Effect of Solvent Polarity in Ionomer Solutions

Srinivas Nomula[†] and Stuart L. Cooper*[,‡]

Department of Chemical Engineering, University of Delaware, Newark, Delaware 19716

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ABSTRACT: A model polyurethane ionomer is synthesized with regularly spaced ionic groups along the polymer backbone. This model system allows study of the effect of ionic interactions on polymer solutions and to understand the behavior of salt-free polyelectrolyte solutions which suffer from the disadvantages of weak scattering and difficulty in filtration and purification. The ionomer has been studied in a variety of solvents by dynamic light scattering. The underivatized polyurethane exists as single chains in solution. The ionomer solution structure depends on the polarity of the solvent and solvent quality with respect to the ionomer backbone. In low-polarity solvents ionic aggregation takes place, and characteristic polyelectrolyte behavior is observed in polar solvents that are good solvents for the ionomer backbone. It is found that in toluene, a low-polarity solvent, the aggregates consist of physically cross-linked chains whereas in dimethylacetamide, a polar solvent, the aggregates consist of polyions and counterions held together due to electrostatic interactions. In very high-polarity solvents, which are usually poor solvents for the ionomer backbone, hydrophobic aggregation results in the formation of micelles consisting of polyol chains at the core with an outer ionic shell. The results provide useful information on the structure of salt-free polyelectrolyte solutions, some aspects of which have been considered controversial, and also explain the disappearance of polyelectrolyte behavior in very high-polarity solvents.

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 paint suspensions and as coating materials. Hence, solution properties of ionomers have attracted considerable interest.[1−7] It has been well established that ionomer solutions show two types of behavior depending on the polarity of the solvents used,[8] namely (1) aggregation due to dipolar attractions between chain segments in nonpolar or low-polarity solvents and (2) polyelectrolyte behavior due to Coulombic interactions in high-polarity solvents. The association of ionomer molecules in nonpolar solvents has been demonstrated by viscosity and light and neutron scattering measurements.[5,8−13] The identification of polyelectrolyte behavior of ionomers in high-polarity ionomer solutions has been supported by viscosity,[8,14−16] static and dynamic light scattering,[6,12,15,16] and small-angle neutron scattering (SANS) experiments.[13,17]

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.[18] Although the polyelectrolyte behavior of salt-free aqueous polyelectrolyte solutions has been extensively studied, its nature is not clear yet. The presence of two diffusion coefficients in dynamic light scattering measurements and a broad single peak in $I(q)$ in small-angle neutron scattering (SANS) and small-angle X-ray scattering (SAXS) measurements are interpreted differently by different researchers, leading to a controversy.[19−21] Several models have been proposed to explain the formation and structure of some kinds of aggregates; however, the molecular structure and thermodynamic driving force that creates such structures are not yet understood.

This research was motivated by two recent publications. In the first, a 5-fold change in dielectric constant of the solvent was found not to affect the dynamics of polyelectrolyte solutions.[22] This is not expected since a change in dielectric constant of the solvent should affect electrostatic interactions in solution through the Debye screening length, which is a measure of the range of electrostatic interactions. In another study, the polyelectrolyte effect of perfluorosulfonate ionomers was found to increase with dielectric constant of the solvent for alcohols and disappear in very high-polarity solvents (higher dielectric constant than water).[23] Electrostatic persistence length arguments were used to explain this behavior, but the measured low values of reduced viscosity in very high-polarity solvents could not be explained.

The diversity in solution properties that can be achieved with ionomer solutions by varying the polarity of the solvent has been observed to be general in all ionomer solutions. The influence of the solvent characteristics on the ionomer solution behavior has not received serious consideration because of the limited solubility of ionomers. This is because ionomers with low ionic content dissolve in only low-polarity solvents while those with high ionic contents are soluble in only high-polarity solvents. 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 possessing a wide range of polarities. By varying the solvent, important experimental parameters such as dielectric constant, viscosity, solvent quality, and charge density can be varied. The dielectric constant, ϵ, has a significant effect on the strength and range of electrostatic interactions (through screening length as well as counterion condensation). The purpose of this work was to study polyurethane ionomer solution structure and

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* To whom correspondence should be sent.

