimidazolinium
(ix) Polyalkylated quaternaries
(x) Polycondensation quaternaries

The widespread uses of cationic quaternary polyelectrolytes are suggested in Table I.2.

TABLE I.2

Uses of Cationic Quaternary Polyelectrolytes

(i) Primary Coagulants
(ii) Flocculants
(iii) Antistatic agents
(iv) Soil Conditioning
(v) Flame retardants
(vi) Hair sprays, shampoo additives etc.
(vii) Sequestering agents
(viii) Grease thickening
(ix) Ekectroconductive coating
(x) Anion-exchange resins
(xi) Biocides
(xii) Dye mordants
(xiii) Pigment retention aids
(xiv) Wet and dry strength additives in paper making
(xv) Emulsifiers and de-emulsifiers
(xvi) Corrosion inhibitors
(xvii) Stiffening agents for fabrics and paper
(xviii) Sensitisers for photographic film
(xix) Polyelectrolyte complexes
(xx) Lube-oil additives
(xxi) Printing inks
(xxii) Adhesives

Ionenes are a particular kind of polycations where the bound cations are in the main chain, as opposed to those materials where the bound positive sites are pendant to the chain. They have been extensively studied by Rembaum (12-14), Razvodskii (15), etc. These materials (fig.I.5) are crystalline and up to n = m = 10, they are water soluble polyelectrolytes. Following the systematic nomenclature of Rembaum, a 6-8 ionene, for example, has n = 6 and m = 8.

(iii) Mixed ions

Polysalts or polyelectrolyte complexes contain cationic and anionic sites on polymeric chains.

When two linear polyelectrolytes of different ionic charge types are mixed in solution, ionic bonded network structures are formed. In such a reaction a separate phase is formed as illustrated by the interaction of gelatine (a polycation) and gum arabic (a polyanion).

The interaction between weakly basic and acid functions leads to the formation of liquid or gel products, called coacervates. The work of Michaels (16) led to the exploitation of the more strongly bonded precipitates formed when a strongly acidic polyanion reacted with a strongly basic polycation. A typical example is the reaction between sodium polystyrene sulphonate and polyvinyl benzyl trimethyl ammonium chloride. (fig.I.6).

A stoichiometric polyelectrolyte complex is formed when the bound ions of opposite signs are equal in number;

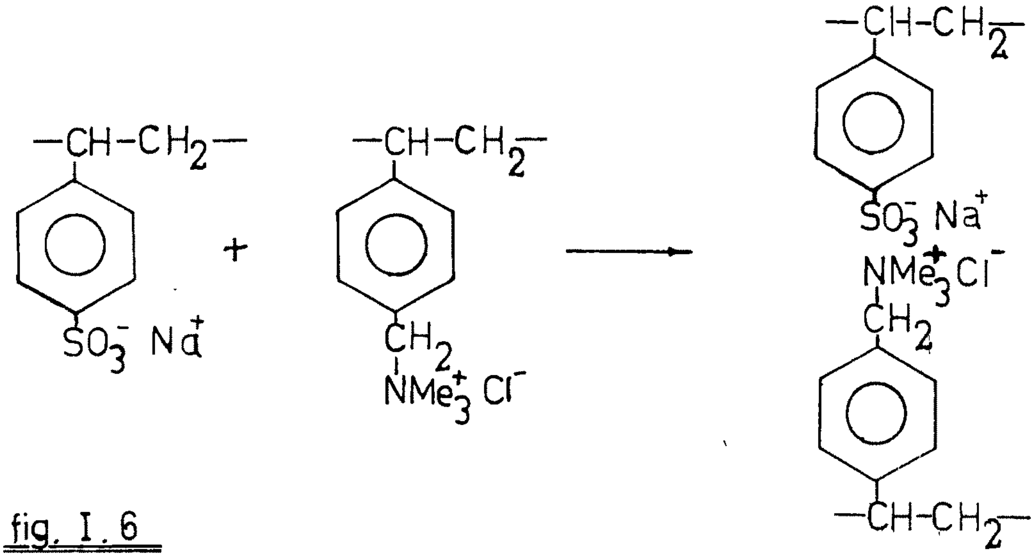
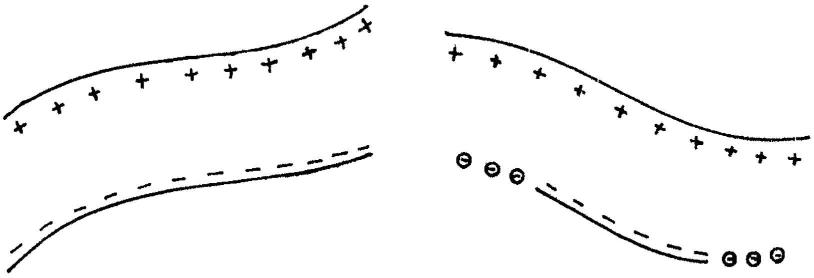


