nylon 3Me6T/nylon 6 blend.

Registry No. Nylon 4 (SRU), 24938-56-5; nylon 4 (homopolymer), 24968-97-6; nylon 46 (SRU), 50327-22-5; nylon 46 (copolymer), 50327-77-0; nylon 6, 25038-54-4; nylon 66, 32131-17-2; nylon 69 (SRU), 28757-63-3; nylon 69 (copolymer), 27136-65-8; nylon 610 (SRU), 9008-66-6; nylon 610 (copolymer), 9011-52-3; nylon 612 (SRU), 24936-74-1; nylon 612 (copolymer), 26098-55-5; nylon 11 (SRU), 25035-04-5; nylon 11 (homopolymer), 25587-80-8; nylon 12 (SRU), 24937-16-4; nylon 12 (homopolymer), 25038-74-8; nylon 3Me6T (SRU), 9071-17-4; nylon 3Me6T (copolymer), 25497-66-9; nylon 6ICOT (SRU), 58814-83-8; nylon 6ICOT (copolymer), 25750-23-6; Bexloy APC-803, 112721-08-1.

References and Notes

(1) Paul, D. R.; Newman, S. *Polymer Blends*; Academic: New York, 1978.
(2) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic: New York, 1979.
(3) Barlow, J. W.; Paul, D. R. *Polym. Eng. Sci.* **1987**, *27*, 1482.
(4) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(5) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(6) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(7) ten Brinke, G.; Rubinstein, E.; Karasz, F. E.; MacKnight, W. J.; Vukovic, R. *J. Appl. Phys.* **1984**, *56*, 2440.
(8) Pfennig, J.-L. G.; Heskkula, H.; Barlow, J. W.; Paul, D. R. *Macromolecules* **1985**, *18*, 1937.
(9) Udea, H.; Karasz, F. E. *Macromolecules* **1985**, *18*, 2719.
(10) Woo, E. M.; Barlow, J. W.; Paul, D. R. *Polymer* **1985**, *26*, 763.
(11) Min, K. E.; Chiou, J. S.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1721.
(12) Fowler, M. E.; Barlow, J. W.; Paul, D. R. *Polymer* **1987**, *28*, 1177.
(13) O'Gara, J. F.; Williams, D. J.; MacKnight, W. J.; Karasz, F. E. *J. Polym. Sci. Polym. Phys. Ed.* **1987**, *25*, 1519.
(14) Min, K. E.; Paul, D. R. *Macromolecules* **1987**, *20*, 2828.
(15) Ellis, T. S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28*, 181.
(16) Ellis, T. S. *Polymer*, in press.
(17) Howe, S. E.; Coleman, M. M. *Macromolecules* **1986**, *19*, 72.
(18) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.
(19) Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.
(20) Balazs, A. C.; Karasz, F. E.; MacKnight, W. J.; Ueda, H.; Sanchez, I. C. *Macromolecules* **1985**, *18*, 2784.
(21) Schulz, O.; Cantow, H. J. *Polym. Bull.* **1986**, *15*, 449.
(22) Epstein, B. N.; Latham, R. A.; Dunphy, J. F.; Pagilagan, R. U. *Advances in Toughened Nylon*; 130th Meeting of the Rubber Division, American Chemical Society, Atlanta, GA, 1986; Paper 26.
(23) Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1976.
(24) Kotliar, A. M. Macromol. Rev. **1981**, *16*, 367.
(25) Kakar, S. K. *Textile Res. J.* **1976**, *46*, 776.
(26) Nishi, T.; Wang, T. T. *Macromolecules* **1975**, *8*, 909.
(27) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953.
(28) Hoffman, J. D.; Weeks, J. J. *J. Chem. Phys.* **1962**, *37*, 1723.
(29) Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1980; Vol. 3.
(30) Ellis, T. S. *J. Appl. Polym. Sci.* **1988**, *36*, 451.
(31) Kitao, T.; Kobayashi, H.; Ikegami, S.; Ohya, S. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 2633.
(32) Ong, E. S.; Kim, Y.; Laverne-Williams, H. *J. Appl. Polym. Sci.* **1986**, *31*, 367.
(33) Kyotani, M. *J. Macromol. Sci., Phys.* **1982**, *B21*, 219.
(34) Verma, A.; Deopura, B. L.; Sengupta, A. K. *J. Appl. Polym. Sci.* **1986**, *31*, 747.
(35) Helfand, E.; Tagami Y. *J. Chem. Phys.* **1971**, *56*, 3592.
(36) Bosma, M.; ten Brinke, G.; Ellis, T. S. *Macromolecules* **1988**, *21*, 1465.
(37) Zimmerman, J.; Pearce, E. M.; Miller, I. K.; Muzzio, J. A.; Epstein, I. G.; Hosegood, E. A. *J. Appl. Polym. Sci.* **1973**, *17*, 849.
(38) Takayanagi, M.; Ogata, T. *J. Macromol. Sci., Phys.* **1980**, *B17*, 591.
(39) Kanakalatha, P.; Vijayan, K.; Sridhar, M. K.; Singh, A. K. *Polymer* **1983**, *24*, 621.
(40) Moore, D. R.; Mathias, L. J. *J. Appl. Polym. Sci.* **1986**, *32*, 6299.
(41) Pillon, L. Z.; Utracki, L. A. *Polym. Eng. Sci.* **1984**, *24*, 1300.

