Macromolecules **2001,** *34,* 2653−2659

Ionomer Solution Structure and Solution Diagram

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Received October 4, 2000; Revised Manuscript Received February 5, 2001

ABSTRACT: Model polyurethane ionomer solution studies revealed that the critical parameters determining the solution behavior of ionomers are solvent polarity, solvent−backbone interactions, and ionic content of the ionomer. The three parameters are used to develop a novel ionomer solution diagram which provides a framework for discussion of ionomer solution behavior. The dissolution process of ionomers in low-polarity solvents is analyzed, and two different mechanisms—dissociation and fragmentation—are identified.

Introduction

Ionomers contain a small number of ionic groups, up to 15 mol %, attached to nonionic backbone chains. Ionomer solutions are commercially very important, for instance as stabilizers for oil-based paint suspensions and as coating materials. Comparison of the solution behavior exhibited by the ionomer solutions to that observed by the corresponding nonionic form of the polymer provides evidence of the unique structure of the ionomer solutions. Previous studies on the solution properties of ionomers have focused primarily on random copolymer ionomers and model telechelic ionomers. Because of the imposition of ionic interactions over polymer−solvent interactions, a model ionomer system would be preferable for these studies. Model telechelic ionomers have ionic groups located at the ends of the polymer chains and are typically of low molecular weight in order to achieve a sufficiently high ionic content. Also, the influence of chain length and ionic content on the morphology of ionomers cannot be studied independently using these systems. Model polyurethane ionomers, developed on the basis of polyurethane chemistry, have regularly spaced ionic groups along the polymer backbone and allow a direct correlation of ionomer structure and properties.[1] Because model polyurethane ionomers provide control of the distance between the ionic groups, the backbone molecular weight can be chosen such that the ionomer is soluble in solvents of a wide range of polarities. Also, the effect of ionic content and solvent quality with respect to the backbone can be studied independently.

Viscosity, light scattering, and fluorescence applied to model polyurethane ionomers in a variety of solvents revealed the importance of solvent polarity, solvent−backbone interactions, and ionic content of the ionomer in determining the solution behavior of ionomers.[1−3] Utilizing these results, in this paper, a general scheme is developed for regularly spaced ionomers to predict the solution behavior. The mechanism of dissolution for an ionomer in a low-polarity solvent is examined. The results obtained from studies of model polyurethane ionomers have also been looked at in the context of other ionomer solution studies. A novel ionomer solution diagram is developed and provides a framework for discussing ionomer solution behavior.

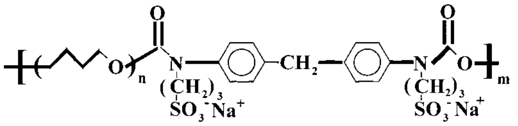

Figure 1. Structure of model polyurethane ionomer.

Table 1. Molecular Characteristics of Polymers

PU sample	M_w[a]	ion content (wt %)
PU-1000	62 500	0.0
PU-4500	56 500	0.0
PU1	77 000	6.5
PU4	60 000	2.0

[a] M_w is the weight-average molecular weight.

Experimental Section

Materials. The synthesis of model sulfonated polyurethane ionomers is described in detail elsewhere.[1] Poly(tetramethylene oxide) (PTMO) of molecular weights 1000 and 4500 were used, and the ionomers are designated PU1 and PU4, respectively. The counterion is the Na^+ ion. The corresponding unsulfonated polyurethanes are denoted by PU-1000 and PU-4500, respectively. The molecular architecture of the model polyurethane ionomer is shown in Figure 1. The precursor polymer has been characterized by gel permeation chromatography (GPC).[1] The values for the ionomer are based on calculation assuming that the sulfonation reaction does not alter the polyurethane backbone. The GPC results based on polystyrene standards are shown in Table 1. The polydispersity of both the unsulfonated polyurethanes was found to be approximately 2. Polymer solutions were prepared by dissolving the ionomer samples in dimethylacetamide and *N*-methylformamide (Aldrich, Spectrophotometric grade) under stirring for 1 day at room temperature.

Measurements. Viscometric experiments were conducted with an automated AVS 300 Schott-Gerate viscometer measuring station with an automatic dilution control unit, a piston buret, and a basic unit with computer output. The kinematic viscosity was measured using KPG-Ubbelohde capillary viscometers (Schott-Gerate), whose size was selected to be appropriate to the viscosity range of the sample under study. In all cases, the flow time was more than 200 s. Kinematic corrections were applied, depending on the specific viscometer used. The measurements were done at concentrations ranging from 0.01 to 0.5 g/dL. The temperature was maintained at 35 ± 0.1 °C in a thermostated bath. Samples were stirred and thermally equilibrated for at least 30 min between dilutions.

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10.1021/ma001731m CCC: $20.00

The measurements were repeated until the error between subsequent measurements was less than 1%. Between samples, the viscometer was cleaned with Chromerge, rinsed with deionized water and then with acetone, and finally dried for at least 12 h at 120 °C.

Results and Discussion

Ionomer Solution Structure. Ionomer solution behavior and selected ionomer solution studies are discussed to reveal the importance of polarity of the solvent, polymer−solvent interactions, and ionic content of the ionomer in determining the solution behavior of ionomers.

