Dilute-solution behaviour of polyurethane ionomers

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The behaviour of some polyurethane thiosulphate and sulphonate ionomers in dilute solutions is reported. Viscosity measurements of the ionomers in *N*,*N′*-dimethylformamide (DMF) showed a 'polyelectrolyte effect', which diminished upon addition of lithium bromide. For water-soluble ionomers, measurements were carried out in aqueous solution. The effect of the counterion was examined. Anomalous molecular-weight distributions of the ionomers were observed by gel permeation chromatography (g.p.c.) using DMF as solvent, which depended on the polymer ionic content, solution concentration and temperature. Normal g.p.c. distributions were obtained, however, in solvent containing 0.5% of lithium bromide.

(Keywords: polyurethane; ionomer; viscosity; solution; gel permeation chromatography)

INTRODUCTION

Ionomers are polymers that contain ionic salt groups at relatively isolated positions along the chain. Although there are numerous investigations of ionomers in the solid state, very few studies have been concerned with the dilute-solution properties of these ionic polymers[1,2]. Results reported for carboxylate and sulphate ionomers revealed abnormal behaviour in which the viscosity was shown to be strongly dependent on, for example, the polarity of the solvent, the nature of the cation and the concentration of the polymer solution[1,3].

Most of the recent work on the dilute-solution properties of ionomers was pioneered by Lundberg *et al.* based on polystyrene sulphonates[4–7]. While these ionomers were regarded as polyelectrolytes of low charge density, they did not display a typical 'polyelectrolyte effect' in low-polarity solvents. The metal sulphonate groups were largely un-ionized in solvents of low polarity; hence their solution behaviour was governed by ion-pair interactions, and not by free ions, as in the case of polyelectrolytes in aqueous solutions. In solvents of high polarity, however, the 'polyelectrolyte effect' was observed in most cases at low concentrations.

Ionomers are also known to influence the gel permeation chromatography (g.p.c.) elution process because of their tendency for intramolecular chain expansion, intermolecular association, or other secondary mechanisms such as adsorption, partition, polymer–solvent or polymer–support interactions. Cha[8] and Coppola *et al.*[9] observed anomalous bimodal distributions in the elution of sulphonated polyacrylonitrile and other ionomers. By using a solution of *N*,*N′*-dimethylformamide (DMF) containing 0.1 M LiBr, the chromatograms of the ionomers were found to have a more symmetrical shape and were eluted at much higher retention volumes than in pure DMF.

This paper reports the dilute-solution viscosity and g.p.c. elution behaviour of some polyurethane ionomers, the preparation of which has been described elsewhere[10,11].

EXPERIMENTAL

Materials

In naming the polyurethanes and their ionomers, the following abbreviations are made for the reactants:

PPG	poly(propylene glycol) of molecular weight of approximately 1025
MDI	diphenylmethane-4,4′-diisocyanate
BD	butane-1,4-diol
TDOL	potassium-*S*-1,2-dihydroxypropyl thiosulphate
SDOL	potassium-*S*-1,2-dihydroxypropyl sulphonate
SDPS	sodium-*S*-1,2-dihydroxypropyl sulphonate

The non-ionic polyurethanes and polyurethane ionomers to be discussed in this paper can now be designated by a polymer code:

	Polymer code	
Polymer composition	Ionic	Non-ionic
PPG/MDI/BD/TDOL	PP-*X*-TH/BD	PP-0
PPG/MDI/BD/SDOL	PP-*X*-S/BD	PP-0
PPG/MDI/BD/SDPS	PP-*X*-SDP/BD	PP-0

Here *X* is the mole percentage of ionic diols in the chain extender mixture. For example, for the synthesis of PP-100-Th/BD, only TDOL was used in the chain extension step, whereas for the synthesis of PP-50-Th/BD, 50 mol% of the TDOL was substituted with

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butane-1,4-diol. All the non-ionic polymers reported have identical compositions. The molar ratios of PPG:MDI:mixed diols in all polymers are 1:3:2.

