(8) Trefonas, P.; West, R.; Miller, R. D. *J. Am. Chem. Soc.* **1985**, *107*, 2737.
(9) Miller, R. D.; Hofer, D.; McKean, D. R.; Willson, C. G.; West, R.; Trefonas, P. In *Materials for Microlithography*; Thompson, L., Willson, C. G., Frechet, J. M. J., Eds.; ACS Symposium Series 266; American Chemical Society: Washington, DC, 1984; pp 293–310.
(10) Miller, R. D.; Hofer, D.; Fickes, G. N.; Wilson, C. G.; Marinero, E.; Trefonas, P., III; West, R. *J. Eng. Sci.* **1986**, *26*, 1129.
(11) Zeigler, J. M.; Harrah, L. A.; Johnson, A. W. *SPIE, Adv. Resist Technol. Process. II* **1985**, *539*, 166.
(12) Carberry, E.; West, R.; Glass, G. E. *J. Am. Chem. Soc.* **1969**, *91*, 5446.
(13) Kira, M.; Bock, H.; Hengge, E. *J. Organomet. Chem.* **1979**, *164*, 277.
(14) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1983; Vol. 9, pp 365–397.
(15) Bock, H.; Kaim, W.; Kira, M.; West, R. *J. Am. Chem. Soc.* **1979**, *101*, 7667.
(16) West, R.; David, L. D.; Djurovich, P. I.; Stearly, K. L.; Srinivasan, R. S. V.; Yu, H. *J. Am. Chem. Soc.* **1981**, *103*, 7352.
(17) Trefonas, P., III; Djurovich, P. I.; Zhang, Xing-Hua; West, R.; Miller, R. D.; Hofer, D. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 819.
(18) Imamura, S.; Tamamura, T.; Harada, K.; Sugawara, S. *J. Appl. Polym. Sci.* **1982**, *27*, 937.
(19) Morita, M.; Imamura, S.; Tanaka, A.; Tamamura, T. *J. Electrochem. Soc.* **1984**, *131*, 2402.
(20) Kobayashi, H.; Ueda, T.; Kobayashi, T.; Tagawa, S.; Tabata, Y. *Nucl. Inst. Meth.* **1981**, *179*, 223.
(21) Kobayashi, H.; Ueda, T.; Kobayashi, T.; Washio, M.; Tagawa, S.; Tabata, Y. *Rad. Phys. Chem.* **1983**, *21*, 13.
(22) Tagawa, S. *Radio. Phys. Chem.* **1986**, *27*, 455.
(23) Gohlke, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 2713.
(24) Loubriel, G.; Zeigler, J. *Phys. Rev. B* **1986**, *33*, 4203.
(25) Takeda, K; Teramae, H.; Matsumoto, N. *J. Am. Chem. Soc.* **1986**, *108*, 8186.
(26) Gill, D.; Jagur-Grodzinsky, J.; Swarc, M. *Trans. Faraday Soc.* **1964**, *60*, 1424.

Ionic Conductivity in Branched Polyethylenimine–Sodium Trifluoromethanesulfonate Complexes. Comparisons to Analogous Complexes Made with Linear Polyethylenimine

Caroline S. Harris, Mark A. Ratner,* and Duward F. Shriver*

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60201. *Received December 23, 1986*

ABSTRACT: Complexes between branched polyethylenimine and $NaSO_3CF_3$ were formed with a polymer repeat unit to salt ratio of 6:1, 12:1, and 20:1. All three complexes are amorphous in contrast to linear polyethylenimine which forms partially crystalline complexes at ratios above 6:1 (lower salt concentrations). The 6:1 complex of branched polyethylenimine has a higher T_g (12 °C) and a lower conductivity (10^{-8} S/cm at 40 °C) than the corresponding complex of linear polyethylenimine (−5 °C and 10^{-7} S/cm). The glass transition temperature of the polymer–salt complex decreases by 43 deg upon decreasing the salt concentration from that of the 6:1 complex to that of the 20:1 complex. Correspondingly, the conductivity of the 20:1 complex at 40 °C is 2 orders of magnitude higher than that of the 6:1 complex. N–H stretching frequencies of linear and branched polyethylenimines and their polymer–salt complexes were studied by infrared spectroscopy. An increase in frequency of the N–H stretching mode of both polymers is seen upon complex formation.

