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Structural Studies of Polyurethane Ionomer Solutions. 1. Dynamic Light Scattering

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ABSTRACT: Viscometry and dynamic light scattering experiments have been used to characterize model polyurethane ionomers in dimethylacetamide (DMAc). The structures in solution are studied as a function of concentration and ionic content. These ionomers have regularly spaced ionic groups and form good model systems to study the effect of ionic interactions on the properties of polymers. These ionomers in DMAc are found to exhibit characteristic behavior of salt-free polyelectrolyte solutions. Viscometric measurements show an upturn in reduced viscosity at very low concentrations. Analysis of dynamic light scattering data by CONTIN indicates the existence of two diffusive modes, a fast mode and a slow mode, differing by 2 orders of magnitude. The diffusion coefficient of the fast mode increases slightly with concentration, whereas the diffusion coefficient corresponding to the slow mode is independent of concentration within the concentration range studied. The rate of increase of the diffusion coefficient of the fast mode with concentration increases with increasing ionic content. The fast mode arises from intermolecular electrostatic interactions while the slow mode is due to motions associated with the formation of domains of associated polymer chains. Both modes do not show any time dependence, suggesting that the solution structures are at equilibrium. The slow mode persists even after filtration through filters with pore sizes that are small compared to the size of domains and therefore the formation of domains is due to reversible interactions in solution. These results indicate that free polyions and associated species coexist in dilute solutions of polyurethane ionomers in polar solvents.

Introduction

Ionomers contain a small number of ionic groups, up to 15 mol %, attached to nonionic backbone chains. The presence of the ionic groups results in improved properties in all physical states of the material. It is generally accepted that the improvement in material properties originates from the aggregation of ions. Though extensive studies have been performed in the bulk, solution properties of ionomers have only recently been investigated.[1,2] Solution studies allow a more thorough understanding of how ionic groups associate and thereby affect the morphology and properties of ionomers.

It has been well established that ionomer solutions show two types of behavior depending on the polarity of the solvents used,[3] 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. 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. The association of ionomer molecules in nonpolar solvents results from strong dipole−dipole interactions among the ionic groups.

In highly polar solvents, ionomers behave identically to aqueous polyelectrolyte solutions[3−6] and exhibit a dramatic increase in reduced viscosity with decreasing polymer concentration. This effect depends strongly on the ionic content and is enhanced with increasing ionic content.[7] This is quite surprising considering the large difference in ionic content that exists between an ionomer and a polyelectrolyte. While ionomers contain relatively low ionic content, polyelectrolytes contain very high ionic content, usually one ionic group per repeat unit. The identification of polyelectrolyte behavior in high-polarity ionomer solutions has also been supported by static and dynamic light scattering[5,6,8,9] and small-angle neutron scattering (SANS) experiments[10,11] 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.[12] Although the polyelectrolyte behavior of salt-free aqueous polyelectrolyte solutions has been extensively studied, its nature is not clear yet. In the classical explanation based on counterion condensation and chain expansion, the polar solvent solvates the ionic pairs due to the high local charge density. In the dilute limit, where single chains exist in solution, the repulsion of the like charges on the same chain leads to chain extension and therefore an increase in reduced viscosity. However, the results from viscosity, light scattering, small-angle X-ray scattering, and neutron scattering suggest some ordered distribution in these solutions even at low concentrations.[13−15] Several models have been proposed to explain the formation and structure of ordered clusters; however, the molecular structure and thermodynamic driving force of such ordered structures is not yet understood. Polyelectrolyte behavior also occurs for polymer latex particles that have a fixed size[16] and for monochelic ionomers that have only one charged group at the end of the chain.[17] In both cases, the explanation of the polyelectrolyte effect due to changes in coil conformation through intramolecular repulsion is impossible, and it has been argued that this behavior could be attributed to intermolecular electrostatic interactions that could lead to an ordered arrangement of the latex particles or polymer chains in solution.[18] Recently, it has been verified that electrostatic interactions, as opposed to phase separation arising out of the hydrophobic backbone, are solely responsible for the appearance of two modes of diffusion in polyelectrolyte solutions, and it was also

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found that a fivefold change in dielectric constant did not affect the electrostatic interactions.[19]

Hara recently reviewed the behavior of polyelectrolytes and ionomers in nonaqueous solution and demonstrated that ionomers offer good model systems to investigate the characteristic behavior of salt-free polyelectrolyte solutions.[20] Ionomer chains with smaller number of charges compared with polyelectrolytes have stronger scattering power because of less destructive interference. Problems associated with aqueous solutions, such as autodissociation of the solvent, can be avoided by using an aprotic solvent. Also, ionomers can have backbone chains compatible with the polar solvent, so no gelation or phase separation occurs as for weakly charged polyelectrolytes in water.

Solution studies of ionomers have focused on telechelic and random copolymer ionomers. Telechelic ionomers have ionic groups only at the chain ends while random copolymer ionomers have ionic groups randomly distributed along backbone chains. Telechelic ionomers have a drawback in that they are typically of low molecular weight, which is necessary for achieving a sufficiently high ionic content. Random copolymer ionomers lack well-defined architecture that can lead to a direct correlation between the observed properties and solution structure. Some basic parameters like the contour length between ionic groups and the number of ionic groups per polymer chain are not well defined. Model polyurethane ionomers form a simple model system with regularly spaced ionic groups and allow a direct correlation of ionomer structure and properties.