Solution Properties of Ionomers. 2. Simple Salt Effect

M. Hara,* J. Wu, and A. H. Lee

Department of Mechanics and Materials Science, Rutgers—The State University of New Jersey, Piscataway, New Jersey 08855-0909. *Received March 21, 1988; Revised Manuscript Received June 9, 1988*

ABSTRACT: The effect of simple salts on the solution properties of sulfonated polystyrene ionomers was studied by viscosity and light scattering measurements. It was shown that the polyelectrolyte behavior of ionomers in a polar solvent was suppressed by the addition of simple salts (LiCl). A single peak in the reduced viscosity vs concentration curve was observed when salt concentration was 1×10^{-4} M. It was found that the addition of simple salts also suppressed the aggregation behavior of ionomers in a low-polarity solvent. However, the addition of excess neutralizing agent (LiOH) seemed to enhance the aggregation at high concentration.

Introduction

Ion-containing polymers, such as polyelectrolytes, biopolymers, glasses, etc., have attracted the attention of researchers for many years.[1-5] The most recent addition to these ion-containing polymers is ionomers which have a small number of ionic groups (i.e., up to 10–15 mol %) along a nonionic backbone chain.[6-8] Because of their special properties, such as excellent mechanical properties, high transparency, and oil resistance, ionomers have mostly been utilized and studied in the solid state. It is now well recognized that the large change in properties of ionomers is due to the clustering of ion pairs in nonionic medium of low dielectric constant.

In contrast to the study of ionomers in the solid state, little work has been done on the solution properties of ionomers. However, during the past several years, the study of solution properties has become active and interesting results have been reported.[9-24] It has now been well established that ionomers show two types of behavior according to the polarity of solvents:[11,23] (1) polyelectrolyte behavior due to electrostatic interactions between ionic groups and small ions in polar solvents; (2) aggregation behavior due to the attraction of ion pairs in low-polarity or nonpolar solvents.

There are many molecular parameters that may influence the solution properties of ionomers. These are molecular weight, ion content, counterion, ion distribution, degree of neutralization, and the presence of simple salts. A systematic study on the effect of ion content was previously reported;[11] the higher the ion content, the larger

0024-9297/89/2222-0754$01.50/0

the polyelectrolyte and aggregation behavior. Light scattering[17,19,21] and neutron scattering[16] give more detailed information on this subject. A systematic study on the counterion effect was recently reported;[20] divalent ions have a larger effect than monovalent ions. Within a series of monovalent ions, the effect on both polyelectrolyte and aggregation behavior increases in the order of Li > Na > K > Cs for carboxylated ionomers, while the order is reversed for sulfonated ionomers. These are understood in terms of solvation–desolvation for various counterion systems.

In this paper, the results of a study on the simple salt effect on the solution properties of ionomers are presented. So far, only limited work has been reported about the salt effect on polyelectrolyte behavior of ionomer solutions.[9,13] Few studies have been reported concerning the salt effect on the aggregation behavior of ionomer solutions.[14]

Experimental Section

Materials. Lightly sulfonated polystyrene (S-SSA) was prepared by solution sulfonation of polystyrene (PS) using the procedure described by Makowski et al.[25] Details of preparation and characterization of ionomers were described elsewhere.[20,22] Ionomer samples with excess neutralizing agent (LiOH) were made as follows: in addition to LiOH needed to neutralize sulfonic acid groups, the calculated amount of excess LiOH (i.e., 100%) was added to acid copolymers in a solvent mixture (benzene/methanol, 90/10 v/v). Then, polymers were recovered by freeze-drying and drying under vacuum at room temperature for at least a week.