Introduction

Solid polymer electrolytes have attracted considerable attention due to their potential application in high energy density batteries.[1,2] These solvent-free systems consist of a solid polymer host in which a salt, usually an alkali metal salt, has been dissolved. Polymer–salt complexes can either be fully amorphous or partially crystalline depending on the polymer and salt employed. Crystalline polymer–salt complexes have the disadvantage of multiphase behavior which greatly complicates the study of their ion-transport and decreases conductivity.[3,4]

Polymer characteristics which should favor polymer–salt complex formation include a low glass transition temperature, T_g, and a high concentration of polar groups.[5] The majority of studies in the past have focused on polymers with ether oxygens as the polar groups. These polymers include linear polymers such as poly(ethylene oxide), PEO, and poly(propylene oxide), PPO, with which the initial studies of polymer electrolytes were made.[2] Other polymer hosts with ether oxygens as the polar group include comblike polymers[6,7] and cross-linked polymer networks.[8,9]

Recently polymers with polar groups other than oxygen have been investigated. One such study from our laboratory utilized poly(alkylene sulfides) to form complexes with the silver salts, silver nitrate and silver trifluoromethanesulfonate.[10] Linear polyethylenimine, LPEI, with secondary nitrogens as the polar groups has been shown by us[11] and others[12] to form conductive polymer–salt complexes with alkali-metal salts. There is also a branched form of polyethyleneimine, BPEI, which has a ratio of primary-to-secondary-to-tertiary nitrogens of 1:2:1.[13,14] BPEI is fully amorphous and has a T_g of 226 K, 27 deg lower than that of LPEI. In the present research, we investigated complex formation between BPEI and sodium trifluoromethanesulfonate, $NaSO_3CF_3$. We determined the conductivity of the BPEI–$NaSO_3CF_3$ complexes and compare our results to our previous study with LPEI.

Experimental Section

BPEI was obtained as a 50% solution in water, average molecular weight 50 000–60 000 (Aldrich Chemical Co.). The polymer was dialyzed under a constant N_2 purge against distilled deionized water which was deaerated by boiling. Cellulose membrane (Union Carbide) was used for the dialysis tubing. After removing the water under reduced pressure, the polymer was further dried under high vacuum (10^{-5} Torr) for 60 h at 58 °C.

Recent grade methanol (MCB) was dried by reflux over iodine-activated magnesium, followed by distillation under a dry nitrogen atmosphere. $NaSO_3CF_3$ was commercial reagent grade material recrystallized from methanol and dried under vacuum at 150 °C. All dried materials were handled in a dry nitrogen or argon atmosphere by using standard Schlenk techniques or in an argon-filled drybox. The polymer–salt complexes were prepared by dissolving stoichiometric quantities of polymer and salt in dried MeOH. After a homogeneous solution was obtained, the methanol was removed under vacuum. The resulting com-

0024-9297/87/2220-1778$01.50/0

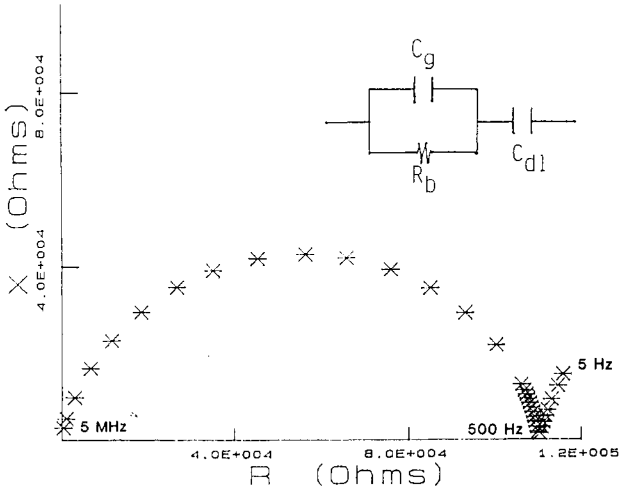

Figure 1. Typical complex impedance plot for BPEI–$NaSO_3CF_3$ complexes with stainless steel electrodes, 6:1 complex at 60 °C. Inset shows equivalent circuit: C_g, geometric capicitance; R_b, bulk resistance; C_{dl}, double-layer capicitance.

plexes were dried at 10^{-5} Torr and 60 °C for 48 h.

Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-2 instrument. Glass transition temperatures were measured at four different heating rates and extrapolated to zero heating rate. X-ray diffraction measurements were obtained with a diffractometer by using Cu Kα radiation. Infrared spectra were obtained with a Nicolet 7199 FT-IR. Sample films were cast from MeOH directly onto Irtran 2 plates (compressed polycrystalline ZnS). The MeOH was evaporated under N_2 purge and the resulting films were dried at 10–5 torr, 70–85 °C for 48 h. A typical polymer film was covered with a thin layer of paraffin oil and then a second plate before removing it from the glovebox and immediately collecting an IR spectrum. The IR spectra of the films showed no bands due to traces of water at the characteristic frequencies, 3400 and 1610 cm^{-1}, when these methods for sample preparation and handling were employed.

Variable-frequency ac impedance and phase-angle measurements were made over the range 50 mHz to 5 MHz by using a Solartron 1250 frequency response analyzer with a Solartron 1286 electrochemical interface and a Hewlett-Packard 4192A LF impedance analyzer. Samples were sandwiched between 12.7-mm diameter stainless steel electrodes in an air-tight cell which was thermostated in an air bath.[15] When the sample was soft a Teflon spacer was used to maintain a constant electrode separation.[16] Spring pressure on the electrodes was used to maintain electrode–sample contact. A representative complex impedance plot for the BPEI–$NaSO_3CF_3$ complexes is whown in Figure 1. This plot is typical for ionic conductors with ion-blocking electrodes in which the spur at low frequencies is attributed to double-layer capacitance.[17]

Results and Discussion

The advantage of BPEI over LPEI is that the former yields homogeneous amorphous salt complexes at low salt concentrations. Complexes were made with nitrogen-to-sodium ratios of 6:1, 12:1, and 20:1. All three complexes were completely amorphous as indicated by the absence of an endotherm in the DSC traces from 210 to 500 K for the 6:1 and 12:1 complexes and 160 to 500 K for the 20:1 complex. The absence of peaks in the X-ray powder diffraction patterns from 5° to 80° (2θ) also indicates the absence of crystallinity in the complexes.

Table I
Glass Transition Temperatures and Conductivity Values for BPEI, LPEI, and Their Complexes with $NaSO_3CF_3$

	T_g, °C	σ(40 °C, S/cm	σ(90 °C), S/cm
BPEI	−47	1×10^{-8}	1×10^{-7}
20:1	−31	2×10^{-6}	7×10^{-5}
12:1	−12	5×10^{-7}	5×10^{-5}
6:1	12	3×10^{-8}	2×10^{-5}
LPEI[11]	−23	$<9 \times 10^{-9}$	
6:1	−5	2×10^{-7}	4×10^{-5}

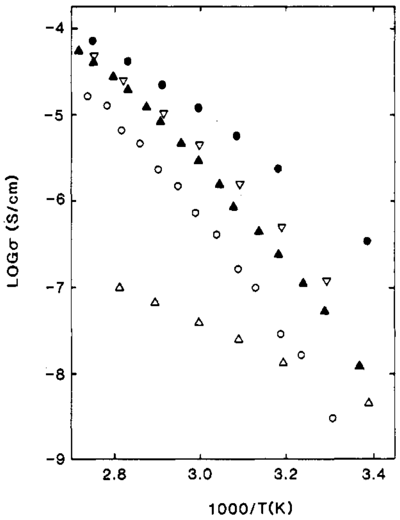

Figure 2. Plot of the temperature-dependent conductivity in Arrhenius coordinates, log σ vs. $1000/T$, for three BPEI–$NaSO_3CF_3$ complexes, nitrogen-to-sodium ratios (○) 6:1, (▽) 12:1, (●) 20:1, and (△) 6:1 (LPEI)[11], (△) BPEI.