Polarity of Solvent. It is very well accepted that solvent polarity is a critical parameter determining ionomer solution behavior.[4−7] Counterion dissociation of ionic polymers depends on the polarity of the solvent since the association strength of the ionic group depends on the dielectric constant. In nonpolar solvents, ionic groups act as dipoles where as counterions dissociate from the polymer chain in a polar solvent. Condensation of counterions occurs in polar solutions of ionic polymers until the free energy of charge repulsion just balances that from the entropy of a free counterion, so that the distance between effective charges on the polyion is the Bjerrum length, l_B.

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T} \qquad (1)$$

In low-polarity solvents, the nonionized ion pairs attract each other, and the resulting aggregation leads to gelation at rather low concentrations. A concentration-dependent equilibrium between intra- and interpolymer chain aggregation was suggested to explain the particular rheological and scattering properties of these solutions. Intermolecular association in ionomer solutions in low-polarity solvents has been demonstrated by viscosity[7−11] and light and neutron scattering experiments.[12,13] The detailed structure of the multiplets (result of association of ionic groups) depends on the dielectric constant of the solvent, the type of ionic group and counterion, and size and structure of the polymer. It has been shown that the type of counterion present has a very important influence on the degree and nature of salt group association.[14] Counterion nature and salt group content play an important role in the structure and structural organization of the salt group aggregates. Temperature and presence of traces of polar substances also have an influence. Cosolvents for salt groups act to disrupt aggregates of the salt groups. As yet, no theory can predict the number of ionic groups per multiplet for a given system. Light scattering measurements on monotelechelic ionomers, which contain a single ionic group, show that there is a preferred configuration of the multiplet and that the variation around an average value of n_m is narrow.[15−17] The random association of macromolecules observed in solutions of ionomers in low-polarity solvents also takes place in solutions of multiblock copolymers in selective solvents and hydrophobically modified water-soluble polymers in water.

In polar solvents, the rheological behavior of diluted solutions usually presents the famous “polyelectrolyte effect”. The identification of polyelectrolyte behavior in high-polarity ionomer solutions has been supported by viscosity,[7,18−20] static and dynamic light scattering (DLS),[12,19−21] and small-angle neutron scattering (SANS) experiments[13,22] that show features that are characteristic of polyelectrolyte solutions. The behavior of polyelectrolytes with added salt is well understood in terms of the screening effect by simple ions of electrostatic interactions among fixed ions and can be described by scaling theory developed for neutral polymer solutions.[23] Although the polyelectrolyte behavior of salt-free aqueous polyelectrolyte solutions has been extensively studied, its nature is not clear yet. The interpretation of viscosity behavior and structure of salt-free polyelectrolyte solutions has been controversial. Recent ionomer solution studies in polar solvents demonstrated that ionomers offer good model systems to investigate the characteristic behavior of salt-free polyelectrolyte solutions.[1,24]

Viscometric and DLS measurements of model polyurethane ionomers PU1 and PU4 demonstrated that sulfonated polyurethane ionomers in DMAc, which is a polar solvent, show polyelectrolyte behavior.[1] The slow mode diffusion coefficient observed in dynamic light scattering measurements has been attributed to domains,[25,26] temporal aggregates,[27] filterable aggregates,[28,29] clusters of higher ionic content polymer chains, particles formed due to hydrophobic aggregation, and aggregates which take considerable time to dissolve. Because of dissociation of counterions, ionomer solutions in polar solvents contain polyions and counterions. Hence, the aggregates correspond to domains consisting of polyions and counterions loosely held together due to electrostatic interactions. In other words, the structures giving rise to the slow mode are *loose aggregates*.[3] The loose aggregate is structurally similar to the domains proposed by Ise[25,26] and Schmitz[27] and consists of polyions and counterions in a small region of solution. The formation of the loose aggregates is attributed to electrostatic interactions between polyions and counterions inside the aggregate. The loose aggregate, as the name suggests, have polyions loosely held together and hence can be disrupted by very weak external/shear forces. It has been concluded that polar solutions of ionomers contain free polyions as well as loose aggregates, aggregates which consist of polyions and counterions held together by electrostatic interactions.[1] Experiments with different polarity solvents in which PU4 exhibits characteristic polyelectrolyte behavior have shown that the size corresponding to the slow mode is related to solvent−backbone interactions and provides further evidence for the presence of loose aggregates in polar solutions of ionomers.[30]

Polymer−Solvent Interactions. Recent studies on Nafion, polyethylene-*co*-methacrylic acid partially neutralized ionomers, model polyurethane ionomers, and polystyrene ionomers have shown the importance of polymer−solvent interactions in determining the ionomer solution behavior in polar solvents.[2,31−33] For ionomers in polar solvents which are poor solvents for the ionomer backbone, the distance between ionic groups along the polymer chain combined with the nonsolubility of the hydrophobic polymer chain induces polymer chain aggregation in order to minimize the polymer−solvent interfacial energy. A colloidal structure results with particles composed of a polymer core and the ionic groups located at the polymer−solvent interface. The shape and size of these polymeric micelles can be expected to be mainly related to the ionic content but is also related to the chemical structure and to the molecular weight of the ionomer.

