

Preparation and Electrical Response of Solid Polymer Electrolytes with Only One Mobile Species

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Abstract: Ionic conductivity has been induced in the quaternary ammonium polymer poly(diallyldimethylammonium) with chloride or (trifluoromethyl)sulfonate counterions by the introduction of a plasticizer, poly(ethylene glycol) (PEG). Similarly, sodium poly(styrene-sulfonate) becomes a sodium ion conductor when plasticized with PEG. Ion transport properties in these materials are similar to those of the well-known class of solid electrolytes poly(ethylene oxide)-alkali metal salt complexes, except that the ac and dc electrical properties can be attributed to known charge carriers. Conductivity of $10^{-5} \Omega^{-1} \text{cm}^{-1}$ at 25 °C has been achieved for the highly plasticized chloride ion conductor. Conductivity measurements were performed by using ac complex impedance analysis and dc experiments by using ion reversible electrodes. Current-voltage response for the sodium ion conductor is linear, or ohmic, for currents up to at least $12 \mu\text{A}/\text{cm}^2$.

The proposed use of solvent-free polymer electrolytes for high energy density batteries^{1,2} has spurred considerable interest in the ion-transport properties of these materials. Most research in this area has focused on alkali metal ion conduction in solid electrolytes formed by alkali metal salts and poly(ethylene oxide)³ (PEO) or poly(propylene oxide)² (PPO). Although cation transport has been substantiated by use of reversible cation electrodes, i.e., alkali metals,⁴⁻⁶ intercalates,¹ and sodium amalgam,⁷ charge transport by anions may be substantial.^{5,6} Knowledge of the relative mobilities of the ions is important for fundamental studies as well as various applications. Here we report studies of solid polymer electrolytes in which one charge, either the cation or the anion, is anchored to the polymer backbone or pendant group on the polymer so that the ac and dc electrical properties are clearly attributable to a known conducting species.

Polyelectrolytes used in ion-exchange resins are normally solvent swollen and have ionic conductivities similar to those of liquid electrolytes, whereas anhydrous polyelectrolytes exhibit very low conductivity on the order of $10^{-14} \Omega^{-1} \text{cm}^{-1}$. Presumably the low conductivity is due to extensive ion pairing and ion clustering which in effect ionically cross-link the polymer, resulting in brittle, glassy materials at room temperature. Use of plasticizers in polymers is known to increase polymer chain flexibility by reducing intermolecular attractions, increase free volume, and decrease the glass transition temperature, T_g . These changes also are known to increase ionic conductivity in solid electrolytes.⁸⁻¹⁰ Therefore the present research was designed to investigate the possibility that plasticizers might increase the flexibility and hence the conductivity of polyelectrolytes.

Experimental Section

Poly(diallyldimethylammonium chloride) (Polysciences) was precipitated from water in acetone and dried for 48 h under vacuum. Poly(diallyldimethylammonium triflate) (DDAT) (triflate = (trifluoromethyl)sulfonate, SO_3CF_3^-) was prepared from the chloride salt following a modified method of a published procedure¹¹ for quaternary ammonium

triflate salts. A slight stoichiometric excess of triflic acid was added to a stirring, aqueous solution of the chloride salt. The polymer precipitated but was redissolved by adding excess water with about 10% methanol to form a solution with 5% solids. The solvent was removed under vacuum. HCl was removed from the polymer by vacuum codistillation with solvent, a 50/50 (vol/vol) solution of acetonitrile and methanol in which the polymer readily dissolved. Solutions with about 10% solids were used and the process repeated four times until the polymer solution tested chloride free as checked by precipitation of AgCl with a solution of silver triflate in 50/50 acetonitrile/methanol. The polymer was finally redissolved and precipitated in anhydrous ethanol to remove excess triflic acid. The precipitate was filtered and rinsed with ethanol for a 77% yield. Sodium poly(styrene sulfonate), MW 6 000 000 (Polysciences), was used without further purification. Lithium poly(styrene sulfonate) was prepared from poly(styrene sulfonic acid), MW 70 000 (Polysciences), and lithium hydroxide by neutralizing an aqueous solution of the polymer to pH 7. The polymer was precipitated in acetone and dried for 15 h under vacuum.

PEG (average MW 300) (Aldrich) was used as is or purified by passing a 50% aqueous solution first through a Dowex 1-X8 ion exchange column in the OH^- form and second through a Dowex 50W-X16 ion exchange column in the H^+ form to remove inorganic impurities, which might contribute to the conductivity. Conductivities of samples using stock or purified PEG were the same within experimental error, indicating that the observed conductivities do not arise from impurities introduced by the plasticizer.

Plasticized quaternary ammonium polymers were prepared by dissolving the chloride form of the polymer in methanol or the triflate form of the polymer in acetonitrile/methanol. The stoichiometric amount of glycol was then added with use of methanol rinses for quantitative transfer. Solvent was then removed under vacuum, and the resulting plasticized polymers were dried for 72 h under vacuum. Inert atmosphere techniques were used throughout sample preparation since the same procedure in the presence of atmospheric moisture results in brittle, cloudy white polymers which do not conduct. For anhydrous samples, physical changes on exposure to air result from the ready absorption of water, which was observed by IR spectroscopy. Prolonged exposure causes the plasticizer to exude from the polymer. Minute amounts of absorbed water, though, could be reversibly removed by vacuum drying.

Plasticized sodium poly(styrene sulfonate) electrolytes were produced by two methods: (1) Stoichiometric amounts of PEG and a suspension of the polyelectrolyte were stirred in methanol for 2 days. This resulted in a flocculent mixture that produced clear, homogeneous samples upon removal of solvent by vacuum. (2) An analogous procedure was used in which small amounts of water were added to the methanol to produce homogeneous solutions. This procedure also produced clear, homogeneous-appearing samples upon removal of solvent by vacuum. Samples were dried for 48 h under vacuum. Characterization was performed with inert atmosphere techniques.