fig. I.6



Stoichiometric arrangement of bound ions

Non-stoichiometric arrangement

fig. I. 7

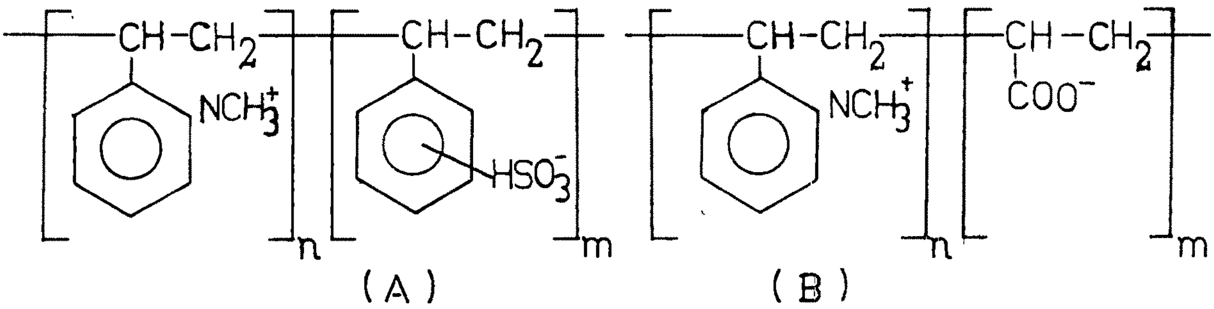


fig. I.8

if the groups can approach close enough, stoichiometric poly-poly salt formations would take place, and the mobile counterions would diffuse away.

Non-stoichiometric complexes also exist, and their behaviour and properties are related to the extent of non-equivalence in bound anions and cations. The excess of bound ions will have the appropriate number of mobile counterions to maintain the balance of electric charges, and will therefore behave like conventional ion-exchange resins. The difference between stoichiometric and non-stoichiometric polyelectrolyte complexes shows up, for example, in their water absorption. The former may absorb 30 % by weight when saturated, the latter up to ten times their dry weight. The distinction between the two types of polyelectrolyte complexes is illustrated diagrametically in fig.I.7.

Following the interest in mosaic membranes for water desalination by piezodialysis (17), attempts have been made to produce analogous structures containing cations and anions on same chains (18,19) as shown in fig.I.8.

Snake-cage polyelectrolytes consist of conventional cation or anion exchangers in which linear polycations or polyanions respectively have been formed by polymerization (20). Structurally these materials are hybrids, since the original ion-exchange material is cross-linked (3-D) whilst the polymerizable counterions produce a chain (1-D) polymer.

3(c) Short covalent chains plus ionic bonds

Metal salts of dicarboxylic acids form an important group of this type of ionic polymers. The studies of the properties of some metal salts of dimerized fatty acids, such as linolic acid or linoleic acid, showed them to be sharp melting, transparent resins from which fibres could be drawn (21).

Invert glasses

As the coherence of the glass network is reduced, by reducing the average number of bridging oxygen atoms per tetrahedron, a stage is reached where discontinuous chains are formed. At this point, Y, the average number of bridging oxygens per tetrahedron is smaller than two and there is less than 50 mole % of SiO_2 in the composition. Assuming the structure to consist of chains, the average chain length $\bar{n}$ (the average number of tetrahedra per chain) is

$$\bar{n} = 2 / (2 - Y)$$

Normally glass formation ceases below this mole ratio, and crystalline products are obtained. This would happen if only one kind of cations was present. However, if two or more kinds of metal ions are used, glass formation can continue to values of $Y < 2$ (22,23). Such glasses are called invert glasses, because there is now a matrix of metal ions in which the chains are embedded (fig.I.9). Certain physical properties pass through an inversion point when $Y = 2$, e.g. there is a minimum in the plot of viscosity against Y.

I.4 Some structural features of ionic polymers

4 (a) Concentration of ionic bonds

Ionic polymers contain bound ions, and free counterions. The bound ion is covalently bonded to the polymer network, as the carboxyl group in the polyacrylates or the quaternary ammonium group in the ionenes. In contrast to this, the counterion is free to move, but the actual mobility depends on various factors such as the strength of the ionic bond, the temperature, the presence of liquid which promotes dissociation, etc. This distinction is easily seen by comparing ionomers with ion - exchange resins, which depend for their operation upon bound ions and mobile counterions.

