Acrylic ampholytic ionomers

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In a continuing study of the preparation of ampholytic ionomers from the polymerization of ion-pair comonomers (cationic–anionic monomer pairs) with nonionic comonomers, the preparation of such ionomers from methyl methacrylate and n-butyl acrylate is described. For both systems, ionomers of varying ion contents were obtained. In the n-butyl acrylate system, a linear relationship of T_g vs. mol % ion content was found, but this did not occur for the methyl methacrylate ionomers. The solubilities of these materials in a wide variety of solvents is discussed. It appears that for n-butyl acrylate ionomers of high ion content in aqueous solution, a new form of polymeric surfactant is obtained.

Keywords Ion-pair comonomers; ampholytic ionomers; polyampholytes; polymerization

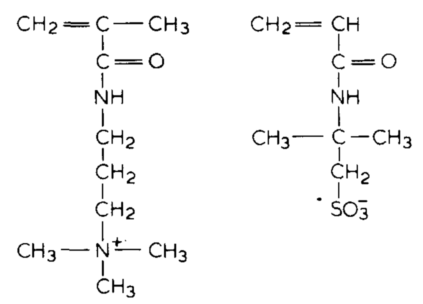
INTRODUCTION

In recent years, the field of ion-containing polymers has been an area of increased academic and industrial research. The high level of activity has manifested itself in the appearance of books, reviews, and conferences dealing with the subject[1–7]. It is well recognized that the introduction of ionic groups into polymeric materials alters the polymer morphology and, consequently, has a profound effect on the physical and chemical properties.

Whereas much attention has been devoted to the morphology and mechanical properties of ionomers, there has been relatively little work done on their solution behaviour. Probably the limited solubility of ionomers in organic solvents has precluded a detailed understanding of their ionic interactions. Otocka *et al.* studied the viscosity of carboxylic acid terminated polybutadiene neutralized with various cations and found that the solution viscosity increased markedly upon neutralization with monovalent and divalent bases[8]. Monakov *et al.* studied the dilute solution viscosity of styrene–methacrylic acid ionomers as a function of concentration, solvent polarity and nature of cation[9]. The solvents employed were dimethyl formamide, dimethyl formamide with a small amount of water, and tetrahydrofuran with a small amount of pyridine or acetic acid. In a variety of studies, Lundberg reported that the solution viscosity of metal sulphonate-containing polystyrene ionomer decreased with the addition of a polar solvent[10–12]. In addition, the effect of temperature on reduced viscosity was quite significant. While for most polymers the solution viscosity decreases monotonically with temperature, Lundberg and Makowski found that the addition of a small amount of polar solvent to the xylene polymer solution changed the viscosity behaviour such that a maximum could be observed with increasing temperature[12].

A new form of polysiloxane ionomer containing no inorganic ions has been reported by Gravier, Baer and Litt, which contains a pendant amphoteric group on a polysiloxane backbone[13,14]. In limited solution property studies it was observed that aggregation increased with increasing concentrations of amphoteric zwitterionic, and this effect was strongly influenced by the nature of the solvent.

Most recently, Salamone *et al.* reported ampholytic polymers which have the positive and negative charges on two pendant groups along the polymer chain[15]. In the course of studies on the mechanism of the spontaneous polymerization of vinylpyridinium salts, a new class of zwitterionic monomeric salts was prepared in which both cationic and anionic components were polymerizable. These new monomeric salts are referred to as cationic–anionic monomer pairs, or more simply as ion-pair comonomers (IPC). For this class of monomer, it is noted that each vinylic moiety is a counterion to an oppositely charged counterpart and each is individually polymerizable. As an example of this class of compound, the ion-pair comonomer of 3-methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate (I) was prepared[16].