In the model polyurethane ionomer PU4 the distance between the ionic groups is slightly less than twice the radius of gyration of the particle, indicating a folded-in structure with ionic groups on the surface.[2] The fact that the radius is approximately half the distance between ionic groups supports the proposed solution structure. In Nafion and polyethylene-*co*-methacrylic acid partially neutralized ionomers the measured radii of the particles are at least twice the distance between ionic groups.[31,32] This means that counterion condensation is taking place and not all ionic groups are located at the surface of the particle. The difference between ellipsoidal and cylindrical shapes can probably be attributed to an effect of polymer–solvent interfacial energy and packing requirements for particle formation.

The colloid structure is characterized by a sharp interface between solvent and polymer phase; the ionomer solutions in highly polar solvents, which are usually poor solvents for the backbone, are colloidal. ESR and NMR spectra of Nafion/NMF solutions are contrary to SANS and SAXS conclusions.[34] The experiments indicated good dissolution of the ionomer, not particle formation. ESR study of VO^{2+} swollen membranes and solutions suggests the alcohol molecules penetrate into the polymer particles.[35] This can happen with other solvents as well, resulting in a diffuse polymer–solvent interface. Thus, a diffuse interface can be present due to the penetration of the solvent molecules inside the particle, creating a solvated region between the dense polymer core and the ionic shell.

The loose aggregate picture we depicted for ionomers in polar solvents has been used to explain this discrepancy.[36] However, particle sizes obtained by Cirkel et al. are much larger compared to those in the literature for the same polymers. Also, a hydrophobic aggregate rather than a loose aggregate is present in polar solutions of ionomers in solvents that cannot dissolve the neutral polymer chain, unless the ionic content is very high.[3] Viscosity measurements[37,38] show the absence of polyelectrolyte behavior, and hence the ionic content of these polymers is not sufficiently high to cause dissolution and subsequent formation of loose aggregate.

Ionic Content of Ionomer. Experiments with different ionic content ionomers in solvents that cannot dissolve the neutral polymer chain showed that smaller particles are formed as the ionic content of the ionomer is increased (as the distance between the ionic groups is decreased).[33,32] Recent studies with higher ionic content ionomer PU1 in NMF have shown that, at sufficiently high ionic content, ionomer solutions exhibit polyelectrolyte behavior even if the solvent is a poor solvent for the backbone.[3] This indicates that ionic content (or distance between the ionic groups) of the ionomer is a critical parameter that influences ionomer solution behavior.

Previously, ionomer solution behavior has been classified solely on the basis of the polarity of the solvent.[7] From the results of studies of model polyurethane ionomer solutions, it can be seen that, in addition to the polarity of the solvent, polymer–solvent interactions (interactions between the ionomer backbone (the nonionic part of the ionomer) and the solvent) and the ionic content of the ionomer are critical in determining the solution behavior of ionomers. In the next section, this information was used to develop an ionomer solution diagram, which provides a framework to discuss solubility and solution behavior of ionomers.

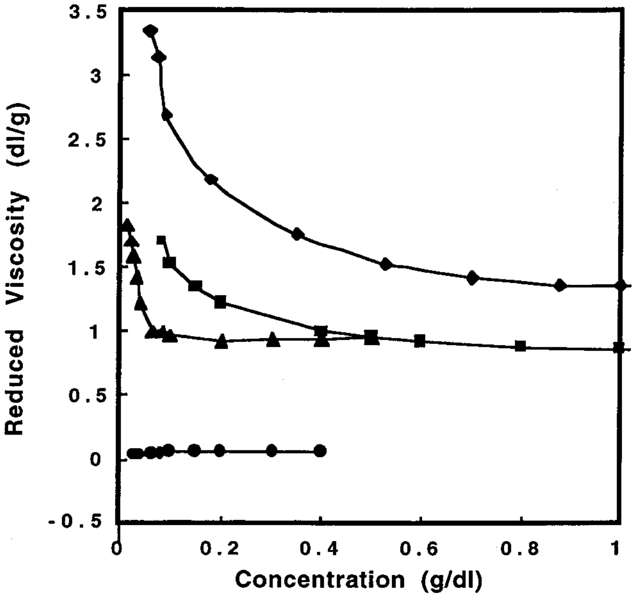

Figure 2. Viscosity behavior of model polyurethane ionomers: (◆) PU1 in DMAc; (■) PU4 in DMAc; (▲) PU1 in NMF; (●) PU4 in NMF.

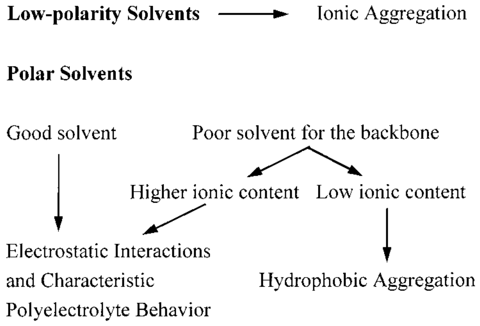

Figure 3. Solution behavior of model polyurethane ionomers.

Figure 2 shows viscosity measurements of the model polyurethane ionomers PU1 and PU4 in DMAc and NMF and demonstrates the importance of the three parameters—polarity of the solvent, polymer–solvent interactions, and ionic content of the ionomer—in determing the solution behavior of ionomers. Both PU1 and PU4 exhibit polyelectrolyte behavior in DMAc, a polar solvent and a good solvent for the backbone, as can be seen from the upturn in reduced viscosity at low concentrations. In another polar solvent NMF, which is a poor solvent for the backbone, PU4 does not show polyelectrolyte behavior. However, PU1, which has a higher ionic content as compared to PU4, has an upturn in reduced viscosity at low concentrations in NMF. Fluorescence measurements have confirmed these observations.[39] The effect of the three parameters on the solution behavior of model polyurethane ionomers is shown in Figure 3.