[†] Present address: Symyx Technologies, Inc., 3100 Central Expressway, Santa Clara, CA 95051.

[‡] Present address: Illinois Institute of Technology, Perlstein Hall, 10 West 33rd Street, Chicago, IL 60616.

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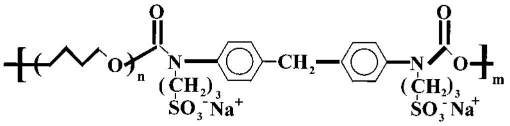

Figure 1. Structure of model polyurethane ionomer.

Table 1. Molecular Characteristics of Polymers[a]

PU sample	M_w	ion content (wt %)
PU-4500	56 500	0.0
PU4	60 000	2.0

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

dynamics in a variety of solvents with different polarities so as to get a better understanding of the interactions in solution. A part of the paper focuses on the importance of Debye (or electrostatic) screening length, κ^{-1}, the length scale for electrostatic interactions, in determining the dynamics in solutions. The results demonstrate the importance of polarity of solvent and polymer−solvent interactions in determining the solution behavior of ionomers and provide an explanation for some poorly understood experimental observations in ionomer and polyelectrolyte solution studies.

Experimental Section

Materials. The synthesis of model sulfonated polyurethane ionomers is described in detail elsewhere.[24] Poly(tetramethylene oxide) (PTMO) of molecular weight 4500 was used, and the unsulfonated polyurethane and the ionomer are designated PU-4500 and PU4, 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).[24] 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. Polymer solutions were prepared by dissolving the ionomer samples in different solvents (Aldrich, Spectrophotometric grade) under stirring for 1 day at room temperature.

Measurements. Dynamic light scattering measurements were conducted with a BI-200SM goniometer (Brookhaven) and a BI-9000AT digital correlator (Brookhaven) at a wavelength of 488 nm from a 300 mW Ar Lexel laser. Measurements were conducted at 35.0 ± 0.1 °C. The temperature of the sample was kept constant through external circulation of water around the sample holder. The channel numbers were 256, of which six data channels were used to determine the baseline. To eliminate dust effects, the data were discarded whenever the difference between measured and calculated baselines was greater than 0.1%. The scattered data from the correlator were transferred to a computer for analysis. Angular measurements were made using a goniometer in the range of scattering angles from 30° to 150°. For ionomer solutions sample times from 0.1 μs to 1 s were used. Solutions were filtered using 0.45 μm syringe filters (Gelman Sciences, Ann Arbor, MI).

Data Analysis

In a dynamic light scattering experiment, the measured intensity correlation function $G^{(2)}(\tau)$ is related to the first-order (or field) correlation function $g^{(1)}(\tau)$ by the Siegert relation

$$G^{(2)}(q,\tau) = B(1 + \beta\, |g^{(1)}(\tau)|^2) \qquad (1)$$

where B is the experimentally determined baseline ($B = G^{(2)}(\infty)$) and the parameter β, $0 < \beta < 1$, is due to experimental variables. β is used either as a parameter in the fitting procedure or in normalizing $G^{(2)}(\tau)$. The background count B (count rate at very long times) is directly measured by the correlator. The electric field correlation function $g^{(1)}(q,\tau)$ is written as