Clearly, an important parameter in ionic polymers is the concentration of bound ions in the structure. In his study of the clustering of ions in organic polymers, Eisenberg (24) defines the concentration of ion pairs in terms of simple stoichiometry as

$$C = \rho \times N / M_i \qquad (1)$$

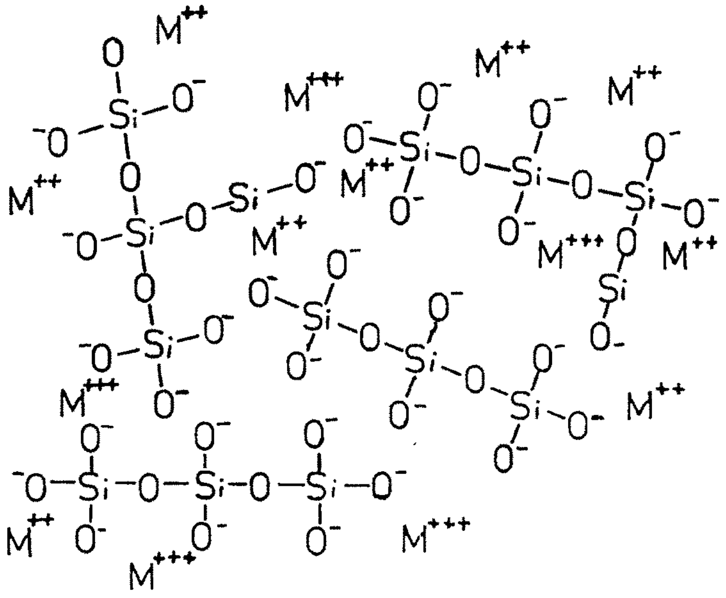


fig. I.9 Invert glass—diagrammatic

Where ρ is the density of polymer, N is the Avogadro number and M_i is the average molecular weight of the chain between ion groups. By definition, this is the concentration of bound ions per cm^3, and it is also a measure of the concentration of ionic bonds. Alternatively one can use the concept of relative number of ionic and covalent network bonds per cm^3, N_{ir} and N_{cr} (1,4) where,

$$N_{ir} = \rho / M_i \qquad (2)$$

$$N_{cr} = \rho \frac{x(X)x(CN)}{2\ M_{ru}} \qquad (3)$$

where

$$CN = \frac{2a + 3b + 4c}{a + b + c} \qquad (4)$$

X = number of covalent network atoms in a repeat unit, CN = average connection number of network atoms and M_{ru} = molecular weight of covalent repeat unit, and a = number of 2-connected, b = number of 3-connected and c = number of 4-connected atoms in the repeat unit. N_{cr} and N_{ir} are molar concentrations.

If a bound ion, of whatever charge or co-ordination number, is counted as generating a single ionic network, the relative number of total network bonds is given by

$$N_r = N_{(c+i)r} = \rho\left\{[1/M_i]+[(X)(CN)/2\,M_{ru}]\right\} \qquad (5)$$

Since most bound ions are univalent, this assumption is not too unreasonable.

Clearly, N_{ir} is an unsophisticated measurement of the concentration of ionic bonds e.g. a high valency and co-ordination number may well give additional stiffness to the network, so that effectively $N_{ir} > \rho < M_i$

Some approximate figures for typical ionic polymers are shown in table I.3.

4(b) Aggregation of ions

It is known that ion association takes place in liquid media of low dielectric constant. Pettit and Bruckenstein (25) have shown that states of aggregation from ion pairs to ion sextets exist in solvents of dielectric constant between 2.27 and 7.38 for salts such as Bu_4NCl and KCl. However, the situation will clearly be somewhat different in ionic polymers, where one ion is bound to a chain, and where it is necessary that the conformation of the chain should accomodate itself to the arragnement of ions if multiplets are to exist.

The simplest form of aggregation is the ion pair, and the probability that these will form in media of low dielectric constant rather than separated ions, is clearly established. The work required to separate an ion pair into dissociated ions for singly charged ions is

$$W = - e^2/r.4.\pi \varepsilon_0 K \qquad (6)$$

where K = the dielectric constant ($\approx$ 2.3 for polyethylene), $1/4\pi\varepsilon_0 = 1$ dyne cm^2. Statcoulomb^{-2} and

TABLE I.3

Proportion of bound ions in ionic polymers

Polymer	$100 \times N_{ir}/(N_{cr} + N_{ir})$
Carboxylated rubbers	0.5 - 2
Ionomers	2
Metal salts of dicarboxylic acids	10
Inorganic glass	~ 15 (covers wide range)
Polyelectrolyte complexes	~ 15
Metal polyacrylates	20
Polyphosphates	25
Linear Silicates	33
Invert glass	> 33

r = distance between the centres of positive and negative charges in the ion pair. If r = 1.5 A° the interaction energy is 7×10^{-12} erg per ion pair, compared with kT = 4×10^{-14} erg at room temperatures. The fraction of dissociated ion pairs is therefore exceedingly small.