Ionomers in solution have four variables: nature of the backbone, distance between the ionic groups, type of ionic group, and solvent. For regularly spaced ionomers, ionic content is inversely proportional to the distance between ionic groups. Though only distance between the ionic groups and solvent have been varied in model polyurethane ionomer solution studies, the results allow conclusions to be made about the effect of the nature of backbone chain and type of ionic group on the solution behavior of ionomers.

Ionomer Solution Diagram. The important constituents of the ionomer−solvent system are solvent, polymer (ionomer backbone), type of ionic group, and ionic content. The structure and interactions in solution are determined by the solvent properties (dielectric constant, solubility parameter of the solvent), the backbone properties (solubility parameter of the polymer and the chain length between ionic groups), and the type of ionic group and ionic content of the ionomer. Temperature influences the solution structure through solvent dielectric constant and the solubility parameters of the polymer and solvent. The ionomer solution behavior can be qualitatively described very well by incorporating these factors in two parameters: a solvent−ionic group index (SII) and a solvent−polymer index (SPI). A new framework has been developed for understanding the gross solution properties of ionomers. The discussion is based on ionomers with regularly spaced ionic groups but is also valid for most block ionomers and can be applied to random copolymer ionomers by considering an average distance between the ionic groups. The two parameters (SII and SPI) show the following characteristics:

$$\begin{aligned} \mathrm{SII} &= \mathrm{SII}_o \qquad \mathrm{SII}_o \le \mathrm{SII}_c \\ &= \mathrm{SII}_c + (1 - \mathrm{SII}_c)\frac{l_B}{l_c} \qquad l_B \le l_c \\ &= 1 \qquad l_B > l_c \end{aligned} \tag{2}$$

$$\begin{aligned} \mathrm{SPI} &= \mathrm{SPI}_o \qquad \mathrm{SPI}_o \le \mathrm{SPI}_c \\ &= \mathrm{SPI}_c + (1 - \mathrm{SPI}_c)\frac{2l_c}{L_c} \qquad l_c \le L_c/2 \\ &= (2 - \mathrm{SPI}_c) - (1 - \mathrm{SPI}_c)\frac{2l_c}{L_c} \qquad l_c > L_c/2 \end{aligned} \tag{3}$$

Here l_c is the distance between the ionic groups, l_B is the Bjerrum length, and L_c is the distance between the ionic groups corresponding to a molecular weight at which the polymer backbone between the ionic groups becomes insoluble in the solvent. SII_o is a zero solvent−ionic group index, determined mainly by the dielectric constant of the solvent and the type of ionic group, and SPI_o is a zero solvent−polymer index, determined by the solubility parameters of the ionomer backbone (δ_p) and the solvent (δ_s).

$$\mathrm{SII}_o = f(\text{solvent, ionic group}) \tag{4}$$

$$\mathrm{SPI}_o = f(\delta_p, \delta_s) \tag{5}$$

$$0 \le \mathrm{SII}_o, \mathrm{SPI}_o \tag{6}$$

SII_c is a critical solvent−ionic group index, above which ionic group dissociation occurs. SPI_c is a critical solvent−polymer index, above which polymer dissolves in the solvent. If $\mathrm{SII}_o > \mathrm{SII}_c$ (ionic group dissociates), SII varies from SII_c for a monochelic ionomer to 1 for a polyelectrolyte. (Counterion condensation takes place such that the distance between the charges on the chain is equal to the Bjerrum length.) Note that for all ionic contents in the counterion condensation regime, SII = 1. Similarly, when $\mathrm{SPI}_o > \mathrm{SPI}_c$ (ionomer backbone dissolves in the solvent), SPI varies from SPI_c for a monomeric backbone (polymer part between the ionic groups) to 1 for half the molecular weight between the ionic groups (i.e., distance between the ionic groups = $L_c/2$) at which the polymer becomes insoluble in the solvent. Solubility decreases with increase in molecular weight, and SPI is defined such that with increase in distance between the ionic groups it increases to a value of 1 and then decreases. Note that l_B and L_c depend on the ionic group, polymer, and solvent. For most polymers soluble in a given solvent, L_c is very large and SPI corresponds to the second part of eq 3.

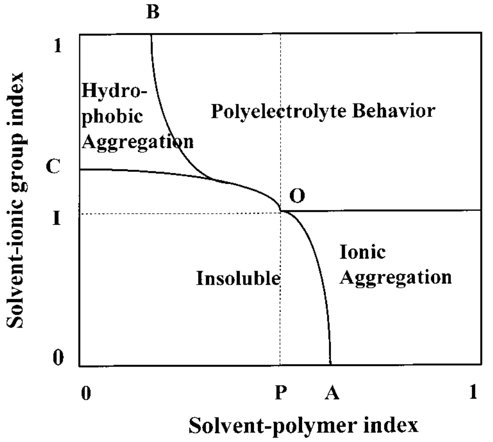

Figure 4. Ionomer solution diagram.