The T_g values of BPEI and the 6:1, 12:1, and 20:1 complexes are listed in Table I. For comparison, the glass transition temperatures of LPEI and the amorphous 6:1 LPEI–$NaSO_3CF_3$ complex are also included. The T_g of both the linear and branched PEI increases when complexes are formed and the T_g values increase with an increase in salt concentration. This increase in T_g can be attributed to an inhibition of polymer segment motion brought about by polymer–salt interactions.[8]

In a branched polymer the increased number of chain ends leads to an increased free volume and a lower T_g.[18] The fact that the T_g of BPEI is 24 deg lower than the T_g of LPEI can be attributed to this branching affect. Binding studies with BPEI and transition-metal salts have shown that it is mainly the primary nitrogens at chain ends that coordinate the metal ions.[19] If we assume that this same behavior occurs with alkali-metal ions, then chain end fluctuations should be restricted upon formation of a polymer–salt complex, causing a large increase in T_g. A comparison of the two polymers shows that, as expected, there is a much greater increase of T_g when BPEI forms a 6:1 complex (+59 deg) than when LPEI forms a 6:1 complex (+18 deg).

Variable-temperature conductivity measurements were carried out from 20 to 95 °C. The measurements were repeated after allowing the samples to cool to room temperature overnight. No hysteresis was observed in the conductivity behavior.

The resulting conductivity values for BPEI, LPEI, and the polymer–salt complexes at 40 and 90 °C are listed in Table I. The conductivity data are plotted in Figure 2. As can be seen in Table I, the polymer–salt complexes with a low salt concentration and a corresponding low T_g are the best conductors. Similar relationships have been reported for other polymer–salt complexes[7,8] and are in agreement with models relating polymer segmental motions to high ionic mobility.[8,20,21] A comparison of the 6:1 complexes of the linear and branched PEI serves to further demonstrate the relationship between T_g and conductivity. The conductivity of the 6:1 LPEI–$NaSO_3CF_3$ complex is closer in magnitude to that of the 12:1 BPEI–$NaSO_3CF_3$ complex than it is to the 6:1 BPEI–$NaSO_3CF_3$ complex. Similarly, the T_g values of the 6:1 LPEI–$NaSO_3CF_3$ and

Table II
VTF Parameters for the BPEI- and LPEI-$NaSO_3CF_3$ Complexes[a]

	T_g, °C	T_0, °C	B_a, eV	A, $S \cdot cm^{-1} \cdot K^{1/2}$	$\lvert T_0 - T_g \rvert$, °C
BPEI					
20:1	-31	-123	0.216	189	92
12:1	-12	-87	0.179	117	75
6:1	12	-66	0.132	226	78
LPEI[11]					
6:1	-5	-80	0.188	306	85

[a] Determined from a least-squares fit of conductivity data to the Vogel–Tamman–Fulcher equation.

12:1 BPEI–$NaSO_3CF_3$ complexes are closer in magnitude differing by only 7 deg, while those of the two 6:1 complexes differ by 17 deg. It appears that for the concentration range we have studied, T_g values of the polymer-salt complexes have a stronger influence than the salt concentration on ionic conductivity.

The non-Arrhenius behavior of the temperature-dependent conductivity of the polymer–salt complexes can be seen in the plots of ln σ vs. $1/T$ in Figure 2. Non-Arrhenius behavior was first observed for PEO- and PPO-salt complexes, explained in terms of a free volume model and described by the Vogel–Tamman–Fulcher (VTF) equation,[2] eq 1, where T_0 is the thermodynamic glass

$$\sigma = At^{-1/2} \exp[-B/(T - T_0)] \qquad (1)$$

transition temperature and B is an "apparent" activation energy. Non-Arrhenius conductivity behavior has also been observed for other polymer–salt complexes and described by the VTF equation or the related William–Landau–Ferry (WLF) equation with varying degrees of success.[3,8,22,23]

The contant T_0 in eq 1 is related to the T_g by the expression of $T_0 \cong T_g - 50$. This expression for T_0 is derived empirically and comes from the relationship between the VTF and WLF equations.[24,25] When the conductivity data for the BPEI complexes are fit to the VTF equation it is found that the resulting T_0 values are more than 50 deg below the experimentally determined T_g. As can be seen in Table II, the T_0 values decrease with salt concentration in the same direction as T_g but the value of $|T_g - T_0|$ does not remain constant. The parameters obtained from fitting the conductivity data to eq 1 are listed in Table II.

