Structural Studies of Polyurethane Ionomer Solutions. 2. Fluorescence

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ABSTRACT: 8-Anilino-1-naphthalenesulfonic acid (ANS) and pyrene fluorescent probes have been used to investigate the interactions in solutions of model polyurethane ionomers PU1 and PU4 in dimethylacetamide (DMAc) and *N*-methylformamide (NMF). PU1 and PU4 solutions in DMAc consist of loose aggregates and have no hydrophobic aggregation. PU4 solutions in NMF show the presence of hydrophobic aggregates due to NMF being a poor solvent for the ionomer backbone. PU1 solutions in NMF have a very small amount of hydrophobic aggregation, indicating that increase in ionic content of the ionomer can eliminate backbone aggregation even in solvents that are poor solvents for the backbone. The results demonstrate the importance of polymer−solvent interactions and ionic content of the ionomer in determining the solution structure of ionomers.

Introduction

Ionomers are polymers that have a small fraction of ionic groups (usually less than 15 mol %) covalently bound to a polymeric backbone. Ionomer solutions have been the subject of a number of investigations in recent years. Traditionally, ionomer solution behavior has been classified on the basis of the polarity of the solvent.[1] In low-polarity solvents association of ionic groups takes place due to strong dipole−dipole interactions among the ionic groups. Viscosity, light, and neutron scattering data obtained on these solutions indicated the formation of multimers and also showed that the extent and average size of the multimers increase with concentration.[1−7] In high-polarity solvents counterions are solvated, and electrostatic interactions in solution result in behavior characteristic of aqueous polyelectrolyte solutions. The identification of polyelectrolyte behavior in high-polarity ionomer solutions has been supported by viscometry,[8−10] static and dynamic light scattering,[6,9−11] and small-angle neutron scattering (SANS) experiments[7,12] that show features that are characteristic of polyelectrolyte solutions. 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. 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.[13]

The influence of solvent characteristics, other than polarity, on the ionomer solution behavior have received serious consideration only recently. Polymer−solvent interactions (interactions between the solvent and the ionomer backbone) were found to play an important role in the solution behavior of ionomers. Studies with perfluorosulfonated ionomers[14] and model polyurethane ionomers[15] in *N*-methylformamide (NMF) showed that colloidal nanoparticles are formed in solution. Consequently, ionomer solution behavior in polar solvents was further classified:[14] (i) ionomer solutions in polar solvents that are able to dissolve the polymer backbone demonstrate characteristic polyelectrolyte behavior, and (ii) ionomer solutions in polar solvents in which analogous neutral polymer is not soluble are characterized by polymer−solvent phase separation, leading to a colloidal dispersion. More recent studies of model polyurethane ionomers in polar solvents showed that ionic content of the ionomer is an important parameter in determining the solution behavior of ionomers.[16]

Ionomer solutions have been extensively studied by techniques such as viscometry, static and dynamic light scattering, small-angle neutron scattering, and even small-angle-X-ray scattering. In comparison, there are few studies using the fluorescence molecular probe technique (FMPT). FMPT is sensitive enough to extend into the dilute solution regime and is unique in its ability to cover a wide range of ionomer concentrations, from 10^{-1} to 10^{-4} M. Fluorescence measurements provide valuable complementary information to that obtained from scattering studies.[17−19] Moreover, it offers the possibility of distinguishing between intra- and interchain interactions.

Excimer fluorescence was used to demonstrate the transition from intra- to intermolecular association with increase in concentration in dilute solutions of telechelic ionomers.[20] The study showed that excimer fluorescence is a very well-suited technique to discriminate intramolecular from intermolecular associations of the ionic end groups of telechelic polymers. Salt group association in sulfonated polystyrene ionomers with different counterions was studied over a wide range of concentrations in tetrahydrofuran (THF) by a fluorescent molecular probe technique using 1,3,6,8-pyrenetetrasulfonic acid tetrasodium salt ((PTS)Na) as the probe.[17] The solution structures in THF and dimethylformamide (DMF) were compared, and it was shown that the salt group association disappears as the solvent is changed from THF to DMF. The transition was also seen through addition of water. When the water content reaches 5 vol %, excimer fluorescence is found to be completely suppressed.