(I)

In structure I, the cationic and anionic moieties are acrylamide derivatives and are expected to have similar polymerization behaviour. This behaviour was used for

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the preparation of novel polyampholytes and ampholytic styrene ionomers. For example, a random polyampholyte was prepared by free radical homo-copolymerization of I in aqueous solution. (N.B. This is a homopolymerization of a monomer which incorporates 2 polymerizable groups.)[16] The novel ionomer was obtained by copolymerizing the ion-pair comonomer I with a large amount of styrene monomer by either emulsion or solution techniques[17,18]. In this copolymerization reaction, with the control of the comonomer input in the starting materials, one can produce an ionomer with a small amount of ionic groups (cationic and anionic) pendantly distributed between blocks of styrene units, as well as having the flexibility of changing the type of ionic groups, the steric factors surrounding these groups, and/or their hydrophilic/hydrophobic character. From the structural point of view, these macromolecules will contain equal amounts of cations and anions pendant from the chain although not necessarily on each polymer molecule.

In preliminary results of studies on the styrene-I ionomer system it was found that the T_g values were linearly dependent on the ion content (and independent on the method of preparation), that the glass transition temperature was unaltered by exposure to moisture, and that the tensile strength was higher than polystyrene[17].

In this work it was of interest to extend the synthesis of ampholytic ionomers to other comonomer systems. For this purpose it was decided to employ a 'soap free' emulsion polymerization technique for copolymerizing a large amount of a neutral 'hard' and 'soft' acrylic comonomer and a small amount of the ion-pair comonomer of methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate (I). The 'hard' monomer used in this investigation was methyl methacrylate and the 'soft' monomer was n-butyl acrylate.

EXPERIMENTAL

Monomers

2-Acrylamido-2-methylpropanesulphonic acid, refined grade (Lubrizol Corporation), was dissolved in methanol and passed through a cation exchange column containing Amberlite IRA-120 in the acid form. The eluent was concentrated under reduced pressure, filtered, and recrystallized. The crystals of the monomeric acid gave a mp 185.5°–186.5°C (lit. 185°C)[19].

Methacrylamidopropyltrimethylammonium hydroxide (*MAPTAOH*). To 20 ml of 50% aqueous solution of methacrylamidopropyltrimethylammonium chloride, obtained from Jefferson Chemical, an equal volume of distilled water was added. This solution was decolourized with activated charcoal and was diluted further with 80 ml of distilled water. It was then passed through a column (I.D. 2.0 cm) containing Dowex IX_4 (2.5 meq/g) anion exchange resin (OH^- form) which had been previously obtained by passing 5% (w/v) solution of sodium hydroxide through the column containing Dowex IX_4 anion exchange resin (Cl^- form), until the eluent was completely free from chloride ion. When the decolourized monomer solution was passed through this column at the rate of about 0.2 ml/min, the eluent, free from chloride ion, was an aqueous solution of methacrylamidopropyltrimethylammonium hydroxide.

Methacrylamidopropyltrimethylammonium 2-acrylamido-2-methylpropanesulphonate (*I*). The freshly prepared solution of methacrylamidopropyltrimethylammonium hydroxide was titrated with a 5% (w/v) aqueous solution of 2-acrylamido-2-methylpropanesulphonic acid to a pH of 6.8. The neutralized solution was freeze-dried to obtain the crude product. The dry sample of the ion-pair comonomer was then treated with chloroform. It was found that the major portion of the crude product dissolved in chloroform, whereas a part of the product was sticky and insoluble in this solvent. The chloroform soluble portion was filtered and concentrated by evaporation under reduced pressure at room temperature. It was then placed inside the freezer for crystallization. The crystals obtained were hygroscopic in nature, yield 48%, mp 146.5°–147°C (lit. 146.0°–147.0°C)[18]. To confirm purity, the monomer pair was further characterized by means of ^1H n.m.r., i.r. and elemental analysis. The results are consistent to those previously reported[16].