Sample code	Ionic groups in the final polyurethanes (mol%)
$X=25$	8.5
$X=50$	17.1
$X=75$	25.6
$X=100$	34.1

Solution viscosity

Viscosity measurements were carried out using a standard Ubbelohde suspended-level viscometer at 25°C in a thermostated water bath. Using a syringe, polymer solutions were filtered directly into the viscometer before any measurement was taken. About 15 min of temperature equilibration was allowed prior to each flow-time measurement. Each flow time was measured at least three times at each concentration and an average value of flow times was recorded.

Gel permeation chromatography

The apparatus consists of a solvent reservoir from which solvent (DMF) was pumped by an h.p.l.c. metering pump (Altex model 110A) at 1.0 ml min^{-1} to a column system composed of a pre-filter, a pre-column and a main column. This main column consisted of crosslinked polystyrene beads (Polymer Laboratories Ltd, PL Gel 300 × 7.5 mm, 5 μm particles of mixed porosity). Sample injection was made through an h.p.l.c. valve with an injection loop fitted between the pump and the column. The eluted sample passed first of all to an ultra-violet detector (Cecil CE 2012 UV monitor), then to a refractive index detector (Knauer differential refractometer) before it was finally collected. Data collection was carried out by a Trilab 2000 computer (Trivector Systems Ltd) at a rate of one point per second.

RESULTS AND DISCUSSION

Dilute-solution viscosity

Viscosity measurements of a number of ionomers under several conditions have demonstrated unusual behaviour. The various effects that have been examined include ion concentration, solvent, counterion and the presence of an electrolyte.

Figure 1a shows a plot of reduced viscosity, $\eta/\eta_0 c$, vs. concentration for the PP-X-Th/BD series of ionomers in DMF at 25°C. The results indicate that, with the exception of the non-ionic polyurethane, PP-0, all the ionomers show an initial fall in reduced viscosity with decreasing concentration, reaching a minimum before starting to rise again. The interpretation of this behaviour is that at high concentration molecular interactions are more favourable than electrostatic interactions. The ionomer chains thus take on a more random conformation and normal viscosity behaviour is observed, i.e. the reduced viscosity decreases with decreasing concentration. As the concentration decreases, there is an increasing volume for the counterions, which tend to distribute themselves at longer distances from the negative ions on the chains. Hence shielding of the fixed charges is reduced, and electrostatic repulsion increases, which tends to expand the polymer chain. This behaviour is most prominent in PP-100-Th/BD and in PP-75-Th/BD with their relatively high ionic contents. The concentration at which the reduced viscosity starts to rise sharply with decreasing concentration corresponds to the onset of chain expansion.

