of transport phenomena developed for the treatment of ordinary electrolytes[26] seems to possess sufficient generality[27] with some underlying simplifications to be reexamined. Still, the pecularities related to the lower symmetry of ionic distributions and to the effect of at certain conditions rather rapid reorientation of the polyions or of the segments of them[28] should be properly incorporated. A more detailed picture of the structure of the solution and in particular of the mutual distribution of the polyions or their segments in equilibrium has also to be known before the fluctuations around it can be studied.

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Electron Spin Resonance Evidence for Specific Solvation Effects in Ionomer Solutions

The solution properties of ionomers are complex and depend on the polymer concentration, the nature of the anion and the cation, the temperature, and the solvent. Relatively few studies have considered how the polarity of the solvent affects the behavior of an ionomer in solution.

Schade and Gartner[1] compared the solution behavior of ionomers derived from copolymers of styrene with acrylic acid, methacrylic acid, and half-esters of maleic acid in tetrahydrofuran (THF), a relatively nonpolar solvent, and dimethylformamide (DMF), a polar solvent.[2] In DMF, they observed a polyelectrolyte effect at low polymer concentrations for Na salts, which they attributed to ionization of the carboxyl group. The increase in the reduced viscosity at very low polymer concentrations is a result of chain expansion due to electrostatic repulsive forces between unshielded anions. With a solvent of lower dielectric constant, such as THF, no dissociation of the ion pair occurs and no polyelectrolyte effect was observed.

Recently several other studies[3-6] have been reported concerning the effect of solvent polarity on the dilute solution viscosity of ionomers. Most of these studies used THF as the nonpolar solvent and DMF as the polar solvent. Lundberg and Phillips[4] studied the solution properties of sulfonated polystyrene (SPS) ionomers in solvents with dielectric constants ranging from 2.2 (dioxane) to 46.7 (Me_2SO). These authors concluded that polar solvents tend to solvate the ions, whereas nonpolar solvents promote ion pairs and interactions between the ionic dipoles.

All the previous studies of ionomer solutions have relied strictly on rheological measurements. Spectroscopic measurements that directly probe the local interactions have not been reported, and such experiments are clearly warranted in view of the complicated solution behavior of these materials. In this communication, we report some electron spin resonance (ESR) results for Mn(II) salts of SPS. Other ESR and infrared spectroscopy studies of these ionomers are reported elsewhere.[7,8]

The SPS ionomers used in this study were prepared from a commercial polystyrene that had a number-average molecular weight of 101 000 and a weight-average molecular weight of 206 000. The procedure of Makowski et al.[9] was used to prepare sulfonated polystyrene containing 2.25 mol % sulfonic acid groups that were converted to the Mn(II) salt by neutralization with manganese acetate. Electron spin resonance (ESR) measurements were made with a Varian E-102E spectrometer at X-band frequency with 100-kHz field modulation. The frequency (ν) was measured with a Varian wavemeter with a crystal detector.

The ESR spectra for 0.5 wt % solutions of MnSPS in THF and DMR are shown in Figure 1. The sharp six-line spectrum for DMF is typical of isolated Mn(II) ions in solution.[10] This result indicates that DMF is able to solvate the dipole interaction to the extent of isolating the Mn(II) ions. Previous infrared spectroscopy (IR) studies[7] also showed that DMF solvates the ion pair, removing the cation from the anion environment. These results are consistent with the observation of a polyelectrolyte effect for SPS in DMF.[4,6] For the THF solution, only a single broad line ESR spectrum is observed. The disappearance of the structure in the spectrum is due to magnetic interactions that occur only in concentrated systems, such as in the case of cation association. This result for SPS in THF is consistent with the absence of a polyelectrolyte effect for this system.[4,6]

Lundberg and Phillips[4] reported that the addition of

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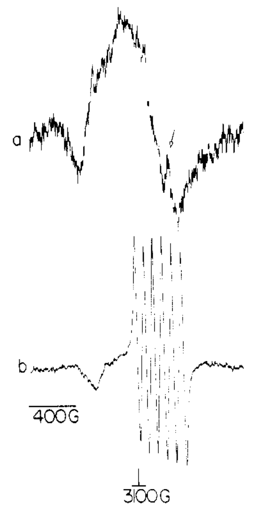

Figure 1. ESR spectra of 0.5% solutions of 2.25 mol % MnSPS in (a) THF (ν = 9.690 GHz), and (b) DMF (ν = 9.574 GHz). Arrow denotes internal cavity resonance.