Infrared measurements were performed on Perkin-Elmer 399 or 283 grating IR spectrophotometers. Films were mounted between salt plates in Nujol to exclude atmospheric moisture. Water was determined by monitoring the 1635cm^{-1} H_2O bending mode on thick films (0.1 mm).

(1) Armand, M. B. Proceedings of the Workshop on Lithium Nonaqueous Battery Electrochemistry, Cleveland, Ohio, June, 1980; pp 261-270.

(2) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In "Fast Ion Transport in Solids"; Vashishta, P., Mundy, J. N., Shenoy, G. K., Eds.; North-Holland: New York, 1979; pp 131-136.

(3) Wright, P. V. *Br. Polym. J.* **1975**, *7*, 319-327.

(4) Weston, J. E.; Steele, B. C. H. *Solid State Ionics* **1982**, *7*, 75-79.

(5) Weston, J. E.; Steele, B. C. H. *Solid State Ionics* **1982**, *7*, 81-88.

(6) Sorensen, P. R.; Jacobsen, T. *Electrochim. Acta* **1982**, *27*, 1671-1675.

(7) Dupon, R. W.; Shitmore, D. H.; Shriver, D. F. *J. Electrochem. Soc.* **1981**, *128*, 715-717.

(8) Papke, B. L.; Raner, M. A.; Shriver, D. F. *J. Electrochem. Soc.* **1982**, *129*, 1694-1701.

(9) Cheradame, H. In "IUPAC Macromolecules"; Benoit, H., Rempp, P., Eds.; Pergamon Press: Oxford, 1982; pp 251-264.

(10) Killis, A.; LeNest, J.-F.; Cheradame, H.; Gandin, A. *Makromol. Chem.* **1982**, *183*, 2835-2845.

(11) Rousseau, K.; Farrington, G. C.; Dolphin, D. *J. Org. Chem.* **1972**, *37*, 3968-3971.

The detection limit for H₂O is 100 ppm. Samples were anhydrous as determined by this technique. Exposure of samples to atmospheric moisture for a few seconds to minutes resulted in readily detectable quantities of H₂O. Anhydrous conditions are important, as indicated by a 10⁴ Ω⁻¹ cm⁻¹ rise in the chloride conductivity (low plasticizer level) on exposure to atmospheric moisture. The effect of moisture on the cation conductors was not very pronounced.

Glass transition temperatures were measured on a Perkin Elmer DSC-2 differential scanning calorimeter with liquid nitrogen as a coolant. Samples were loaded under an argon atmosphere in hermetically sealed aluminum pans, quenched from room temperature at 320 K/min, and heated at rates of 10, 20, and 40 K/min after equilibration. Samples from different preparations for the same materials normally gave good agreement.

Samples for polarized optical microscopy were prepared in a nitrogen atmosphere by sealing thin films between a microscope slide and coverslip with epoxy. All samples, viewed through a Leitz Wetzlar polarizing microscope equipped with a Mettler FP52 hot stage, did not rotate polarized light, indicating that they are amorphous. Samples were heated at a rate of 10 °C/min to observe any physical changes that occur upon heating.

Alternating current impedance measurements over the frequency range 5–5 × 10⁵ Hz were made with a Hewlett Packard 4800A vector impedance meter. Polymer samples were pressed with a 1/2 in. die hand press (maximum pressure 1000 psi) in a nitrogen-filled glove box and loaded in a sealed holder between Pt-disk electrodes. Variable-temperature measurements were carried out with the sample in a thermostated heating chamber controlled by a Bruker B-ST temperature-control unit. For experiments with calomel or sodium amalgam electrodes, a sealed glass cell similar to one described previously⁷ was used. DC potentials were applied with a PAR Model 363 potentiostat-galvanostat and recorded on a strip chart recorder with a full scale response time of 0.5 s. Owing to the thin film nature of mercurous chloride on mercury, steady-state currents with these electrodes were determined on short time scales of ~10 s.

Calomel electrodes were prepared from triply distilled mercury, reagent grade nitric acid, and NaCl as previously described.¹² Sodium amalgam was prepared by dissolving reagent grade sodium in triply distilled mercury to give a solid-liquid amalgam mixture (mole fraction of sodium = 0.086) in order to maintain a constant activity of sodium during polarization experiments.

Results and Discussion

Recently the mechanism of ion transport has been discussed for PEO^{2,8} and PPO²-alkali metal salt complexes or PEO-urethane elastomer networks.^{9,10} Cation-dipole interactions are considered to be the driving force for solvation of alkali metal salts by the polymers, and energetics for these interactions have been discussed.⁸ Little attention has been paid to anion-polymer interactions in these systems which would be ion-van der Waals interactions where the charge on the anion is diffuse and polarizable. These interactions may be weaker than those of the polymer with the cation, so facile anion motion may be likely. The proposed free volume mechanism for ion transport in amorphous solid polymer electrolytes is well supported by experiment, and ionic conductivity has been shown to be much higher in amorphous rather than crystalline materials at the same temperature.^{13,14} Above *T_g* the high amplitude conformation fluctuations of the polymers couple to the ions to enhance their mobility. These factors are important for the design of new polymer electrolytes such as the plasticized polyelectrolytes presented here, where amorphous materials possessing large fractions of free volume were expected as a result of presence of the plasticizer.

