Macromolecules **1993,** *26,* 2767–2770

Characterization of a Stoichiometric Range of Sodium Salt Complexes of Amorphous Poly[(oxymethylene)oligo(oxyethylene)] by Differential Scanning Calorimetry and ^{23}Na NMR

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Received January 11, 1993; Revised Manuscript Received February 19, 1993

ABSTRACT: Sodium salt complexes of poly[(oxymethylene)oligo(oxyethylene)], $[OCH_2(OCH_2CH_2)_m]_n$ (m = 8–10), are characterized by (1) DSC between 190 and 295 K and (2) ^{23}Na NMR spectroscopy between 208 and 358 K using an inversion–recovery pulse sequence. The complexes studied (polymer$_x$NaAn, An = ClO$_4$ and I, x = 8–150) crystallize near 280 K only for $x > 25$; higher salt concentrations result in complexes which remain amorphous throughout the temperature range studied. Glass transition temperatures are determined for each complex, and the conductivity–temperature plots fit to the VTF equation using the relation $T_0 = T_g - 27$ K. ^{23}Na NMR studies on complexes with x = 50, 25, and 8 show two components distinguished by relaxation rates. Mole fraction, molal concentration, and T_2^* are determined for each component over the temperature range studied, and observed trends are discussed in terms of mobile charge carriers and cross-link sites.

Introduction

Amorphous polyether–salt complexes can exhibit high ionic conductivities and are presently being considered for applications as electrolytes in energy storage devices.[1] Poly(ethylene oxide) (PEO)–salt complexes have been demonstrated to perform adequately above the melting point of the complex (typically 60–100 °C) but are predominantly crystalline, and therefore far less conductive, at ambient temperature. Booth and co-workers[2–4] have described a simple chemical route to high-molecular-weight poly[(oxymethylene)oligo(oxyethylene)] copolymers, $[OCH_2(OCH_2CH_2)_m]_n$, subsequently denoted as (poly(ME$_m$), which are amorphous at ambient temperature. As the synthesis involves the oxymethylene linkage of a distributed sample of poly(ethylene glycol), the average value for m is presented (m_{avg} = 8.7 when PEG 400 is utilized). Complexes of poly(ME$_{8.7}$) with alkali-metal salts are also amorphous at ambient temperature and exhibit ionic conductivities on the order of 10^{-4}–10^{-5} S cm^{-1}.[2–6] We have previously described the characterization of a range of stoichiometries for two sodium salt complexes—poly(ME$_{8.7}$)$_x$NaClO$_4$ and poly(ME$_{8.7}$)$_x$NaI, x = 15–150—by IR spectroscopy, X-ray diffraction, impedance, and dc measurements between 283 and 343 K.[6] Broad maxima in the ionic conductivities were found at x = 25–50, and there was no significant difference in the results obtained on the two salt complexes studied. To further evaluate the relation between polymer dynamics and ionic conduction in amorphous polyether–salt complexes, we here describe results obtained on these complexes using differential scanning calorimetry and ^{23}Na NMR spectroscopy.

Experimental Section

Poly(ME$_{8.7}$) was prepared by a modification of the method published by Booth and co-workers.[3] The ^{13}C and ^{1}H NMR spectra obtained on the resulting polymers closely matched those reported previously for high-molecular-weight polymers.[2] All subsequent manipulations were performed in a drybox or under dry N$_2$ to exclude moisture.

NaClO$_4$ (EM, reagent grade) and NaI (Mallinckrodt, analytical reagent, recrystallized from ethanol/water) were evacuated for several days at 70 °C. CH$_3$CN (Mallinckrodt, HPLC grade) was distilled over P$_2$O$_5$ prior to use. Salt complexes were prepared by codissolving stoichiometric quantities of the polymer and salt in CH$_3$CN, removing the solvent by evacuation, and heating at 70 °C in vacuo for several hours to remove traces of solvent or volatile impurities.

