(12) Bruckner, S.; Campbell, J. S.; Yoon, D. Y.; Griffin, A. C. *Macromolecules* **1985**, *18*, 2709.
(13) Samulski, E. T. *Polymer* **1985**, *26*, 177.
(14) Erman, B.; Flory, P. J. *Macromolecules* **1983**, *16*, 1607.
(15) Queslel, J.-P.; Erman, B.; Monnerie, L. *Macromolecules* **1985**, *18*, 1991.

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Low-Angle Light Scattering Study of Polyelectrolyte Behavior of Ionomers in Polar Solvent

Ionomers are a new class of ion-containing polymers which have ions in concentrations up to 10–15%, randomly distributed in nonionic backbone chains, and have been widely studied in the solid state.[1-3] Recently, the solution properties of ionomers have begun to be studied[4-10] because of their unique properties: (1) in nonpolar solvents, ionomers show aggregation behavior due to dipole–dipole attractions between ion pairs; (2) in polar solvents, they show polyelectrolyte behavior due to the repulsion between fixed ions in polymer chains. Even ionomers with only a few percent of ions show characteristic polyelectrolyte behavior. Lundberg et al.[5] studied this polyelectrolyte behavior using viscosity measurements; the reduced viscosity increased remarkably with decreasing polymer concentration. MacKnight et al.[10] studied the polyelectrolyte behavior using neutron scattering; the scattering curves exhibit a broad single maximum. Here, we study the polyelectrolyte behavior of an ionomer (lightly sulfonated polystyrene) in a polar solvent (DMF) using light scattering measurements.

Although much work has been done to elucidate the structure of salt-free polyelectrolytes in aqueous solution, the exact structure of polyelectrolytes is still not clear.[11] One of the reasons is the difficulty in obtaining reliable data for salt-free polyelectrolyte solutions. For example, only a few light scattering data are available.[12-14] One of the reasons for the scarcity of data is that the scattered intensity from salt-free polyelectrolyte solutions is very small: the excess scattering from a salt-free polyelectrolyte in aqueous solution over that of water is only 10–100%; i.e., the reduced scattered intensity, $R_\theta = (0.1\text{–}1) \times 10^{-6}$.[13] Therefore, it is very difficult to obtain reliable data for this system. Another reason is that optical clarification is difficult for aqueous solution systems.

By using ionomers dissolved in polar solvents to study polyelectrolyte behavior, we can overcome these problems. In ionomer solutions, the excess scattered intensity is twenty to several hundred percent of that from solvent; i.e., $R_\theta = (1\text{–}20) \times 10^{-6}$. Therefore, the scattered intensity from ionomer/polar organic solvent solutions is more than 10 times larger than that from polyelectrolyte/water solutions. Also, optical clarification is easier due to the low viscosity of the ionomer solution. Therefore, we can obtain reliable light scattering data for polyelectrolyte behavior in the absence of salts. The purpose of the present work is to study the characteristics of salt-free polyelectrolytes by using ionomers in polar solvents. It should be mentioned that even though the characteristic polyelectrolyte behavior is smaller for ionomer solutions than for polyelectrolytes, they maintain the essential features.

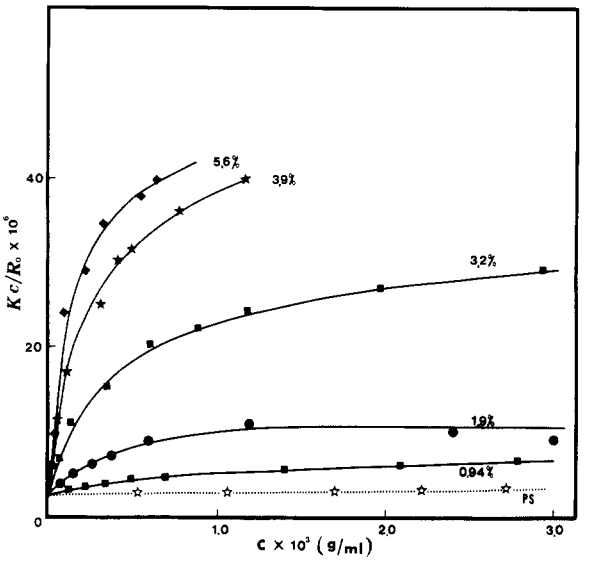

Figure 1. Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against c for S-xSSA-Na of various ion contents as well as PS in DMF.