Methyl methacrylate (*MMA*) obtained from Rohm and Haas contained hydroquinone as an inhibitor. The inhibitor was removed by washing the monomer several times with sodium hydroxide (10% w/v) and water. It was then dried overnight over anhydrous calcium chloride. The monomer was decanted from the drying agent, fractionally distilled under reduced pressure (bp 46°/100 mm Hg), and stored under nitrogen in the refrigerator until used.

n-Butyl acrylate (*BuAc*) (Rohm and Hass) was purified by employing the same method as described for methyl methacrylate. It was distilled at 101 mm Hg at a temperature of 84°–85°C. The first and last fractions were discarded and the middle fraction was collected. It was preserved under nitrogen inside the refrigerator until used.

Potassium persulphate. A saturated solution of potassium persulphate (Aldrich) in water was prepared. The solution was left inside the hood at room temperature to evaporate. When about two-thirds of the water evaporated, the solution was kept at a temperature of about 4°C to crystallize. The crystals were filtered, dried and preserved in a vacuum desiccator.

Polymerizations

(1) Methyl methacrylate and I

In a polymerization tube, 5.0 g of methyl methacrylate (50 mmol), 1.175 g of ion-pair comonomer I (30 mmol), 13.5 mg of $K_2S_2O_8$ (0.05 mmol) and 11.0 ml of distilled water were placed. The contents were degassed by the freeze-thaw technique until air was completely expelled from the tube. The tube was sealed with a flame torch and allowed to cool. Once the constriction part was cold, the reaction mixture was thawed. It was then placed in a shaker in such a way that it was completely immersed into a thermostatically controlled bath maintained at 45°C. The reaction was allowed to continue for 8 h. As the shaker tumbled, the contents of the tube were obtained in the form of white, pellet-type beads. The reaction mixture was lyophilized, yield 96% (MMA-1).

The dry sample (MMA-1) was washed with and then filtered first with methanol, followed by equal volumes of methanol and water and finally with water. The filtrate on evaporation gave an insignificant amount of solid. The residue was tested for solubility in different solvents. It was found that the swelling of the polymer was greatest in chloroform compared to other common organic solvents, and a part of it dissolved in chloroform giving a highly viscous mass. In order to ensure that complete isolation of chloroform soluble material took place, more chloroform was added while the mixture was magnetically stirred. The mixture was then centrifuged and the supernatant was filtered through a fine fritted disc filter. The processes of addition of chloroform, stirring and filtering, were repeated until no further change in viscosity of the added solvent was noticed. The chloroform soluble fraction was reprecipitated from methanol giving a fibrous material. It was dried under vacuum, yield 26%. This fraction of polymer was labelled as MMA-2. The insoluble fraction was washed with fresh chloroform and dried in a vacuum oven giving a yield of the dried polymer of 49% (MMA-3). The elemental analyses and mol % ion compositions are reported in *Table 1*.

(2) n-Butyl acrylate and I

In a polymerization tube, 3.7 ml of n-butyl acrylate (25 mmol), 0.489 g of ion-pair comonomer I (1.25 mmol), 6.7 mg of $K_2S_2O_8$ (0.025 mmol) and 5.5 ml water were mixed. The mixture was degassed by the conventional free-thaw technique until air was completely expelled from the tube. The tube was then sealed and placed in a constant temperature bath maintained at 45°C. With the help of a shaker, the contents of the reaction tube were tumbled continuously and uniformly inside the bath. The reaction was allowed to take place at this temperature for 7 h. A partly coagulated emulsion was obtained. The latex was dialysed exhaustively against deionized water, followed by lyophilization. The obtained polymer was translucent and elastic in nature, yield 91%.

The polymer was washed with methanol, methanol–water mixtures (1:1 by volume) and water. The supernatant from the methanol was clear but those from the methanol–water mixture and water were slightly turbid. These solutions did not clarify even after being filtered through a 0.22 μ Millipore filter or by centrifugation at 4000 r.p.m. for 1 hour. These fractions when combined and lyophilized gave a fluffy, white material.