Polyurethane (PU) ionomers contain alternate ionic hard segments and nonionic soft segments. The model polyurethane ionomers are synthesized as a 1:1 copolymer of a diisocyanate and a macroglycol without a chain extender. The ionic groups in these ionomers are bonded solely to the urethane nitrogen, resulting in regular positioning of the ionic groups. These systems make an excellent model for studying ionomer morphology because they allow control of (1) the separation distance between the ionic groups by varying the polyol molecular weight and (2) the compatibility of the ionic groups with the polymer chain by varying the polyol type. Advantages of these systems are the regular and well-known distribution of the ionic groups along the polymeric backbone and the overall molecular weights larger than 50 000 that can be synthesized.

Aqueous solutions of polyurethane ionomers are of particular importance. Polyurethane ionomers have been utilized in applications that require water dispersions since the ionic groups act as internal emulsifiers, which yields better dispersion stability and finer particle size.[21−24] The polyol hydrophilicity also has a strong effect on the blood contacting response of the water-soluble sulfonated polyurethanes that show antithrombogenic effects.[25−28] Viscometric experiments on polyurethane ionomer solutions have focused on the study of the changes of the behavior of solutions in organic solvents, such as acetone, upon addition of water. When water is added in solutions of these ionomers in acetone, a phase inversion can occur[21,29−33] that depends on the relative amount of the two solvents. Viscosity and conductometric studies have been performed to study this phase inversion;[21,29−31,34] however, the details of this process are still unknown.

Though the structure−property relationship of model polyurethane ionomers has been very well characterized in the bulk,[35−38] ionomer solution characterization has not been very extensive. The strong effect of solvent type on the structure and morphology of these ionomers is illustrated when they are cast using different solvents, which results in a dramatic change in both thermal and mechanical properties.[29,36,39] Therefore, characterization of the chain conformation and dimensions of these ionomers in solution will lead to a better understanding of the behavior in not only the solution state but the solid state as well.

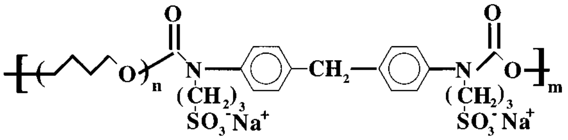

Figure 1. Structure of model polyurethane ionomer.

Previous work on polyurethane ionomer solution properties was mainly in terms of viscometric measurements. The aim of the present study is to study the structures in solution as a function of concentration and ionic content so as to get a better understanding of ionic interactions in solution. This study is focused on the characterization of the polyurethane ionomer solutions by viscometry and dynamic light scattering (DLS) and the influence of ionic content on structures in solution. DLS studies were done over a broad range of delay times and identify two relaxation modes confirming the polyelectrolyte behavior demonstrated by viscometric measurements.

Experimental Section

Materials. The polyurethanes were synthesized in a solution-phase two-step condensation polymerization, according to the method of Hwang et al.[40] Oligomers of poly(tetramethylene oxide) (PTMO) in *N*,*N*-dimethylacetamide (DMAc) were reacted with methylenebis(phenyl isocyanate) (MDI). These materials were then derivatized by a bimolecular nucleophilic displacement of the urethane nitrogen using sodium hydride, followed by a ring-opening reaction with 1,3-propanesultone. The polyurethanes were derivatized by replacement of 100 mol % of urethane hydrogens with propyl sulfonate groups. The polymers were extracted in toluene for 48 h in a Soxhlet extractor to remove low molecular weight material. Elemental analysis was performed by Galbraith Laboratories (Knoxville, TN), and the results were consistent with stoichiometric calculations.

Infrared (IR) spectroscopy was used to confirm that almost all the urethane nitrogens were sulfonated. The spacing between ionic groups was varied by varying the molecular weight of PTMO. The structure is shown in Figure 1. Sodium (Na) was used as the counterion since it strongly interacts with the sulfonate group, which results in strong interactions in solution. Two different samples were synthesized from PTMO of molecular weight 1000 and 4500, respectively. The underivatized samples are designated PU-1000 and PU-4500 to indicate the molecular weight of the PTMO used in the synthesis. The corresponding sulfonated samples are designated PU1 and PU4, respectively.

Polymer solutions were prepared by dissolving the ionomer samples in DMAc (Aldrich: spectrophotometric grade) under stirring for 1 day at room temperature. Ionomer samples dissolved easily. Karl Fischer titration was performed after the experiment to check the water content in the polymer solutions. In all cases, water content was found to be less than 0.15%.

Measurements. Size exclusion chromatography (SEC) was performed with a Beckman liquid chromatography unit with DMAc containing 2.0 g/L $LiNO_3$ as the eluent at a flow rate of 0.5 mL/min at 30 °C. Standard polystyrenes were used for calibration.

The 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 polymers were dissolved in DMAc, and measurements were done at concentrations ranging from 0.01 to 3.0 g/dL. The temperature was maintained at 35 ± 0.1 °C in the thermostat bath. Samples were stirred and thermally equilibrated for at least 30 min between dilutions. 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.

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 ± 0.1 °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 6 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 microcomputer for analysis. The scattering intensity is increased by either increasing the laser power or the aperture size (scattering volume). 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.

