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Complex Formation of Poly(ethylenimine) with Sodium Triflate and Conductivity Behavior of the Complexes

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ABSTRACT: Poly(ethylenimine)–$NaCF_3SO_3$ complexes were formed with a polymer repeat unit to salt ratio ranging from 6:1 to 4:1. The complexes change from amorphous to crystalline as the salt concentration is increased. The glass transition temperatures of the amorphous complexes are approximately 15 °C lower than that of the crystalline 4:1 complex. The conductivities of the amorphous complexes are significantly higher than that of the crystalline material. The conductivity plots of all of the complexes follow nearly linear Arrhenius type behavior over the temperature range studied.

Introduction

The potential application of solvent-free polymer–salt complexes as electrolytes in high energy density batteries,[1,2] has stimulated considerable investigation of the fundamental factors governing the behavior of these systems. Most of the focus has been on poly(ethylene oxide) (PEO), which forms complexes with various alkali-metal salts.[2] Vibrational spectroscopy, X-ray diffraction, and EXAFS have provided detailed structural information on PEO–salt complexes.[3,4,5] Free volume and configurational entropy models describe the temperature-dependent and concentration-dependent behavior of the dc conductivity.[2,6] NMR has given insight into the ionic transport mechanism involved in the conductivity behavior of these systems; results indicate that conduction occurs primarily in the amorphous regions of the complexes.[7] The importance of the amorphous phase to ionic transport also is indicated by the enhancement of conductivity seen when a crystalline complex is in a metastable amorphous phase.[8] A set of polymer characteristics that should favor polymer–salt complex formation includes a high concentration of polar groups, polymer flexibility, and low polymer cohesive energy density.[3] Linear poly(ethylenimine) (PEI) ($(CH_2CH_2NH)_n$) has the required closely spaced polar groups and low cohesive energy density. For example, the melting temperature for PEI, 60 °C, compares favorably with that of PEO, 65 °C. In the present research we investigated complex formation between high molecular weight PEI (MW = 100 000) and $NaCF_3SO_3$ (NaTf) and determined the conductivity of these complexes. During the course of our research an independent investigation of low molecular weight PEI (MW = 2000) complexes with NaI was reported.[9]

Experimental Methods

Linear PEI was prepared from poly(ethyloxazoline) (Dow Chemical Co.), average molecular weight 200 000, by acid hydrolysis as described in the literature for a lower molecular weight material.[10] The product was dried at 0.02 torr and 90 °C for 15 h. Ashing of the polymer revealed only 0.02% of inorganic impurities. The product was characterized by a comparison of ^1H NMR spectra,[11] X-ray diffraction patterns,[12] and DSC thermograms[11] with those reported in the literature. Anal. Calcd for $(C_2H_5N)_n$: C, 55.77; H, 11.70; N, 32.50. Found: C, 54.17; H, 11.66; N, 31.19.

Reagent grade methanol (MCB) was dried by reflux over iodine-activated magnesium, followed by distillation under a dry nitrogen atmosphere. Sodium trifluoromethanesulfonate either was commercial reagent grade material or was prepared by neutralizing an aqueous HCF_3SO_3 solution with NaOH to pH 5. All salts were recrystallized from methanol and dried under vacuum at 150 °C. IR spectra of the salt showed no bands due to traces of water at the characteristic frequencies, 3400 and 1610 cm^{-1}.

The polymer–salt complexes were prepared by dissolving stoichiometric quantities of polymer and salt in anhydrous MeOH. After a homogeneous solution was obtained, the methanol was removed under vacuum. The complexes were dried under vacuum at 50–60 °C for 2 days. IR spectra of thin films of the complexes were inspected for bands in the regions around 3400 and 1610 cm^{-1}, arising from trace amounts of water. A broad band at 3300 cm^{-1} due to the N–H stretch of the complexed PEI and smaller bands around 1650 cm^{-1} due to N–H bending partially obscure the water modes and make accurate water detection impossible.

X-ray diffraction measurements were obtained with a diffractometer using Cu Kα radiation. Differential scanning calorimetry (DSC) measurements were performed on a Perkin-Elmer DSC-2 instrument; melting temperatures were obtained at a scan rate of 10 °C/min.