Table 2. Properties of Solvents

solvent	dielectric constant (ϵ) (25 °C)	viscosity (η) at 35 °C (cP)
toluene	2.4	0.499
1-propanol	20.1	1.514
1-methyl-2-pyrrolidinone	32	1.666
dimethylacetamide	37	0.536
dimethyl sulfoxide	47	1.771
formamide	109	
N-methylformamide	182	1.385

$$g^{(1)}(q,\tau) = \int_0^{\infty} G(\Gamma,q) \exp(-\Gamma\tau)\, \mathrm{d}\Gamma \qquad (2)$$

where the line width Γ (or decay rate or relaxation rate) is related to the particle diffusion coefficient D by $\Gamma = Dq^2$, q is the amplitude of the scattering wave vector defined as $q = 4\Pi n/\lambda \sin(\theta/2)$, and $G(\Gamma)$ is the normalized distribution function of the line widths and contains detailed information on the distribution of diffusivity, particle size, or relaxation times.[25] The inversion of the integral equation, to obtain the desired molecular information, is an ill-posed problem.[26−28] One of the most reliable analyses for the solution of this problem is the algorithm developed by Provencher.[29−32] It is based on the principle of parsimony to detect the most probable solution and also takes into account the noise in the data. The deconvolution by CONTIN yields the spectrum of decay rates (or relaxation times) for the various processes in the scattering samples as a series of amplitudes $G(\Gamma)$, along a grid of Γ values. Equation 2 is modified to plot $\Gamma G(\Gamma,q)$ vs $\log(\Gamma/q^2)$ so that the plot is in an equal area representation, and the area under each peak corresponds to the weight of the peak.[33,34]

$$g^{(1)}(q,\tau) = \int_{-\infty}^{\infty} \Gamma G(\Gamma,q) \exp(-\Gamma\tau)\, \mathrm{d} \log(\Gamma/q^2) \qquad (3)$$

The weighted average decay rate $\langle\Gamma\rangle$ is calculated as the first moment of $G(\Gamma,q)$ divided by the zeroth moment of $G(\Gamma,q)$. The average effective diffusion coefficient is defined by $\langle\Gamma\rangle/q^2 = D_{\mathrm{eff}}$ where $\langle\Gamma\rangle$ is the average value of Γ. An effective hydrodynamic radius, R_h, can be evaluated using the Stokes−Einstein relation:

$$D_{\mathrm{eff}} = kT/6\Pi\eta R_{\mathrm{h}} \qquad (4)$$

where k is the Boltzmann constant, η is the solvent viscosity, and T is the absolute temperature of the solution.

Results and Discussion

The model polyurethane ionomer PU4, synthesized from PTMO of molecular weight 4500, is soluble in solvents with a wide range of dielectric constants. Dynamic light scattering (DLS) was applied to PU4 solutions in different solvents at a concentration of 0.2 g/dL to investigate the solution structure. The solvents used and their properties are shown in Table 2.

Dynamic light scattering (DLS) was applied to the ionomer solutions to characterize the structures in the solution. A complex correlation function is obtained from solutions made from some of the solvents. Figure 2 shows a typical normalized autocorrelation functions obtained from DMAc. The autocorrelation function

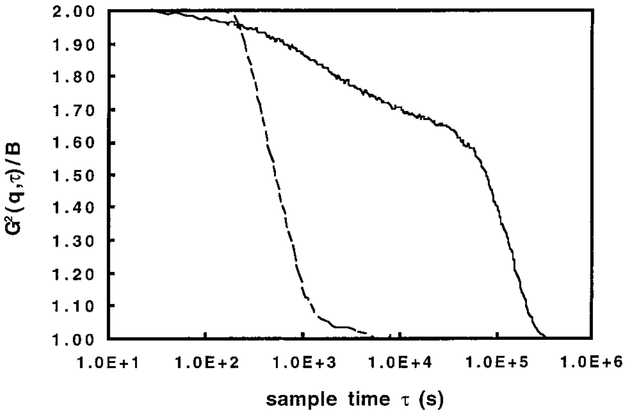

Figure 2. Decay of normalized autocorrelation function of sulfonated and unsulfonated polyurethane at a concentration of 0.2 g/dL in DMAc. *B* is the background count. The dotted line corresponds to the unsulfonated polyurethane.