Theory

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

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

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

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

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.[41] The inversion of the integral equation, to obtain the desired molecular information, is an ill-posed problem. One of the most reliable analyses for the solution of this problem is the algorithm developed by Provencher.[42−45] 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.

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

Data analysis with CONTIN provides information on the moments of the relaxation time distribution from which the z-average diffusion coefficient may be evaluated. The mutual diffusion coefficient for nonaggregating polymers (systems with weak interactions) is given by the generalized Stokes−Einstein equation as

$$D = \frac{M(1 - vc)}{N_A f(c)}\left(\frac{\partial \Pi}{\partial c}\right) \tag{4}$$

where M is the molecular weight, v is the partial specific volume, $f(c)$ is the frictional coefficient, c is the concentration of the polymer, $\partial\Pi/\partial c$ is the inverse osmotic compressibility, and N_A is Avogadro's number. For strongly interacting systems, by using the Zernicke−Prins equation for light scattering analysis with the Born−Green approximation it can be shown[46] that

$$\frac{Kc}{R_0} \propto \left(1 + \frac{N}{V} m_0\right) \tag{5}$$

where Kc/R_0 is the reduced scattered intensity at zero angle, N/V is the number of particles per unit volume, and m_0 is the intermolecular excluded volume. From fluctuation theory it is shown[47] that

$$\frac{Kc}{R_0} \propto \left(\frac{1}{RT}\frac{\partial \Pi}{\partial c}\right) \tag{6}$$

The reduced scattered intensity at zero angle Kc/R_0 is a function of concentration and is a measure of intermolecular excluded volume as well as inverse osmotic compressibility. For strongly interacting systems, the inverse osmotic compressibility term in eq 4 dominates[48] and

$$D \propto \left(\frac{\partial \Pi}{\partial c}\right) \tag{7}$$

From the above three equations,

$$D \propto \frac{\partial \Pi}{\partial c} \propto \left(1 + \frac{N}{V} m_0\right) \tag{8}$$

Also, we have inverse osmotic compressibility

$$\frac{\partial \Pi}{\partial c} = \frac{RT}{M}(1 + 2A_2 c + ...) \tag{9}$$

where A_2 is the second virial coefficient.

An effective hydrodynamic radius, R_h, can be evaluated using the Stokes−Einstein relation:

$$D_{\mathrm{eff}} = kT/6\pi\eta(1/R_h) \tag{10}$$

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

Results

Gel Permeation Chromatography. The polymers have been characterized by gel permeation chromatography (GPC). The GPC results based on polystyrene standards are shown in Table 1. Note that GPC was done using the polymer samples before they were

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] Weight-average molecular weight.

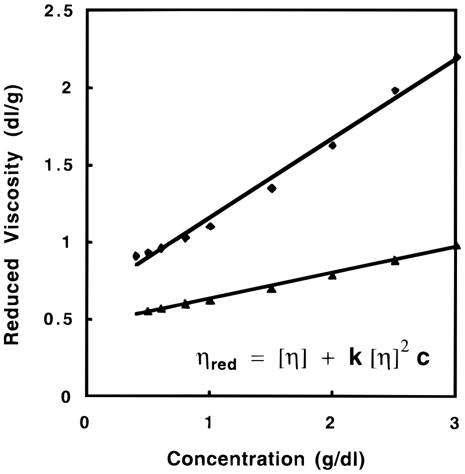

Figure 2. Viscometric measurements for unsulfonated polyurethanes: (◆) PU-1000; (▲) PU-4500.

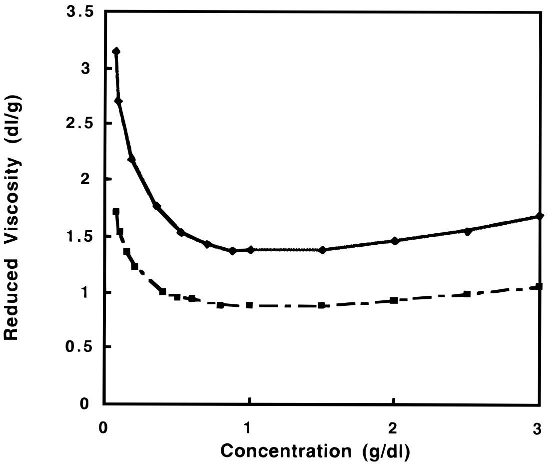

Figure 3. Viscometric measurements for sulfonated polyurethanes: (◆) PU1; (■) PU4.

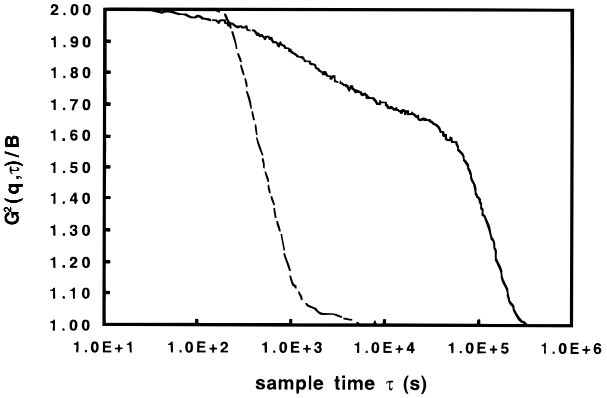

Figure 4. Decay of normalized autocorrelation functions of PU-1000 and PU1 at a concentration of 0.1 g/dL, at an angle of 60°. *B* is the background count. The dashed line corresponds to PU-1000.

sulfonated and the molecular weights were corrected for sulfonation later. This is because GPC of ionic polymers results in anomalously high molecular weights because of interactions between ions and polymer, or solvent, or column material.[49,50] The samples may also form aggregates which clog the column. It was determined previously that the sulfonation step did not alter much the molecular weight distribution of the polyurethanes.[28] The polydispersity was found to be 2.2.