The higher form of aggregation is the multiplet, and it is assumed that they are randomly distributed throughout the matrix. It is further assumed that they are distributed on a cubic lattice, and that each multiplet consists of a spherical drop. The inside of the drop contains the ion pairs in the multiplet, whilst the outside of the drop accomodates the hydrocarbon chain which accompanies the bound ions. It is assumed that sequential ion pairs are not found in the same multiplet.

By simple arguements, Eisenberg showed that

$$r_m = 3.\ V_P/S_{ch} \qquad (7)$$

where r_m = radius of the multiplet,
V_P = volume of the ion pair and S_{ch} = The contact surface of the chain

If, for an ethylene-sodium methacrylate copolymer there are a relatively large number of $-CH_2-$ segments between the carboxylate ions, the minimum segment to be accomodated on the surface of the drop can reasonably be assumed to be $-CH_2-\underset{|}{C}H-CH_2$ - with the bound ion attached to the middle carbon atom. On this basis, if V_P = 12 $A^{\circ 3}$,

$r_m = 3$ Å and V_m the volume of the multiplet = 100 Å^3. This gives a maximum value of 8 pairs for perfect volume occupation, but the number is likely to be less than this for the packing of such groups as - COO^-Na^+.

The multiplet drops are coated with non-ionic chains making this type of higher aggregation possible; the situation however is more complicated. A number of different models can be considered, but whichever the model is chosen, the following factors will be involved.

(1) Upon cluster formation, work is done to stretch the segments of polymer chain between ionic groups from the distance corresponding to randomly dispersed multiplets to the distance corresponding to the oriented clusters.

(2) Electrostatic energy is released when multiplets aggregate.

(3) The cluster is not infinitely stable, and above some temperature (Tc) the cluster decomposes. At this temperature electrostatic and elastic forces balance.

(4) Some ring formation will take place between sequential ion pairs incorporated in the same cluster.

At low ion concentrations, as the speciang between the ionic groups increases, the stage will be reached when there will be more physical entanglements than ionic groups. Since these entanglements act as cross-links, they will oppose the aggregation of multiplets into clusters. The nature of the polymer chain-for example its stiffness or the presence of bulky side groups—will also play a large part. Similarly at high ionic concentrations, the stage may be reached where extensive cluster formation is impeded by the highly entangled and hindered nature of the structure. Thus the most orderly arrangement of the ions may be found at some intermediate range of concentrations.

The most direct evidence on ion aggregation comes from x-ray studies, as might be expected, These studies confirm the existance of ionic heterogeneities in the materials which have been examined, but these cover only a narrow range of compositions - crystalline and amorphous copolymers of carboxylic acids containing relatively small proportions of ionic groups. This is the range of compositions which comprises the materials generically termed ionomers.

In the case of ethylene ionomers, the original du Pont work (26) suggested that ionic domains exist. The X-ray peak which is observed with the neutralized copolymer persists above the melting point - in fact upto 300°C. Small amounts of water intensify the peak, which virtually disappears if the sample is saturated with water. It was inferred from this evidence that this was a three-phase system, with amorphous and crystalline polyethylene regions, and ionic domains of diameter $\sim$ 100 A°.

Roe (27) examined the caesium salt of a material similar to that of the du Pont workers (5 mole % acrylic acid; 75 % neutralized) and found no evidence of cluster formation, but strong evidence for the existence of duplets and quadruplets. Three other investigations are of interest. Macknight (28) examined a typical ethylene ionomer (4.1 mole % methacrylic acid; various counterions) and concluded that the salt groups are largely concentrated in spherical clusters of diameter 16-20 Å located in the amorphous phase. Marx, et al (29) investigated an ethylene ionomer and a rubber copolymer of butadiene and methacrylic acid and concluded that the aggregation of the scattering sites corresponded to multiplet formation - from dimers to tetramers and above, depending on the salt concentration. Eisenberg (30) examined a number of styrene ionomers and found two peaks in the X-ray pattern at ~22 Å which he tentatively assigned to multiplet and cluster formation respectively. Presumably these can co-exist in the same material. This work confirms the existence of primary aggregates or multiplats, but leaves the existence of clusters at the level of working hypothesis (30).

Other evidence of the aggregation of ions comes from various directions, such as viscoelastic studies of ionomers and carboxylated rubbers, etc. The work of Tobolsky (31,32) supported the idea of ionic domains of unspecified size, and therefore of unknown degree of aggregation. The work on the polyethylene ionomers was complicated by the presence of crystallinity, but the results obtained with the amorphous carboxylate rubbers were simpler to interpret. The high strength of these materials was ascribed to hard ionic clusters which give rise to a two-phase reinforced structure. In a separate study of a rubbery copolymer of butadiene-lithium methacrylate, Otocka and Eirich (33) postulated the existence of quadrupolar (i.e. multiplet) links.