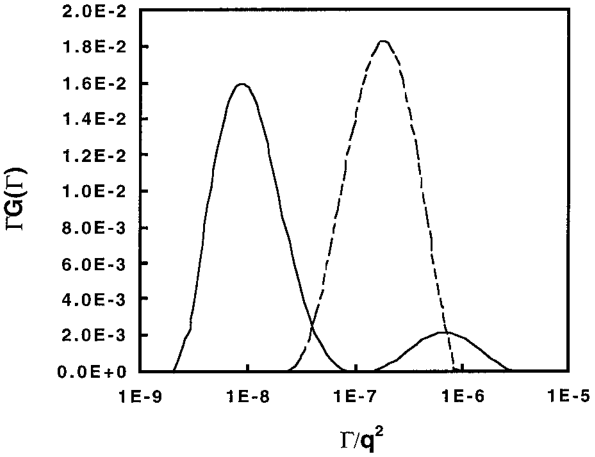

Figure 3. Spectrum of decay rate, Γ, normalized by q^2, of sulfonated and unsulfonated polyurethane at a concentration of 0.2 g/dL. The dotted line corresponds to the unsulfonated polyurethane.

corresponding to a single relaxation time is sigmoidal in shape. It can be clearly seen that there exist more than one relaxation time, and so the scattering data cannot be described by a single-exponential function. The results of data analysis by CONTIN, in terms of spectrum of decay rates (or, equivalently, relaxation time distributions), of the ionomer as well as the underivatized polyurethane are shown in Figure 3. There are two distributions of decay rates over a wide range of time scales for the ionomer solution, whereas only one distribution of decay rate is obtained for the underivatized polyurethane. There are two distributions of effective diffusion coefficients for the ionomer solution corresponding to the two relaxation modes identified.

The two modes for the ionomer differ by 2 orders of magnitude and show q^2 dependencies. A relaxation mode in which D is independent of q^2 is an indication of a translational diffusion mode. The q^2 dependence of the diffusion coefficients contains the effect of polydispersity, internal motions (chain flexibility/rotational diffusion coefficient), and electrostatic interactions, and it is very difficult to decompose it into its various components. Polydispersity causes broadening of the relaxation time distribution. At a fixed ionomer concentration (the solution structure fixed), the relative amount of fast diffusion coefficient shows a definite increase with q^2. The q^2 dependence of the diffusion coefficients is complicated, and diffusion coefficients extrapolated to zero q are used to discuss the results. The q^2 dependence of the fast mode diffusion coefficient for ionomer solutions in polar solvents arises primarily due to electrostatic interactions and is interpreted qualitatively using coupled mode theories.

PU4 solutions in toluene, 1-propanol, 1-methyl-2-pyrrolidinone, and dimethylacetamide (DMAc) have two diffusion coefficients differing by about 2 orders of magnitude. The fast diffusion coefficient is termed the fast mode, and the slow diffusion coefficient is termed the slow mode. PU4 solutions in dimethyl sulfoxide (DMSO), formamide, and *N*-methylformamide have a single diffusion coefficient.

Ionic Aggregation. In low-polarity solutions of ionomers association of ionic groups takes place due to dipole–dipole interactions. For ionomer solutions in toluene, the diffusion coefficient corresponding to the fast mode (6×10^{-7} cm²/s) is found to be slightly higher than the diffusion coefficient of the unsulfonated polymer PU-4500 (1.3×10^{-7} cm²/s). This can be attributed to a decrease in the size of single chains due to intrachain association. The slow mode corresponds to the diffusion of the aggregated ionomer chains in solution. These results are in agreement with the vast literature on aggregation behavior of ionomers in nonpolar solvents.[5,8–16,35–37] The aggregate size can be calculated from the slow mode diffusion coefficient (5×10^{-8} cm²/s) using the Stokes–Einstein equation, and a hydrodynamic radius of 90 nm is obtained. The solutions that were originally filtered with 1 μm filters were further filtered with 0.2 μm filters. The slow mode diffusion coefficient increased to 6.4×10^{-8} cm²/s (corresponding to a hydrodynamic radius of about 70 nm), and the amplitude of the slow mode decreased. The fast mode diffusion coefficient was unaffected. This implies that larger ionic aggregates were lost upon filtration of solutions with small filters, resulting in a decrease of the average aggregate size. A corresponding decrease in the intensity of the scattered light was also observed. Cursory investigation showed that the new diffusion coefficients do not correspond to a decreased ionomer concentration resulting from the loss of polymer during filtration. These results show that (1) the aggregates are physically cross-linked, which is what is expected, and (2) the solution structures may not be at equilibrium, i.e., the aggregates are not formed in the solution through the association (aggregation) of individual ionomer chains; instead, they are insoluble fragments remaining from a partial dissolution process. Further discussion of this observation is made in another publication.[38] Similar behavior was seen in tetrahydrofuran (THF), another low-polarity solvent (dielectric constant, $\epsilon = 8$).