In this paper, 8-anilino-1-naphthalenesulfonic acid (ANS) and pyrene fluorescent probes have been used

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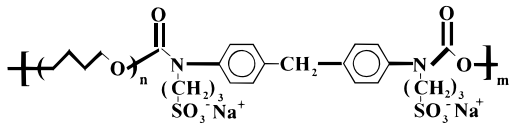

Figure 1. Structure of model polyurethane ionomer.

Table 1. Molecular Characteristics of Polymers; M_w Is the Weight-Average Molecular Weight

PU-sample	M_w	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

to investigate the interactions in polar solutions of model polyurethane ionomers. The results obtained from these probes enables one to determine how the solution structure changes with solvent polarity. The importance of polymer−solvent interactions and ionic content of the ionomer in determining the solution behavior of ionomers is demonstrated.

Experimental Section

Materials. The synthesis of model sulfonated polyurethane ionomers is described in detail elsewhere.[21] Poly(tetramethylene oxide) (PTMO) of molecular weights 1000 and 4500 was used, and the ionomers are designated PU1 and PU4, respectively. 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 polymers have been characterized by gel permeation chromatography (GPC).[21] The values for the ionomers 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 (by using magnetic stirrers for agitation) for 1 day at room temperature.

Measurements. Fluorescence spectra were measured on a SLM Aminco 8100 spectrofluorometer at 30 ± 0.1 °C. Quartz cuvettes filled with 3.0 mL aliquots of the ionomer solution were used. Stock solutions of 8-anilino-1-naphthalenesulfonic acid (ANS) with a concentration of 0.5 mM were prepared in DMAc and NMF. The concentrated solution of ANS was added to the ionomer solutions to give an ANS concentration of 2.5×10^{-6} M. The probe and the polymer were added to the solution at the same time. The solutions were heated at 40−50 °C with stirring for 2 h to equilibrate the fluorescent probe and the structures in solution. The solutions were excited at a wavelength of 385 nm, and the emission intensity was measured between 400 and 650 nm. Stock solutions of pyrene with a concentration of 2×10^{-4} M were prepared in DMAc and NMF. Pyrene was used at a concentration of 5×10^{-8} M with excitation wavelength at 346 nm, and the emission intensity was measured between 360 and 550 nm. The fluorescence intensity of the same volume of ionomer at the same concentration (which was generally very small) was subtracted from the emission intensity of the ionomer solution with the probe ($\Delta I = I$(ionomer + probe) − I(ionomer)). At least three measurements were taken, and the results were averaged.

The probe concentration confidence limit was tested using different probe concentrations. A probe concentration was chosen such that the emission intensity was linear with probe concentration. (For both the probes, the intensity doubled when the concentration was doubled.) Most difference was observed at low probe concentration; this means that at higher probe concentrations most of the probe remains in solution. Finally, two probe concentrations have been used. A longer integration time was used for data acquisition at lower probe concentrations. Solutions were filtered using 0.45 μm syringe filters (Gelman Sciences, Ann Arbor, MI).