Viscometry. The results of viscometric measurements are presented in the form of reduced viscosity vs concentration diagrams. Figure 2 contains the data obtained for the unsulfonated samples. For a neutral polymer, the reduced viscosity increases linearly with polymer concentration as suggested by the Huggins equation

$$\eta_{red} = [\eta] + k'[\eta]^2 c \tag{11}$$

where $[\eta]$ is the intrinsic viscosity and k' is the Huggins constant. The data fit the Huggins equation very well. As expected, the results scale with molecular weight; the higher molecular weight PU-1000 has higher values of reduced viscosity at any concentration. The reduced viscosity—concentration curves for different ionic contents are shown in Figure 3. An upturn in reduced viscosity is seen at low concentrations. This is in agreement with the results obtained by many investigators for different kinds of polyurethane ionomers in polar solvents.[32,51]

Dynamic Light Scattering. Dynamic light scattering (DLS) was applied to the ionomer solutions to characterize the structures in the solution. Figure 4 shows normalized autocorrelation functions for PU-1000 and PU1 at 0.1 g/dL and at an angle of 60° in DMAc. The autocorrelation function 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 analysis of the experimental data from DLS experiments is, in general, a mathematically ill-posed problem.[52−54] So, the data analysis was carried out using CONTIN, a robust algorithm developed by Provencher. CONTIN provides an evaluation of all the moments of the particle size distribution as well as the detection of all characteristic modes of diffusion that are expected to be imposed due to the ionic interactions. The results of data analysis by CONTIN, in terms of the spectrum of decay rates (or equivalently, relaxation time distributions), of the ionomer as well as the underivatized polyurethanes are shown in Figure 5. The decay rate distributions are shown as plots of $\Gamma G(\Gamma)$ rather than $G(\Gamma)$, as this representation allows for an equal-area representation of all possible modes of diffusion in the logarithmic time scale, and therefore the significance of each mode can be better visualized.[55] In this study, CONTIN was applied by setting IQUAD = 1, in which case the results obtained by CONTIN are in terms directly of $\Gamma G(\Gamma)$ which are equivalent to $\tau w(\tau)$. It has been shown that such a solution scheme is more precise than first solving for $G(\Gamma)$ and then multiplying by Γ.[56] Figure 5 shows two distributions of decay rates over a wide range of time scales for the ionomer solution, whereas only one distribution of decay rates is obtained for the underivatized polyurethanes. This demonstrates characteristic polyelectrolyte behavior since polyelectrolytes in aqueous solutions show two separate decay modes. These results are also in agreement with those obtained for sulfonated polystyrene ionomers.[57]

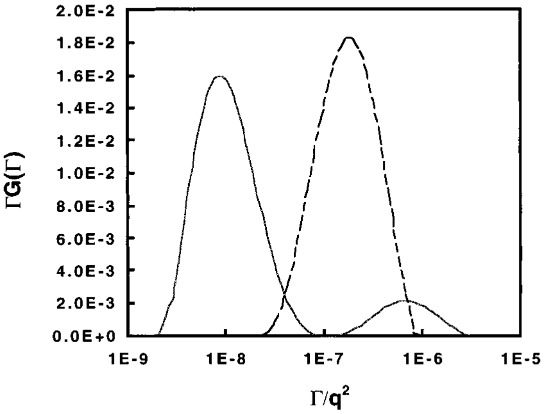

Figure 5. Spectrum of decay rate, Γ, normalized by q^2, of PU-1000 and PU1. The dashed line corresponds to PU-1000.

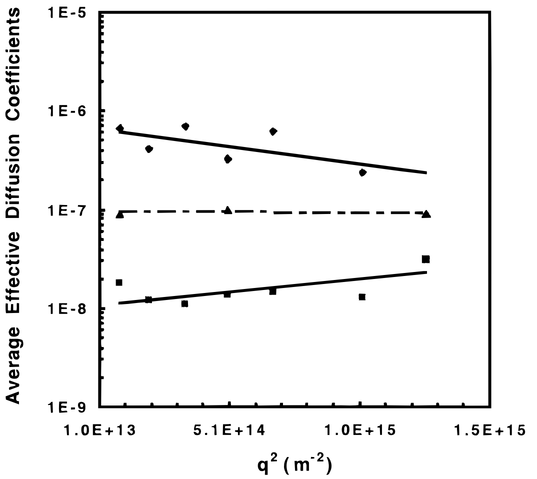

Figure 6. Average effective diffusion coefficients (in cm^2/s) vs q^2 for PU1 at a concentration of 0.1 g/dL: (◆) fast diffusion mode; (■) slow diffusion mode; (▲) diffusion data for the unsulfonated precursor polymer PU-1000.