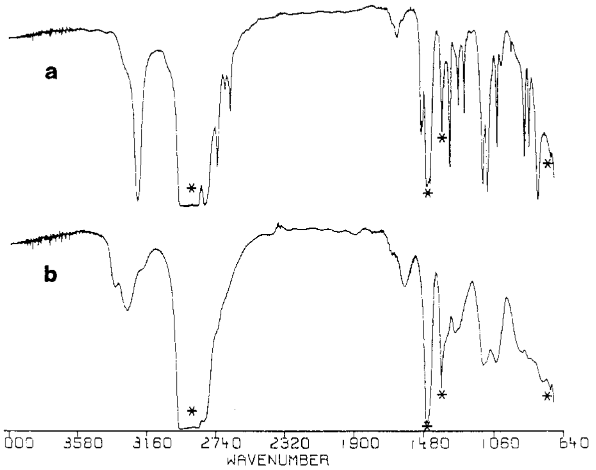

Figure 3. Infrared spectra of (a) linear polyethylenimine and (b) branched polyethylenimine recorded as films on Irtran 2 material plates with paraffin oil. Asterisk indicates paraffin oil bands.

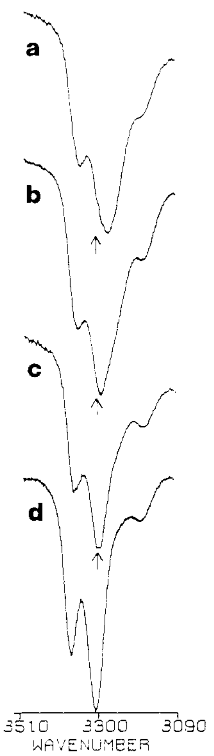

Figure 4. Comparison of N–H stretches in the 3500–3100-cm^{-1} infrared region for branched PEI and BPEI–$NaSO_3CF_3$ complexes: (a) BPEI; polymer repeat unit to salt formula unit ratio (b) 20:1; (c) 12:1; (d) 6:1. Arrows are placed at 3300 cm^{-1} as a guide for comparing band shifts.

The infrared spectra of BPEI and LPEI are shown in Figure 3. The broadness of the bands in the BPEI spectrum is characteristic of the random interactions which occur in amorphous polymers.[26] The primary amino groups in BPEI give rise to symmetric and asymmetric N–H stretching bands at 3277 and 3352 cm^{-1}, respectively; the shoulder at 3190 cm^{-1} is an overtone of the NH_2 deformation at 1594 cm^{-1}.[27] The N–H stretch of the secondary amines coincides with the ν_s(NH) at 3277 cm^{-1}. The secondary amino groups in LPEI give rise to an N–H stretch at 3220 cm^{-1}. Is is unusual for N–H bending modes of secondary amines to give rise to bands above ~1400 cm^{-1}.[28] The band at 1643 cm^{-1} in the LPEI spectrum is more probably due to the C=O stretching mode of the 2% residual acyl groups detected by ^{1}H NMR. This band corresponds to the strong ν(CO) band at 1653 cm^{-1} of the LPEI precursor, poly(ethyloxazoline).

In dilute solution ν_{as}(NH) and ν_s(NH) of primary amines occur around 3500 and 3400 cm^{-1}, respectively. The N–H stretch of secondary amines occurs in the 3350–3310-cm^{-1} region. Hydrogen bonding causes these bands to shift to lower frequencies.[29] For both LPEI and BPEI we see that the NH stretches are well below those of (free) amines. X-ray structure analysis of the LPEI indicates that the polymer forms double-stranded helices which allow every NH group to participate in hydrogen bonding.[30] The low frequency of the NH stretch in LPEI provides further evidence for this hydrogen bonding. The low frequencies of the NH stretching bands of BPEI indicate that hydrogen bonding also occurs in this polymer though perhaps not as strongly.