Results and Discussion

Previous studies of model polyurethane ionomer PU4 solutions in toluene, DMAc, and NMF by viscometry and light scattering have shown that they consist of ionic aggregates, loose aggregates and hydrophobic aggregates, respectively.[22] Aggregation of ionic groups due to dipolar interactions takes place in toluene, a low-polarity solvent, resulting in the formation of ionic aggregates. In DMAc, a polar solvent and a good solvent for ionomer backbone, single polyions as well as loose aggregates consisting of polyions and counterions held together due to electrostatic interactions are found. In NMF, a highly polar solvent and a poor solvent for the ionomer backbone, backbone aggregation takes place, resulting in the formation of hydrophobic aggregates, particles consisting of a polymer core and an outer ionic shell. Though aggregate transition from an ionic crosslink to a loose one (where no ionic aggregation is present) has been demonstrated,[17] the transition to a hydrophobic aggregate (from a loose aggregate with no hydrophobic aggregation) has not been demonstrated. The self-association of hydrophobes occurs either within a single polymer chain or among different polymer chains, or both, depending on the chemical structure of the polymers. In general, in highly dilute aqueous solutions, hydrophobic associations may preferentially occur within a polymer chain, but with an increase in the polymer concentraton, a tendency for interpolymer association increases.

Hydrophobic aggregation typically leads to the formation of micelles. Because of the importance of the micellization process in a wide range of industries, much attention has been devoted not only to experimental studies of micelles but also to thermodynamic and theoretical investigations.[23] It was found that the micellization process of block copolymers as well as some low molecular mass amphiphiles is sufficiently cooperative to yield colloidal particles with a narrow size distribution and a high aggregation number. The micellization process in these systems obeys the scheme of closed association.[24] The thermodynamic factors responsible for the association of block copolymers in organic solvents are different from those for amphiphiles in aqueous media. Micelle formation by amphiphiles is mainly due to a positive standard entropy of micellization.[25] In this case, an attractive force arises from the hydrophobic interactions which are a result of a reorganization of the structure of water which takes place when the hydrocarbon units are removed from it. On the other hand, for block copolymers in selective organic solvents, it was shown that the enthalpy contribution to the free energy change is solely responsible for the association.[26]

Fluorescence studies of hydrophobic association in polymer solutions rely on the use of a dye, either free or chemically bound. Using a free probe, which is usually introduced into a polymer solution by injection of a small amount of dye solution in a water-miscible solvent, is convenient. However, as pointed out by Winnik,[27] because the probes necessarily have a very low solubility in water, microcrystals of the probes almost always form when they are introduced into water solutions of polymers. The microcrystals disappear slowly as the probe dissolves in the hydrophobic do-

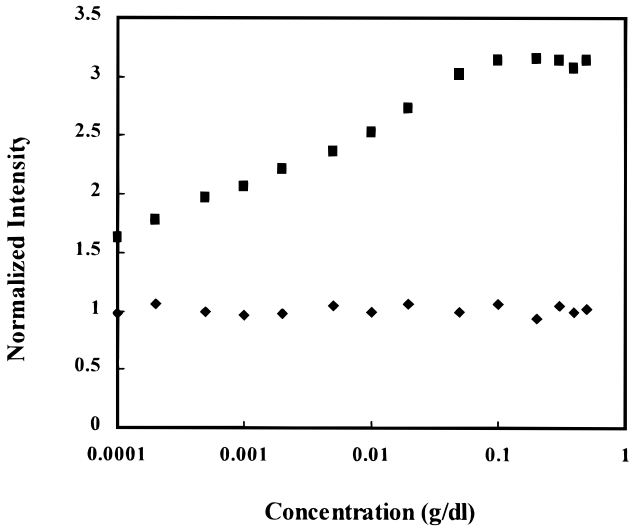

Figure 2. Normalized fluorescence intensities as a function of ionomer concentration for PU4 in DMAc (◆) and PU4 in NMF (■).