Data analysis with CONTIN provides information on the moments of the relaxation time distribution from which the z-average diffusion coefficient may be evaluated. The diffusion coefficient is defined in the limit of small scattering vector q as $D_z = \lim_{q \to 0} \Gamma/q^2$. If only translational motion is present, the relaxation time decreases with scattering angle and the diffusion coefficient D is independent of q, or similarly Γ varies as q^2. In addition, D varies linearly with concentration in the dilute solution regime, and therefore the diffusion coefficient is defined as that at the limit of zero concentration. In the analysis that follows in this paper, the data are presented in terms of an effective diffusion coefficient, $D_{\mathrm{eff}}(q,c) = \Gamma(q,c)/q^2$, which is a function of both scattering angle and concentration. There are two distributions of effective diffusion coefficients corresponding to the two relaxation modes identified. 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. Figure 6 shows the average effective diffusion coefficients corresponding to the two modes of PU1 and the single mode of unsulfonated polyurethane PU-1000 as a function of q^2. A straight line is drawn through the diffusion coefficients corresponding to each mode by the method of least squares. 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.[58,59] A relaxation mode in which D is independent of q is an indication of a translational diffusion mode. The q^2 dependence of the diffusion coefficients, which contains the effect of polydispersity, internal motions (chain flexibility/rotational diffusion coefficient), and electrostatic interactions, will not be analyzed because it is very difficult to decompose it into its various components. Polydispersity causes broadening of the relaxation time distribution.

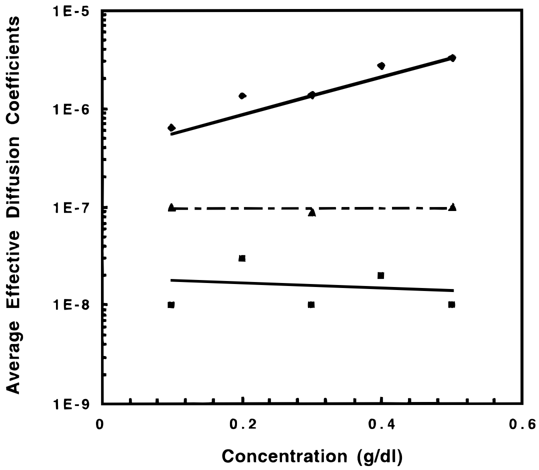

Figure 7. Average effective diffusion coefficients (in cm^2/s) vs concentration for PU1: (◆) fast diffusion mode; (■) slow diffusion mode; (▲) diffusion data for the unsulfonated precursor polymer PU-1000.

The hydrodynamic radius, R_{h} is influenced by both geometric dimensions and hydrodynamic interactions. Dynamic light scattering of unsulfonated polyurethanes gave hydrodynamic radius values of 10.5 nm for PU-4500 and 13 nm for PU-1000, independent of measurement angle and concentration. The hydrodynamic radius calculations based on viscometric measurements and the relation $R_{\mathrm{h}} = (3/4\pi N_{\mathrm{A}})^{1/3}([\eta]M)^{1/3}$ yielded sizes of 10.2 nm for PU-4500 and 11.4 nm for PU-1000. The agreement between the values obtained from the different measurement techniques is reasonable.

The effect of concentration on the effective diffusion coefficients that are evaluated from the two relaxation modes observed in the ionomer solutions of PU1 and from the single relaxation mode observed in solutions of PU-1000 is shown in Figure 7. The concentration dependence can be analyzed at each q. The effective diffusion coefficients extrapolated to zero q, to eliminate effects associated with the q^2 dependence, are plotted against concentration. From the figure we can see that the fast mode increases slightly with concentration. In polyelectrolyte solutions, a significant increase in the fast mode with polymer concentration was reported.[58,59] The slow mode is seen to remain constant within statistical error and so is independent of concentration. The slow mode was found to have a significant concentration dependence in salt-free polyelectrolyte solutions. No correlation is found between the relative amounts of fast and slow modes and concentration.

The studies have been repeated for PU4, which has a lower ionic content than PU1, and the results are shown in Figure 8. The results were very similar except the increase in the fast mode with concentration is not as high as in PU1, suggesting that the fast mode is due

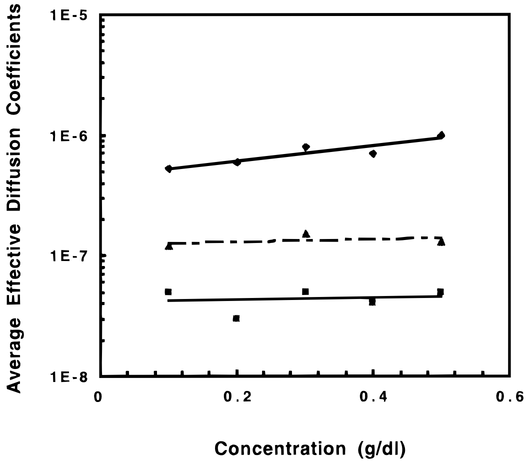

Figure 8. Average effective diffusion coefficients (in cm^2/s) vs concentration for PU4: (◆) fast diffusion mode; (■) slow diffusion mode; (▲) diffusion data for the unsulfonated precursor polymer PU-4500.

to electrostatic interactions. The slope decreases with a decrease in ionic content, and since concentration effects can be expected to be similar in both ionomers, the slope seems to be a measure of electrostatic interactions.