DSC data were obtained between 190 and 295 K using a Netzsch, Inc., STA 419C scanning calorimeter with a low-temperature measuring head and liquid-nitrogen-cooled heating element. Samples (approximately 10 mg) were loaded into aluminum pans in a dry atmosphere and made airtight by wrapping with Teflon tape. The DSC sample chamber was evacuated prior to use and back-filled with dry He. Samples were stabilized by slow cooling to 190 K and subsequently heated at 10, 5, and 2 K/min. Reported transition temperatures are extrapolated to zero heating rate.

^{23}Na NMR data were obtained using a Bruker 400-MHz spectrometer with a 5-mm broad-band probe. Neat samples of polymer–salt complexes were loaded into the tubes under an inert atmosphere. An inversion–recovery (INVREC) pulse sequence at 105.8 MHz, with variable delays in the range of 10 μs to 1 s, was utilized to examine samples between 208 and 358 K at intervals of 15 K.

Results and Discussion

Arrhenius plots of the impedance data for the poly(ME$_{8.7}$)$_x$NaClO$_4$ and poly(ME$_{8.7}$)$_x$NaI were previously reported for x = 150–15[6] and are presented (Figure 1) for poly(ME$_{8.7}$)$_x$NaI to include recent results for the complex with x = 8. Data were also obtained for poly(ME$_{8.7}$)$_x$NaClO$_4$ complexes and are essentially identical. The curved-line response observed in the temperature–conductivity plots is consistent with the VTF behavior common in polymer electrolytes. A rapid decrease in conductivity is observed below 293 K for lower salt concentrations. This effect, due to the formation of a crystalline complex, occurs well above ambient temperature for the corresponding PEO complexes.[1] DSC data (Table I, Figure 2) are presented for poly(ME$_{8.7}$)$_x$NaI and poly(ME$_{8.7}$)$_x$NaClO$_4$ complexes and agree with data obtained by other workers[7,8] on related materials. A melting transition is observed near 280 K at lower salt concentrations (x = 150, 50) only, indicating that poly(ME$_{8.7}$)$_x$NaAn complexes with $x < 50$ do not crystallize in the temperature range studied. These results therefore follow the trends observed in the conductivity–temperature plots. The glass transition for the poly(ME$_{8.7}$) complexes is markedly stronger at higher salt concentra-

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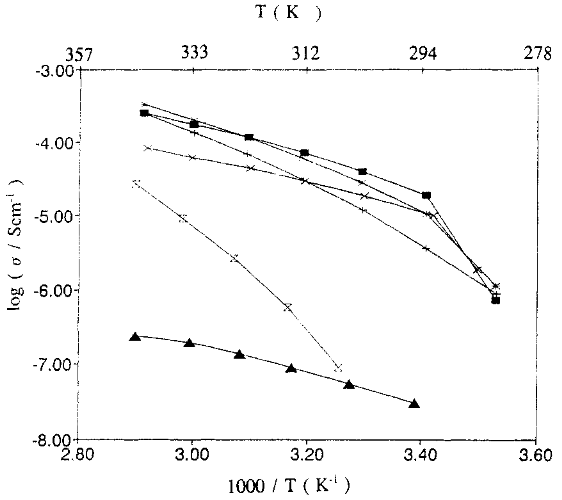

Figure 1. Arrhenius plots for poly(ME$_{8.7}$)$_x$NaI: (⧗) x = 8; (+) x = 15; (*) x = 25; (■) x = 50; (×) x = 150; (▲) uncomplexed poly(ME$_{8.7}$).

Table I. DSC Results Obtained on Poly(ME$_{8.7}$)$_x$NaI Complexes and Calculated VTF Parameters Using T_0 = T_g − 27 K

aPEO$_x$NaI

x	T_g (±3K)	T_m (±3K)	B (eV)	A (S K$^{1/2}$ cm^{-1})
aPEO	205	281		
150	212	278	0.063	0.15
50	211	272	0.080	1.6
25	220		0.090	6.0
15	234		0.090	9.7
8	262		0.103	28.0

aPEO$_x$NaClO$_4$

x	T_g (±3K)	T_m (±3K)
aPEO	205	281
150	208	278
75	214	274
50	211	280
25	220	
15	228	
8	258	

tions, which is reasonable as the entire sample is amorphous for these complexes and undergoes the glass transition. As with other polyether complexes, the glass transition temperature increases with salt concentration, reflecting a change in polymer dynamics due to polymer–salt interactions. The conductivity plots above T_m were fit to the VTF equation:

$$\sigma = (A/T)\exp(-B/(T - T_0)) \qquad (1)$$

and the calculated parameters A and B are presented in Table I. The experimental T_g data were employed directly to determine T_0 (T_0 was taken to be T_g − 27 K to minimize undue correlation between the parameters employed in the fit).