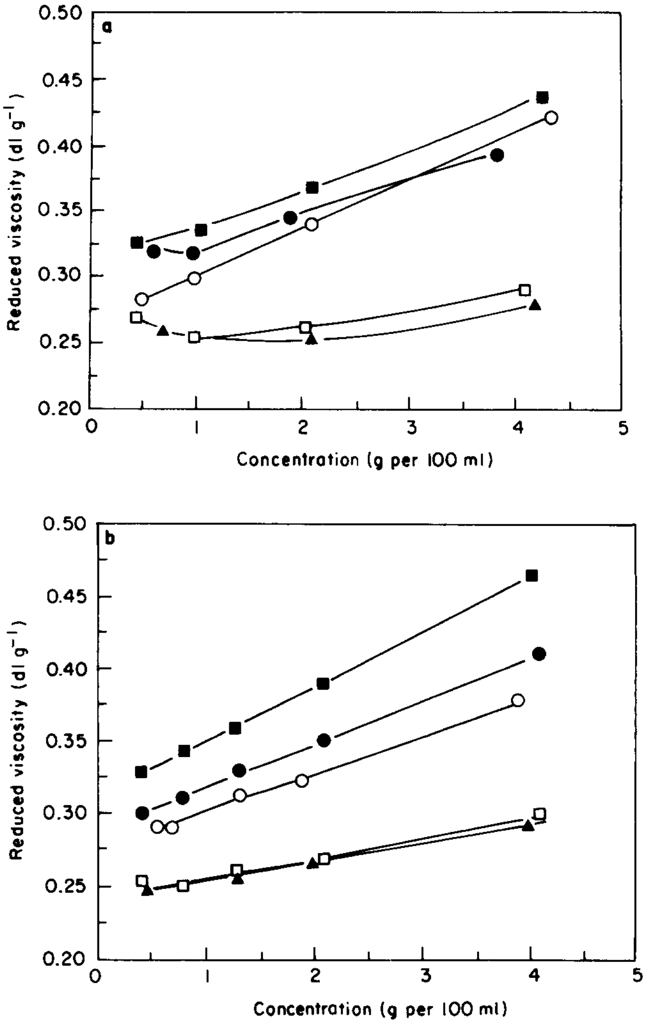

Figure 1 Reduced viscosity vs. concentration for (a) PP-X-Th/BD in DMF at 25°C and (b) PP-X-Th/BD in DMF+0.5% LiBr at 25°C: (○) PP-0; (■) PP-25-Th/BD; (●) PP-50-TH/BD; (□) PP-75-Th/BD; (▲) PP-100-Th/BD

The effect of 0.5% lithium bromide on the viscosity behaviour of the PP-X-Th/BD series of ionomers in DMF at 25°C is illustrated in *Figure 1b*. Upon addition of LiBr, the viscosity of all the ionomers appears to behave similarly to conventional non-ionic polymers. Thus, 0.5% of LiBr effectively shields the ionic groups on the ionomer chains and reduces electrostatic repulsions between ions. Similar effects of LiBr on the viscosity behaviour of ionomers have been reported by other workers[12,13]. The result also shows a gradual decrease in viscosity with increasing ionic content of the ionomers, suggesting an apparent decrease in molecular weight.

The high solubility of PP-100-S/BD and PP-100-SDP/BD in water enabled the viscosity of these two ionomers to be measured in aqueous solution. These two ionomers, which contain relatively high concentrations of ionic groups, may be referred to as polyelectrolytes with low charge density. The results for PP-100-S/BD and PP-100-SDP/BD presented in *Figures 2a* and *2b* show the effect of different concentrations of LiBr on the viscosity of these two systems. In the absence of LiBr,