The structures in solution have been examined for time dependence. Although the mechanism for time dependence is not known, DLS experiments for some systems have shown that the larger aggregates dissociate into smaller entities as time proceeds until equilibrium is achieved. For some polyelectrolyte solutions, the contribution of the slow diffusive mode was found to decrease with time and even to disappear altogether on a very long time scale (up to several months).[60] If the time dependence is confirmed, the slow mode can be attributed to the translation of large clusters in the solution which disaggregate with time, indicating that salt-free polyelectrolyte solutions only slowly tend to equilibrium. No time dependence has been found for the systems studied here. The samples gave identical results after 4 months.

To examine the nature of the structures giving rise to the slow mode, the ionomer solutions were filtered with 1.0, 0.45, and 0.2 μm pore size filters. The size of the domains giving rise to the slow mode was calculated from the Stokes–Einstein relation (eq 10) to be around 0.5 μm. The slow mode did not change upon filtration with even the smallest size filter, suggesting the domains formed in the solution are due to interactions between individual polymer chains which are easily disrupted.

Discussion

Two decay modes have been identified for PU ionomers in DMAc, in agreement with the viscometric results which indicated characteristic polyelectrolyte behavior.[58,59,61] Both modes are q^2 dependent and are diffusive processes.

The fast mode can be explained in terms of a large inverse osmotic compressibility. If we consider the generalized Stokes–Einstein equation (eq 4), the diffusion coefficient is directly proportional to the inverse osmotic compressibility. Since the inverse osmotic compressibility is very large for polyion solutions due to repulsive interactions which lead to large intermolecular excluded volume (see eq 8), higher diffusion coefficients are expected for polyion solutions. The diffusion coefficients are significantly enhanced due to intermolecular electrostatic interactions.

The light scattering intensities from the polyurethane ionomer solutions are very small and may be partly the reason why they have not been studied so far by techniques other than viscometry. The small scattering from polyurethane ionomer solutions denotes a small value of osmotic compressibility (see eq 6). The observation that most of the scattered intensity is in the slow mode is consistent with that seen for polyelectrolyte solutions,[62] which have a very small osmotic compressibility.

The fast mode can also be explained in terms of what can be called polyion–counterion coupling. Since the ionomer 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,[63] and so the significant increase in the diffusion coefficient of single ionomer chains as compared to the underivatized polyurethane is not unreasonable. The fast mode shows an angular dependence and hence cannot be attributed to internal motions. The explanation of the fast mode in terms of the electrostatic interactions is also consistent with the observed effect of ion content on its slope with respect to concentration.

The concentration dependence of the diffusion coefficient is observed to be linear, which is similar to the behavior that would be expected for a nonionic polymer solution in the dilute concentration regime. For a nonionic polymer solution in the dilute solution regime, $D_{\text{eff}} = D_z(1 + k_D c)$, where k_D is the concentration coefficient of the diffusion constant that includes both thermodynamic and hydrodynamic contributions.[47] The slope is a measure of interactions in solution. The concentration dependence in the case of strong intermolecular interactions comes only through the inverse osmotic compressibility term. So, the slope should correspond to the second virial coefficient in osmotic pressure measurements. The positive slope of the diffusion coefficient vs concentration curve indicates repulsive interactions in solution and is in agreement with the sign of the second virial coefficient expected. The increase in slope with increase in ionic content can be explained based on the increase in repulsive interactions in solution. A theory (or a model) of the second virial coefficient dependence on the interactions (or ion content) can be tested against these data.

The slow mode of diffusion can be attributed to macroscopic fluctuations of short structural domains. If the Stokes–Einstein relation (eq 10) is used to calculate the sizes corresponding to the diffusion coefficients of the slow mode, sizes corresponding to more than 10 times the size of underivatized polymer are obtained. Therefore, the slow mode in the DLS data can be explained in terms of large-scale heterogeneities existing in solution. Similar behavior reported for salt-free polyelectrolyte solutions, sodium poly(styrenesulfonate)[59,61] and quaternized PVP[58] in water, have been interpreted as arising from large-scale domains in the solution.[64] Theories have been proposed to explain the formation of such domains in salt-free polyion solutions. In the two-state model by Ise et al.,[14] the formation of domains is explained in terms of attractive interactions between different polyions through intermediary counterions. There exist free (single polyions and counterions) and lattice domains. The lattice structures are stabilized by direct electrostatic interactions between small ions and polyions whose positions are affixed to particular locations within the lattice such that the energy is minimized. According to the temporal aggregate model by Schmitz et al.,[65] the aggregates are formed due to dipole−dipole type attractions through the distortion of counterion clouds. Counterions screen direct repulsive interaction between the polyions and provide a "fluctuating dipole" interaction. Thus there exist free and temporal aggregate domains. The critical size and hence stability of these aggregates are proposed to result from a balance between attractive forces arising from fluctuations in the small ion and polyion distributions and the disruptive Brownian forces. The temporal aggregate model stresses the dynamic character of counterions and is the electrodynamic analog of the electrostatic two-state model. Electrodynamic refers to the fluctuating electrical forces arising from asymmetric distributions of interacting small ions and polyions.