Electrostatic Interactions. Solutions in polar solvents had low scattering, and very long measurement times (up to 5 h) were found to be necessary to obtain both the full amplitude $1 + \beta^2$ of the intensity–intensity correlation function and a good asymptotic value at large times (typically 1 ± 0.001). Dynamic light scattering of the model polyurethane ionomers in polar solvents yields two relaxation times. Both relaxations originate from diffusive processes.[39] The fast mode arises due to polyion–counterion coupling and the slow mode due to the presence of loose aggregates.[24] The loose aggregates consist of polyions and counterions loosely held together due to electrostatic interactions. The interpretation of the two modes is dealt with extensively in two other papers.[24,40]

The slow mode diffusion coefficient has not been well understood, and its interpretation has been controversial. Studying the effect of solvent polarity on the two modes can be expected to provide an insight into their origin. The polar solvents studied are 1-propanol, 1-methyl-2-pyrrolidinone, and dimethylacetamide (DMAc). The polar solutions exhibit two diffusive modes. The two modes differ by 2 orders of magnitude with the fast mode ($\sim 10^{-6}$ cm^2/s) showing a small negative q^2 dependence and the slow mode ($\sim 10^{-8}$ cm^2/s) showing a small positive q^2 dependence. The negative slope of the fast mode and the positive slope of the slow mode were also reported for salt-free polyelectrolyte solutions.[41,42]

The fast mode can be explained in terms of polyion–counterion coupling using coupled mode theories.[43] Briefly, since the polyelectrolyte solution contains both polyions and counterions (since counterions dissociate from the charged polymer in a polar solvent), the fast moving counterions coupled to the polyions by Coulombic interactions make the polyions move faster, leading to larger polyion diffusion coefficients. Under salt-free conditions the diffusion coefficient can be shown to approach that of the small ions.[44]

Coupled diffusion, multicomponent theories explicitly consider the dynamics of polyions, gegenions, and co-ions and provide a detailed understanding of dynamic coupling phenomena. The theoretical formulation of the multicomponent, coupled diffusion problem is quite complex, and the mathematical treatment requires gross simplification. Current calculations treat all components as point particles exhibiting different mobilities and charges which obviously represent a rather poor approximation for the polyion structure. Since it is a mean-field theory (a mean force field is assumed around each particle instead of considering local force field fluctuations), the multicomponent approach is expected to yield meaningful results in the low q limit, i.e., on large length scales, where local fluctuations are averaged to a mean value. Despite serious approximations and restrictions, multicomponent theories describe essential features of polyelectrolyte dynamics, such as coupled diffusion, plasmon modes, and Nernst–Hartley diffusion.[39] The important result is that the effective diffusion coefficient of polyelectrolytes is enhanced by the forces exerted by the ionic atmosphere. This is because in addition to the concentration gradient as given by Fick's diffusion law, the local electric field due to the neighboring ions also contributes to the particle flux of ions. It is found that the fluctuations of ions become coupled if $\kappa^2 V^{2/3} \gg 1$, where V is the experimentally probed volume and κ is the Debye screening length. In scattering experiments fluctuations are probed in a volume $V = q^{-3}$, so that coupling takes place when $\kappa^2/q^2 \gg 1$. One can define $\lambda = \kappa^2/q^2$. For $\lambda \ll 1$ (weak coupling), the apparent diffusion coefficient is identical to the diffusion coefficient of the polyions. In the intermediate coupling regime, the diffusion coefficient is an increasing function of κ_p; i.e., it increases with increasing polyion concentration. The origin for the enhanced mobility of the polyions is the coupling to the motion of the small counterions as a consequence of local electroneutrality.