Lightly sulfonated polystyrene (S-SSA) was prepared by the sulfonation of polystyrene, using acetyl sulfate as a sulfonating agent.[15] The starting polystyrene was a polystyrene standard (Pressure Chemical Co.) with a narrow molecular weight distribution ($M_w = 4.0 \times 10^5$, $M_w/M_n < 1.06$). The acid content, which was controlled by changing the amount of acetyl sulfate, was 0.94, 1.9, 3.2, 3.9, and 5.6 mol %. The acid copolymers were converted to ionomers by adding the proper amount of methanolic sodium hydroxide in benzene/methanol (90/10), freeze-drying, and drying at room temperature under vacuum. The ionomers were easily dissolved in dimethylformamide (DMF). Light scattering measurements were conducted with a KMX-6 low-angle light scattering photometer (Chromatix-LDC/Milton Roy) 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/LDC-Milton Roy) at 25 ± 0.1 °C.

Figure 1 shows the results of light scattering for S-xSSA-Na in DMF for various ion contents. Again, ionomers show typical polyelectrolyte behavior;[16] the reciprocal reduced scattered intensity (Kc/R_0) rises steeply from the intercept at zero concentration, bends over, and becomes nearly horizontal at higher concentration. From the intercept, the weight-average molecular weight, M_w, is obtained as 4.0×10^5 for all ionomers. Therefore, the ionomers are molecularly dispersed in DMF.

In order to analyze the light scattering data from the ionomers in a polar solvent, we used a simple effective potential model with an effective diameter. This model, which treats the macroions as if they were neutral but have an effective size, was originally introduced by Doty and Steiner[16] for their analysis of light scattering data from macroions and then used by Benmouna et al.[17] for their explanation of the origin of the peak observed in X-ray and neutron scattering curves obtained from salt-free polyelectrolytes. Doty and Steiner[16] derived the following equation for macroions in water by considering the long-

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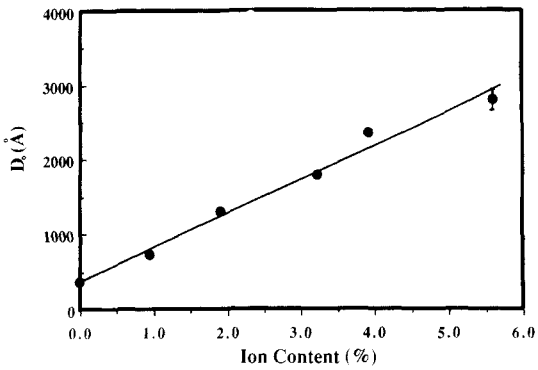

Figure 2. Plots of effective diameter at zero concentration, D_0, against ion content for S-xSSA-Na in DMF.

range Coulombic interaction and nonrandom arrangement (ordering) of macroions:

$$\frac{Kc}{R_\theta} = \frac{1}{MP(\theta)}\left\{1 + \frac{2B'}{M}c\Phi(hD)\right\} \quad (1)$$

where $\Phi(x) = (3/x^3)(\sin x - x \cos x)$, $h = (4\pi/\lambda') \sin(\theta/2)$, and $B' = (2\pi/3)D^3N_0$. Also, $P(\theta)$ represents the particle scattering factor, λ' the wavelength of light in the medium, θ the scattering angle, and N_0 Avogadro's number. Here, D is the effective ionic diameter of macroions, which is a decreasing function of concentration.