In this work lithium was used as a counterion instead of sodium. Also, lithium chloride (LiCl) was used as an added salt. We use the following designation of ionomers;[6] S-0.026SSA-Li means the copolymer of styrene (S) with lithium styrenesulfonate, whose mole fraction is 0.026. Therefore, this ionomer has 2.6 ionic groups per 100 repeat units of PS. The starting polystyrene was a polystyrene standard (Pressure Chemical Co.) with a narrow molecular weight distribution ($M_w = 4.0 \times 10^5$, $M_w/M_n < 1.06$).

Measurements. Ionomer samples obtained by freeze-drying were dissolved in a proper solvent (DMF, THF) under stirring for a day at room temperature. The detailed procedure for viscosity and light scattering measurements was described elsewhere.[20,21] Also, preliminary dynamic light scattering experiments were conducted with a BI-200 SM photogoniometer (Brookhaven) and a BI-2030 correlator (Brookhaven). Details on experiments and data analysis will be reported in the near future.[26]

Results and Discussion

Polyelectrolyte Behavior. It is now well established that ionomers show polyelectrolyte behavior in polar organic solvents.[9,11,13,20] Figure 1 shows the effect of added salt (LiCl) on the viscosity behavior of sulfonated polystyrene ionomer in DMF. It is seen that the reduced viscosity for the no salt system increases sharply with decreasing polymer concentration. This is the typical behavior of classical polyelectrolytes in water.[1-3] By adding simple salts, it is seen that the viscosity decreases, a maximum is observed, and finally, neutral polymer behavior is observed. This is due to the screening of ionic charges along the chain by simple salts. This seems to be the first example that a peak is observed in ionomer/polar organic solvent systems, although many examples are reported for polyelectrolyte/water systems.[1-3] The intrinsic viscosity, $[\eta]$, is plotted as a function of salt concentration in Figure 2. The straight line is obtained between log $[\eta]$ and log C_s, where C_s represents the salt concentration. A similar relationship between log $[\eta]$ and log C_s has been reported for various polyelectrolyte systems, although the slope of the line for the ionomer solution (−0.12) is smaller than for polyelectrolyte systems (−(0.2–0.5)). This is probably due to the smaller change in chain size with the addition of salts for ionomers than for polyelectrolytes, since the number of charges along the chain of the former is much smaller than for the latter.

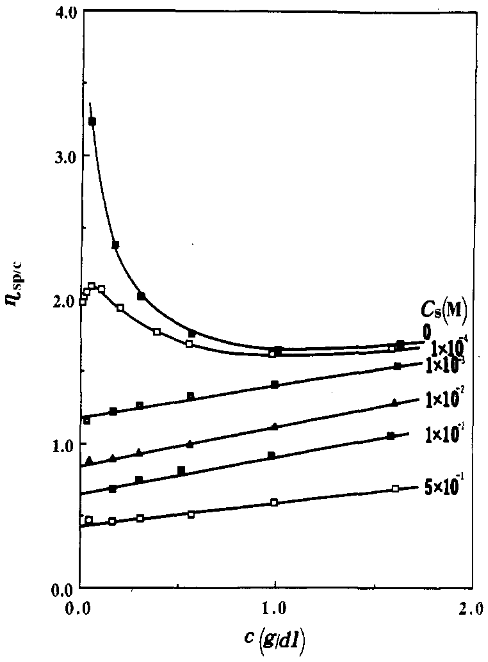

Figure 1. Reduced viscosity, η_{sp}/c, against polymer concentration for S-0.026SSA-Li in DMF with various salt (LiCl) concentrations.

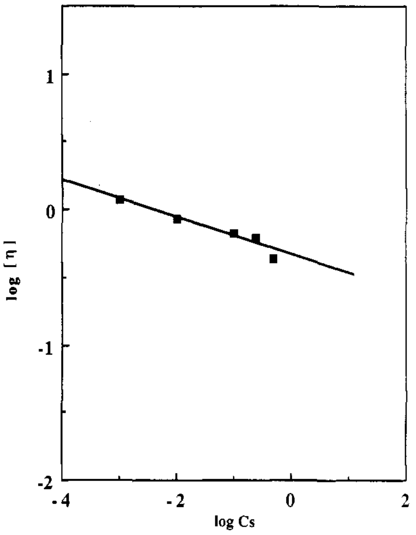

Figure 2. Intrinsic viscosity, $[\eta]$, against salt (LiCl) concentration, C_s, for S-0.026SSA-Li in DMF.