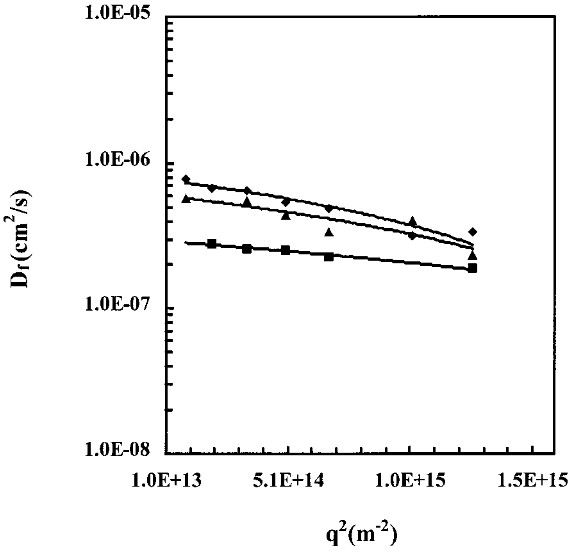

Figure 4. Average effective diffusion coefficients corresponding to the fast mode (in cm^2/s) vs q^2 for PU4 at a concentration of 0.2 g/dL in different polar solvents: propanol (■), 1-methyl-2-pyrrolidinone (▲), and dimethylacetamide (◆).

Table 3. Diffusion Coefficients (Extrapolated to Zero Angle) for PU4 at 0.2 g/dL in Different Polar Solvents[a]

solvent	dielectric constant	D_f (cm^2/s)	D_{un} (cm^2/s)	PE
1-propanol	20	3×10^{-7}	1.8×10^{-7}	1.67
1-methyl-2-pyrrolidinone	32	6×10^{-7}	2.3×10^{-7}	2.61
N,*N'*-dimethylacetamide	37	8×10^{-7}	2×10^{-7}	4.0

[a] D_f is the fast mode diffusion coefficient, D_{un} is the diffusion coefficient of the unsulfonated polymer, and PE is the polyelectrolyte effect (a ratio of D_f to D_{un}).

The fast mode diffusion coefficient D_f shows a negative q^2 dependency as shown in Figure 4. This can be interpreted in terms of the range of electrostatic interactions using coupled mode theories. As explained above, coupling of fluctuations of ions occurs when $\kappa^2/q^2 \gg 1$. For strong coupling, $q^{-1} \gg \kappa^{-1}$. Thus, maximum coupling is measured at low angles. With an increase in angle, q increases resulting in a decrease in coupling. The decrease in coupling leads to a decrease in the diffusion coefficient D_f. Thus, D_f has a negative q^2 dependency. It is important that a distinction be made between the magnitude of the fast mode diffusion coefficient and its amplitude with respect to the slow mode. The amplitude of fast mode increases with increase in angle. This is easily understood as due to the size of structures giving rise to the fast mode being much smaller than those giving rise to the slow mode.

