V.

SUMMARY

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Ionic polymer is either inorganic or organic and contains both covalent and ionic bonds in its chains or network structure. Its range is very wide and includes such dissnimilar materials as glass, ionomers, alginate gels, polyelectrolytes, etc. The introduction of ionic bonds into covalent solids affects their ion exchange characteristics, rigidity, thermal lability, etc. They are classified in terms of chains and network types into three groups; (i) covalent network containing ionic bonds, (ii) long covalent chains carrying ionic bonds and (iii) short covalent chains with ionic bonds. In terms of ion types they are classified into (i) polyanions, (ii) dianions, (iii) mixed ions and amphoterics (iv) dications and (v) poly cations.

Long covalent chains carrying ionic bonds are exemplified by (i) polyanions, such as, linear silicates, linear phosphates, ionomers, polyacrylates, polysaccharides, salts of carboxylated rubbers, anionic polyelectrolytes, etc., (ii) polycations, such as quaternary ammonium polymers and (iii) mixed ions, such as poly salts or polyelectrolyte complexes.

Concentrations of ions pairs can be derived from the expression

$$C = \rho \times N \div M_i$$

where ρ is the density of the polymer, N is Avogadro number and M_i is the average molecular weight of the chains between the ion groups. Ions aggregate to form ion pairs, ion multiplets and ion clusters. For ethylene-sodium methacrylate copolymers a maximum value of 8 ion pairs has been suggested for perfect volume occupation (1-3).

Eisenberg (4) suggested that for the linear silicates, phosphates and polyacrylates, the glass transition temperature (Tg) can be represented by the following equation for fully neutralized polymers:

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

where q is the counter ion charge, 'a' is internuclear distance between the cation and the anion at closest approach and A and B are constants.

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. 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 (5,6). Ionic polymer cover the whole range of hydrolytic stabilities (1, 7).

Styrene-acid copolymers and their salts and derivatives have been of wide interest. These have been prepared and studied for blending them with elastomers (8), glassfibers (9), etc., for improving fluidity of coal slurries (10), in latex paints (11), etc. Viscosity of the salts of these copolymers has been studied with reference to pH, degree of neutralization, nature of metal ions, cross-links, etc. (12-14).

Considerable work has been carried out in our laboratories on ionic polymers, eg. on semiconductivity of chelate polymers (15), pyrolysis of polychelates (16), chelating polymers (17), ion exchange resins (18), etc. The results obtained by me as my studies on ionic polymers at the Master's degree level, enthused to continue work in the field. It was planned

(i) to prepare polyanhydrides from various di and polyacids such as adipic acid, sebacic acid, si isophthalic acid,EDTA, etc. and to prepare polymers from hydroxy and amino benzoic acids under similar conditions and to study their acid content, hydrolytic stability, etc.

(ii) to prepare sets of copolymers with varying compositions using styrene and acrylic acid, fumaric acid, maleic anhydride, etc and to study their acid content, IR spectra, solubility, viscosity in solution, etc.

(iii) 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, solubility, viscosity in solution, etc.

(iv) to prepare the copolymers of styrene, methyl methacrylate and acrylic acid or fumaric acid and to study their acid content, viscosity in solutions, etc.

(v) to prepare Na(I), Cu(II), Zn (II), Ba (II), and Ca (II) salts of the above polyanhydrides copolymers and tercopolymers by partial neutralization,etc. and to study their viscosity in solution.

The investigations were carried as planned and the results of these investigations are correlated and discussed.

Poly(fumaric acid) and poly(maleic anhydride) were prepared by addition polymerization and poly (sebacic anhydride), poly (adipic anhydride), poly (isophthalic anhydride), poly(fumaric anhydride), etc. were prepared by condensation polymerization. They were unstable to hydrolysis or were obtained in poor yields and were not studied further.

Poly(p-amino benzoate) and poly(p-hydroxybenzoate) were prepared by condensation polymerization and are suggested to have the degree of polymerization (d.p.) of 4-5.

Copolymers of styrene with maleic anhydride, fumaric acid, acrylic acid or methyl methacrylate and of divinyl benzene with fumaric acid or acrylic acid were prepared. Preliminary studies of these copolymers led to the preparation of sets of copolymers of styrene with maleic anhydride, fumaric acid or acrylic acid. These copolymers were studied for their acid content, IR spectra, viscosity in solution, etc. These acidic copolymers were converted into partial salts by replacing H of the acidic group partially by Na, Cu, Zn, Ca or Ba. The salts were studied for their viscosity in solutions. Huggin's equation, Martin's equation and Kraemer's equation were used to evaluate intrinsic viscosity and the effects of the nature of ion, the degree of substitution, etc are considered (12, 20).

Tercopolymers of styrene and divinyl benzene with acrylic acid, methacrylic acid or fumaric acid were prepared.

These were insoluble and hence their salts were not prepared. Tercopolymers of styrene and methyl methacrylate with acrylic acid or fumaric acid were prepared. Their acid content, IR spectra and viscosity in solution were obtained. These tercopolymers were converted into partial salts by replacing H of the acidic group partially by Na, Cu, Zn, Ba or Ca. Their viscosity in solution was determined. Their intrinsic viscosity was evaluated and the effects of the nature of the ion, degree of substitution etc are considered.

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