Table 1 Elemental analyses and composition of MMA ampholytic ionomers

Sample	%C	%H	%N	%S	Mol. % ion content based on %N
MMA–1	58.69	8.75	1.64	1.45	4.40
MMA–2	58.99	6.31	0.14	0.35	0.35
MMA–3	50.23	7.64	2.64	2.11	7.70

The residue was allowed to swell in toluene while it was stirred with a magnetic stirrer. Later, it was reprecipitated in methanol. The precipitated polymer was dried in a vacuum oven. The polymerization reaction was repeated by using different comonomer ratios as given in *Table 2*. In each of these experiments an insoluble rubbery fraction, designated series L (Low ion content), and a water-soluble powdery fraction, designated series H, (High ion content) were obtained. The elemental analyses and compositons of these fractions are presented in *Tables 3* and *4*, respectively.

Thermal analysis

The determination of the glass transition temperature was first attempted with a Perkin-Elmer differential scanning calorimeter, DSC 1B. A linearly programmed heating rate of 10°C min^{-1} was used and the temperature was calibrated against indium (mp 429 K) and crystals of steric acid (mp 345 K). However, in the d.s.c. thermogram the baseline shift was not discernible even up to 600 K. Therefore, a Perkin-Elmer thermal mechanical analyser model TMS-1 was used. To prepare the sample, a small piece of the material was cut to fit onto the quartz sample platform properly. The bottom surface of the sample was made as flat as possible to avoid any false penetration resulting from the softening of the concave edges. The temperature program control UU1 was used in conjunction with TMS-1 to program the temperature. For determination above room temperature the Dewar was filled with water, and for low temperature liquid nitrogen was used.

Table 3 Elemental analysis and composition of low ion content BuAc ampholytic ionomers

Sample	%C	%H	%N	%S	Mol. % ion content based on %C
BuAc–1L	65.08	9.53	0.1	0.2	1.36
BuAc–2L	65.18	9.52	0.1	0.1	0.98
BuAc–3L	65.51	9.12	0.1	0.1	0.23

Table 4 Elemental analyses and composition of high ion content BuAc ampholytic ionomers

Sample	%C	%H	%N	Mean % mol. ion content based on %N
BuAc–1H	44.29	8.29	8.61	55.9
	44.37	8.08	8.45	
BuAc–2H	45.32	8.36	8.25	50.8
	45.19	8.09	8.05	

Table 2 Polymerization of n-butyl acrylate with I at varying comonomer concentration*

Sample	BuAc (g)	I (g)	[I]/[BuAc] (mol %)	Vol of solution (ml)	Initiator (mg)	Time (h)	Yield (%)
BuAc–1	3.20	0.49	4.8	9.2	6.7	6.5	91.2
BuAc–2	3.20	0.39	3.8	14.7	6.7	22.0	81.8
BuAc–3	6.40	0.19	0.99	29.4	13.0	16.0	71.0

* Reaction temperature = 45°C

Determination of particle size

The self-stabilized emulsion polymerization of the ion-pair comonomer and n-butyl acrylate resulted in a partially coagulated latex. The latex was filtered through glass wool and diluted with distilled water. A tiny drop of this diluted latex was placed on the surface of a copper grid which had been previously coated with a thin carbon film. After the water was evaporated, the pictures of the particles were taken by using a JEOL INC model JEM 100 transmission electron microscope.

N.m.r. measurements

Nuclear magnetic resonance spectra were obtained in a JEOL PS-100 instrument coupled with a Fourier Transform computer.

RESULTS AND DISCUSSION

Preparation of ion-pair comonomer

The ion-pair comonomer I was obtained by titrating a freshly prepared solution of methacrylamidopropyltrimethylammonium hydroxide with a 5% aqueous solution of 2-acrylamido-2-methylpropanesulphonic acid as discussed in the Experimental. This titration involved dilute aqueous solutions of a strong acid and a strong base. The neutralization point was detected by following the pH with a pH meter. The resulting salt, i.e., I, was soluble in water. At the neutralization point slight opalescence of the solution was observed. During the process of purification of the salt pair by recrystallization from chloroform, it was found that about 87% of the product was soluble in chloroform. The chloroform solution was filtered, concentrated and crystallized. Upon recrystallization, only 48% of pure monomeric salt pair was obtained.