Formation of micelles with a hydrophobic core surrounded by a corona of charges was shown to be possible in polyelectrolyte solutions at certain conditions. The slow mode here is not due to micellar aggregation because the polyurethane backbone is compatible with the polar organic solvent, DMAc, used and so hydrophobic aggregation can be ruled out. Also, formation of polymeric micelles, which are compact aggregates with a dense core of minimal solvation, is usually accompanied by a pronounced increase in scattering intensity due to increase in the apparent molecular weight of the aggregate. The formation of domains in ionomer solutions is accompanied by a marked decrease in scattering intensity, suggesting that domains in ionomer solutions are rather loose objects. The decrease in scattering intensity is caused mainly by the decrease in the osmotic compressibility of the solution as a whole due to the presence of charge interactions.

The slow mode of diffusion has been attributed by others to a small, residual population of undissolved aggregates and/or other particles, which could be permanently removed by proper initial filtration of the samples.[66,67] Accordingly, the slow mode represents a nonequilibrium state of the polyelectrolyte solution and so is basically a time effect. This study showed no time dependencies and so the two modes are due to equilibrium structures. Also filtration of the samples through filters smaller than the domain size found preserved the slow mode, showing that the domains giving rise to the slow mode are in dynamic equilibrium.

Conclusions

The polyurethane ionomers studied have regularly spaced ionic groups which allow a direct correlation of observed properties and solution structure. They form good model systems to study the effect of ionic interactions and also to understand the behavior of salt-free polyelectrolyte solutions which suffer from the disadvantages of weak scattering and difficulty in filtration and purification.

Viscometric and DLS measurements were used to demonstrate that sulfonated polyurethane ionomers in DMAc, which is a polar solvent, show polyelectrolyte behavior. CONTIN analysis of the DLS data reveals two diffusive modes for the ionomer solutions. The unsulfonated samples show a single relaxation time distribution. The two diffusion coefficients for the ionomer solutions differ by 2 orders of magnitude. The fast mode shows a negative q^2 dependence and the slow mode shows a small positive q^2 dependence. The fast mode increases with concentration and is due to intermolecular electrostatic interactions. The slope of the fast mode with concentration is found to decrease with a decrease in ionic content, suggesting that the slope is a measure of electrostatic interactions. The slow mode is independent of concentration within the concentration range investigated and corresponds to the existence of large-scale "heterogeneities", whose origin, nature, and structures are currently controversial. DMAc is a good solvent for the polyurethane and hence the slow mode is not due to aggregates arising out of poor backbone solvation. The slow mode is unaffected by filtering using filters with pore size smaller than the calculated aggregate size. This suggests that the domains which give rise to the slow mode are formed due to dynamic interactions in solution. Both modes are not time-dependent and so the structures in the solution are at equilibrium. It appears that both free polyions and associated species coexist in dilute solutions of PU ionomers.

Current investigations include extension of the DLS technique to different systems to isolate various effects which give rise to fast and slow modes so as to obtain a basic understanding of their origin. More detailed results, focused on the structures and the forces responsible for their formation, will be reported in the future.

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References and Notes

(1) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1821.
(2) Siadat, B.; Lundberg, R. D.; Lenz, R. W. *Macromolecules* **1981**, *14*, 773.
(3) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(4) Rochas, C.; Domard, A.; Rinuado, M. *Polymer* **1979**, *20*, 76.
(5) Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1757.
(6) Hara, M.; Wu, J. L. *Macromolecules* **1988**, *21*, 402.
(7) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.
(8) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(9) Hara, M.; Wu, J. L. *Multiphase Polymers: Blends and Ionomers*; Utracki, L. A., Weiss, R. A., Eds.; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989.
(10) MacKnight, J.; Lantman, C. W.; Lundberg, R. D.; Sinha, S. K.; Peiffer, D. G. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1986**, *27*, 327.
(11) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1339.
(12) Mandel, M. In *Polyelectrolytes; Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993.
(13) Ise, N. *Acc. Chem. Res.* **1980**, *13*, 303.
(14) Ise, N. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 323.
(15) Wang, J.; Wang, Z.; Peiffer, D. G.; Shuely, W. J.; Chu, B. *Macromolecules* **1991**, *24*, 790.
(16) Yamanaka, J.; Matsuoka, H.; Kitano, H.; Ise, N. *J. Colloid Interface Sci.* **1990**, *134*, 92.
(17) Wu, J.; Wang, Y.; Hara, M.; Granville, M.; Jerome, R. J. *Macromolecules* **1994**, *27*, 1195.
(18) Ise, N.; Okubo, T.; Kunugi, S.; Matsuoka, H.; Yamamoto, K.; Ishii, Y. *J. Chem. Phys.* **1984**, *81*, 3294.
(19) Ermi, B. D.; Amis, E. J. *Macromolecules* **1996**, *29*, 2701.

(20) Hara, M. Polyelectrolytes in Nonaqueous Solution. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993.

(21) Dieterich, D.; Keberle, W.; Witt, H. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 40.

(22) Dieterich, D.; Rieck, J. N. *Adhes. Age* Feb 1978, *24*.

(23) Rosthauser, J. W.; Nachtkamp, K. In *Advances in Urethane Science and Technology*; Frisch, K. C., Klempner, D., Eds.; Technomic: Lancaster, PA, 1987; Vol. 10, p 121.