Consider the ionomer solution diagram in Figure 4. In the figure I and P are used for SII_c and SPI_c, respectively. If the backbone is insoluble, SPI (=SPI_o) is less than SPI_c. Similarly, above an SII of SII_c, the ionic group dissociates. There are four possibilities: (1) the backbone is insoluble ($\mathrm{SPI} < \mathrm{SPI}_c$), and counterion (ionic group) dissociates ($\mathrm{SII} > \mathrm{SII}_c$) (hydrophobic aggregation can be expected to take place); (2) the backbone is soluble ($\mathrm{SPI} > \mathrm{SPI}_c$), and the ionic group does not dissociate ($\mathrm{SII} < \mathrm{SII}_c$) (ionic aggregation can be expected to take place); (3) the backbone is soluble ($\mathrm{SPI} > \mathrm{SPI}_c$), and counterion dissociation occurs ($\mathrm{SII} > \mathrm{SII}_c$) (polyelectrolyte behavior is exhibited); and (4) the backbone is insoluble ($\mathrm{SPI} < \mathrm{SPI}_c$), and counterion does not dissociate ($\mathrm{SII} < \mathrm{SII}_c$) (ionomer is insoluble in the solvent).

If the ionic group does not dissociate ($\mathrm{SII} < \mathrm{SII}_c$) and the backbone is insoluble ($\mathrm{SPI} < \mathrm{SPI}_c$,) the ionomer is clearly *insoluble*. If both backbone dissolution and ionic group dissociation take place, electrostatic interactions in solution result in *polyelectrolyte behavior*. In general, if ionic dissociation does not take place but the backbone is soluble, ionic aggregation takes place. Similarly if the backbone is insoluble and ionic groups dissociate, *hydrophobic aggregation* takes place. However, the ionomer is *insoluble* (1) when the backbone dissolves and there are a large number of ionic groups and (2) when ionic group dissociation takes place but there are few ionic groups. For example, PU1 does not dissolve in toluene, and monochelic polystyrene does not dissolve in water. This results in the regions bound by OAP and OCI depicting *insoluble* ionomer behavior. Even in the presence of *hydrophobic aggregation*, *polyelectrolyte behavior* may be seen in some cases (usually at higher ionic contents), as has been observed for PU1 in NMF and poly(styrenesulfonate) in water. This results in a new boundary OB for *polyelectrolyte behavior*. The different regions are indicated in Figure 4.

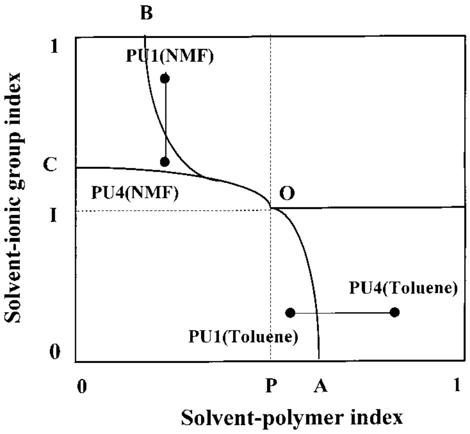

Figure 5. Ionomer solution diagram for PU1 and PU4 in toluene and *N*-methylformamide.

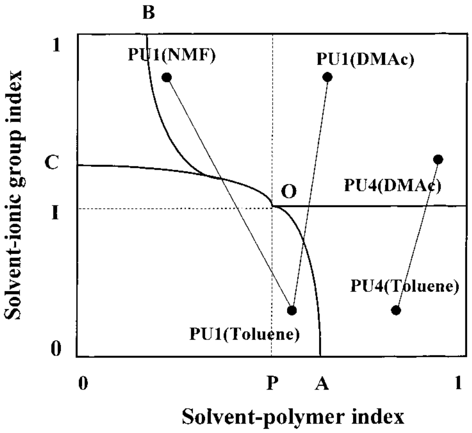

Figure 6. Ionomer solution diagram for PU1 and PU4 in toluene and DMAc and PU1 in NMF.

The behavior of an ionomer in a solvent can be predicted, given the ionic group, distance between the ionic groups, dielectric constant of the solvent, and solubility parameters of the ionomer backbone and solvent. The first step is to calculate SII_o and SPI_o. However, the calculation is a formidable task because there is no theory available to compute these values. For example, we can define $SII_o = F_iSII_c$ and $SPI_o = F_pSPI_c$, such that ionic group dissociation occurs for $F_i > 1$ and the backbone soluble for $F_p > 1$. F_i can be calculated considering that ionic group dissociation occurs when thermal energy overcomes the electrostatic potential energy.

$$F_i = \frac{4\pi\epsilon\epsilon_0 k_B T}{K(ze)^2} \tag{7}$$

K is a parameter that depends on the type of ionic group, solvent, coordinating abilities of the counterion, etc., and *z* is the valence of the counterion. However, similar calculation of F_p, which is a function of solubility parameters of polymer and solvent, is not trivial. This is because solubility parameter based calculations do not give good agreement with experimental results in the presence of any specific interactions including hydrogen bonding.[40] In the simple treatment here, it is assumed that the values of SII_o and SPI_o are available. Detailed analysis is beyond the scope of this work. Also, SII_c and SPI_c can be arbitrarily set (for example, equal to 0.5) but is not done to keep the treatment general. Qualitative comparison will be made on the basis of available information.