Small-angle light scattering data are shown in Figure 3. For a no-salt system, the characteristic curve for a polyelectrolyte system[19,27,28] is obtained; the reciprocal scattered intensity increases sharply and levels off at higher concentration. We showed in previous papers[19,22] that all curves for ionomer samples with different ion content seemed to converge to the same intercept corresponding to the inverse of weight-average molecular weight. It is also seen that neutral polymer behavior is observed for the 0.1 M LiCl system. The intercept seems to give the correct molecular weight (4.0×10^5), although we used the dn/dc value for undialized samples (we could not dialize the system, because DMF attacks the regenerated cellulose membrane). This is primarily due to the fact that the dn/dc value is relatively insensitive to salt concentration for the ionomer/DMF system. It was reported that for some polyelectrolyte/water systems, dn/dc values for dialized samples and for undialized samples were almost the same.[29]

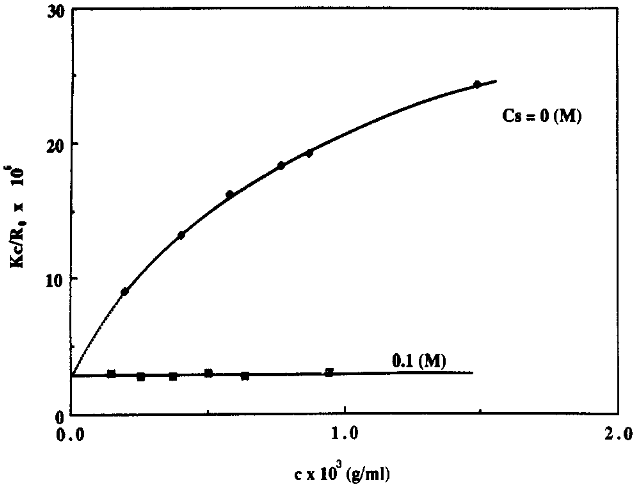

Figure 3. Reciprocal reduced scattered intensity at zero angle, K_c/R_0, against polymer concentration for S-0.026SSA-Li in DMF as well as S-0.026SSA-Li with 0.1 M LiCl.

Finally, the preliminary dynamic scattering data also show the suppression of polyelectrolyte behavior. The cumulant analysis of the data for S-0.026SS-Li in DMF shows a deviation of the correlation curve from single exponential due to the long-range ionic interactions. However, with the addition of LiCl, the second cumulant is very small and the correlation curve is almost the same as that of the PS precursor, i.e., the correlation curve is single exponential. Therefore, the polyelectrolyte behavior of ionomers due to the ionic interactions is completely suppressed by the addition of simple salts. Systematic dynamic light scattering studies of these ionomer solutions will be reported soon.[26]

Aggregation Behavior. The aggregation behavior due to dipolar attractions of ion pairs in nonpolar solvents has been studied extensively. However, most of the studies reported have been conducted for no-salt systems. Figure 4 shows the effect of added salt (LiCl) on the aggregation behavior of ionomers. It was shown that the viscosity behavior is interpreted in terms of intra- and intermolecular aggregation;[11,30] at dilute concentration, the viscosity of the ionomer is smaller than that of its precursor (ex. PS) due to the dominant intramolecular interactions. At higher concentrations, the viscosity of the ionomer is larger than that of its precursor due to the dominant intermolecular interactions. This behavior is observed for the no-salt system of S-0.026SSA-Li ionomer in THF. However, with the addition of simple salts (LiCl), it is seen that both intra- and intermolecular aggregation is suppressed (Figure 4). We showed in a previous study[20] that the interaction between fixed ions and counterions in nonpolar solvents is essentially similar to that in polar solvents. The only difference is that more ion pairs are formed in nonpolar solvents than polar solvents. If this is the case, the suppression of aggregation behavior by the addition of simple salts may be understood in the same way as the suppression of polyelectrolyte behavior by the addition of simple salts: interaction between ionic species is shielded by the ionic atmosphere of added salts.[1,2].