The residue from this recrystallization, which was insoluble in chloroform, was tacky. It was insoluble in water and methanol but swelled appreciably in these solvents. To explore the nature of this product, it was purified by swelling in water and reprecipitating from chloroform. The precipitate was filtered and dried in a vacuum oven. An infra-red spectrum of the purified product did not show the presence of any vinyl moiety in the material, but had the appearance of the homocopolymer of I. This result indicates that during the preparation and purification of I, a part of the monomer pair had undergone spontaneous polymerization, apparently yielding a crosslinked product.

Preparation of ampholytic MMA ionomers

The method of preparation of ionomers of MMA and I was attempted by the soap-free emulsion polymerization technique[17]. However, this technique was not effective for the MMA system, where a suspension polymerization resulted. It was found that in the polymerization mixture, sample MMA-1 was a combination of two major distinct products; one soluble in chloroform, sample MMA-2, and the other chloroform insoluble, sample MMA-3. An insignificant amount of solid product was obtained from methanol, methanol–water and water-soluble fractions, as had been found previously in the formation of ampholytic styrene ionomers in the n-butyl acrylate ionomers discussed below[17]. From the elemental analyses (*Table 1*) the chloroform soluble fraction was shown to have an ion content of 0.35 mol% and the chloroform insoluble fraction had an ion content of 7.7 mol%.

An attempt was made to obtain more information on the composition of MMA-ionomers by spectroscopic measurements. The infra-red spectrum of MMA-2 is essentially that of poly(methyl methacrylate), with no peaks for the substituted amide groups due to the ion-pair comonomer being discernible. From the proton n.m.r. of this sample in $CDCl_3$ solution, the presence of the ion-pair comonomer also could not be detected. However, this same effect was noted for styrene ionomers in the absence of polar cosolvents[17,18].

The percentage of nitrogen (0.14%) in sample MMA-2 is very low. Such a low concentration may appear within the range of experimental error but in this case it appears reasonable. This is supported from the following considerations: (i) an analysis of authentic poly(methyl methacrylate) did not show any detectable amount of nitrogen and (ii) the viscosity of a solution of MMA-2 was unusually higher than a solution of poly(methyl methacrylate) prepared by suspension polymerization under comparable conditions. Increased viscosity in this sample is most likely related to the ionic aggregation in the resulting ionomer.

From the infra-red spectrum of sample MMA-3, it can be seen that in addition to the peaks characteristic of poly(methyl methacrylate), it also exhibits peaks at 330, 1660 and 1220 cm^{-1} indicating the presence of a substituted amide group. In addition, the solubility characteristics of the high charge density MMA ionomer were rather interesting. The solvents studied included acetone, acetonitrile, benzene, benzyl alcohol, chloroform, carbon tetrachloride, dimethyl sulphoxide, methyl ethyl ketone and toluene. It was found that only benzyl alcohol would dissolve MMA-3 and that all other singular or mixed solvents, including those containing the polar cosolvent methanol, only caused, at best, swelling. This result appears consistent with the solubility characteristics of high charge density ampholytic styrene ionomer[18].

T_g *values of MMA ionomers*

The introduction of small amounts of ionic groups into a hydrocarbon polymer is known to exert a profound effect on the physical properties of the resultant system[11]. Among the properties which are affected are glass transition temperature, density, viscosity, modulus, and water absorption.

In the case of the MMA-1 ionomers, the glass transition temperatures as a function of mol% ionic content are reported in *Table 5*. Although it was not possible to measure the T_g for sample MMA-3, for the samples studied it appeared that the glass transition temperature increased with increasing amount of ion content in the ionomer. However, there was no linear relationship

Table 5 Glass transition temperature of MMA–I ionomers

Sample number	Ion content (mol %)	T_g (°C)
PMMA	0.00	97.0
MMA–1	4.40	115.0
MMA–2	0.35	109.5
MMA–3*	7.70	–

* With sample MMA–3, no transition was observed; at temperatures above 260°C, the ionomer became brown coloured

Table 6 Glass transition temperatures of BuAc–I ionomers

Sample	Mol % ion content	T_g (°C)
BuAc–1L	1.36	−44.0
BuAc–2L	0.98	−45.0
BuAc–3L	0.23	−50.0
BuAc	0.00	−51.0

between these two quantities as was previously reported for styrene-I ampholytic ionomers[17].