The case of polyelectrolyte complexes is complicated by the presence of water as an essential third component, as anhydrous polyanion-polycation complexes exist but are of little practical interest. The presence of dissolved, mobile counterions further complicates the situation. From the studies of mechanical properties (34) it was concluded that a polyelectrolyte complex was made up of regions of varying intensity of polyion-polyion interactions.

I.5 Some Physical Properties of Ionic Polymers

5.(a) Glass Transitions in ionic polymers

The transitions from a glassy to a rubbery consistency is a characteristic of many polymeric solids. At some stage of increase in temperature, the segmental mobility increases to the point where rubber-like deformation under a small applied stress becomes possible. It can be expected that this segmental mobility will depend upon the nature of the inter-chain forces, and in the case of ionic polymers upon the degree of ionisation, the presence of ionic bonds and the nature of counter-ions.

In very highly cross-linked carbon polymers there has been no indication of a glass transition below the decomposition temperature of the polymer. At lower concentrations of cross-links, it was found that the glass-temperature increases with the degree of cross-linking (35,36).

In practice, many of the commercially important solid ionic polymers have a relatively low concentration of bound ions.

Eisenberg (10) compared the behaviour of linear silicates, polyphosphates and polyacrylates. These are all polyanions, two being inorganic and one organic. Despite the wide differences in structure, the behaviour of these materials was very similar. For this limited range of materials, the glass transition temperature can be represented approximately by an equation of the following general form for the fully neutralized polymers:

$$T_g = A\ (q/a) + B$$

where q is the counterion charge in units of 1 electron, 'a' is internuclear distance between the cation and the anion at closest approach and A and B are constants.

The individual equations are as follows:

$T_g = 625\ (q/a) - 12$ polyphosphates—partly or fully neutralized

$T_g = 635\ (q/a)+132$: Linear silicates ($M_2O:SiO_2=1$)

$T_g = 730\ (q/a)-67$ Polyacrylates—fully neutralized only

5 (b) Melting transition

The process of melting is a reversible one, i.e. the bonds which are broken on melting must be capable of reforming on cooling. It means that there must be enough thermally labile bonds to disrupt the polymer structure sufficiently, so that flow becomes possible i.e. it must dissociate into 1—D fragments. The softening or melting behaviour of a polymer, depends on the nature and strength of all the cohesive forces which bond the material together. Thus, in addition to the ionic bonds which will be present in an ionic polymer, there will also be a 1—D or 3—D continuous arrangement of covalent bonds, as well as van der Waal's bonds and possibly hydrogen bonds as well.

The following facts regarding the behaviour of polymers which do not contain ionic bonds are of importance in considering the softening behaviour of ionic polymers.

(i) Carbon polymers melt if their structure is 1—D and if the cohesive forces between their chains are not too great.

(ii) Some inorganic oxide polymers such as silica melt reversibly on heating, despite the fact that they have a 3-D structure. In this case, the network bonds themselves such as Si - O are capable of reversible bond switching on heating.

The melting behaviour of ionic polymers also depends on the nature of ionic bonds, i.e. whether the ionic bonds themselves are thermally labile at a temperature below the decomposition temperature of the polymer.

When ionic solids melt, the melting point depends upon the ratio of the heat of fusion to the entropy of fusion ($T_f = \Delta H_f / \Delta S_f$), and it may vary over a very wide range.

5 (c) Viscoelastic properties

As with the glass transition and melting transition, the viscoelastic properties of ionic polymers - for example flow, stress relaxation and creep-involve a number of features which are unique to these materials. These include some factors discussed above namely

(i) the lability of the ionic bond or cross-link,
(ii) the relative lability of the main chain bonds,
(iii) the formation of ion multiplets, clusters or other microaggregates, and
(iv) the effect of ion aggregation on crystallization

behaviour, when crystallizable main chains are present.

It is seen that the ionic bond acts as a kind of cross-link, and the high viscosity of ionic polymer melts provides evidence that its effect persists above the melting point. In the case of carbon polymers, the ionic bond is more labile than the covalent cross-link with which it is compared, in its response to heat or longterm stress.

5 (d) Flow behaviour

The poorer flow properties, as evidenced, for example, by a drop in melt index, show that the presence of ionic bonds leads to a greater inter-chain attraction. As might be expected, the viscosity increases as the concentration of ions increases.

Brown (2) found that the monovalent salts of carboxylic elastomers containing 0.1 ephr of carboxyl groups become plastic when warmed, and mill and sheet normally, in contrast to the zinc salts which crumble at the same temperature. At a higher temperature, however, the zinc salts also become somewhat plastic.