It is of interest to consider the effects of excess neutralizing agent on the aggregation behavior of ionomers (Figure 5). It is seen that excess LiOH enhances the intermolecular interactions, while the degree of intramolecular interaction seems to stay the same. Although we do not know the mechanism of enhancement at this stage, it should be mentioned that in the solid state, the enhancement of physical properties of ionomers by the addition of excess neutralizing agent has been observed.[31,32]

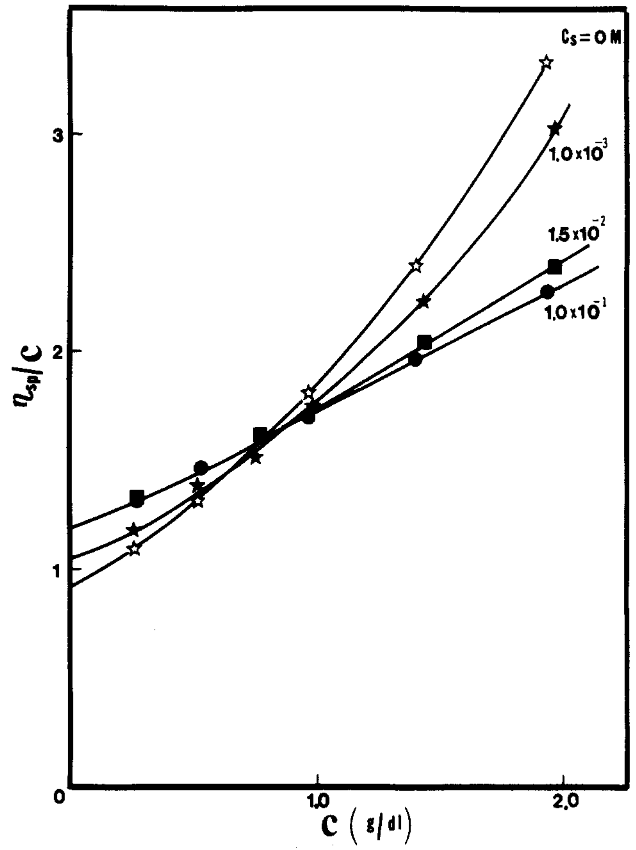

Figure 4. Reduced viscosity, η_{sp}/c, against polymer concentration for S-0.026SSA-Li in THF with various salt (LiCl) concentrations.

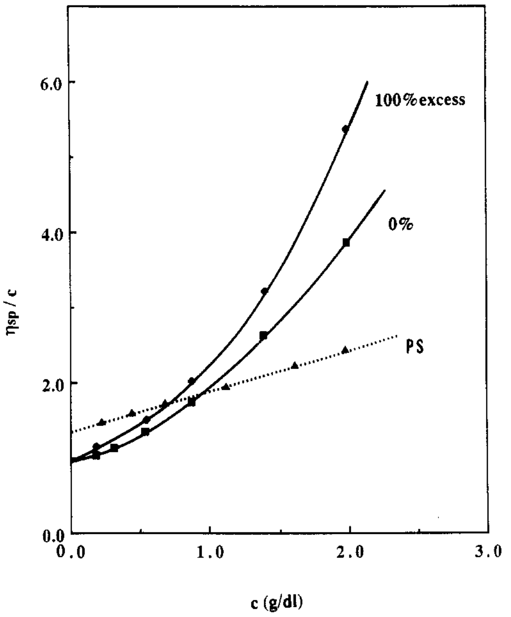

Figure 5. Reduced viscosity, η_{sp}/c, against polymer concentration for S-0.0026SSA-Li in THF for S-0.026SSA-Li as well as S-0.26SSA-Li with 100% excess LiOH.

It is suggested that the excess neutralizing agent strengthens the ionic aggregates and helps to prevent ion hopping. This seems to be consistent with our results in solution.

