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Communications to the Editor

Polyelectrolyte Behavior of Halato-Telechelic Ionomers in Polar Solvent

Polyelectrolyte behavior, which is typically observed for salt-free polyelectrolytes in aqueous solution, is not well understood[1] in terms of the structure of the solution and the essential factors causing the behavior. One of the reasons is the difficulty in obtaining reliable data for salt-free polyelectrolytes in aqueous solutions. Recently, it has been shown that ionomers that have a small number of ionic groups (i.e., up to 10–15 mol % in concentration) offer good model systems to investigate the characteristics of salt-free polyelectrolytes.[2-5] Ionomers can be dissolved in polar organic solvents, which eliminates the various problems associated with aqueous solutions, such as self-dissociation of solvent (water), complex water structure, etc. Moreover, measurements such as light scattering and viscosity are easier to conduct in organic solvents due to the strong scattering and low viscosity of ionomer solutions. For example, the excess scattered intensity, R_θ, from ionomer/organic solvent systems is $(1–20) \times 10^{-6}$, while that from polyelectrolyte/water is $(0.1–1) \times 10^{-6}$.[3] It has been pointed out[5] that the polyelectrolyte behavior of ionomer/polar solvent systems is essentially the same as that for polyelectrolyte/water systems: viscosity,[2,6,8] static light scattering,[3,4,9] dynamic light scattering,[10] neutron scattering,[11] and osmotic pressure[6] measurements all show similar effects.

Hara et al.[5] studied the characteristics of polyelectrolyte behavior using polystyrene-based ionomers that had ionic groups randomly distributed along the chain. In their work, the role of intra- and intermolecular interactions on polyelectrolyte behavior of random ionomers was studied by changing the number of ionic groups per chain, since it was expected that the importance of intramolecular interaction decreased with decreasing number of ionic groups per chain. It was observed that even ionomers with a very small number of ions (e.g., less than one ionic group per chain on average) showed characteristic polyelectrolyte behavior. It was suggested that the essential factor causing polyelectrolyte behavior was intermolecular interactions not intramolecular interactions as is usually assumed in conventional explanations.[1] Although the results seem to be clear, there is the possibility that some polymer chains have a larger number of ionic groups than other chains due to the random distribution of ionic groups. In order to study further the role of intermolecular interactions in polyelectrolyte behavior, we use in this work halato-telechelic ionomers, in which ionic groups are located only at chain ends.

The polystyrene-based halato-telechelic polymers were prepared by an anionic polymerization in THF at −78 °C. The resulting dimethylamino-telechelic polystyrene was quaternized with 1-bromoethane in refluxing THF for 3 weeks. The functionality determined by potentiometric titration was 1.85. The weight-average molecular weight determined by light scattering was 12 000. Details concerning the preparation were described elsewhere.[12]

Polymer solutions were prepared by dissolving the dried samples in dimethylformamide (DMF) under stirring for a day at room temperature. The polymers were easily dissolved in DMF. The reduced viscosity was measured with a modified Ubbelohde viscometer at 25 ± 0.05 °C. Light scattering measurements were conducted with a KMX-6 low-angle light scattering photometer (Chromatix) at a wavelength of 633 nm at 25 ± 0.5 °C, and the specific refractive index increment, dn/dc, was measured with a KMX-16 differential refractometer (Chromatix) at 25 ± 0.1 °C. The optical clarification of the solution was carried out by passing the solution through two membranes, whose pore sizes were 0.5 and 0.2 μm, in succession. Details concerning the viscosity[5] and light scattering[4] experiments and data analysis were described elsewhere.