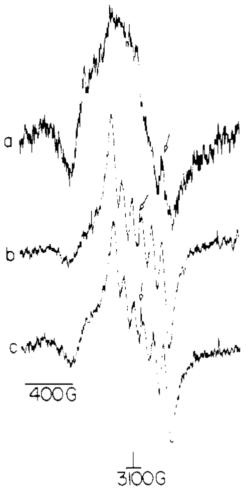

Figure 2. ESR spectra of 0.5% solutions of 2.25 mol % MnSPS in (a) THF (ν = 9.690 GHz), (b) 97% THF + 3% water, and (c) 94% THF + 6% water (ν = 9.123 GHz). Arrow denotes internal standard.

Figure 3. ESR spectra of 0.5% solutions of 2.25 mol % MNSPS in (a) toluene, (b) 97% toluene + 3% methanol, and (c) 94% toluene + 6% methanol. All ν = 9.067 GHz. Arrow denotes internal standard.

water (ϵ = 78.5) to an SPS/THF solution results in solvation of the ion pair and polyelectrolyte behavior. Spectroscopic evidence for this is shown in Figure 2, which gives the ESR spectra of MnSPS in THF/water mixed solvents. Although the six hyperfine lines appear when water is added to the THF solutions, the spectra are built on a broad background. This broad background is probably due to incomplete solvation of the cation, indicating that both isolated Mn(II) and associated species are present in the solution.

Similar ESR spectra are observed for mixed-solvent systems containing toluene (ϵ = 2.4) and methanol (ϵ = 32.6), Figure 3. MnSPS is insoluble in toluene alone; toluene-swollen samples exhibit a single broad line ESR spectrum that is characteristic of predominately associated cations. In order to dissolve MnSPS a polar cosolvent is required. Upon the addition of 3% methanol the hyperfine structure begins to be resolved. The addition of more than 5% methanol has no further influence on the ESR spectrum. As with the THF/water solutions, the spectra in Figure 3 are broader than would be expected if all the Mn(II) species were isolated. It is worth noting here that despite the fact that methanol is capable of ionizing the sulfonate ion pair, a fact confirmed by IR, no polyelectrolyte effect was observed in dilute solution.[4,6] The reason for the similarity of the ESR spectra but differences in the dilute solution behavior for the THF/water and toluene/methanol systems is not clear. This may be due to differences in the relative populations of isolated and associated species in the two solutions. Lundberg[11] has observed similar phenomena and reports that Na NMR experiments indicate that the THF/water solutions of NaSPS contain a higher concentration of isolated Na ions than do toluene/methanol solutions.

The ESR results presented in this communication clearly support the rheological data obtained for ionomer solutions. These specific solvation effects may have important implications in the formation of the bulk microstructure of ionomers isolated from solution. This subject is discussed separately in another paper.[8]

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(2) Although we refer to THF as a nonpolar solvent, as correctly pointed out by one of the reviewers, synthetic chemists consider it to be relatively polar. The key word here is "relatively". From a chemist's perspective, the "nonpolar" nature of THF is manifested by its ability to separate the ion pair in anionic polymerization. We, in fact, have IR evidence (ref 7) that similarly in our systems, THF is able to weaken the polarization of the sulfonate anion by the metal cation. The fact that THF does not, however, completely ionize the metal sulfonates is demonstrated by the absence of a polyelectrolyte effect. Therefore, we conclude that, although THF weakens the cation–anion interaction, it does not completely separate the anion from the electrostatic field of the cation. In our work, we have adopted the operational definition of a polar solvent as one that is capable of completely solvating the ion pair and a nonpolar solvent as one that does not.
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Photon Correlation Spectroscopy of Poly(vinyl acetate)