Anion conductivity is induced in the quaternary ammonium polymer poly(diallyldimethylammonium chloride) (I, DDAC) by the addition of varying amounts of poly(ethylene glycol) (II, PEG) which acts as a plasticizer. Conductivity of 10⁻⁵ Ω⁻¹ cm⁻¹ has been achieved at 25 °C for the highly plasticized chloride ion conductor. When chloride is replaced by (trifluoromethyl)sulfonate, SO₃CF₃⁻

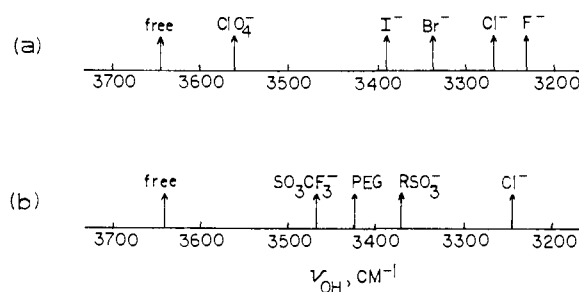
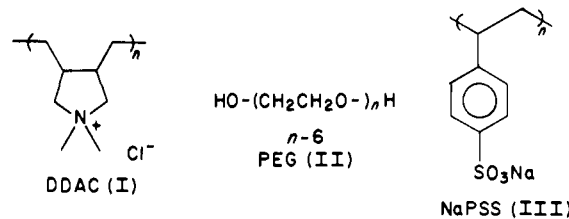


Figure 1. Frequencies of $\nu(\text{O-H})$ for free and H-bonded alcohols: (a) for methanol in CCl₄ from ref 19; (b) free hydroxyl of propylene glycol in CCl₄ from ref 20, neat PEG, and PEG in polymer electrolytes. The species to which the alcohols are hydrogen bonded are listed above the frequency.

or triflate, the conductivity remains high despite the larger bulk of this anion. Cation conductivity also was achieved in sodium poly(styrene sulfonate) (III, NaPSS) when plasticized with PEG, although the interactions are probably different from the anion conductors. It appears that hydroxyl-sulfonate as well as sodium ion-ether oxygen interactions facilitate the formation of these amorphous electrolytes. The conductivities are higher than for their crystalline counterparts, PEO-sodium salt electrolytes, at low temperatures but lower at high temperatures (>60 °C).



Transparency is a very sensitive method for the detection of heterogeneity in polymers. Cloudiness is a characteristic feature of immiscible materials in which the refractive index for the two materials is 0.1 or greater.¹⁵ A good example is that only 0.01% of polystyrene in poly(methyl methacrylate) produces cloudiness due to inhomogeneity.¹⁶ All of the NaPSS-PEG and DDAC-PEG samples used in conductivity measurements were clear and flexible at room temperature, indicating that the plasticizer is incorporated homogeneously into these polyelectrolytes.

Anion Conductors. An important reason for the use of DDAC is that the positive quaternary nitrogen is surrounded by four alkyl groups, thus separating the opposite charges and reducing tight ion pairing. Ion pairing has been shown to significantly reduce the mobility of charge carriers in solid polymer electrolytes.¹⁷ The conductivity of DDAC at 25 °C was not measurable on our instruments, which indicates a conductivity of much less than 10⁻⁹ Ω⁻¹ cm⁻¹, as expected. A number of esters and ethers were tested for compatibility as plasticizers with DDAC. Brittle, cloudy white films resulted when mixtures of DDAC with diisodecylphthalate, dibutyl phthalate, dibutyl sebacate, tetraethylene glycol dimethyl ether, PEO, or poly(vinyl alcohol) (88% hydrolyzed) were cast from methanol or methanol/water solutions at 25 or 60 °C. Segregation of the plasticizer occurred in some cases. The only plasticizer found to be effective was PEG. Since the similar compound tetraethylene glycol dimethyl ether was incompatible, the hydroxyl groups on the polyether must play an important role in the plasticizing interaction. PEG was also found to plasticize the quaternary ammonium triflate polymer, though attempts to plasticize a sulfate-exchanged polymer were unsuccessful.

Infrared spectroscopy substantiates the hypothesis that hydrogen bonding is important in the plasticizer interaction with the polyelectrolytes. Study of the glycol hydroxyl stretches in different polymer electrolyte environments compared to model studies of

(12) Hills, G. J.; Ives, D. J. G. In "Reference Electrodes, Theory and Practice"; Ives D. J. G., Janz, G. J. Eds.; Academic Press: New York, 1961; pp 127-178.

(13) Stainer, M.; Hardy, L. C.; Whitmore, D. H.; Shriver, D. F. *J. Electrochem. Soc.* **1984**, *131*, 784-790.

(14) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91-95.

(15) Masanori, H.; Eisenberg, A. *Macromolecules* **1984**, *17*, 1335-1340.

(16) Yuen, H. K.; Kinsinger, J. B. *Macromolecules* **1974**, *7*, 329-336.

(17) Dupon, R. W.; Papke, B. L.; Ratner, M. A.; Whitmore, D. H.; Shriver, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 6247-6251.