Conclusion

The effect of simple salts (LiCl, LiOH) on the solution properties of sulfonated polystyrene ionomer was studied. It was observed that the polyelectrolyte behavior of ionomers in a polar solvent was suppressed by the addition of LiCl, as expected from the behavior of polyelectrolytes in water. The single exponential correlation function obtained for ionomer salt systems also shows the suppression of charge effects by small salts. This result also suggests that the molecular weight distribution of ionomers is not affected by the sulfonation reaction of the polystyrene precursor. A similar shielding effect of a simple salt (LiCl) on the aggregation behavior of ionomers in a low-polarity solvent was observed, although it did not completely suppress the aggregation. Also, it was observed that the addition of excess neutralizing agent (LiOH) enhanced intermolecular aggregation. This seemingly opposite effect of different simple salts is of interest in connection with the control of degree of aggregation in ionomer systems. This behavior is currently under investigation by dynamic light scattering technique.

Acknowledgment. We thank I. Chen and Y. Lin for their technical assistance and Drs. J. Scheinbeim and U. P. Strauss for useful discussions. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work is also partly supported by NSF (DMR-8513893).

Registry No. LiCl, 7447-41-8; LiOH, 1310-65-2.

References and Notes

(1) Rice, S. A.; Nagasawa, M. *Polyelectrolyte Solutions*; Academic: New York, 1971.
(2) Oosawa, F. *Polyelectrolytes*; Marcel Dekker: New York, 1971.
(3) Selegny, E., Ed. *Polyelectrolytes*; D. Reidel: Dordrecht, Holland, 1974.
(4) Holliday, L., Ed. *Ionic Polymers*; Applied Science: London, 1975.
(5) Walton, A. G.; Blackwell, J. *Biopolymers*; Academic: New York, 1973.
(6) Eisenberg, A.; King, M. *Ion*-Containing *Polymers*; Academic: New York, 1977.
(7) MacKnight, W. J.; Earnest, T. R. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 41.
(8) Pineri, M.; Eisenberg, A., Ed. *Structure and Properties of Ionomers*; D. Reidel: Dordrecht, 1987.
(9) Roches, C.; Domard, A.; Rinaudo, M. *Polymer* **1979**, *20*, 76.
(10) Lundberg, R. D.; Makowski, H. S. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1821.
(11) Lundberg, R. D., Phillips, R. R. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1143.
(12) Broze, G.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1981**, *14*, 224; **1982**, *15*, 920; **1982**, *15*, 1300.
(13) Niezette, J.; Vanderschueren, J.; Aras, L. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1845.
(14) Tant, M. R.; Wilkes, G. L.; Storey, R. F.; Kennedy, J. P. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1984**, *25*, 118.
(15) Fitzgerald, J. J.; Weiss, R. A. *ACS Sym. Ser.* **1986**, *No. 302*, 35.
(16) 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.
(17) Lantman, C. W.; MacKnight, W. J.; Peiffer, D. G.; Sinha, S. K.; Lundberg, R. D. *Macromolecules* **1987**, *20*, 1096.
(18) Aldebert, P.; Dreyfus, B.; Pineri, M. *Macromolecules* **1986**, *19*, 2651.
(19) Hara, M.; Wu, J. *Macromolecules* **1986**, *19*, 2887.
(20) Hara, M.; Lee, A. H., Wu, J. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1407.
(21) Hara, M.; Wu, J. *Macromolecules* **1988**, *21*, 402.
(22) Hara, M.; Lee, A. H., Wu, J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1985**, *26*(2), 257; **1986**, *27*(1), 335; **1986**, *27*(2), 177; **1987**, *28*(1), 198.
(23) Marina, M. G.; Monakov, Y. B.; Rafibov, S. R. *Uspekhi Kim* **1979**, *48*, 722.
(24) Shade, H.; Gartner, K. *Plaste Kautschuk* **1974**, *21*, 825.
(25) Makowski, H. S.; Lundberg, R. D.; Singhal, G. H. U.S. Pat. 3 870 841, 1975 (assigned to Exxon Research and Engineering Co.).
(26) Hara, M.; Wu, J. *Macromolecules*, to be submitted for publication.
(27) Doty, P.; Steiner, R. F. *J. Chem. Phys.* **1952**, *20*, 85.
(28) Oth, A.; Doty, P. *J. Phys. Chem.* **1952**, *56*, 43.
(29) Tan, J. S.; Gasper, S. P. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1785.
(30) Hara, M.; Wu, J.; Lee, A. H. *Macromolecules* **1988**, *21*, 2214.
(31) Bagrodia, S.; Tant, M. R.; Wilkes, G. L.; Kennedy, J. P. *Polymer* **1987**, *28*, 2207.
(32) Jar, P.; Sauer, J. A.; Hara, M. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1987**, *28*(2), 367.