A large exotherm near 230 K is reproducibly observed at x = 50 for both sodium salt complexes and is unaffected by thermal cycling of the samples. The origin of this transition is uncertain, but it is perhaps significant that the transition is observed only at a stoichiometry of x = 50, which is near the maximum salt concentration for the formation of a crystalline phase.

^{23}Na NMR spectroscopy has been employed to examine the chemical environment for Na$^+$ in amorphous polyether complexes. Two Na$^+$ species, distinguished on the basis of relaxation rates, have been detected by Greenbaum and co-workers[8–14] and other groups.[15–17] These two components to the ^{23}Na signal have been ascribed to mobile and bound sodium species, corresponding to the Na$^+$ species with short and long relaxation times, respectively.

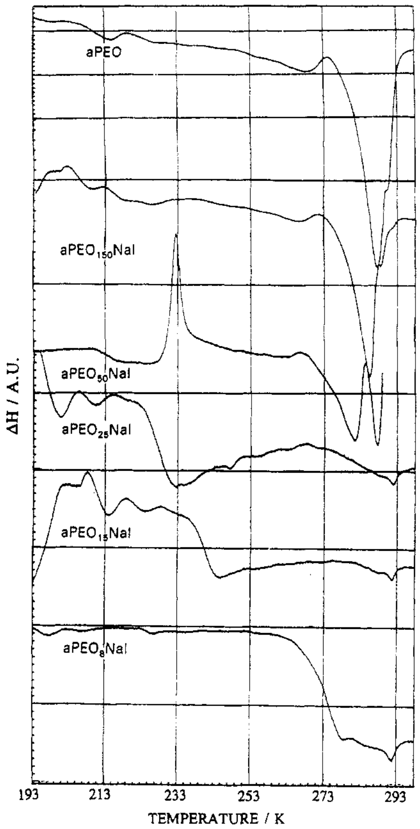

Figure 2. Differential scanning calorimetry data obtained on poly(ME$_{8.7}$)$_x$NaI. Traces shown were collected at 5 K/min.

The inversion–recovery method is employed to examine polymer–salt complexes with three different salt concentrations (x = 8, 25, and 50) in the temperature range of 208–358 K. Complexes with salt concentrations lower than x = 50 are difficult to study because of the low concentration of Na$^+$ in the sample, which is compounded in these complexes because, below T_m, much of the Na$^+$ is in a crystalline phase and cannot be detected. The results we describe agree well with those of other workers and extend the NMR technique to the examination of a range of stoichiometries.

A typical series of NMR spectra obtained (Figure 3) displays the inversion of two overlapping peaks, one sharp and one broad, which are ascribed to Na$^+$ species Na$_A^+$ and Na$_B^+$, respectively. The typical separation of 2 orders of magnitude for the T_1 relaxation times of these signal components provides a unique solution for the relation

$$I(\tau) = M_A e^{-\tau/T_{1A}} + M_B e^{-\tau/T_{1B}} + C \qquad (2)$$

where I = total signal intensity, τ = pulse delay, M_A and M_B = magnetization coefficients for Na$_A^+$ and Na$_B^+$, T_{1A} and T_{1B} = spin–lattice relaxations for these two species, and C = a machine constant. Parameters derived by fitting the peak integrals in Figure 3 are displayed in Table II, and a plot of these calculated and experimental values is displayed in Figure 4. The mole fractions of Na$_A^+$ and Na$_B^+$ are then determined from magnetization coefficients:

$$\chi_A = M_A/(M_A + M_B) \qquad (3a)$$

$$\chi_B = M_B/(M_A + M_B) \qquad (3b)$$

and molal concentrations (mol/kg polymer), c_A and c_B, for Na$_A^+$ and Na$_B^+$ can be derived using the mole fraction and the overall salt concentration.