Table I

	mol ratio X ⁻ :hydroxyl	T _g ^b , °C	conductivity, Ω ⁻¹ cm ⁻¹ (activation energy, eV) ^a			
			26 °C	34 °C	98 °C	90 °C
Cl ⁻	2:1	-39 (20)	7 × 10 ⁻⁸	(0.84)	1 × 10 ⁻⁵	(0.52)
	1:1	-53 (10)	4 × 10 ⁻⁶	(0.57)	1 × 10 ⁻⁴	(0.39)
	0.67:1	-58 (10)	1 × 10 ⁻⁵	(0.55)	3 × 10 ⁻⁴	(0.41)
SO ₃ CF ₃ ⁻	2:1	-43 (40)	2 × 10 ⁻⁷	(0.79)	2 × 10 ⁻⁵	(0.57)
	0.67:1	-75 (20)	6 × 10 ⁻⁶	(0.48)	1.5 × 10 ⁻⁴	(0.39)
Na ⁺ : -(CH ₂ CH ₂ O-)	0.25:1	-29 (20)	3 × 10 ⁻⁷	(0.81)	5 × 10 ⁻⁵	(0.50)
	0.17:1	-39 (10)	2 × 10 ⁻⁶	(0.74)	1 × 10 ⁻⁴	(0.33)

^a From the slope of the tangent line using the first three or the last three points on the graph. ^b Heating rate (°C/min) follows T_g in parentheses.

hydrogen bonding of alcohols explains the nature of the interaction of glycol hydroxyl groups with the polyelectrolytes. In comparison with IR data for an isolated hydroxyl group, hydrogen bonding of alcohols to electronegative atoms or ions reduces the frequency and broadens the IR band associated with the O-H stretch. For example, previous hydrogen-bonding studies of methanol with quaternary ammonium halide salts in CCl₄ have shown the monomeric ν(O-H) to shift from a sharp 3644-cm⁻¹ band to a broad 3272-cm⁻¹ band on addition of a chloride salt to the solution.¹⁸ Figure 1a shows that the size of the frequency change upon hydrogen bonding generally increases in the order I⁻ < Br⁻ < Cl⁻ < F⁻. For the perchlorate ion, which has very low basicity, the decrease in ν(O-H) is only ca. 100 cm⁻¹.¹⁹

The utilization of shifts in ν(O-H) for indications of hydrogen bonding between PEG and various anions is complicated by intra- and intermolecular hydrogen bonding within the PEG. Even at high dilution of PEG intramolecular hydrogen bonding will occur between the O-H groups and ether or hydroxyl oxygen atoms which are part of the same molecule. Free hydroxyl groups on glycols are found to have ν(OH) values similar to those of other free alcohols.²⁰ Thus in Figure 1b we employ a value of ca. 3640 cm⁻¹ for ν(O-H) of free hydroxyls in PEG, which contrasts with the value for the neat material which we find to be ca. 3430 cm⁻¹ and is reported in the literature²¹ as ca. 3425 cm⁻¹.

In the plasticized polymer electrolytes, anions compete with oxygen atoms in PEG as hydrogen-bonding acceptors. Figure 1b shows that hydrogen bonding between PEG and anions in plasticized polymer electrolytes occurs and that the shifts in ν(O-H) from that of free hydroxyl follow the same general trends as with the methanol/CCl₄ model studies. When PEG is added to DDAC in the ratio of one hydroxyl to two chlorides, ν(O-H) shifts down to ~3250 cm⁻¹, indicating hydrogen bonding to the more electronegative chloride ion. For the same plasticizer level with triflate rather than chloride, ν(O-H) is 3470 cm⁻¹. This shift indicates that the hydrogen-bonding interaction with triflate dominates over hydrogen bonding with oxygen atoms of PEG. The frequency shift is similar to that between methanol and perchlorate, and this is consistent with the similarity in basicity of perchlorate and triflate ions.¹¹ These results indicate that hydrogen bonding between PEG and triflate is important for plasticizer-polymer compatibility.

Polarized optical microscopy confirms the amorphous nature of the plasticized polymers as no birefringence is observed. Hot-stage optical microscopy indicates the loss of PEG from the plasticized chloride polymers at temperatures above 100 °C. At ambient temperatures, the plasticized electrolytes are stable for at least 1 year. Electrolytes with 0.32, 0.48, and 0.58 weight fractions of PEG were prepared, and these correspond to mole ratios of chloride to hydroxyl group of 2, 1, and 0.67, respectively. Contrary to our earlier communication,²² DSC results indicate

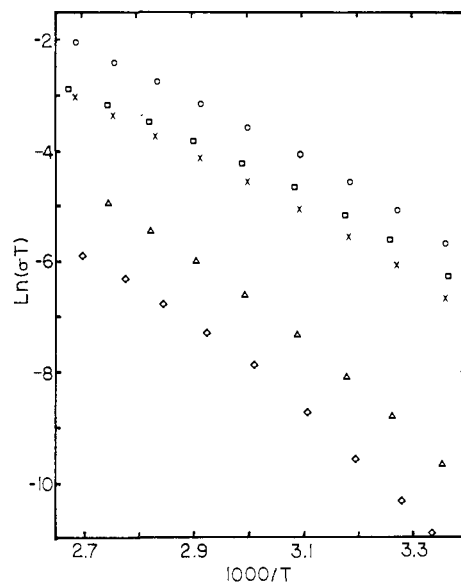


Figure 2. Ionic conductivity (Ω⁻¹ cm⁻¹) vs. temperature plotted as ln(σT) vs. 1000/T for various mole ratios of chloride ion in polymer to hydroxyl group in the plasticizer—(◇) 2:1, (×) 1:1, (○) 0.67:1—and triflate ion in polymer to hydroxyl group—(Δ) 2:1, (□) 0.67:1.

a lowering of T_g as the plasticizer level increases (see Table I). T_g's were broad, normally covering 15 to 25 °C, as would be expected for plasticized polymers.²³ ΔC_p transitions for polymers with low plasticizer levels were weak, necessitating faster scan rates. No endotherms are observed for the melting of pure PEG in the chloride electrolytes, though the highly plasticized triflate electrolyte appears to contain some PEG which gives an endothermic melt (-17 °C) near that of PEG (-30 °C) and it has a T_g of -75 °C which is close to that seen for PEG at -78 °C. T_g for PEG (MW = 194) has been reported as -69 and -70 °C with broadline NMR and torsion pendulum techniques,²⁴ while T_g for diethylene glycol it is found to be -76 and -83 °C with the same techniques, respectively. The low T_g found for PEG (av. MW = 300) may be due to the distribution of molecular weight in the compound as well as the different technique used to measure T_g. The glass transitions seen in the plasticized polymers are most likely due to motions of the plasticizer backbone. A second, higher T_g arising from the polyelectrolyte was not observed because PEG exuded from the sample at higher temperatures.