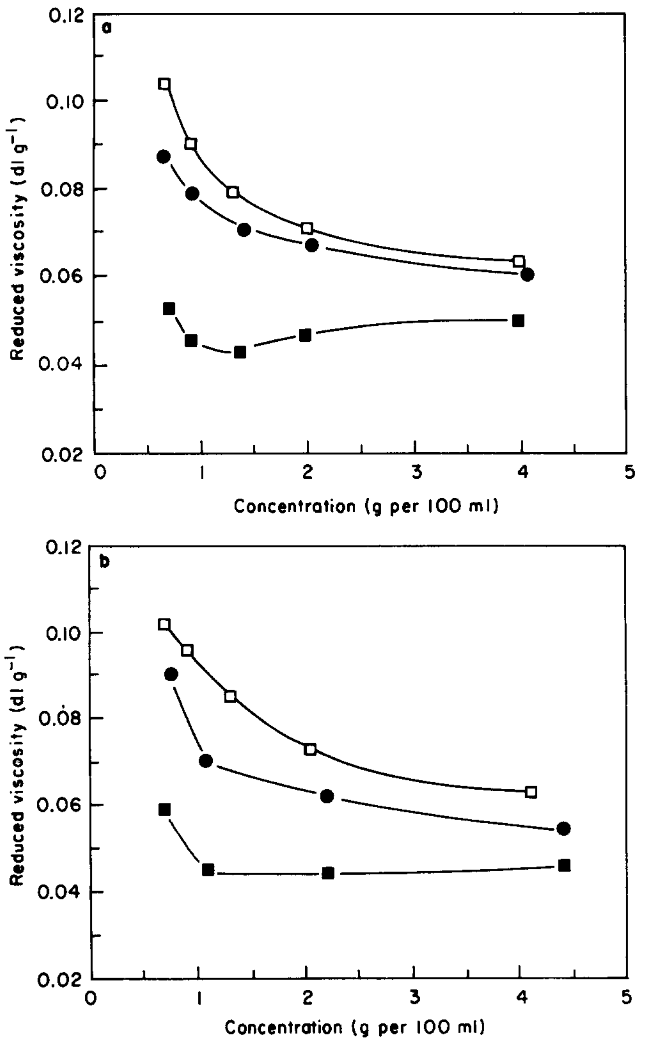

Figure 2 Reduced viscosity vs. concentration for (a) PP-100-S/BD in water at 25°C and (b) PP-100-SDP/BD in water at 25°C: (□) without LiBr; (●) 0.01% LiBr; (■) 0.1% LiBr

both PP-100-S/BD and PP-100-SDP/BD display typical polyelectrolyte behaviour in dilute aqueous solutions. Comparing the two systems in the absence of any inorganic salt, it appears that the rise in reduced viscosity in PP-100-S/BD is slightly sharper than that of PP-100-SDP/BD. The increase in reduced viscosity is directly related to the strength of the counterion binding the sulphonate group. A potassium ion, which is slightly larger than a sodium ion, will have slightly less binding strength to the sulphonate group than the sodium ion and therefore exhibits a slightly greater 'polyelectrolyte effect'. The results also indicate that the ability of the LiBr to neutralize and shield the sulphonate ions depends on the concentration of the added salt. While little effect on the viscosity is seen at very low levels of addition of LiBr, a clear difference is observed at a level of 0.1%.

Gel permeation chromatography

G.p.c. separation of ionic polymers is much more complicated than that of non-ionic polymers owing to the various interactions between ions and polymer, or solvent, or column material. The presence of these interactions often leads to apparent molecular weights that are much higher than that of the same corresponding non-ionic polymer, and in most cases results in anomalous molecular-weight distributions[8,9,14].

Effect of ionic groups on the retention time

Figures 3 and *4* show the g.p.c. chromatograms of the PP-X-Th/BD series of ionomers at three different solution concentrations, using DMF as eluant. The dramatic effect of ionic groups on the elution behaviour is immediately apparent when comparing the chromatogram of the ionomers to that of the non-ionic polymer PP-0. Two major differences between the ionomers and the non-ionic polymer are noticed:

(a) Bimodal-type distributions and varying peak positions at solution concentrations of 0.3% are observed in the chromatograms of all the ionomers.

(b) The position and shape of the peaks of all the ionomers are found to vary with solution concentration.

The results show that the retention time of the ionomers is much shorter than that of the non-ionic polymer at the same concentration (0.3%). In addition, more than one peak is observed in the chromatograms of PP-25-Th/BD and PP-50-Th/BD, which is unexpected.

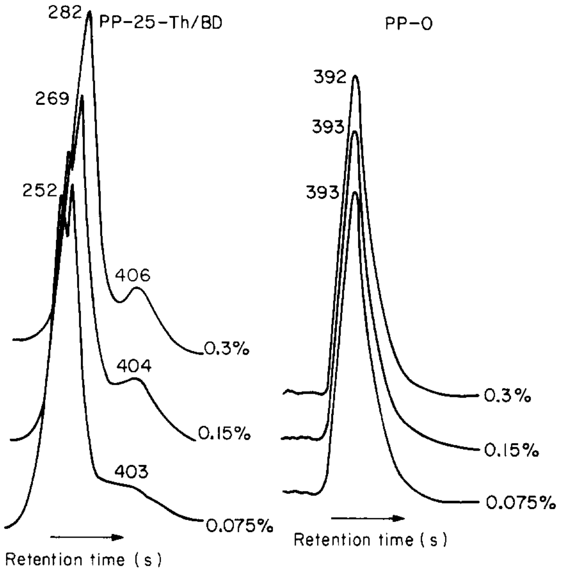

Figure 3 G.p.c. chromatograms of PP-0 and PP-25-Th/BD at three different concentrations