Variable-frequency ac impedance and phase-angle measurements were made over the range 5 Hz to 500 kHz by using a Hewlett-Packard 4800A vector impedance meter. Samples were contained in an airtight cell which was thermostated in an air bath. For these measurements, samples were pressed into the form of disks and sandwiched between Pt electrodes. At temperatures above 60 °C the pressure on the electrodes causes the 5:1 and 6:1 samples to flow, resulting in a short circuit of the cell or changes in the sample thickness. To prevent flow, the samples were pressed onto a Teflon spacer between the electrodes.[13]

Results and Discussion

In a previous study on the acid hydrolysis of poly(*N*-benzoylethylenimine) ($(CH_2CH_2NC(O)C_6H_5)_n$) to give linear PEI, no change was observed in the degree of polymerization from starting polymer to product. On the

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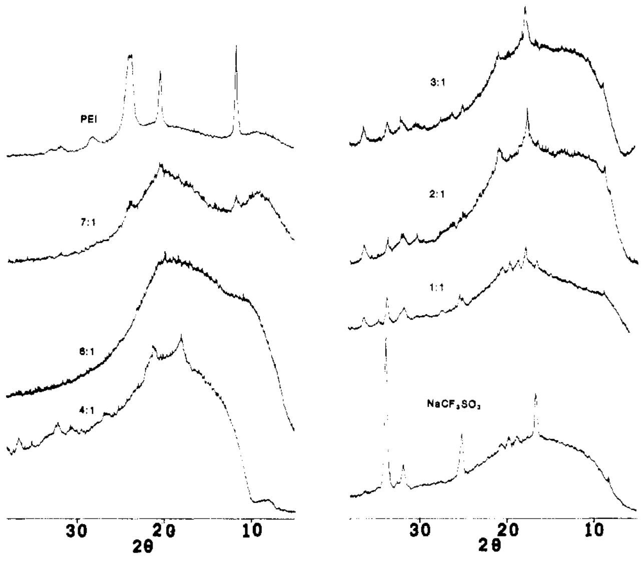

Figure 1. X-ray powder diffraction patterns for PEI–$NaCF_3SO_3$ complexes and for PEI and $NaCF_3SO_3$.

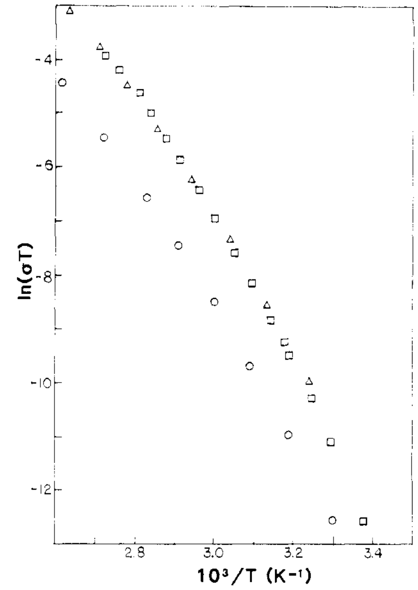

Figure 2. Plot of the temperature-dependent conductivity as ln (σT) vs. 1000/T (K^{-1}) for three $[(EI)_xNaCF_3SO_3]_n$ complexes: (○) x = 4; (△) x = 5; (□) x = 6.

Table I
Glass Transition Temperatures and Conductivity Values for PEI–NaTf Complexes

$[(EI)_xNaTf]_n$	T_g,[a] °C	σ, Ω^{-1} cm^{-1}
$x = 6$	−5	2.4×10^{-7} (41 °C), 5.4×10^{-5} (94 °C)
$x = 5$	−3	3.1×10^{-7} (41 °C), 6.3×10^{-5} (97 °C)
$x = 4$	+9	5.6×10^{-8} (41 °C), 1.2×10^{-5} (95 °C)

[a] Values extrapolated to zero heating rate.