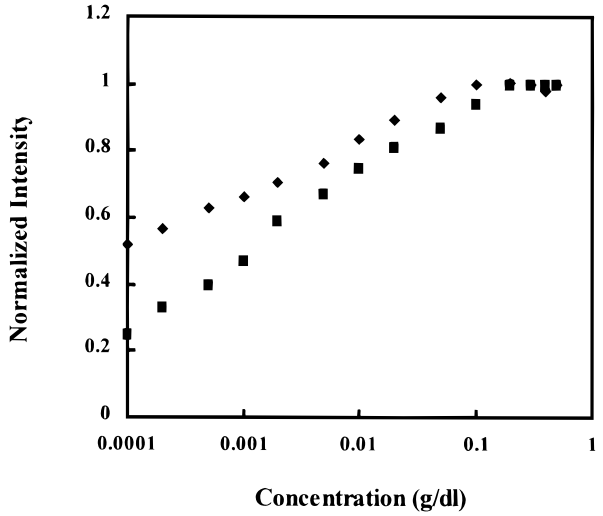

Figure 3. Normalized fluorescence intensities at two different concentrations, 2.5×10^{-6} M (◆) and 5×10^{-6} M (■), of ANS as a function of ionomer concentration for PU4 in NMF.

mains. In addition, the location of the probe is not known with certainty because it is free to diffuse through the entire sample although it may be preferentially solubilized in the hydrophobic environment.

The fluorescent probe, ANS, is sensitive to the local environment. When the probe enters a region of different polarity, the wavelength at which a maximum in emission intensity occurs will shift. When there is no hydrophobic association, the emission maximum remains at 500 nm. With increase in hydrophobic association, the excimer emission shifts to 490 nm and increases in intensity. ANS does not fluoresce in an aqueous environment but exhibits a fluorescence maximum when in a nonpolar, hydrophobic environment.[28] When binding occurs, the fluorescence spectrum changes dramatically from that exhibited by the dye in an aqueous environment. When excited at 377 nm, the single broad band that has an emission peak at 520 nm in water can shift to a wavelength as low as 462 nm when the dye is in a hydrophobic region. Simultaneously, the intensity of the fluorescence may increase as much as 2 orders of magnitude. These two quantities are measures of the dielectric constant or polarity of the dye environment. For systems in which hydrophobic aggregation takes place, at higher concentrations the emission intensity increases and the maximum in intensity shifts to lower wavelengths, indicating that the dye is in a hydrophobic environment. If intensity (neglecting peak shift) is plotted as a function of concentration, a rapid increase should occur at lower concentrations for more hydrophobic solutions.

Preliminary experiments were performed in order to determine the most appropriate ANS concentration to use, and a concentration of 2.5×10^{-6} M was used. Fluorescence emission spectra for PU4−NMF were measured, and at all concentrations the emission intensity increases and the maximum in intensity shifts to lower wavelengths, indicating that the dye is in a hydrophobic environment. To eliminate solvent effects, the intensity at the maximum, I_{max}, normalized with fluorescence emission intensity from pure solvent containing only the probe, is plotted against ionomer concentration. I ($=I_{max}/I_0$) as a function of ionomer concentration is shown for solutions of PU4 in DMAc as well as NMF in Figure 2. The emission intensities have a maximum at 463 and 484 nm for DMAc and NMF solutions, respectively. The emission intensity does not change with increase in concentration for PU4 solutions in DMAc. This shows that there is no significant aggregation of the probe with the polymer. Also, the shift in wavelength of the excitation peak from the 463 nm found for the dye is negligible over the entire concentration range of the ionomer. So it can be hypothesized that the dye does not bind to the ionomer and is therefore presumptive evidence that no hydrophobic region or binding site for the dye exists on the polymer. An observation consistent with the above is that there is no significant difference in binding between unionic and ionic polyurethanes, PU-4500 and PU4, in DMAc.

The emission intensities of PU4 solutions in NMF rapidly increase with increase in concentration, indicating hydrophobic aggregation. As the ionomer concentration is increased, more hydrophobic aggregates are present and so more of the probe resides in hydrophobic regions, thus resulting in an increase in emission intensity. Note that the emission intensity has enhanced values at the lowest ionomer concentration at which measurements were made, indicating that hydrophobic aggregates exist even at very dilute concentrations. For DMAc solutions, addition of ionomer does not make any difference to the emission intensities, providing evidence for the absence of hydrophobic aggregation. The results show that as the solvent is changed from DMAc to NMF in PU4 solutions, the aggregates change from a loose aggregate (with no hydrophobic aggregation) to an aggregate formed due to hydrophobic association.