Cooper (37) studied the flow behaviour of the divalent metal salts of a low molecular weight copolymer of butadiene and methacrylic acid and observed that E_{vis}, the activation energy for viscous flow

(i) increased with the acid content of the copolymer, and hence the number of ionic cross-links,

(ii) was higher than that of the hydrocarbon polymer segments, and

(iii) depended on the nature of the cation values being approximately equal for Zn, Ca, Sr and Pb but were about twice as great for Mg and Cd.

5 (e) Relaxation behaviour

A discussion of relaxation behaviour is concerned mainly with creep, stress-relaxation and dynamic mechanical properties. Studies of these phenomena have thrown light on the behaviour both of ionic and covalent bonds under the effect of thermal and mechanical stress.

When there is no bond inter-change as with polystyrene or polymethyl-methacrylate, the principle of time-temperature superposition applies, i.e. a single master curve for log $E_r(t)$ Vs log t will fit all the data, if the curves are shifted horizontally along the time axis on to one reference curve. It can be explained by postulating that the relaxation mechanism above Tg consists of an irreversible movement of chain segments, a process which speeds up as the temperature is increased.

Similar evidence has been presented by Bonotto and Bonner (38) in their extensive study of ethylene-acrylic acid copolymer salts. Also the process of ion exchange is very clearly shown up in glasses. If a glass containing sodium ion is immersed in molten potassium nitrate, an exchange of cations takes place, so that potassium ions enter the glass and sodium ions enter the melt.

5 (f) Stiffness

It is known that the normal effect of cross-linking is to increase the modulus, so that it might be expected that if ionic bonds increase the connectivity in a material, the stiffness will increase.

The Pioneer work of Brown (2) on carboxylic elastomers showed that a divalent ion is more effective in raising the modulus than a manovalent ion for this system. Other workers (32), using a tercopolymer of butadiene - acrylonitrile-methacrylic acid, found that the zinc salt has a modulus three times that of the unneutralized material at an ambient temperature. They also found that the modulus of the zinc salt approximated to that of the sulphur-cured material.

Bonotto and Bonner (38) have made a thorough study of the bulk physical properties of salts of ethylene-acrylic acid copolymers. The salt form showed a modulus increase of six times, which is already attained at a conversion of the acid groups of $\sim$ 30 %.

Using a similar type of ionomer, it was found that aliphatic diamines also produce salt-like cross-links and hence increase the stiffness of the acid copolymers.

The metal salts of polyacrylic and polymethacrylic acids as well as copolymers of lower carboxyl content have been investigated by Nielsen (3,39). The flexural modulus of zinc polyacrylate is 2½ times that of polyacrylic acid at normal temperature . Furthermore, whilst the modulus of polyacrylic acid falls off sharply in its transition region of ~ 90°C, the modulus of the zinc salt remains high upto 300°C.

It can be generalised that

(i) the stiffening effect of ionic bonds is greater in the rubbery region, where large elastic strains are possible.

(ii) The use of univalent ions leads to an increase in modulus.

(iii) The use of divalent ions leads to a greater increase in modulus than univalent ions. This effect is most marked with elastomers.

(iv) where an excess of metal oxide is used in preparing the salt form, as in some of the work on rubbers, it will act as an inert filler and will increase the modulus slightly in accordance with normal composite experience (40).

(v) Where ion clustering occurs to form a macroscopic ionic phase, it may also increase the modulus by the mechanism mentioned in (iv) above.

5.(g) Strength

Since the introduction of ionic bonds increases stiffness, it would be expected that it would also increase strength. This in fact is observed despite a concomitant reduction in strain to failure. Usually the increase in strength is less than the increase in stiffness. The results obtained with the metal polyacrylates in flexure were anomalous and explained by imperfections in the specimens (3).

In the case of rubbers, it appears that a divalent ion has a greater effect on strength than a univalent ion. This is in line with the experience with stiffness.

5 (h) Thermal expansion

Barker (41) showed that the following very approximate relationship is valid for a large number of materials.

$$E \alpha^2 \simeq 15 Nm^{-2} \,{}^\circ C^{-2}$$

where E is Young's modulus and α is the coefficient of linear expansion. Since the introduction of ionic bonds into polymer increases E, it can be expected that it will reduce the coefficient of expansion.

5 (j) Hydrolytic stability

From the available information it has been concluded that ionic polymers cover the whole range of hydrolytic stabilities, from those which disintegrate in water, to those which swell but remain coherent, to those which are completely stable.

Bonotto and Bonner (38) studied the water absorption by ethylene-acrylic acid copolymer salts as a function of conversion, with five cations. Their results showed great difference between potassium and sodium on one hand,and lithium, magnesium and calcium on the other. A higher absorption was accompanied by a reduction in stiffness, indicating that water had a plasticizing effect. The results showed that at 60 % conversion to the salt form, approximately 2 molecules of water were absorbed per ion pair for the potassium salt, 1 molecule for the sodium salt, and 0.2 molecule per ion pair for Li, Ca and Mg.