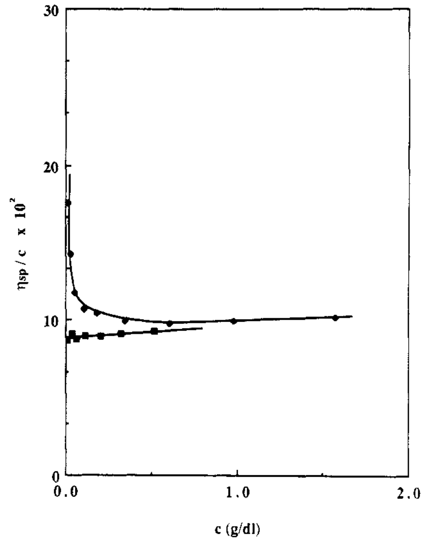

Figure 1. Reduced viscosity against polymer concentration for halato-telechelic ionomer (◆) in DMF as well as for unquaternized polymer (■).

Figure 1 shows the results on viscosity measurements for the halato-telechelic ionomer in DMF, as well as for the unquaternized sample. While the unquaternized sample behaves as a neutral polymer, the quaternized sample (ionomer) shows typical polyelectrolyte behavior:[1] the reduced viscosity, η_{sp}/c, increases remarkably with decreasing polymer concentration. Similar behavior has been observed for various ionomers[2,5-8] which have ionic groups randomly distributed along backbone chains, as well as salt-free polyelectrolytes in water.[1]

In order to confirm the results, the low-angle light scattering measurements were conducted for the same samples as those used for viscosity measurements. Figure 2 shows the light scattering results for the halato-telechelic ionomer in DMF, as well as for the unquaternized sample. The unquaternized sample shows neutral polymer behavior: reciprocal reduced scattered intensity, Kc/R_0, increases linearly with polymer concentration in the concentration range studied. From the intercept, the weight-average molecular weight is found to be 12 000. However, the quaternized sample shows typical polyelectrolyte behavior:[13] the Kc/R_0 rises steeply from the intercept, bends over, and becomes nearly horizontal at higher concentration. Similar behavior was reported for polystyrene-based ionomers,[3,4,9] in which the ionic groups were randomly distributed along the chain, as well as for salt-free polyelectrolytes in water.[13,14]

From these experiments, there is no doubt that the polystyrene-based halato-telechelic ionomer shows polyelectrolyte behavior which is typically seen in random

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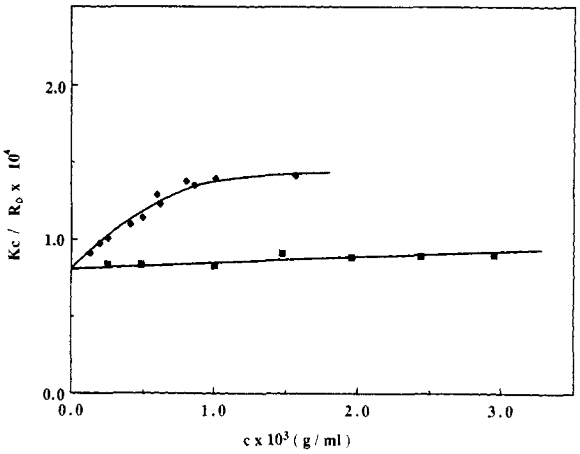

Figure 2. Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against polymer concentration for halato-telechelic ionomer (◆) in DMF as well as for unquaternized polymer (■).

ionomers in polar solvents or in polyelectrolytes in water.

Hara et al.[5] showed that random ionomers (i.e., lightly sulfonated polystyrene) with a very small number of ionic groups (e.g., less than one ionic group per chain on average) showed polyelectrolyte behavior. It was suggested from these observations that the necessary condition to cause polyelectrolyte behavior is the existence of ionic groups in polymer chains, whatever their number is, and that the intermolecular interactions play a major role in polyelectrolyte behavior. The present results on halato-telechelic ionomers seem to confirm the previous conclusions. Since only two ends of the polymer chain have ionic groups that are separated by more than 100 repeating units, it is difficult to apply the conventional explanation of polyelectrolyte behavior; i.e., the intramolecular repulsion between fixed ions on the same chain causes the expansion of the chain, leading to polyelectrolyte behavior.

In addition, as is shown in the value of the functionality (1.85), many chains have only one ionic end group. This fact reinforces our conclusion that the effects observed are intermolecular in nature.