Once the solvent, ionic group, and the backbone are fixed, SII_o and SPI_o can be calculated. Then both SII and SPI are functions of only the distance between the ionic groups (ionic content). The effect of different parameters on the solution structure can be examined. The following examples show how ionomer solution diagram incorporates the importance of polarity of solvent, distance between the ionic groups, and polymer–solvent interactions.

Consider solutions of ionomers PU1 and PU4 in toluene. For both ionomers, because the polarity of the solvent is too low for counterion dissociation, $SII < SII_c$. SPI for PU4 is greater than SPI for PU1 because of larger distance between the ionic groups (see eq 3). From Figure 5 it can be seen that though PU1 is insoluble in toluene, PU4 is soluble, and ionic aggregation takes place in solution. It can be seen that solubility of an ionomer in a good solvent for the backbone can be improved by increasing the distance between the ionic groups (i.e., by lowering the ionic content). Consider solutions of ionomers PU1 and PU4 in *N*-methylformamide (NMF). The solution behavior exhibits the competing effects of the quality of solvent toward the hydrophobic backbone of the chains and the dielectric property of the solvent affecting the solvation of counterions of the ionic groups. For both ionomers, because the polarity of the solvent is very high, counterion dissociation takes place, and SII for PU1 is greater than SII for PU4 because of its higher ionic content (see eq 2). Since the backbone is insoluble in the solvent, $SPI < SPI_c$ for both PU4 and PU1. From Figure 5 it can be seen that PU1 in NMF exhibits polyelectrolyte behavior whereas hydrophobic aggregation takes place in PU4 solutions in NMF. The above two examples illustrate the critical role of the distance between the ionic groups in determining the solution behavior of ionomers.

If the solvent is changed, both SII and SPI change, and the amount and nature of change will determine the resulting solution behavior. To determine the effect of polarity of solvent on the ionomer solution behavior, consider PU1 in toluene, DMAc, and NMF and PU4 in toluene and DMAc. From Figure 6 it can be seen that ionic aggregation takes place in toluene solutions of PU1 and PU4 whereas DMAc solutions of PU1 and PU4, and NMF solutions of PU1 exhibit polyelectrolyte behavior. The influence of polymer–solvent interactions on the ionomer solution behavior can be seen by examining the solution behavior of PU4 in DMAc and NMF. Ionic groups dissociate in both solvents, and so $SII > SII_c$. Since the backbone of PU4 is insoluble in NMF, $SPI < SPI_c$ whereas $SPI > SPI_c$ in DMAc. Hence, as seen in Figure 7, DMAc solutions of PU4 exhibit polyelectrolyte behavior whereas hydrophobic aggregation takes place in *N*-methylformamide.

Solubility studies were done to determine the interaction of polyurethane ionomers with different solvents. The solubility of PU1 was examined in a series of solvents. The data are shown in Table 2 and allow comparison of trends in solubility, dielectric constant, and solubility parameter components. The results clearly show that the dielectric constant is not the sole controlling factor. According to Hansen, the solubility parameter $\delta^2 = \delta_p^2 + \delta_h^2 + \delta_d^2$, where δ_p, δ_h, and δ_d are polar, hydrogen-bonding, and dispersion parameters. If the three-dimensional solubility parameter is considered, the dispersion parameter seems to have little effect

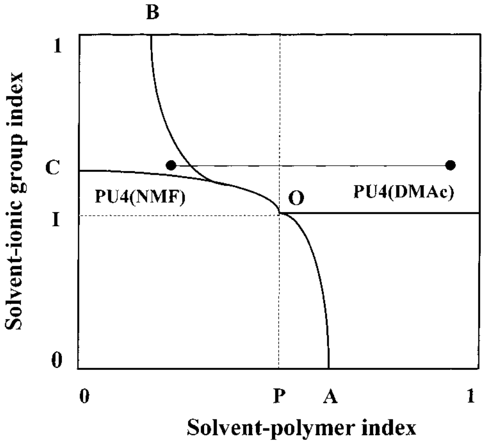

Figure 7. Ionomer solution diagram for PU4 in dimethylacetamide and *N*-methylformamide.

Table 2. Results of Solubility Studies for PU1

solvent	solubility/deg of swelling	δ_d	δ_p	δ_h	δ	ϵ
formamide	soluble	17.2	26.2	19.0	36.6	109.0
DMA	soluble	16.8	11.5	10.2	22.7	59.0
DMSO	soluble	18.4	16.4	10.2	26.6	46.7
acetonitrile	slight[a]	15.3	18.0	6.1	24.6	37.5
DMF	soluble	17.4	13.7	11.3	24.8	36.7
1-methyl-2-pyrrolidinone	soluble	18.0	12.3	7.2	22.9	32.0
ethanol	medium[a]	15.8	8.8	19.4	26.6	24.0
2-butanone	medium[a]	16.0	9.0	5.1	19.0	18.5
2-propanol	slight[a]	15.8	6.1	16.4	23.5	18.3
cyclohexanone	high[a]	17.8	6.3	5.1	19.6	18.0

[a] Degree of swelling.

compared to the polar and hydrogen-bonding parameters. No direct conclusions could be drawn about the solubility based solely on the solubility parameter and the dielectric constant. The polar and hydrogen-bonding parts of the solubility parameter seem to be more important. The results are in good agreement with those obtained by Al-Salah et al.[41] and Peiffer et al.[42]