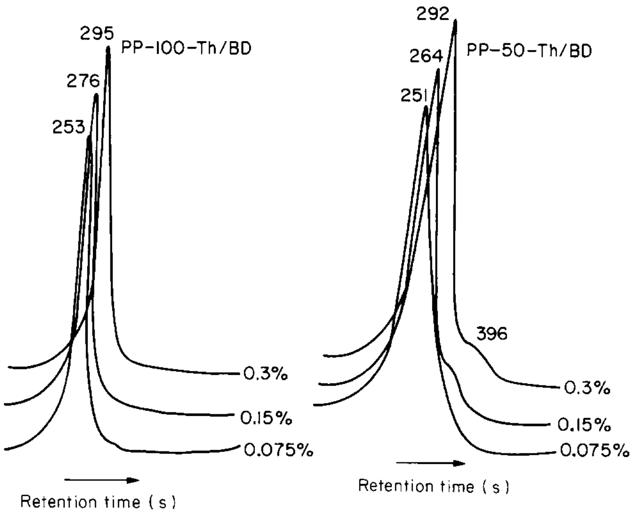

Figure 4 G.p.c. chromatograms of PP-50-Th/BD and PP-100-Th/BD at three different concentrations

Several factors may be responsible for the apparent high molecular weight of the ionomers. In good solvents, such as DMF, both the ionic and non-ionic polyurethanes generally have a moderately open conformation, owing to solvation and intramolecular associations between urethane groups. The presence of ionic groups along the polymer chain causes the chains to expand because of electrostatic repulsion. The amount of chain expansion depends on the concentration of ionic groups in the polymer. Hence the amount of chain expansion in PP-100-Th/BD should be greater than that of PP-50-Th/BD or PP-25-Th/BD. The fact that all ionomers seem to have broadly similar retention times suggests that there must be other factors involved apart from electrostatic repulsion.

One other cause for the multiple peaks is the intermolecular association between the ionic groups, which gives rise to the formation of aggregates composed of different numbers of individual chains. This is likely to be the major factor responsible for the abnormal increase in molecular weight. The stability of the ionic aggregates depends on the electrostatic forces and therefore on the number of ionic groups holding the different chains together. For the lower-ionic-content polymers, there are fewer ionic groups (fewer association points) and it is possible that some chains exist in the unassociated form. In addition, intramolecular association between the urethane groups in the polymer chains also occurs, which results in a more close-packed conformation. The ionic groups in the close-packed chains have less tendency to undergo intermolecular association. This is demonstrated clearly in the chromatograms of PP-25-Th/BD and PP-50-Th/BD. It appears that, even in PP-25-Th/BD, the number of unassociated chains is much smaller compared to the number of aggregates.

Effect of sample concentration on the retention time

The second type of behaviour exhibited by all the ionomers is their shorter retention times with decreasing solution concentrations. The behaviour of ionic polymers in dilute solution depends strongly on the ionic strength of the solution and therefore on the concentration of the ions present. At lower concentrations, i.e. lower ionic strength, DMF acts effectively as a relatively poor solvent for the highly polar ionomers, and there is a strong tendency for intermolecular associations to take place between polymer chains. As the concentration increases, molecular motions disrupt the aggregates. Consequently, the aggregates at higher concentrations are of smaller sizes and hence appear at longer retention times. Thus, for PP-25-Th/BD, having a low ionic concentration results in less stable aggregates. The disruption of larger aggregates to form smaller ones may be the origin of the multiple peaks observed in this system.

Effect of lithium bromide on the retention time

Figure 5 shows the chromatograms of the PP-*X*-Th/BD series of ionomers in DMF containing 0.5% lithium bromide. The addition of LiBr seems to have no effect on the retention time of the non-ionic polyurethane. On the other hand, the retention times of the ionomers are drastically changed in the presence of the electrolyte. Upon addition of LiBr, all the unexpected g.p.c. behaviour disappears completely and a normal distribution curve is obtained. The LiBr effectively screens the ionic groups, diminishes the repulsive forces and allows the polymer chains to take on a smaller hydrodynamic volume. This results in an increase in retention time. Furthermore, addition of LiBr effectively shields the charges on the polymer chains, which makes ionic