basis of this result and the molecular weight indicated by the manufacturer, the molecular weight of the PEI is estimated to be 100 000. The X-ray diffraction patterns for $[(EI)_xNaTf]_n$ (n is the degree of polymerization and x is the number of ethylenimine repeat units), x = 1, 2, 3, 4, 6, and 7, and for the pure polymer and salt are shown in Figure 1. The minimum concentration of salt at which all the polymer is complexed occurs at the 6:1 polymer repeat unit per salt formula unit. For example, when the salt concentration is reduced to give a 7:1 complex, reflections are seen at 2θ = 23.75°, 20.50°, and 11.65°, which correspond to reflections of the uncomplexed PEI. The 6:1 and 5:1 complexes are largely amorphous, as indicated by the lack of reflections in the X-diffraction patterns. Small irregular endotherms are seen by DSC for the 6:1 and 5:1 complexes. These indicate the presence of a small amount, 10%, of crystallinity. This behavior has been recognized in other polymer–salt complexes.[7,8] The presence of a small amount of crystallinity in the 6:1 and 5:1 complexes also can be seen by optical polarized microscopy.

When the salt concentration is increased to the 4:1 stoichiometry, a partly crystalline complex is formed. A comparison of the X-ray diffraction patterns of the uncomplexed NaTf and PEI with that of the 4:1 complex shows that the major reflections of the complex at 2θ = 18.1°, 21.2°, 32.2°, and 36.7° do not correspond to major reflections of NaTf or PEI. These reflections are attributed to a crystalline complex formed with a stoichiometry of 4:1. A broad endotherm around 160 °C is seen in the DSC of the 4:1 material and is assigned to the melting of the crystalline complex. This assignment is supported by the disappearance of birefringence, indicating a crystalline to amorphous transition around 165 °C.

The maximum amount of salt that can be incorporated into the PEI–NaTf complex is surpassed when the salt concentration is increased to a 3:1 polymer repeat unit to salt ratio. At this concentration the X-ray diffraction pattern has a reflection at 2θ = 33.7°, which corresponds to the strongest reflection of NaTf. The excess salt also can be seen by optical polarized microscopy. As the salt concentration is increased to give 1:1 stoichiometry, the reflections in the X-ray diffraction pattern arising from free salt become more prominent.

Plots of ln (σT) vs. T^{-1} for the three complexes $[(EI)_xNaTf]_n$, x = 6, 5, and 4, are shown in Figure 2. The 6:1 and 5:1 complexes display similar conductivity values, while the conductivity of the 4:1 complex is almost an order of magnitude lower (Table I). The conductivity of the uncomplexed PEI was less than 8.7×10^{-9} Ω^{-1} cm^{-1} from room temperature up to 57 °C. In contrast, a conductivity value of ca. 6×10^{-8} Ω^{-1} cm^{-1} at 60 °C was found in a previous study of a lower molecular weight PEI.[9] The high conductivity observed in that study was probably due to residual NaOH or salt. The rigorous washing and drying procedures used in the present research gave a high-purity polymer with conductivity values that are negligible compared to those of the polymer–salt complexes.

The conductivity data for the three complexes can be fit to the Arrhenius expression, eq 1.

$$\sigma = AT^{-1} \exp(-E_a/RT) \qquad (1)$$

The activation energy (E_a) and the exponential prefactor (A) are obtained from plots of ln (σT) vs. 1/T (Figure 2 and Table II). As an alternative analysis, the conductivity data for the 4:1 complex were separated into a low- and a high-temperature region with the division at $T \simeq 65$ °C. The values for E_a and A from the two regions are listed in Table II. This two-region conductivity behavior has been observed for several crystalline PEO–salt complexes,[2,14-16] with an analogous decrease in the activation energy on going from the low-temperature to the high-temperature region. The transitions in the PEO–salt complexes have been attributed to the melting of small regions of pure or slightly doped PEO.[16] In the case of the 4:1 PEI–NaTf complex, the transition temperature of 65 °C corresponds to a partial melting of the 4:1 complex observed by optical microscopy, and this is close to the melting temperature of pure PEI, 60 °C.