Diffusion coefficients extrapolated to zero angle, corresponding to the fast mode in different polarity solvents, are shown in Table 3. The fast mode diffusion coefficient can be seen to increase with the polarity of the solvent showing that the diffusion coefficient of single polyions is enhanced by electrostatic interactions. Since as the solvent changes specific solvent properties like viscosity change, it is best to compare the fast mode diffusion coefficient with the diffusion coefficient of the un-ionized polymer. Hence, a parameter PE (for polyelectrolyte effect) can be defined as the ratio of the fast mode diffusion coefficient (D_f) to that of the diffusion coefficient of the un-ionized polymer (D_{un}) to examine the effect of solvent polarity. PE is a measure of the increase in D_f due to ionic interactions. From Table 3 it can be seen that PE increases with polarity of the solvent showing that the diffusion coefficient of single polyions is enhanced by electrostatic interactions, and

Table 4. Hydrodynamic Radii Corresponding to the Slow Mode for PU4 at 0.2 g/dL in Different Polar Solvents

solvent	dielectric constant	R_h (nm)
1-propanol	20	75
1-methyl-2-pyrrolidinone	32	50
N,*N*′-dimethylacetamide	37	100

Table 5. Diffusion Coefficients (Extrapolated to Zero Angle) for PU4 at 0.2 g/dL in Different High-Polarity Solvents

solvent	dielectric constant	D (cm^2/s)	R_h (nm)
dimethyl sulfoxide	47	4.04×10^{-8}	32
formamide	109	1.99×10^{-8}	
N-methylformamide	182	4.75×10^{-8}	35

ionomer solution behavior is influenced by a change in the dielectric constant of the solvent.

Polyelectrolyte behavior increases with increase in dielectric constant, ϵ. This is because of increase in interparticle coupling as a result of increase in κ^{-1}. Thus, D_f increases with increase in ϵ. This is in agreement with the viscosity measurements which show an increase in polyelectrolyte behavior, a measure of intermolecular coupling, with increase in dielectric constant.

The change in the loose aggregate as a function of solvent polarity can be monitored in terms of hydrodynamic radius. The hydrodynamic radii calculated from the slow mode diffusion coefficients are shown in Table 4. The size of the loose aggregate first decreases and then increases with dielectric constant. The results can be understood in terms of the interaction of the solvent with the ionomer backbone. 1-Methyl-2-pyrrolidinone is a poor solvent for the ionomer backbone, and hence the aggregate is smaller. Considering propanol and DMAc, both of which are good solvents for the backbone, it can be seen that the loose aggregate size increases with dielectric constant. Thus, the size corresponding to the slow mode responds to the solvent–backbone interactions and provides evidence for the presence of loose aggregates in polar solutions of ionomers.

The results present evidence of two species in solution: single polyions as well as loose aggregates, which are polyions held together due to electrostatic interactions. Ionomer solution dynamics is found to be influenced by solvent dielectric constant.

Hydrophobic Aggregation. There exists a single diffusion coefficient for PU4 solutions in the highly polar solvents dimethyl sulfoxide (DMSO), formamide (FMD), and *N*-methylformamide (NMF) (see Table 5). These solvents are polar, and consistent with ionomer solution behavior discussed previously, two modes of diffusion are expected. As was shown earlier in this paper, the polyelectrolyte effect, PE, increases with increase in dielectric constant of the solvent due to an increase in Debye screening length, which is a measure of range of electrostatic interactions in solution. Since only the slow diffusion mode is observed, the results in Table 5 do not indicate polyelectrolyte behavior. This seems to indicate that the polyelectrolyte behavior (presence of two diffusive modes in dynamic light scattering measurements) disappears beyond a certain value as the solvent dielectric constant is increased.

An interesting thing to note about these solutions is the unusually high scattering observed, much higher than the weak scattering that is obtained from solutions made with DMAc and other polar solvents. This indicates either the formation of micelles or high ordering in solution since the necessary condition for scattering is a difference in index of refraction. The difference in scattering is not due to difference in the refractive indices of the solvents.

The solution structure of PU4 in NMF has been investigated in detail.[45] Counterions always dissociate from the polymer chain in polar solutions of ionomers. In general, in high-polarity solvents, incompatibility between the solvent and the nonpolar backbone can be expected. It turns out that the polyurethane ionomer backbone is not soluble in these solvents. Thus, hydrophobic aggregation can be used to explain the experimental data obtained from very high-polarity solvents, DMSO, FMD, and NMF. The diffusion coefficient can be identified as that corresponding to hydrophobic aggregates of ionomer chains with a polymer core and an outer ionic shell.