In recent reports, Wang and Fischer[1] have presented a theoretical derivation which leads to the conclusion that the photon correlation function of light isotropically scattered by bulk amorphous polymers near the glass transition temperature is equivalent to a measurement of the time-dependent longitudinal compliance. This conclusion was bolstered by an experimental study[2] of light scattered by poly(vinyl acetate) (PVac) in which the relaxation spectrum evaluated from the photon correlation data was found to be closely similar to that which characterized the bulk compliance of PVAc by McKinney and Belcher.[3]

In the discussion of their PVAc light scattering data, Fytas et al. note[2] that their data are not in agreement with an earlier study in our laboratory.[4] They assign the discrepancy to the analytical problems which derive from the splicing procedures used to generate correlation functions in our study. By contrast, their experiment utilized a logarithmic correlator, thus avoiding the need to splice data sets. While this experimental difference may influence the comparison of their data with ours, we write this paper to point out that the difference between the two studies is, in fact, for the most part due to the difference in glass transition temperatures of the two samples. The sample used in our study[4] was of molecular weight $M_w = 4.4 \times 10^6$ and $T_g = 32 \pm 2$ °C; for the sample of Fytas et al.[2], $M_w = 15\,000$ and $T_g = 17$ °C. It is not therefore surprising that at comparable temperatures, the average relaxation times $\langle \tau \rangle$ measured by Fytas et al.[2] are several orders of magnitude larger than ours.

To illustrate this, we have plotted in Figure 1 relaxation time data in the form log $\langle \tau \rangle$ vs. $(T - T_g)$, the temperature distance from T_g. Clearly, our $\langle \tau \rangle$ values are reasonably consistent with those of Fytas et al.[2] for $(T - T_g) \sim 15$ °C. However, Figure 1 indicates that, for our data which extend into a temperature regime closer to T_g, the apparent activation energy is significantly smaller than would be calculated from the WLF equation which fits the data of Fytas et al.[2] A further difference between the two sets of data is that, as stated by Fytas et al.[2], the exponent β, estimated from fractional exponential fits to experimental correlation functions, i.e., $\phi = \exp(-t/\tau)^{\beta}$, is found to be somewhat larger in our work (0.45 vs. 0.35).

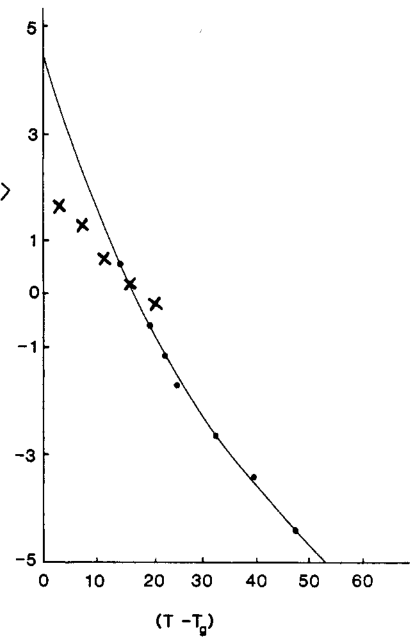

Figure 1. Logarithm of the average relaxation time derived from photon correlation analysis of light isotropically scattered by poly(vinyl acetate) in the bulk state near T_g, plotted vs. the temperature distance $(T - T_g)$: (●) data of Fytas et al.;[2] (×) data of Tribone et al.;[4] the solid line is a WLF fit to the data of Fytas et al.

These differences may indeed be the result of the errors attendant to analysis of spliced correlation functions as stated by Fytas et al.[2] However, it is worth noting that at least two studies[5,6] have observed that the apparent activation energy of viscoelastic properties just above or below T_g may be smaller than that predicted by extrapolation based on the WLF equation applicable for $T \gg T_g$. Also, for a low-T_g polymer, it is possible that the width of the relaxation spectrum may be increased because of the molecular weight distribution and the associated spread in T_g. This could be a contributing factor in the smaller β-parameter observed by Fytas et al.[2] Definitive comparison between different experimental data sets under circumstances where T_g is molecular weight dependent requires identical or at least closely similar samples.

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Solid-Phase Block Copolymer Synthesis by the Iniferter Technique

In 1982 we proposed the concept of an iniferter (*ini*tiator–trans*fer* agent–*ter*minator) for design of polymer

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