It can be seen that dielectric constant is not a principal factor determining the solubility of an ionomer, but it becomes important when the ion content of the polymer is high. The coincidence of solubility parameters between solvent and polymer is also important when the ion content is low. The critical parameters are polarity of the solvent, the solvent–backbone interactions, and the distance between the ionic groups. However, the type of ionic group plays an important role since it determines the ionomer structure in bulk. This is why even changing the counterion of an ionomer affects its solubility. As shown in a recent study,[43] ionomer or polyelectrolyte behavior of ionomers is determined not only by the type of solvent (high or low polarity) but also by the coordinating abilities of the cation, the pH, and the type of ionic groups in the system. The solubility boundary is given by the curve AOC in Figure 4. It is not possible to quantitatively predict this boundary because of the complications involved.

Dissolution of Ionomers. To understand the dissolution process, consider what happens when a polymer sample is put in solution. High dielectric constant solvents solvate the counterions and disperse ion pairs and multiplets present in an ionomer. Depending on the backbone–solvent interactions and ionic content of the ionomer, either loose aggregates or hydrophobic aggregates are formed. However, if the counterion cannot be solvated because of low dielectric constant of the solvent and the solvent is a good solvent for the ionomer backbone, one of two things may happen. (1) All the multiplets dissociate (without the solvation of the counterion), and the resulting solution structure is based on a closed or open association model of aggregation of ionic groups. (2) Only a few or none of the multiplets dissociate, leading to a solution consisting of fragments (typically submicron multichain particles). Most literature data on ionomer solutions in low-polarity solvents have been interpreted in terms of the first process. Several experimental results support the possibility of occurrence of the second process.

It has been observed that both melt viscosity values and solution behavior can vary according to the solvent history of sulfonate ionomers.[44] Intramolecular interactions that prevailed in dilute solution and that remained “locked in” the solid polymer upon freeze-drying are still maintained upon dissolution in a solvent of low polarity such as xylene. Equilibration upon dilution either does not occur or is very slow. The addition of cosolvents such as alcohols expedites this equilibration. These observations suggest that sample preparation of sulfonate ionomers could be very important in determining physical properties of such systems.

System-specific relations for aggregation were found for poly(sodium acrylate)-*g*-poly(ethylene oxide) graft copolymers.[45] Two parameters were found to be relevant: structure of the copolymer as architecture has direct implications on the characteristics of the microdomains and especially on the aggregation number; and thermodynamic properties of the components as described using Flory–Huggins interaction parameters.

Block copolymer ionomer solutions were found to be not at equilibrium.[46] It was found that the solubility of sulfonated SEBS (styrene–(ethylene-*co*-butylene)–styrene triblock copolymer) ionomers decreased with increasing storage time even when the solids were under sealed and dry conditions.[47] The solutions contained large species (~500 nm) which dissolved very slowly in THF with the dissolution process following first-order kinetics. The results suggest that the origin of “association of sulfonated SEBS ionomers” should be reconsidered; namely, these large species were not formed from individual chains in solution but instead were fragments produced in the dissolution process.

For many kinds of ionomers in low-polarity solvents, it is likely that the observed very large species were not formed in the solution through the association (aggregation) of individual ionomer chains; instead, they are small insoluble fragments remaining from a partial dissolution process. The “multiplets” or ionic aggregates that exist in an ionomer in solid state are not disrupted by the solvent. However, the backbone is solvated, resulting in breaking of the polymer sample put in a low-polarity solvent. These fragments can be microgels, “starlike” clusters, or even trimers and dimers, depending on the strength of the ion-pair clusters formed in the bulk. According to the solubility of corresponding sulfonated SEBS samples,[47] the strength of the ion-pair clusters is in the order $Mg^{2+} > Na^{+} \sim Mn^{2+} > Zn^{2+} \sim Cu^{2+} \sim Ni^{2+} > Co^{2+}$.

The dissolution process depends on the specific system (ionomer and solvent) under consideration, specifically the type of ionic group, solvent, and the nature of multiplet in the solid state. The exact mechanism (association or fragmentation) can be determined by examining the reproducibility of data obtained from different solutions of the same concentration, made from different initial concentrations or different methods. Absence of reproducibility points to absence of equilibrium. If solutions of same concentration of ionomer made differently are not identical, the dissolution is clearly by fragmentation. Even when dissolution is by fragmentation, larger aggregates may dissociate into smaller entities as time proceeds until equilibrium is achieved. The two mechanisms for dissolution can be easily understood by considering that polymers are swollen by solvent before dissolution.

Conclusions

Ionomer solution structure is determined by interactions between the solvent and the polymer (nonionic backbone) and the solvent and the ionic group. Hence, solubility parameters of the solvent and the polymer (which determine backbone–solvent interactions) and the polarity of the solvent are critical parameters. The ionomer solution diagram described in this paper provides a framework for discussion of ionomer solution behavior and shows why ionic content (distance between the ionic groups) plays an important role. The dissolution process of ionomers in low-polarity solvents is analyzed, and two different mechanisms—dissociation and fragmentation—are identified.

Acknowledgment. We thank Dr. Chang Zheng Yang of Nanjing University for synthesizing the polyurethane ionomers used in this work. We are grateful to National Science Foundation for financial support through Grant DMR 9531069.