Preparation of ampholytic BuAc ionomers

In the preparation of ampholytic ionomers from n-butyl acrylate, self-stabilized emulsion polymerization was employed and appeared to be effective. The emulsion system consisted of the ion-pair comonomer I, n-butyl acrylate, water and potassium persulphate. It was anticipitated that the monomer pair would cause micelle formation or would do so shortly after the initiation of polymerization.

It has been found previously that in the self-stabilized emulsion polymerization of styrene and I, the monomer pair by itself was not able to emulsify the mixture of styrene and distilled water prior to initiation. However, as the polymerization proceeded for a short while, a stable emulsion free of coagulation resulted. The particles were not monodisperse and had sizes between 0.2 to 0.6 μ[17,18].

In the BuAc-I system a partially coagulated latex was obtained. Within a short time after the initiation of reaction, no phase separation was observed. However, with time some of the particles coagulated giving small lumps of rubbery polymer. This process of coagulation might have been aided by the fact that the polymer was much above its glass transition temperature and, therefore, when the particles came into contact with each other, some of the particles flowed and collapsed to form larger particles.

The latex was dialysed exhaustively against deionized water followed by lyophilization. The polymer thus obtained was translucent and elastic in nature. It was washed and centrifuged successively with methanol, methanol–water mixtures and water. The supernatant solutions from these washes were combined and lyophilized, giving an amorphous material. The residue was allowed to swell in toluene, then reprecipitated from methanol and dried in a vacuum oven.

In this investigation, ionomers of BuAc and I were prepared using varying comonomer ratios (*Table 2*). As has been mentioned before, two fractions were obtained in these polymerization reactions. The major fraction (~70%), was a rubbery polymer, designated as series L in *Table 3* and the other fraction (~20%), an amorphous polymer, designated as series H in *Table 4*.

The compositions of these fractions were calculated from the elemental analyses data given in *Tables 3* and *4*. For the polymer series L (*Table 3*), the per cent content of nitrogen and sulphur were very low. Thus, in this particular series, instead of the nitrogen and sulphur per cents being used for calculation of ion content, the per cent carbon was employed instead. It appeared from these results that the rubbery polymer contained a small concentration of ionic moieties whereas the amorphous fraction contained a larger concentration. Comparing the conditions of reaction (*Table 2*) and the ionic composition of the resulting rubbery polymer, (*Table 3*), it can be seen that the ion content in the polymer increased with increased ion-pair comonomer to n-butyl acrylate ratio. It is interesting to note that the concentration of ionic groups in these polymers was about 25% of the concentration of the ion-pair comonomer in the initial reaction mixture.

In order to substantiate further the incorporation of the ionic comonomer into the polymer chain, infra-red spectra of both fractions, i.e., samples containing low ionic content (0.23–1.36 mol%) and a sample containing a high ionic content (50.8 mol%) were taken. For the preparation of i.r. samples of ionomers with low ion contents, the polymers were initially brought to a temperature slightly lower than their processing temperature, thus allowing them just to flow. It was at this point that the polymers were transferred to an NaCl plate and pressed hard between the plates. The i.r. spectra of samples containing 0.23–1.36 mol% of ionic content were determined in this fashion. As expected, the i.r. spectrum of the ionomer with an 0.23 mol% ionic content was virtually superimposable to the spectrum of homopoly-n-butyl acrylate. However, as the concentration of the ionic moiety increased, it could be seen that the absorption at 1660 cm^{-1}, due to the amide groups of the ionic moieties, successively increased.

The i.r. spectrum of sample BuAc–2H containing a high content of ionic moiety (50.8 mol%) showed the characteristics of BuAc peaks in addition to the absorption band for the secondary amide of the ionic moiety. The relative intensities of the ester and amide adsorptions clearly demonstrated the high ionic content of this ionomer.