The measurements for PU4 solutions in NMF at two different probe concentrations are shown in Figure 3. The emission intensities plotted are normalized so that the maximum normalized intensity is unity for each probe concentration. The plateau is reached earlier for the lower probe concentration, because more of the probe (as a percentage of the total amount of the probe added to the solution) present in the solution resides in hydrophobic regions.

The normalized emission intensities for PU1 solutions in DMAc and NMF are shown as a function of concentration of PU1 in Figure 4. Similar to PU4, hydrophobic aggregation is not expected for PU1 when DMAc is used

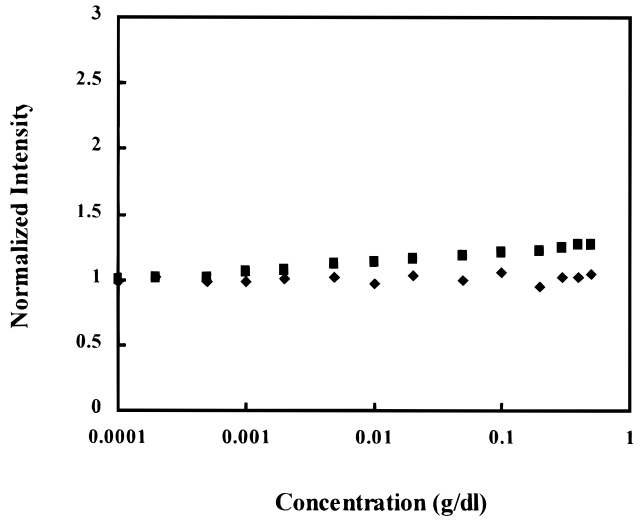

Figure 4. Normalized fluorescence intensities as a function of ionomer concentration for PU1 in DMAc (◆) and PU1 in NMF (■).

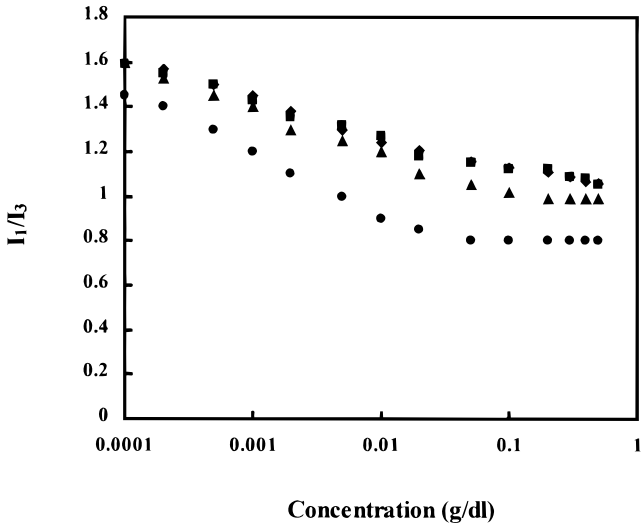

Figure 5. Intensity ratio I_1/I_3 in the pyrene emission spectrum as a function of ionomer concentration for solutions of PU1 in DMAc (◆), PU4 in DMAc (■), PU1 in NMF (▲), and PU4 in NMF (●).

as the solvent. This is confirmed by the data in Figure 4; the emission intensities do not change much with an increase in PU1 concentration in DMAc. For PU1 solutions in NMF the emission intensity increases very slowly with concentration, indicating a very small amount of hydrophobic aggregation.