The NH stretching bands of both polymers shift to higher frequencies when the polymer–salt complexes are formed, Table III and Figure 4. Upon forming a 6:1 complex the NH band of LPEI splits and shifts to 3301 and 3316 cm^{-1}: The asymmetric and symmetric NH_2 stretching bands of BPEI shift to 3374 and 3309 cm^{-1}. In

Table III
N-H Stretching Frequencies of BPEI, LPEI, and Their Complexes with $NaSO_3CF_3$[a]

	ν_{as}(NH), cm^{-1}	ν_s(NH), cm^{-1}		ν_{as}(NH), cm^{-1}	ν_s(NH), cm^{-1}
BPEI	3352	3277	LPEI		3219
20:1	3362	3300	6:1		3317, 3302
12:1	3371	3300			
6:1	3374	3309			

[a] Recorded as films on Irtran 2 material plates with paraffin oil.

the polymer–salt complexes the lone pairs on the nitrogen atoms are involved in solvation of the sodium ions and are no longer available for hydrogen bonding, causing a shift to higher frequency and sharpening of the NH stretching bands, Figure 4, as expected.[28] The transition from a crystalline to an amorphous state, as occurs when LPEI forms a complex, can also influence the NH stretching frequency. The lower density of the amorphous state gives rise to longer interchain distances resulting in weaker hydrogen bonds which would cause an increase in frequency of the NH stretch of the polymer–salt complexes. Such an effect has been observed for nylons in which the NH streching frequency of the amorphous nylon is 10 cm^{-1} higher than that of the analogous crystalline nylon.[31]

Hydrogen bonding to CF_3SO_3 also may occur in the polymer–salt complexes. It is known that perchlorate ions form hydrogen bonds in liquid ammonia though these bonds are weaker than the self-association interactions of ammonia, causing shifts of ν(NH) to higher frequencies.[32] This same behavior may occur for $CF_3SO_3^-$ in the polymer–salt complexes as indicated by similar trends for hydrogen bonding to alcohols[33] and similar basicities for $CF_3SO_3^-$ and ClO_4^-.[34] Inductive effects may also influence the NH stretching frequencies of the polymer–salt complexes by removing electron density from the N–H bonds upon coordination of the sodium ions.[35] Shifts of ν(NH) to lower frequencies by as much as 75 cm^{-1} have been seen for dialkylamines upon coordination of cupric halides. In the case of cupric halides, intramolecular hydrogen bonding and Cu–X π bonding may also contribute to the shift of ν(NH).[36] For the polymer–salt complexes smaller inductive effects would be expected on the basis of the smaller charge of the sodium ion and the greater ionic character of the nitrogen–sodium interactions.

Other changes in the spectrum of BPEI which occur upon complex formation include shifts of the bands at 1128 and 1051 cm^{-1} to 1107 and 1079 cm^{-1}. These bands have been assigned to the asymmetric C–N stretch of primary and secondary amino groups, respectively.[27] The tentative nature of these assignments, though, does not allow a detailed analysis of the specific polymer–salt interactions which could cause these band shifts. Thus the formation of polymer–salt complexes causes band shifts in the infrared spectrum of BPEI which may be useful in studies of the nature of BPEI–salt interactions.

In conclusion, both branched and linear PEI form conductive polymer–salt complexes. The 6:1 complexes of both polymers are amorphous but the glass transition temperature of the 6:1 LPEI complex is lower and the conductivity is higher than that of the BPEI complex. As the concentration of salt is reduced in branched PEI the T_g values decrease and ionic conductivity increases. Around a 20:1 ratio of polymer repeat units to salt, branched PEI is a better conductor than linear PEI because the former is amorphous whereas the latter contains a crystalline phase.

Acknowledgment. This research was supported by the Office of Naval Research and by the NSF Materials Research Laboratory Program through the Northwestern Materials Research Center.