Eisenberg (30) made use of the water absorption data for styrene-sodium methacrylate ionomers to support the argument that the increase from 1 water molecule per ion pair to 3-5 water molecules per ion pair with the increase in ion content reflected a change in the degree of aggregation of the ions. The data of Bonotto and Bonner, and of Eisenberg indicated that the factors involved in controlling water uptake were (i) ion type (ii) ion aggregation and (iii) nature of the chain.

I.6 Some examples of ionic polymers

6 (a) Thermoplastic ionic polymers : Ionomers

The range of compositions of homogeneous random copolymers of ethylene and methacrylic acid neutralized partially or completely with sodium or zinc ions is such that they can be fabricated by conventional plastics processing equipment into finished products.

The weight fraction of metal ion in the commercial ionomers is only a few percent. This should be enough to form cross-linked gel if suitably combined, however it is remarkable that the ionomers show no tendency to gel, either in the solid state or in solution. They remain truly thermoplastic even after exposure to the elevated temperatures encountered in processing.

Ionomers, being flexible, tough and truly thermoplastic, can be extruded into films by blow moulding. They can be injection moulded into solid objects and blow moulded into bottles. The films and sheets can be postformed by various methods into skin and blister packages.

The translucency of the copolymer and the ethylene homopolymer is due to their spherulitic crystallinity. The transparency of the ionomers led the workers to suppose that similar crystallinity was either absent or present to a small degree in these materials.

6(b) Carboxylated elastomers

Commercially, latices are the most important form of carboxylated elastomers. The carboxyl functional group confers important advantages such as the ability to use sulphurless curing systems, e.g. a metal oxide, cross-linking with other functional polymers and high adhesive strength. The increased polarity of the polymer increases its compatibility with, and affinity for, polar surfaces encountered in fibres and inorganic fillers.

6(c) Rigid, highly carboxylated ionic polymers

The polyacids are characterised by a mole ratio of COOH:C of about 1:3. In poly (acrylic acid) this ratio is exactly 1:3 while in poly (itaconic acid) it becomes 2:5. These ionic polymers are diverse in character. They may be formed in the solid state as with Nielsen's ionic polymer salts, or in aqueous solution as in the case with the dental ionic polymer cements and certain soil stabilisers. Fabrication can be by acid-base reaction between polyacids and cation-releasing bodies or by polymerizations of a metal acrylate in situ (soil stabilization).

(c-i) Ionic polymer cements

The ionic polymer cements are the products of the hardening reaction that occurs when aqueous solutions of polyacids e.g. poly(acrylic acid) are brought into intimate contact with certain simple or complex metal oxides. These oxides act as sources of cations which serve to ionically cross-link the polyanionic chains to form a hard gel matrix. These materials are of interest in being intermediate between a filled organic polymer and an inorganic cement. They are novel as polymers in that the matrix is a hydrocolloid and can be described as an ionic polymer gel.

(c-ii) Monolithic plastics formed from metal polyacrylate salts

Ionic polymers prepared by Nielsen (42,43) by reacting zinc and other metal oxides with solid poly (acrylic acid) possessed improved properties over normal plastics, characterised by higher shear moduli, lower thermal expansion, and good thermal stability. The main drawback of these materials for building applications was their brittleness, and hence they have found no practical application.

(c-iii) Acrylic soil conditioners

The use of salts of acrylic acid, its polymers and derivatives as soil conditioners was stimulated by the need to construct temporary roads and runways quickly during the second world war. A particular objective was to eliminate the nuisance of dust raised by aeroplanes on landing and taking off.

6(d) Metal dicarboxylates - Halatopolymers

The behaviour of these materials both in solution and in the melt has been sufficiently characterised to conclude that the metal dicarboxylates are indeed polymers (42,43); on the other hand it has been pointed out that metal dicarboxylates such as the metal sebacates tend to crystallize in a salt structure. The ability of these metal dicarboxylates to display both polymeric and salt-like properties appears to be unique. The term 'halatopolymers' has been introduced to describe that group of materials which can display salt and polymer properties. The transition of a metal sebacate salt into a polymer is referred to as a 'halatopolymeric transition'.

The feature which distinguishes the metal dicarboxylates from other polymers is the presence of highly ionic bonds in the main chain of the polymer. The presence of such bonds in the main chain results in strong dipole interaction between chains and corresponding brittleness in material.

6(e) Polyelectrolyte complexes

Polyelectrolyte complex resins, also called polysalts or poly ion complexes, are the reaction products of two oppositely charged, strong polyelectrolytes.

The polyelectrolyte complex resin structure is especially interesting because ionic and covalent forces contribute equally to the network structure.