The variable-temperature electrical-conductivity data yield curved plots of ln(σT) vs. 1/T for the chloride and triflate conductors (Figure 2). This behavior, which is similar to that of diffusion of small molecules through polymers (diffusion α(σT)), has been seen previously for other polymer electrolytes.^{2,11} This type of ion transport has been described by WLF-type equa-

(18) Allerhand, A.; Schleyer, P. *J. Am. Chem. Soc.* **1963**, *85*, 1233-1237.

(19) Symons, M. C. R. In "Electron-Solvent and Ion-Solvent Interactions"; Kevan, L., Webster, B. C. Eds.; Elsevier Scientific Publishing Co.: New York, 1976; pp 311-341.

(20) Buc, H.; Neel, J. C. R. *Hebd. Seances Acad. Sci.* **1961**, *252*, 1786-1788. Masson, M.; Royer, H.; Dupuyrat, R. C. R. *Hebd. Seances Acad. Sci., Ser. B* **1972**, *274*, 62-65.

(21) Matsuura, H.; Miyazawa, T. *Spectrochim. Acta* **1967**, *23A*, 2433-2447.

(22) Hardy, L. C.; Shriver, D. F. *Macromolecules* **1984**, *17*, 975-977.

(23) Shen, M. C.; Tobolsky, A. V. In "Plasticization and Plasticizer Processes"; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1965; pp 118-124.

(24) Faucher, J. A.; Koleske, J. V.; Santee, E. R.; Stratta, J. J.; Wilson, C. W. *J. Appl. Phys.* **1966**, *37*, 3962-3964.

(25) Arai, K.; Eisenberg, A. *J. Macromol. Sci.-Phys.* **1980**, *817*, 803-832.

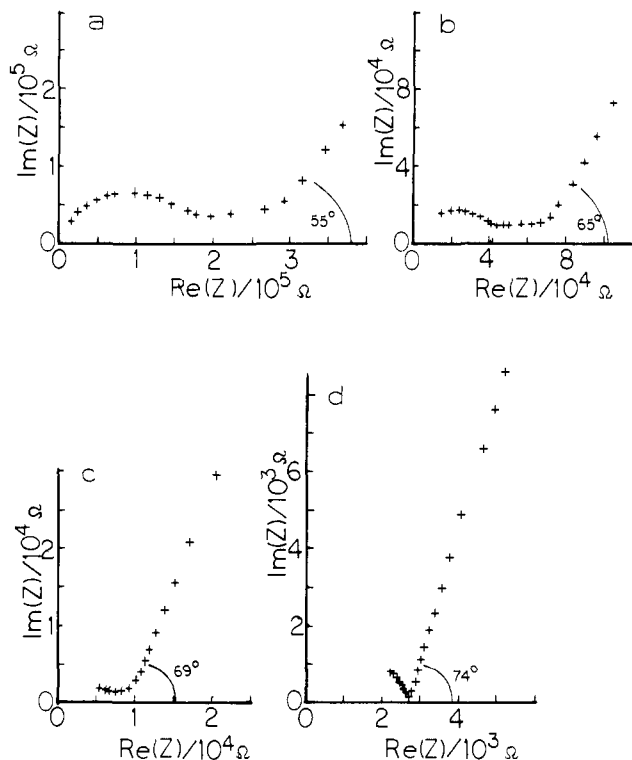


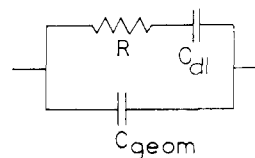
Figure 3. Plots of the imaginary part vs. the real part of the impedance, Z , using ion blocking electrodes. Mole ratio of the Cl^- : OH group at various temperatures: (a) 2:1, 41 °C; (b) 2:1, 60 °C; (c) 2:1, 98 °C; (d) 0.67:1, 26 °C. See text for interpretation.

tions,^{9,10,25} the Vogel-Tammann-Fulcher relation,² and the similar Gibbs configurational entropy model⁸ rather than the Arrhenius law. As seen most clearly with the chloride conductor, increasing the level of plasticizer reduces T_g and hence increases the conductivity (see Table I). Comparison of chloride and triflate conductivities with the same mole fraction of plasticizer is interesting. At the low plasticizer level triflate ion has higher conductivity than chloride ion, while at the higher plasticizer level this trend is reversed. As the plasticizer level is increased, the changes in free volume, electrostatic interactions, and hydrogen bonding may affect conductivity differently, depending on the mobile ion. Since these interactions are subtle and probably have cooperative effects, the proposal of a specific mechanism for this behavior would be speculative. In general though, hydrogen bonding of the plasticizer to the mobile anion probably reduces electrostatic attraction to the counterion and the additional free volume created by the plasticizer enhances ion transport.

Complex impedance plots are typical of those seen for ionic conductors with ion-blocking electrodes (Figure 3). In particular, the spur found at low frequencies is ascribed to double-layer capacitance in a cell with an ion blocking electrode configuration²⁶ (Figure 4). Notable is that the angle of the spur to the horizontal tends toward the ideal 90° as the free volume is increased by increasing either the temperature or the plasticizer level. This behavior may be qualitatively explained as more ideal formation of the double-layer capacitance as the free volume increases, enabling a high concentration of charge-balancing ions to develop at the electrode-electrolyte interface. Deviations of the spur from ideal have been discussed²⁶⁻²⁸ and may be due to a number of physical properties such as surface roughness, large mobility ratios, and some degree of incomplete blocking.