As a first step of an analysis, we analyzed the initial slope of the Kc/R_0 vs. c curve. From the above equation, the initial slope is obtained as

$$\text{initial slope} = \left[\frac{\mathrm{d}}{\mathrm{d}c}\left(\frac{Kc}{R_0}\right)\right]_{c=0} = \frac{4\pi N_0}{3M^2}D_0{}^3 \quad (2)$$

here, D_0 represents the effective diameter of a macroion at zero polymer concentration. We also used the relations $P(0) = 1$ and $\Phi(0) = 1$. By using eq 2, we calculated the effective diameters from the initial slopes, which were obtained by curve fitting of a third-degree polynomial.

The effective diameters at zero concentration are plotted as a function of ion content in Figure 2. It is seen that D_0 is a linear function of ion content. The effective diameter is a measure of distance of closest approach of centers of macroions and therefore reflects the range of interaction of macroions with other macroions.[16] The large change in effective diameter with ion content—for example, at 4% ion content, D_0 increases to 2200 Å from 420 Å for PS—is consistent with the observed large change in viscosity.[5]

In summary, polyelectrolyte behavior was studied by using ionomers in a polar solvent. Light scattering data show that the polyelectrolyte behavior is enhanced with increasing ion content. It is found that the effective diameter of ionomers increases linearly with ion content at least up to the 5% ion content level. More detailed experiments and analysis of the light scattering data are under way and will be reported.

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References and Notes

(1) Holliday, L. *Ionic Polymers*; Applied Science: London, 1975.
(2) Eisenberg, A.; King, M. *Ion-Containing Polymers*; Academic: New York, 1977.
(3) MacKnight, W. J.; Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(4) Rochas, C.; Domard, A.; Rinaudo, M. *Polymer* **1979**, *20*, 76.
(5) Lundberg, R. D.; Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(6) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1982**, *15*, 920.
(7) Niezette, J.; Vanderschueren, J.; Aras, L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1845.
(8) Tant, M. R.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1980**, *25*, 118.
(9) Fitzgerald, J. J.; Weiss, R. A. *ACS Symp. Ser.* **1986**, *302*, 35.
(10) 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*, 327.
(11) Hayter, J.; Jannink, G.; Brochard-Wyart, F.; de Gennes, P. G. *J. Phys. (Paris)* **1980**, *41*, L-451.
(12) Nagasawa, M.; Takahashi, A. *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic: New York, 1972; Chapter 16.
(13) Oth, A.; Doty, P. *J. Phys. Chem.* **1952**, *56*, 43.
(14) Alexandrowicz, Z. *J. Polym. Sci.* **1959**, *40*, 91.
(15) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Patent 3 870 841, 1975 (assigned to Exxon Research and Engineering Co.).
(16) Doty, P.; Steiner, R. F. *J. Chem. Phys.* **1952**, *20*, 85.
(17) Benmouna, M.; Weill, G.; Benoit, H.; Akcasu, Z. *J. Phys. (Paris)* **1982**, *43*, 1679.

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A Finite Element Method for Determining the Stiffnesses of Tube-Polymer Frameworks

In earlier papers a discussion of known and potential inorganic and organic polymers with tube frameworks has been given, Figure 1.[1-3] Many of these very unusual polymers have frameworks with linkage arrangements that lead to inherent stiffness. Some of the frameworks, because of the details of their linkage arrangements, are connsiderably stiffer than others.

In view of the probable importance of tube polymers and the novel and substantial differences in the stiffnesses of their frameworks, it is desirable to have a technique suitable for quantitatively determining these stiffnesses. However, no such technique has been described. Our interest in having such a technique has led us to investigate the methods used in engineering to determine the stiffnesses of trusses and other large, complex structures.

One method currently used for this purpose is the finite element method.[4] In this method, the properties of a structure are represented by the properties of a set of structural elements (e.g., a set of pipes, I-beams, or blocks), and the properties of these are appropriately summed to determine the global behavior of the structure. Since in many cases this method requires considerable computation, it is commonly carried out with the aid of an appropriate program.

One such program is SAP IV.[5] This is an established program that can be applied to structures whose complexity and size require models having not only several types of elements but also thousands of them.[6] The program can be used for the static analysis of structures and

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