References and Notes

(1) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. *Ext. Abstr. Int. Conf. Solid Electrolytes, 2nd* **1978**, abstr. 6.5.
(2) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Trasport in Solids*; Vashista, P., Mundy, J. N., Shenoy, G. K., Eds.; North-Holland: New York, 1979; pp 131–136.
(3) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.
(4) Lee, Y. L.; Crist, B. *J. Appl. Phys.* **1986**, *60*, 2683.
(5) Papke, B. L.; Ratner, M. A.; Shriver, D. F. *J. Phys. Chem. Solids* **1981**, *42*, 493–500.
(6) Hall, P. G.; Davies, G. R.; McIntyre, J. E.; Ward, I. M.; Bannister, D. J.; LeBroq, K. M. F. *Polym. Commun.* **1986**, *27*, 98.
(7) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
(8) Cheradame, H. In *IUPAC Macromolecules*; Benoit, H., Rempp, P., Eds.; Pergamon: New York, 1982; p 251.
(9) Bouridah, A.; Dalard, F.; Deroo, D.; Cheradame, H.; Le Nest, J. F. *Solid State Ionics* **1985**, *15*, 233.
(10) Clancy, S.; Shriver, D. F.; Ochrymowycz, L. A. *Macromolecules* **1986**, *19*, 606.
(11) Harris, C. S.; Shriver, D. F.; Ratner, M. A. *Macromolecules* **1986**, *19*, 987.
(12) Chiang, C. K.; Davis, G. T.; Harding, C. A.; Takahashi, T. *Macromolecules* **1985**, *18*, 825.
(13) Dick, C. R.; Ham, G. E. *J. Macromol. Sci., Chem.* **1970**, *A4*, 1301.
(14) Jones, G. D.; MacWilliams, D. C.; Braxtor, N. A. *J. Org. Chem.* **1965**, *30*, 1994.
(15) Dupon, R. W. Ph.D. Thesis, Northwestern University, 1983.
(16) Clancy, C. F. Ph.D. Thesis, Northwestern University, 1985.
(17) Billmeyer, F. W., Jr. *Textbook of Polymer Science*, 2nd ed.; Wiley: New York, 1971; p 231.
(18) Takagishi, T.; Okuda, S.; Kuroki, N.; Kozuka, H. *J. Poly. Sci., Poly Chem. Ed.* **1985**, *23*, 2109.
(19) Druger, S. D.; Ratner, M. A.; Nitzan, A. *Phys. Rev. B.: Condens. Matter* **1985**, *31*, 3939; *Solid State Ionics* **1983**, *9/10*, 1115.
(20) Papke, B. L.; Ratner, M. A.: Shriver, D. F. *J. Electrochem. Soc.* **1982**, *129*, 1694.
(21) Watanabe, M.; Oohashi, S.; Sanui, K.; Ogata, N.; Kobayashi, T.; Ohtaki, Z. *Macromolecules* **1985**, *18*, 1945.
(22) Fontanella, J. J.; Wintersgill, M. C.; Calame, J. P.; Smith, M. K.; Andeen, C. G. *Solid State Ionics* **1986**, *18/19*, 253.
(23) Williams, M. L.; Landel, R. F.; Ferry, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 3701.
(24) Adams, G.; Gibbs, J. H. *J. Chem. Phy.* **1965**, *43*, 139.
(25) Zbinden, R. *Infrared Spectroscopy of High Polymers*; Academic: New York, 1964; p 18.
(26) Spell, H. L. *Anal. Chem.* **1969**, *41*, 902.
(27) Colthrup, N. B.; Daly, L. H.; Wiberley, S. S. *Introduction to Infrared and Raman Spectroscopy*; Academic: New York, 1964; p 279.
(28) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 127.
(29) Chatani, Y.; Kobatake, T.; Tadokoro, H.; Tanaka, R. *Macromolecules* **1982**, *15*, 170.
(30) Skrovanek, D. J.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1986**, *19*, 699.
(31) Lemley, A. T.; Roberts, J. H.; Plowman, K. R.; Lagowski, J. J. *J. Phys. Chem.* **1973**, *18*, 2185.
(32) Hardy, L. Charles; Shriver, D. F. *J. Am. Chem. Soc.* **1985**, *107*, 3823.
(33) Rousseau, K.; Farrington, G. C.; Dolphin, D. *J. Org. Chem.* **1972**, *37*, 3968.
(34) Cotton, F. A. In *Modern Coordination Chemistry*; Lewis, J., Wilkins, R. G., Eds.; Interscience Publishers, Inc.: New York, 1960; p 361.
(35) Gerrard, W.; Goldstein, M.; Mooney, E. F. *J. Inorg. Nucl. Chem.* **1969**, *31*, 107.
(36) Tanaka, R.; Ueoka, I.; Takaki, Y.; Kataoka, K.; Saito, S. *Macromolecules* **1983**, *16*, 849.
(37) Johnson, T. W.; Klotz, I. M. *Macromolecules* **1974**, *7*, 149.
(38) Takahashi, T.; Davis, G. T.; Chiang, C. K.; Harding, C. A. *Solid State Ionics* **1986**, *18/19*, 321.