To provide a definitive assignment of the low-frequency spur, calomel electrodes were employed in a second set of complex impedance experiments. The spur seen previously for ion-blocking

Equivalent circuit



Ideal plot

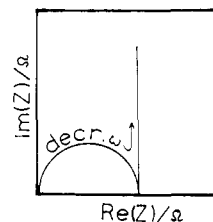


Figure 4. Ideal equivalent circuit and corresponding complex impedance plot for a polymer electrolyte with ion-blocking electrodes. R = bulk resistance, C_{geom} = geometric capacitance, C_{dl} = double-layer capacitance.

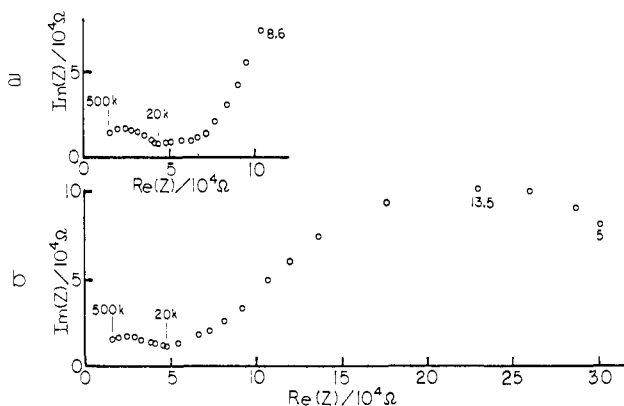


Figure 5. Plots of the imaginary part vs. the real part of the impedance Z for the 2:1 chloride to hydroxyl electrolyte at 60 °C. Frequencies (5 Hz–500 kHz) are listed next to the data points: (a) with Pt electrodes; (b) with $\text{Hg}/\text{Hg}_2\text{Cl}_2$, calomel, electrodes.

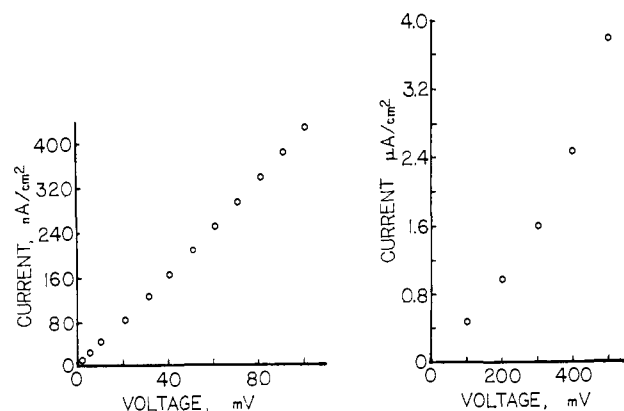


Figure 6. Variation of the steady-state current vs. applied voltage for the 2:1 Cl^- : OH group electrolyte at 60 °C with calomel electrodes.

electrodes (Figure 5a) is now converted to an arc (Figure 5b). According to impedance/frequency response theory,²⁶ this arc can be ascribed to charge-transfer resistance at the chloride ion reversible electrode. This type of response is well characterized for other polymer electrolyte systems with cation reversible electrodes.^{5,6} For electrolytes with both the low and high plasticizer level, the frequency behavior of the charge transfer arc is similar,

(26) Macdonald, J. R. *J. Chem. Phys.* **1974**, *61*, 3977–3996.

(27) Macdonald, J. R. *J. Electroanal. Chem.* **1975**, *66*, 143–147.

(28) Macdonald, J. R.; Garber, J. A. *J. Electrochem. Soc.* **1977**, *124*, 1022–1030.

and this indicates that the electrode kinetics, rather than the electrolyte kinetics, are the rate-limiting factor in the transfer of the chloride ion.

DC studies with ion-reversible calomel electrodes indicate that steady-state currents due to chloride ion transport can indeed be obtained. Plots of steady-state current vs. voltage are shown in Figure 6. The resistance calculated from the slope arises from bulk resistance plus electrode-electrolyte charge-transfer resistance. Good agreement between the dc and ac impedance values is obtained if care is taken to compare data at the same potential. For example, the ac results which are obtained at 270 mV rms (Figure 5b) indicate a total resistance of ~ 350 k Ω whereas the dc resistance for the same sample at the same potential is 325 k Ω . The 7% discrepancy between these two values is within the limits of experimental error. Conversely, if the dc resistance is calculated in the 1–10 mV range, the total resistance is 450 k Ω or a 29% increase over the results determined in the ac experiment.

Cation Conductors. Although PEO readily forms complexes with alkali metal salts, attempts to form complexes of PEO with NaPSS as well as other polyelectrolytes were unsuccessful. But the use of low molecular weight poly(ethylene glycol) analogues of PEO results in clear, compatible films which are flexible at room temperature. Alkali metal ion complexation by low molecular weight PEG is well-known, and thought to be similar to complexation by crown ethers, although weaker.²⁹ Recent studies of polymer blends between polystyrene-poly(methyl methacrylate) copolymer ionomers and PEO have shown that the ion-dipole interaction facilitates formation of blends¹⁵ by similar interactions as in the materials formed in this study.

Plasticization of NaPSS ionomers with glycerol has previously been reported,³⁰ but on materials with only $\sim 2\%$ of the styrene groups sulfonated. In this study, completely sulfonated polystyrene is used to maintain a high salt concentration, thus avoiding localized electrostatic potential wells which might occur in a fractionally substituted polystyrene such as an ionomer (~ 5 – 10% sulfonated).