Polyelectrolyte complex resins containing equimolar quantities of polyanion and polycation are described as 'neutral'. These are strongest, most easily prepared, and generally preferred. Other formulations containing upto 0.1 milli-equivalent excess of polyanion or polycation per gram of resin are described as 'non-stoichiometric'. As would be expected, the non-stoichiometric materials display an enhanced capacity to sorb water and electrolytes and have found favour in biological and biomedical applications.

Alone, polyelectrolyte complex resins are hard, brittle, readily ground, and preferably handled as fine powders. Plasticized with 1-10% salts, certain acids, and oxy-sulphurous compounds, the resins become tough, horn like and leathery. Water equilibrated, the same materials behave as hydrogels with unusually good chemical stability and strength. Versatility is thus a key feature of these resins.

Polyelectrolyte complex resins appear slightly amber and are completely odourless and tasteless. They are insoluble in water, acids, bases and all organic

Solvents. They are soluble in a few three-component solvents comprising water, an electrolyte, and a high polarity organic solvent.

I.7 Present Work

In recent years, styrene-acrylic acid copolymers and their derivatives and compositions have been prepared and studied for (i) their physico-chemical, mechanical and processing properties (44), (ii) their blending with elastomers (45), (iii) immobilization of enzymes (46), (iv) their thermal stability (47), (v) compounding them with glass fibres (48), (vi) latex paints (49), (vii) improving fluidity of coal slurries (50), (viii) their rheological properties (51), (ix) their IR spectra (52), (x) cluster formation in solution (53), (xi) differences in sequence distribution (54,55), (xii) their NMR spectra, FTIR analysis and PG chromatograms (56), etc.

Styrene-fumaric (or maleic) acid copolymers and their derivatives and compositions have been prepared and studied in recent years for (i) their use as suspension stabilizers (57), (ii) their improved processibility (58,59), (iii) rheological properties of their blends (60), (iv) their use as cutting fluids (61), (v) their IR spectra (62,63) etc.

These polymers have been investigated for their solution viscosity. It was observed that the viscosity of sodium salts (ionomers) of styrene-acrylic acid copolymers is proportional to $\exp^{n}$ where n is the degree of neutralization (64). Viscosity of partially neutralized acrylic acid -styrene copolymers decreased initially on successive dilution with water (65), In acrylic acid-styrene ionomers replacement of H by Na,Li or Pb led to increase in $[\eta]_{max}/[\eta]_{o}$ (66). Ionic groups attached at wide intervals along nonpolar polymer chains produce strong associating interactions in solution (67). Rheological similarity of physical networks was discussed with reference to styrene-acrylic acid copolymers (68). Viscosity of concentrated solutions of styrene-acrylic acid copolymer was found to be a function of degree of neutralization (69). Effect of adding styrene or methacrylic acid to the solutions of styrene-methacrylic acid copolymers on their viscosity was discussed (70). Viscosity of solutions of styrene-methacrylic acid over a range of pH and of its salts was studied (71-73). Pfeiffer (74) has observed that solution properties of ionomers are controlled through intermolecular interactions. Thus viscosity of ionic polymers has been studied with reference to pH, degree of neutralization, nature of metal ions, cross links etc.

Considerable work has been carried out in our laboratories on different aspects of a wide variety of polymers. Studies were made on (i) Semiconductivity of chelate polymers (75), (ii) Pyrolysis of chelate polymers (76), (iii) chelating polymers (77), (iv) ion-exchange resins (iii) and redox polymers (78), sorption and swelling of polymers (79), etc. At the master's degree level, I worked on ionomers of styrene-acrylic acid. The results fascinated me and I prepferred to continue to work in the field.

Hence it was planned

i) to prepare polyanhydrides from various di & poly acids such as adipic acid, sebacic acid, isophthalic acid, EDTA, etc and to prepare polymers from hydroxy and amino acids under similar conditions and to study their acid content, solubility, etc.

ii) to prepare sets of copolymers with varying compositions using sytrene and acrylic acid, fumaric acid or maleic anhydride and to study their IR spectra, acid content, viscosity of solutions, etc.

iii) to prepare Na, Cu, Zn, Ba and Ca salts of these copolymers by partial neutralization and to study their viscosity in solutions.

iv) to prepare copolymers of divinyl benzene with acrylic acid or fumaric acid and tercopolymers of styrene, divinyl benzene and acrylic acid or fumaric acid and to study their acid content and viscosity of solutions.

v) to prepare tercopolymers of styrene, methyl methacrylate and acrylic acid or fumaric acid and to study their acid content and viscosity of solutions, and

(vi) to prepare Na, Cu, Zn, Ba & Ca salts of these tercopolymers and to study their viscosity in solution.

The experiments carried out and the results obtained are presented and discussed in the following pages.