The conductivity data for the 5:1 and 6:1 complexes show a slight deviation from Arrhenius behavior. Curva-

Table II
Activation Energies and Exponential Prefactors[a,b]

	$[(EI)_6NaTf]_n$		$[(EI)_5NaTf]_n$		$[(EI)_4NaTf]_n$	
	E_a, eV	A[c]	E_a, eV	A[c]	E_a, eV	A[c]
Vogel–Fulcher, T_0 = −100 °C[d]			0.230[e]	9.46×10^2		
Vogel–Fulcher, T_0 = −80 °C[d]	0.188[e]	3.06×10^2				
Vogel–Fulcher, T_0 = −50 °C	0.111[e]	7.26	0.111[e]	7.022		
Arrhenius	1.131	1.00×10^{13}	0.972	4.27×10^{11}	1.020	4.36×10^{11}
Arrhenius, T < 65 °C					1.162	7.51×10^{13}
Arrhenius, T > 65 °C					0.891	6.80×10^9

[a] Determined from a least-squares fit of conductivity data to the Vogel–Fulcher expression. [b] Determined from a least-squares fit of conductivity data to the Arrhenius expression. [c] Units are Ω^{-1} cm^{-1} K for the Arrhenius expression and Ω^{-1} cm^{-1} K$^{1/2}$ for the Vogel–Fulcher expression. [d] T_0 value obtained from a least-seuares fit of the conductivity data to the Vogel–Fulcher expression. [e] This is the apparent activation energy, as determined by the least-squares fit to eq 2; in free volume theory, it is related to the reciprocal expansivity.

ture in the conductivity data plotted with Arrhenius coordinates is typical for amorphous polymer–salt complexes and is usually explained in terms of a free volume[2] or configurational entropy[6] regime. It has been shown for a series of amorphous PEO and PPO salt complexes that the temperature dependence of the conductivity can be fit to the Vogel–Fulcher expression, eq 2,[2] where T_0 is the

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

thermodynamic glass transition temperature, the value of which is related to T_g, $T_g \geq 1.15T_0$,[17] and B is an "apparent" activation energy. The curvature in the present data was not large enough to obtain a reliable fit to eq 2. A fit to eq 2 might be obtained if conductivity data were extended to higher temperatures.[18] It is possible that for temperatures which exceed T_0 only slightly, kinetic limitations on free volume motion result in inapplicability of the Vogel–Fulcher form. To check for the possibility that residual water contributes to the conductivity, ac impedance measurements were repeated on a sample after it was subjected to an additional 12 h under high vacuum at 60 °C. No significant change in the conductivity was observed.

As seen in Table I, an increase in salt concentration, from the amorphous 6:1 complex to the semicrystalline 4:1 complex, gives rise to an increase of the T_g of almost 15 °C. This change is paralleled by a drop in magnitude of the conductivity. Similar relationships between T_g and conductivity have been reported for other polymer–salt complexes[19,20] and are in agreement with models relating a lower conductivity and a higher T_g to the inhibition of polymer segmental motions by increased salt concentrations.[6,20,21]

The chemical versatility of PEI makes it attractive for other studies as a possible polymer host in solid electrolytes. For example, the polymer backbone can be chemically modified either by replacement of the hydrogen atom on nitrogen or by quaternizing the nitrogen to produce a polyelectrolyte.[11,22,23] Poly(ethylenimine) also can form complexes with transition-metal salts. Complexes of PEI with the chlorides of Ni, Co, Rh, and Pd with a repeat unit to salt ratio of 2:1 have been reported.[24] In our laboratory preliminary investigations[25] have shown that high molecular weight linear PEI also forms complexes with $CuCl_2$, $CuSO_4$, and $ZnCl_2$. All of these complexes are amorphous, with T_g > 25 °C. Comparison of the present results with a previous study[9] indicates that high and low molecular weight PEI are similar in their tendency to form complexes with sodium salts. However, the 6:1 complexes differ in their physical properties. The high molecular weight 6:1 PEI complex of the present study is elastomeric, whereas the low molecular weight PEI complex is a paste.[26]

We have demonstrated that PEI forms complexes with alkali-metal salts. The ionic conductivity of these complexes follows a temperature dependence similar to that of PEO–salt complexes. The greater chemical versatility of PEI should lead to a variety of interesting ion transport and redox polymers.

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