(24) Tirpak, R. E.; Markusch, P. H. *Proc. Water-Borne Higher-Solids Coat. Symp., 13th* **1985**.

(25) Grasel, T. G.; Cooper, S. L. *J. Biomed. Mater. Res.* **1989**, *23*, 311.

(26) Okkema, A. Z.; Cooper, S. L. *Biomaterials* **1991**, *12*, 668.

(27) Silver, J. H.; Karayianni, E.; Cooper, S. L. *J. Colloid Interface Sci.* **1996**, *178*, 219.

(28) Silver, J. H.; Marchant, J. W.; Cooper, S. L. *J. Biomed. Mater. Res.* **1993**, *27*, 1443.

(29) Chan, W. C.; Chen, S. A. *Polymer* **1988**, *29*, 1995.

(30) Chen, S. A.; Chan, W. C. *J. Polym. Sci., Part B: Polym. Phys.* **1990**, *28*, 1515.

(31) Lipatov, Y. S.; Tsukruk, V. V.; Dmitruk, N. V.; Polyatskova, N. V.; Shilov, V. V.; Shevchenko, V. V. *Polym. Commun.* **1983**, *24*, 197.

(32) Al-Salah, H. A.; McLean, J. A., Jr.; Frisch, K. C.; Xiao, H. X. *J. Macromol. Sci., Phys.* **1987**, *B26*, 447.

(33) Rajan, H.; Rajalingam, P.; Radhakrishnan, G. *Polym. Commun.* **1991**, *32*, 93.

(34) Rembaum, A. *J. Elastoplast.* **1972**, *4*, 280.

(35) Lee, D. C.; Register, R. A.; Yang, C. Z.; Cooper, S. L. *Macromolecules* **1988**, *21*, 1009.

(36) Ding, Y. S.; Register, R. A.; Yang, C. Z.; Cooper, S. L. *Polymer* **1989**, *30*, 1204.

(37) Register, R. A.; Yu, X. H.; Cooper, S. L. *Polym. Bull.* **1990**, *22*, 565.

(38) Register, R. A.; Cooper, S. L.; Thiyagarajan, P.; Chakrapani, S.; Jerome, R. *Macromolecules* **1990**, *23*, 2978.

(39) Chen, S. A.; Chan, W. C. *Makromol. Chem.* **1988**, *189*, 1204.

(40) Hwang, K. K. S.; Speckhard, T. A.; Cooper, S. L. *J. Macromol. Sci., Phys.* **1984**, *B23*, 153.

(41) Burchard, W.; Lang, P.; Bauer, J. *Makromol. Chem., Macromol. Symp.* **1992**, *58*, 21.

(42) Provencher, S. W.; Hendrix, J.; De Maeyer, L.; Paulussen, N. *J. Chem. Phys.* **1978**, *69*, 4273.

(43) Provencher, S. W. *Makromol. Chem.* **1979**, *180*, 201.

(44) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.

(45) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 229.

(46) Bodycomb, J.; Hara, M. *Macromolecules* **1994**, *27*, 7369.

(47) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper and Row: New York, 1971.

(48) Pusey, P. N.; Tough, R. J. A. In *Dynamic Light Scattering*; Pecora, R., Ed.; Plenum: New York, 1985.

(49) Cha, C. Y. *J. Polym. Sci., Polym. Lett. Ed.* **1969**, *7*, 343.

(50) Coppola, G.; Fabbri, P.; Pallesi, B. *J. Appl. Polym. Sci.* **1972**, *16*, 2829.

(51) Chan, W. C.; Chen, S. A. *Polymer* **1993**, *34*, 1265.

(52) Kratochvil, P. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: London, 1972.

(53) Burchard, W.; Lang, P.; Bauer, J. *Makromol. Chem., Macromol. Symp.* **1992**, *25*, 61.

(54) Stock, R. S.; Ray, W. H. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1393.

(55) Stepanek, P. In *Dynamic Light Scattering*; Brown, W., Ed.; Oxford University Press: New York, 1993.

(56) Jakes, J. *Czech. J. Phys.* **1988**, *38*, 1305.

(57) Bodycomb, J.; Hara, M. *Macromolecules* **1995**, *28*, 8190.

(58) Forster, S.; Schmidt, M.; Antoniette, M. *Polymer* **1990**, *31*, 781.

(59) Sedlak, M.; Amis, E. *J. Chem. Phys.* **1992**, *96*, 817.

(60) Mathiez, P.; Mouttet, C.; Weisbuch, G. *Polymer* **1981**, *20*, 2381.

(61) Sedlak, M.; Amis, E. J. *J. Chem. Phys.* **1992**, *96*, 826.

(62) Sedlak, M. *J. Chem. Phys.* **1994**, *101*, 10140.

(63) Berne, B. J.; Pecora, R. *Dynamic Light Scattering*; Wiley: New York, 1976.

(64) Sedlak, M. *Macromolecules* **1993**, *26*, 1158.

(65) Schmitz, K. S.; Lu, M.; Gauntt, J. *J. Chem. Phys.* **1983**, *78*, 5059.

(66) Smits, R. G.; Kuil, M. E.; Mandel, M. *Macromolecules* **1994**, *27*, 5599.

(67) Norwood, D. P.; Benmouna, M.; Reed, W. F. *Macromolecules* **1996**, *29*, 4293.

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