T_g *values of BuAc ionomers*

It was found that the T_g values of the n-butyl acrylate ionomers were higher than that of the homopolymer of BuAc and that they increased with the increase of the ion content of the ionomer (*Table 6*). The ion content of these polymers were 0.23–1.36 mol% and within this range an apparently linear relationship between the T_g and the ion content was obtained (*Figure 1*). The slope of this plot, d T_g/dC, is 5.5°C/mol%. Linear relationships between the T_g and the ion content have also been reported for metal counterion ionomers[20] as well as the ampholytic styrene-I ionomers[17].

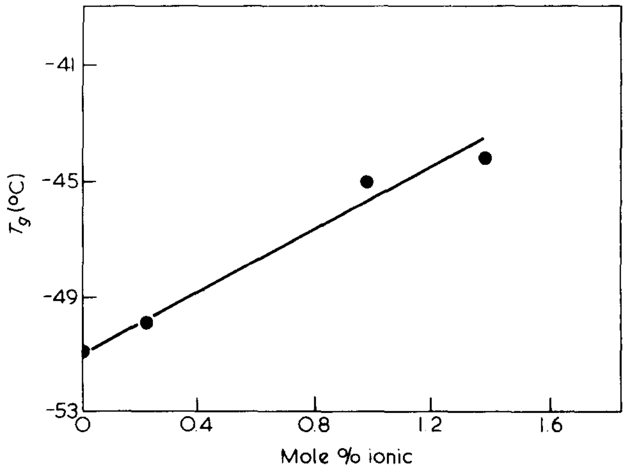

Figure 1 Plot of T_g vs. mol % ionic content for n-butyl acrylate ampholytic ionomers (correlation coefficient = 0.99)

Table 7 Solubility tests for BuAc–I ionomers (Series L)

Solvent	Observation
Benzene	high swelling, forms gel
Toluene	high swelling, forms gel
Xylene	high swelling, forms gel
Methylene chloride	high swelling
Chloroform	high swelling
Tetrahydrofuran	high swelling
Ethylene chloride	high swelling
Ethyl acetate	moderate swelling
Dimethyl formamide	slight swelling
Dimethyl sulphoxide	slight swelling
Methyl ethyl ketone	insoluble
Butanol	insoluble
Benzyl alcohol	highly dispersed

BuAc-1 latex particle size

About 2.0 ml of the latex was saved from each reaction mixture for the particle size determination. This was done by using a transmission electron microscope and comparing the micrographs with that of a standard monodisperse polystyrene. It was found that the particles were not uniform in size and shape due to their collapsing tendency as was previously indicated. Sometimes, as the solvent evaporated, there was a tendency for the particles to form a continuous film. This was probably aided by the fact that these polymers were much above their glass transition temperature, where they were soft and sufficiently mobile to flow and fill the voids left by escaping water. Because of this, it was very difficult to determine the particle size quantitatively. However, for samples BuAc-1H and BuAc-2H, which were prepared under identical conditions varying only the concentrations of I, larger particles of average size of 0.6 μ were found.

Solubility of n-butyl acrylate ionomers

The solubilities of the n-butyl acrylate ionomers was surprising. The low ion content ionomers were found to be insoluble in most of the common organic solvents (*Table 7*). Mixed solvent systems such as chloroform, benzene or toluene with variable amounts of methanol or dimethyl sulphoxide did not dissolve the ionomers. These results were related to those of the MMA-1 ionomers, but, surprisingly, the low ion content BuAc-I ionomers did not dissolve even in benzyl alcohol. Because of this lack of solubility, no further solution properties in organic solvents were studied. However, the high ion content ionomers were surprisingly soluble in water and in aqueous salt solution. In these solutions, at concentrations of 0.5 wt%, they formed a colloidal, foaming solution. Because of the unusual nature of this class of polymer in aqueous solutions, we hope to report further studies on their solution behaviour in the near future.

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