Several models based on intermolecular interactions may be considered to explain the results: Wolff[15] stated that chains were entangled and decreased in size with concentration in the concentration range where the Fuoss equation was applicable. Similar arguments, based on homogeneously entangled semidilute polyelectrolyte solutions, are given by using a scaling approach,[16,17] although this considers a locally rodlike conformation arising from intramolecular repulsion in a very dilute polyelectrolyte solution. Hara and Nakajima[18] suggested the existence of "lamps" which are formed due to inhomogeneous entanglements of polymer chains under repulsive interactions. Ise et al.[19] proposed the formation of a second phase made of macroions, caused by the net attraction of charges having the same sign, via counterions with opposite sign. Whether the interaction is attractive or repulsive, our data strongly suggest the importance of intermolecular interactions in the solution behavior of salt-free polyelectrolytes. More detailed experiments on halato-telechelic ionomers are under way to find the best model to explain the observed behavior.

In summary, typical polyelectrolyte behavior was observed for halato-telechelic ionomers that had ionic groups only at chain ends. Both viscosity and low-angle light scattering experiments showed similar results as those obtained for random ionomers. Although some solution properties of halato-telechelic ionomers have been reported,[20-22] this is the first time that polyelectrolyte behavior is reported for this type of ionomer. It is suggested that the essential factor causing polyelectrolyte behavior is intermolecular in nature. More detailed experiments on the halato-telechelic ionomers are under way. Analyses on these systems and the proper models to explain the results will be reported.

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References and Notes

(1) See, for example: Mandel, M. *Encyl. Polym. Sci. Eng.* **1987**, *11*, 739.
(2) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(3) Hara, M.; Wu, J. *Macromolecules* **1986**, *19*, 2887.
(4) Hara, M.; Wu, J. *Macromolecules* **1988**, *21*, 402.
(5) Hara, M.; Wu, J.; Lee, A. H. *Macromolecules* **1988**, *21*, 2214.
(6) Rochas, C.; Domard, A.; Rinaudo, M. *Polymer* **1979**, *20*, 1979.
(7) Niezette, J.; Vanderschueren, J.; Aras, L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1845.
(8) Hara, M.; Lee, A. H.; Wu, J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1407.
(9) Lantman, C. W.; MacKnight, W. J.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(10) Hara, M.; Wu, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29*(2), 360.
(11) MacKnight, W. J.; Lantman, C. W.; Lundberg, R. D.; Sinha, S. K.; Peiffer, D. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27*(1), 327.
(12) Granville, M.; Jerome, R. J.; Teyssie, P.; DeSchryver, F. C. *Macromolecules*, in press.
(13) Doty, P.; Steiner, R. F. *J. Chem. Phys.* **1952**, *20*, 85.
(14) Oth, A.; Doty, P. *J. Phys. Chem.* **1952**, *56*, 43.
(15) Wolff, C. *J. Phys. (Les Ulis, Fr.)* **1978**, C2-39, 169.
(16) Odijk, T. *Macromolecules* **1979**, *12*, 688.
(17) de Gennes, P.-G.; Pincus, P.; Velasco, R. M.; Brochard, F. *J. Phys. (Les Ulis, Fr.)* **1976**, *37*, 1461.
(18) Hara, M.; Nakajima, A. *Polym. J.* **1980**, *12*, 703.
(19) Ise, N. *Angew. Chem.* **1986**, *25*, 323.
(20) Broze, G.; Jerome, R.; Teyssie, P. *Macromolecules* **1982**, *15*, 920.
(21) Broze, G.; Jerome, R.; Teyssie, P. *Macromolecules* **1982**, *15*, 1300.
(22) Tant, M. R.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*, 118.
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Brønsted Acidity at Polyethylene-Solution Interfaces

Acid-base chemistry is probably one of the most fundamental aspects of organic chemistry and has received extensive study.[1] It is also widely recognized that acid-base interactions including hydrogen-bonding, proton