Polarized optical microscopy indicates that the films are amorphous as no birefringence is observed. The stoichiometries used are 0.49 and 0.59 wt % of PEG which correspond to ratios of Na⁺ to $-(\text{CH}_2\text{CH}_2\text{O}-)$ of $\sim 0.25:1$ and $0.17:1$, respectively. Variable-temperature microscopy for the 0.25:1 electrolyte indicates slow exudation of the plasticizer above ~ 65 °C which ceases when the temperature is lowered again. The sample became only slightly cloudy at 80 °C. The exudation rate was slow enough so that only a small change in the stoichiometry occurred in the time scale of the experiments as indicated by the reproducibility of conductivity plots for the same sample. Both stoichiometries of the plasticized electrolytes are stable for at least 2 months at ambient temperatures. The same type of behavior was also observed for the 0.17 stoichiometry, but this was accompanied by gradual clouding of the sample initiating at 60 °C. After cooling, the sample reverted to its original clear state within a few hours. Here again, conductivity plots are reproducible, indicating that the composite is stable long enough at high temperatures to study its physical properties. As in the case of the anion conductors, DSC indicates a lowering of T_g as the plasticizer level increases (Table I). No endotherms for melting of pure PEG are present, indicating that the components are intimately mixed. Attempts to form similar materials with PEG-dimethyl ether (MW = 400) resulted in cloudy, brittle films, indicating that hydroxyl groups are important in the plasticizing interaction. IR spectroscopy indicates that hydroxyl groups are hydrogen bonded to the sulfonate groups (see Figure 1).

Ionic conductivity and activation energies of these plasticized polyelectrolytes are similar in magnitude to PEO-alkali metal salt complexes (see Figure 7 and Table I). The dramatic increase in conductivity over the unplasticized polymer may be attributed to

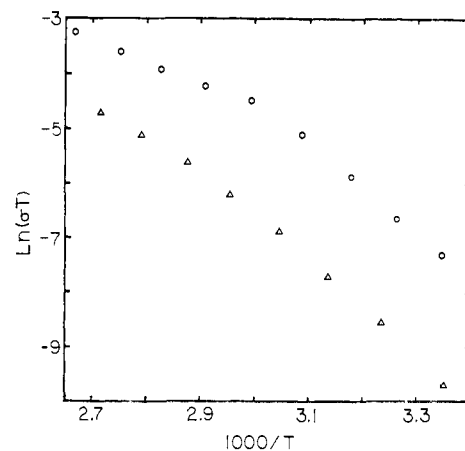


Figure 7. Ionic conductivity, σ ($\Omega^{-1} \text{ cm}^{-1}$), vs. temperature plotted as $\ln(\sigma T)$ vs. $1000/T$ for various mole ratios of Na⁺:ether oxygen in glycol: (Δ) 0.25:1; (O) 0.17:1.

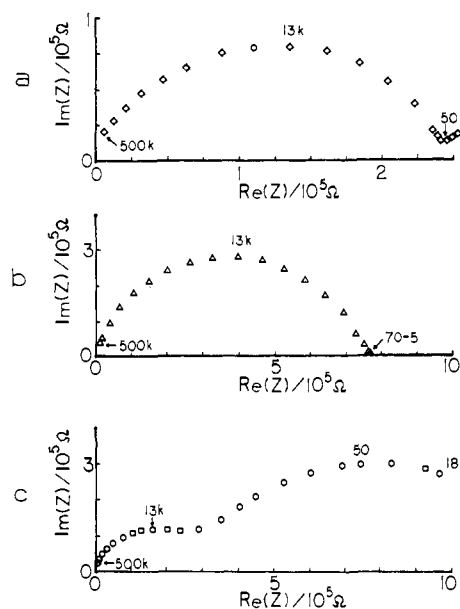


Figure 8. Plots of the imaginary part vs. the real part of the impedance (Z) for the 0.25:1 Na⁺: ether group electrolyte at 25 °C. Frequencies (5 Hz–500 kHz) are listed next to the data points: (a) with Pt electrodes; (b) with sodium amalgam electrodes; (c) with sodium electrodes. Cell constants for the three experiments differ, resulting in varying impedances and thus different arc sizes.

a substantial decrease in tight ion pairing brought about by the PEG-ion interactions mentioned earlier. In addition, a substantial increase in free volume introduced into the polymer by the high concentration of freely rotating end groups of the glycol would be expected to increase the conductivity. With the low plasticizer level, a curved conductivity plot is observed and may be described along the lines described for the anion conductors. For the high plasticizer level, a two-sloped plot is apparent where the temperature with the break in slope corresponds to the temperature of the onset of clouding as noted previously in optical microscopy experiments.

As with the anion conductors, complex impedance plots for the sodium conductors are typical of those seen for polymer electrolytes. Figure 8 shows impedance plots for the 0.25 stoichiometry with differing electrodes. In Figure 8a the beginning of the spur for double-layer capacitance is seen when Pt-ion-blocking electrodes are used. This spur is absent (Figure 8b) when sodium amalgam electrodes are employed, because the double-layer capacitance is eliminated by the reversible Na⁺ transfer at the electrode-electrolyte interface. In addition, no arc for charge-transfer resistance is present as seen with the chloride conductor using calomel electrodes. Sodium metal electrodes result in an

(29) Yanagida, S.; Takahashi, K.; Okahara, M. *Bull. Chem. Soc. Jpn.* 1977, 50, 1386–1390.

(30) Lundberg, R. D.; Makowski, H. S.; Westerman, L. In "Ions in Polymers"; Eisenberg, A., Ed.; American Chemical Society: Washington, DC, 1980; pp 67–76.