Comparison of the data for PU1 and PU4 in NMF in Figures 2 and 4 shows that though hydrophobic aggregates are formed in the case of PU4, the amount of hydrophobic aggregation of PU1 is insignificant. Absence of hydrophobic aggregation in PU1 solutions in NMF indicates dissolution of PU1 in NMF. This has also been demonstrated through viscometry and light scattering experiments.[16]

Although these observations of the fluorescence of bound ANS provide some qualitative clues on the solution structure of ionomers in different solvents, the picture is incomplete without the results from viscometry and light scattering. In particular, these observations provide no estimate of the magnitude of the association constant or of the size of the presumed aggregates, when present. This is because fluorescence is insensitive to the particle size distribution, but only to the amount of the hydrophobic microdomains (nanoparticles) formed in the dispersion because the change in fluorescence signal is related to the change of the hydrophility around the probe molecules.[17]

The vibronic fluorescence spectrum of pyrene exhibits five peaks. The I_1 peak, which arises from the (0,0) transition from the lowest excited electronic state, is a "symmetry-forbidden" transition that can be enhanced by the distortion of the π electron cloud. So I_1, occurring at 373 nm, yields enhanced values of fluorescence intensity in polar solvents or environments. On the other hand, the I_3 peak (at approximately 383 nm) is not forbidden and thus is relatively solvent-insensitive (insensitive to solvent polarity). In a wide variety of aromatic hydrocarbons, forbidden vibronic bands in weak electronic transitions show marked intensity enhancements under the influence of solvent polarity. Hence, the ratio I_1/I_3 of the intensities of the first to the third peaks is an index of the polarity of the probe microenvironment.[29,30] These values range from 1.8 to 1.9 in water, to 0.95 for a polystyrene film, and to about 0.5 for nonpolar solvents such as hexane and are thus very helpful for determining the location of the pyrene probe in the micelles. Since pyrene prefers the nonpolar regions very strongly, its water solubility is only about 5×10^{-7} M—the value of the ratio starts to decrease already at a very low volume fraction of the hydrophobic domains. Upon micellization, the ratio I_1/I_3 generally decreases over a rather narrow concentration range. If there is hydrophobic aggregation, I_1/I_3 can be expected to decrease with increase in polymer concentration.

Preliminary experiments have been performed as explained in the Experimental Section, and 5×10^{-8} M was determined to be the most appropriate concentration in pyrene. Figure 5 shows ionomer concentration dependence of the intensity ratio (I_1/I_3) in the pyrene emission spectrum for PU1 and PU4 in DMAc as well as NMF. For pyrene solutions in DMAc and NMF, without any ionomer added, I_1/I_3 has a value of 1.6. For PU4 solutions in NMF, no sudden decrease in I_1/I_3 is observed with increase in ionomer concentration, so hydrophobic aggregates exist even in very dilute solutions. Also, at the lowest concentration at which measurements were made, I_1/I_3 has a value of 1.45, which is smaller than the value of 1.6 that is obtained for solutions containing only pyrene. A plateau value of ~0.8 at the ionomer concentration higher than 0.1 g/dL indicates the complete transference of pyrene molecules from the solvent to the hydrophobic environment of the colloidal particles. These results show that hydrophobic aggregation takes place in NMF solutions of PU4. Surprisingly, the I_1/I_3 values for the solutions of PU1 in DMAc and NMF and for PU1 in NMF also decrease with increase in ionomer concentration, though not as significantly as those for PU4 solutions in NMF. We interpret this as arising due to association of pyrene with the hydrophobic backbone of the ionomers, but not due to solubilization of the probe in a hydrophobic aggregate. Also, the higher plateau value indicates that though the probe environment may be hydrophobic, some contact with solvent still remains.

The results from the two probes, ANS and pyrene, are consistent. PU1 and PU4 solutions in DMAc have no hydrophobic aggregation. PU4 solutions in NMF show the presence of hydrophobic aggregates where as

PU1 solutions in NMF have a very small amount of hydrophobic aggregation.