As temperature is increased, the polymer chains inside the aggregate as well as the ionic groups on the surface can rearrange so as to have the maximum number of ionic groups on the surface leading to decrease in the size of the aggregate. Dynamic light scattering of PU4 solutions in NMF at 35, 45, and 55 °C yielded the same size aggregates, indicating that the size is determined by the number of ionic groups that could occupy the surface. The effect of added salt was also examined and was found to not influence the aggregate size.

In a recent study a 5-fold change in dielectric constant of the solvent was found not to affect the dynamics of polyelectrolyte solutions.[22] The results here show that solvent dielectric constant does affect the interactions in solutions of ionic polymers in polar solvents, even though the polymer–solvent interactions do not change drastically. 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 whereas 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.

$$l_B = \frac{e^2}{4\pi\epsilon\epsilon_0 k_B T} \tag{5}$$

As the solvent polarity is changed from polar to nonpolar, there is a critical dielectric constant beyond which counterion condensation takes place. Counterion condensation almost always takes place in polyelectrolyte solutions because of their high charge density. In the case of ionomer solutions, counterions are completely dissociated in all high-polarity solvents. The counterion condensation regime can be introduced by either decreasing the solvent dielectric constant or increasing the ionic content of the ionomer. The Debye screening length in the absence of salt arises due to counterions and is given by

$$\kappa^{-1} = \left(\frac{\epsilon\epsilon_0 k_B T}{e^2 N_A c_c}\right)^{1/2} \tag{6}$$

In the counterion condensation regime, the concentration of free counterions, c_c, is proportional to the dielectric constant of the solvent, ϵ, and so the Debye screening length does not change. In this regime the electrostatic interactions remain constant. For every ionic polymer, there exists a critical solvent dielectric constant corresponding to counterion condensation. The diffusion coefficient can be expected to remain constant below this critical ϵ and should increase with ϵ above this value. So the effect of dielectric constant of the solvent on the dynamics of ionic polymer solutions in polar solvents can best be studied using ionomers that have a small number of ionic groups.

Typically very high-polarity solvents are poor solvents for the low-polarity ionomer backbone because of incompatibility due to the polarity difference. The disappearance of polyelectrolyte behavior in high-polarity solvents[23] can be understood in terms of a change in solvent quality which causes a change in solution structure and consequently the dominant interactions in solution. Ionomer solution behavior is thus found to be determined not only by solvent polarity but also by the solvent quality with respect to the backbone (polymer−solvent interactions).

High-polarity solvents can be good solvents even for ionomers with low-polarity backbones if the ionic content is sufficiently high. In another study[40] it was shown that as the ionic content of the ionomer is increased, the second virial coefficient changes from negative in NMF solutions of PU4 to positive in NMF solutions of a polymer similar to PU4 but containing a higher ionic content. This indicated that NMF changed from a poor solvent to a good solvent as the ionic content of the polymer increased.

Conclusions

The polyurethane ionomer studied has regularly spaced ionic groups which allow a direct correlation of observed properties and solution structure. This model system allows study of the effect of ionic interactions on the properties of polymers. We have identified three different regimes in the solution structure of polyurethane ionomers depending on the polarity of the solvent and polymer−solvent interactions. Low-polarity solutions are found to contain single chains or small aggregates formed due to intrachain association and large aggregates made of chains physically cross-linked due to ionic association. In polar solvents that are good solvents for the ionomer backbone single polyions and loose aggregates are present. Hydrophobic aggregates are present in very high-polarity solvents which are usually poor solvents for the ionomer backbone. The results also provide evidence for the presence of loose aggregates in polar solvents that are good solvents for the ionomer backbone through the influence of backbone−solvent interactions on the sizes corresponding to the slow diffusion coefficient. For the model polyurethane ionomer PU4 studied here, a structural inversion is found to take place as solvent polarity changes—the solution structure changes from association of ionic groups to loose aggregates to hydrophobic association.

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