References and Notes

(1) Nomula, S.; Cooper, S. L. *Macromolecules* **1997**, *30*, 1355–1362.
(2) Nomula, S.; Cooper, S. L. *J. Colloid Interface Sci.* **1998**, *205*, 331–339.
(3) Nomula, S.; Cooper, S. L. *J. Phys. Chem. B* **2000**, *104*, 6963.
(4) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1821.
(5) Siadat, B.; Lundberg, R. D.; Lenz, R. W. *Macromolecules* **1981**, *14*, 773.
(6) Gebel, G.; Loppinet, B.; Williams, C. E. *J. Phys. Chem. B* **1997**, *101*, 1884–1892.
(7) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(8) Tant, M. R.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28* (1), 1.
(9) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Maromol. Chem. Phys.* **1988**, *C28*, 99.
(10) Lantman, C. W.; MacKnight, W. J. *Annu. Rev. Mater. Sci.* **1989**, *19*, 295.
(11) Lundberg, R. D. In *Structure and Properties of Ionomers*; Pineri, M., Eisenberg, A., Eds.; D. Reidel Publishing Company: Dordrecht, Holland, 1986; Vol. 198, p 387.
(12) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(13) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1339.
(14) Bakeev, K. N.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 4578–4582.
(15) Vanhoorne, P. Ph.D. Thesis, University of Liege, 1994.
(16) Pispas, S.; Hadjichristidis, N.; Mays, J. W. *Macromolecules* **1994**, *27*, 6307–6317.
(17) Chassenieux, C.; Johannsson, R.; Durand, D.; Nicolai, T.; Vanhoorne, P.; Jerome, R. *Colloids Surf. A* **1996**, *112*, 155–162.
(18) Rochas, C.; Domard, A.; Rinuado, M. *Polymer* **1979**, *20*, 76.
(19) Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1757.
(20) Hara, M.; Wu, J. L. *Macromolecules* **1988**, *21*, 402.
(21) Hara, M.; Wu, J. L. In *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; American Chemical Society: Washington, DC, 1989; Vol. 395, p 446.
(22) MacKnight, J.; Lantman, C. W.; Lundberg, R. D.; Sinha, S. K.; Peiffer, D. G. *Polym. Prepr.* **1986**, *27*, 327.
(23) Mandel, M. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993; p 1.
(24) Hara, M. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993; p 193.
(25) Ise, N. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 323.
(26) Matsuoka, H.; Schwahn, D.; Ise, N. *Macromolecules* **1991**, *24*, 4227.
(27) Schmitz, K. S.; Lu, M.; Singh, N.; Ramsay, D. *Biopolymers* **1984**, *23*, 1637.
(28) Smits, R. G.; Kuil, M. E.; Mandel, M. *Macromolecules* **1994**, *27*, 5599–5608.
(29) Norwood, D. P.; Benmouna, M.; Reed, W. F. *Macromolecules* **1996**, *29*, 4293–4304.
(30) Nomula, S.; Cooper, S. L. *Macromolecules* **2001**, *34*, 719.
(31) Gebel, G.; Loppinet, B. *J. Mol. Struct.* **1996**, *383*, 43–49.
(32) Gebel, G.; Loppinet, B.; Hara, H.; Hirasawa, E. *J. Phys. Chem. B* **1997**, *101*, 3980.
(33) Li, M.; Jiang, M.; Wu, C. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1593.
(34) Szajdzinska-Pietek, E.; Schlick, S. *Langmuir* **1994**, *10*, 2188–2196.
(35) Li, H.; Schlick, S. *Polymer* **1995**, *36*, 1141.
(36) Cirkel, P. A.; Okada, T.; Kinugasa, S. *Macromolecules* **1999**, *32*, 551.
(37) Aldebert, P.; Gebel, G.; Loppinet, B.; Nakamura, N. *Polymer* **1995**, *36*, 431–434.
(38) Gebel, G.; Loppinet, B. In *Ionomers: Characterization, Theory and Applications*; Schlick, S., Ed.; CRC Press: New York, 1996; p 83.
(39) Nomula, S.; Cooper, S. L. *Macromolecules* **2000**, *33*, 6402.
(40) Grulke, E. A. In *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1989.
(41) Al-Salah, H. A.; McLean, J. A., Jr.; Frisch, K. C.; Xiao, H. X. *J. Macromol. Sci., Phys.* **1987**, *B26*, 447–463.
(42) Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Chem.* **1982**, *22*, 1757.
(43) Kruczala, K.; Schlick, S. *PMSE Prepr.* **1998**, *39*, 475.
(44) Lundberg, R. D.; Phillips, R. R. In *Coulombic Interactions in Macromolecular Systems*; Eisenberg, A., Bailey, F. E., Eds.; American Chemical Society: Washington, DC, 1986.
(45) Hourdet, D.; L'alloret, F.; Durand, A.; Lafuma, F.; Audebert, R.; Cotton, J. P. *Macromolecules* **1998**, *31*, 5323–5335.
(46) Zhou, Z.; Peiffer, D. G.; Chu, B. *Macromolecules* **1994**, *27*, 1428–1433.
(47) Wu, C.; Woo, K.; Jiang, M. *Macromolecules* **1996**, *29*, 5361–5367.

MA001731M