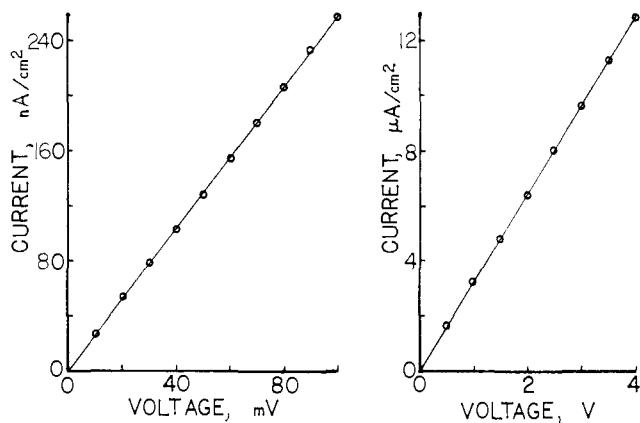


Figure 9. Variation of the steady-state current vs. applied voltage for the 0.25:1 Na⁺:ether oxygen with sodium amalgam electrodes: (a) 25 °C, $1/\text{slope} = 7.80 \times 10^5$ and corresponds to impedance seen in Figure 8b; (b) 29 °C.

arc corresponding to charge-transfer resistance (Figure 8c). This is attributed to the reaction of sodium with the glycol hydroxyl groups to form a passivating layer on the sodium electrodes. Electronic conductivity has been shown to be negligible for similar sodium ion conductors.⁷

Current-voltage behavior is of fundamental interest for conducting materials but has not previously been determined for polymer electrolytes. The current voltage response of NaPSS can be determined by dc methods because this electrolyte contains only one mobile ion, Na⁺, and there is negligible charge-transfer resistance between this material and sodium amalgam electrodes. Figure 9 shows the linear current response for NaPSS-PEG between sodium amalgam electrodes over a range of applied potential from 10 mV to 4 V, indicating ohmic behavior. The current is directly proportional to the applied field for currents up to at least $12 \mu\text{A}/\text{cm}^2$. Higher current densities should be achieved by reducing the pellet thickness below 1 mm which was used for these experiments. For ionic conductors where two mobile species are present, current-voltage response might not be expected to be linear as the activation energies of the charge carriers will in general be different.

Conductivity values from ac and dc methods with sodium amalgam electrodes agree within experimental error (1–3%). A polarization experiment using 100 mV applied voltage shows an immediate response with a constant current for a duration of 2 h (a 3% drop in current occurred which was correspondingly seen in the ac conductivity and may be attributed to a slow reaction of sodium with PEG). For similar experiments in which two mobile species are present, the current has been seen to decrease substantially during this time period.³¹ This polarization experiment may be considered as a control experiment for the method of determining the transport number of ions, indicating

that other mechanisms, such as polymer reorganization, may not contribute significantly to the drop in current over long periods of time. It is important to emphasize the origin of the agreement between ac and dc resistances. The dc resistance, $7.8 \times 10^5 \Omega$, is determined from Figure 9a as $(\text{slope})^{-1}$ and the corresponding ac impedance is determined by the point at which the arc meets the $\text{Re}(Z)$ axis in Figure 8b. The agreement between these two measurements arises because the current is carried by cations only. Similar comparisons with electrolytes containing both mobile cations and anions may not agree because both types of ions contribute to the ac conductivity, whereas the steady-state dc current arises only from the mobile species for which ion-reversible electrodes are used.

Attempts to form lithium analogues of the NaPSS-PEG materials were unsuccessful. The material with 0.25 Li⁺ per ether oxygen is clear and flexible at room temperature after preparation, but it irreversibly becomes cloudy and exudes PEG when heated to ~ 42 °C. Similarly, stoichiometry of the 0.17:1 Li⁺ per ether oxygen was not homogeneous as indicated by its cloudiness and flow properties. A possible explanation for this behavior is a stronger lithium ion-sulfonate ion interaction that cannot be overcome by complex formation with PEG.

Conclusions

Ion-dipole and hydrogen-bonding interactions appear to be important for the formation of the plasticized polyelectrolytes investigated here. Ion transport in these materials is similar to that for other solid, solvent-free polymer electrolytes, but the ac and dc electrical response can be attributed solely to one conducting species. Anionic conductivity, which is not dramatically decreased by substituting the more bulky triflate ion for chloride, is of the same order of magnitude with activation energies similar to those of PEO solid electrolytes and the cation conductor plasticized polyelectrolyte NaPSS-PEG. Current-voltage response for the sodium conductor is ohmic from 10 mV to 4 V.

The success of these experiments indicates that new polymer electrolytes with unity transport for a specified ion may be designed by using internal plasticization, i.e., the copolymerization of ion-containing monomers with plasticizing monomers.³² This technique would overcome the phase-segregation problem due to heat as seen with the cation conductors, or due to water with the anion conductors. The great sensitivity of the chloride ion conductivity to atmospheric moisture indicates potential use for an internally plasticized chloride ion conductor as a sensing device for low levels of moisture.

Acknowledgment. This research was partially supported by the Office of Naval Research. L.C.H. was the recipient of a PPG Industries fellowship.

Registry No. I, 7398-69-8; III, 9080-79-9; DDAT, 96445-41-9; PEO, 25322-68-3; LiPSS, 9016-91-5.

(31) Clancy, S.; Shriver, D. F., manuscript in preparation.

(32) Immergut, E. H.; Mark, H. F. In "Plasticization and Plasticizer Processes"; Gould, R. F., Ed.; American Chemical Society: Washington, DC, 1965; pp 1–26.