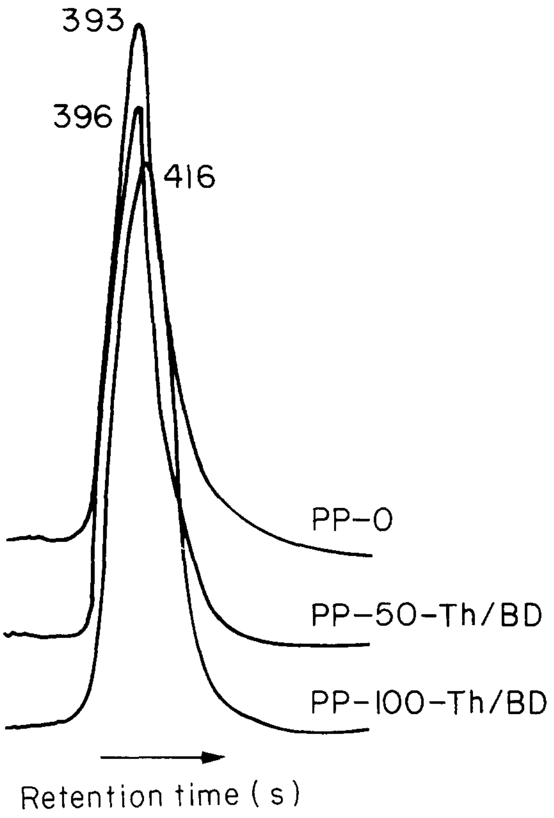

Figure 5 G.p.c. chromatograms of PP-*X*-Th/BD series containing 0.5% LiBr

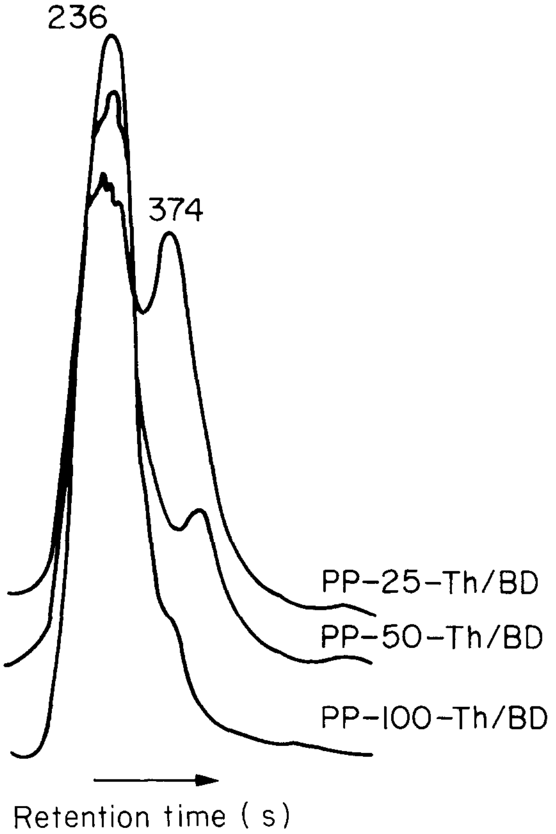

Figure 6 G.p.c. chromatograms of PP-*X*-Th/BD series at 80°C

aggregation less likely. Hence the polymers are eluted apparently as single species.

Effect of temperature on the retention time

The chromatograms of the PP-X-Th/BD series of ionomers at 80°C in DMF are presented in *Figure 6*. Inspection of these chromatograms reveals a number of differences from those obtained at room temperature. The retention times for all the ionomers appear to be slightly shorter at high temperature than at lower temperature. This is expected, as the viscosity of the polymer solution depends strongly on the temperature. For PP-25-Th/BD, the peak at 80°C is 374 s, instead of 406 s at room temperature. This suggests that increasing the temperature reduces the stability of the ionic aggregates. A similar effect is observed in PP-50-Th/BD. For PP-100-Th/Bd, in addition to the broadening of the peak, which is due to the breakdown of larger aggregates, there appears to be a slight shoulder at around 374 s. This may correspond to the elution of single polymer chains.

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