Conclusions

Low-polarity model polyurethane ionomer solutions are found to contain single chains or small aggregates and large aggregates, made of chains physically cross-linked due to ionic association. In polar solvents, single polyions and loose aggregates are present. Hydrophobic aggregates are present in very high-polarity solvents (higher dielectric constant than water). The nature of interactions inside an aggregate change with the polarity of the solvent, polymer−solvent interactions, and ionic content of the ionomer. PU1 and PU4 solutions in DMAc consist of loose aggregates and have no hydrophobic aggregation. PU4 solutions in NMF show the presence of hydrophobic aggregates due to NMF being a poor solvent for the ionomer backbone. PU1 solutions in NMF have a very small amount of hydrophobic aggregation, indicating that increase in ionic content of the ionomer can eliminate backbone aggregation even in solvents that are poor solvents for the backbone. The results demonstrate the importance of polymer−solvent interactions and ionic content of the ionomer in determining the solution behavior of ionomers.

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References and Notes

(1) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(2) Tant, M. R.; Wilkes, G. L. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 1.
(3) Fitzgerald, J. J.; Weiss, R. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1988**, *C28*, 99.
(4) Lantman, C. W.; MacKnight, W. J. *Annu. Rev. Mater. Sci.* **1989**, *19*, 295.
(5) 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.
(6) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(7) Lantman, C. W.; MacKnight, W. J.; Sinha, S. K.; Peiffer, D. G.; Lundberg, R. D.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1339.
(8) Rochas, C.; Domard, A.; Rinuado, M. *Polymer* **1979**, *20*, 76.
(9) Peiffer, D. G.; Lundberg, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1757.
(10) Hara, M.; Wu, J. L. *Macromolecules* **1988**, *21*, 402.
(11) 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.
(12) MacKnight, J.; Lantman, C. W.; Lundberg, R. D.; Sinha, S. K.; Peiffer, D. G. *Polym. Prepr.* **1986**, *27*, 327.
(13) Mandel, M. In *Polyelectrolytes: Science and Technology*; Hara, M., Ed.; Marcel Dekker: New York, 1993; p 1.
(14) Gebel, G.; Loppinet, B.; Williams, C. E. *J. Phys. Chem. B* **1997**, *101*, 1884−1892.
(15) Nomula, S.; Cooper, S. L. *J. Colloid Interface Sci.* **1998**, *205*, 331.
(16) Nomula, S.; Cooper, S. L. *J. Phys. Chem. B*, in press.
(17) Bakeev, K. N.; MacKnight, W. J. *Macromolecules* **1991**, *24*, 4578.
(18) Li, M.; Jiang, M.; Wu, C. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 1593.
(19) Li, M.; Jiang, M.; Zhang, Y.; Fang, Q. *Macromolecules* **1997**, *30*, 470.
(20) Granville, M.; Jerome, R.; Teyssie, P.; De Schryver, F. C. *Macromolecules* **1988**, *21*, 2894.
(21) Nomula, S.; Cooper, S. L. *Macromolecules* **1997**, *30*, 1355.
(22) Nomula, S.; Cooper, S. L. Submitted to *J. Polym. Sci., Part B: Polym. Phys.*
(23) Astafieva, I.; Zhong, X. F.; Eisenberg, A. *Macromolecules* **1993**, *26*, 7339.
(24) Elias, H. G. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: London, 1972.
(25) Tanford, C. *The Hydrophobic Effect: Formation of Micelles and Biological Membranes*; John Wiley & Sons: New York, 1980.
(26) Price, C.; Stubbersfield, R. B.; El-Kafrawy, S.; Kendall, K. D. *Br. Polym. J.* **1989**, *21*, 391.
(27) *Polymer Surfactants*; Winnik, F., Goddard, E., Ananthapadmanabham, K., Eds.; CRC Press: London, 1992; Chapter 9.
(28) Muesing, R. A.; Nishida, T. *Biochemistry* **1971**, *10*, 2952.
(29) *The Chemistry of Excitation at Interfaces*; Thomas, J. K., Ed.; American Chemical Society: Washington, DC, 1984.
(30) Kalyanasundaran, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039.

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