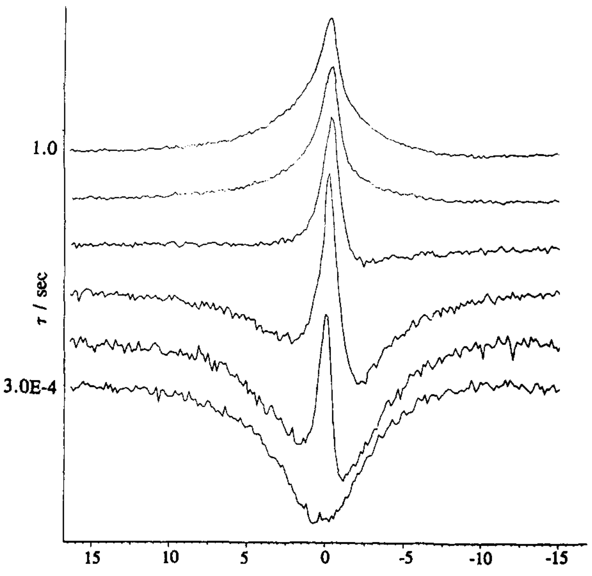

Figure 3. ^{23}Na NMR spectra obtained on poly($ME_{8.7}$)$_{25}$NaI at 343 K using an inversion–recovery pulse sequence with τ = 10 μs to 1 s.

Table II. Parameters Derived for Poly($ME_{8.7}$)$_{25}$NaI by Fitting Equation 2 to the Integrated Peak Intensities from the INVREC Experiment

temp (K)	T_{1A} (s)	T_{1B} (s)	M_A	M_B	C	χ_A	χ_B
358	0.0012	0.12	31	73	115	0.30	0.70
343	0.0009	0.12	38	103	116	0.27	0.73
328	0.0008	0.14	52	130	108	0.29	0.71
313	0.0010	0.16	52	157	87	0.25	0.75
298	0.0014	0.19	38	131	79	0.22	0.78
283	0.0024	0.19	53	159	62	0.25	0.75
268	0.004	0.21	73	185	51	0.28	0.72
253	0.008	0.24	87	184	54	0.32	0.68
238	0.0098	0.14	74	179	15	0.29	0.71
223	0.10	0.11	52	206	−3	0.20	0.80
208	0.14	0.11	33	237	−5	0.12	0.88

In addition, line widths were measured at appropriate pulse delays, τ, to provide T_2^* for each of the Na^+ species. The parameters c_A, c_B, T_{2A}^*, and T_{2B}^* were evaluated for each complex at each of 11 temperatures.

The line width for Na_A^+ increases markedly near the glass transition temperature (Figure 5), demonstrating that the relaxation rate for Na_A^+ is correlated to polymer dynamics. In contrast, the relaxation rate for species Na_B^+ is continuous through the glass transition temperature. These observations indicate that Na_A^+ is involved in charge transport and that a principal mode of relaxation involves ionic motion. The number of charge carriers should therefore be dependent on c_A, although the exact relation cannot be determined without the transport number of Na_A^+. The preexponential factors (A) derived from the VTF relation, which are directly related to the total number of charge carriers in the complexes, and the values obtained for c_A show similar trends for the complexes studied.

The results obtained strongly argue against the notion that Na_A^+ represents a single ion and Na_B^+ an ion aggregate since (1) the concentration ranges examined are all beyond the range where free ions predominate[4] and (2) χ_A increases, rather than decreases, with salt concentration. A more plausible explanation is that these two species are distinguished by their degree of interaction with the polymer (hence the previous notation mobile and bound). The VTF behavior of these complexes already suggests that the mobility of Na_A^+ is dependent on polymer dynamics; Na_B^+ must be still more strongly bound.

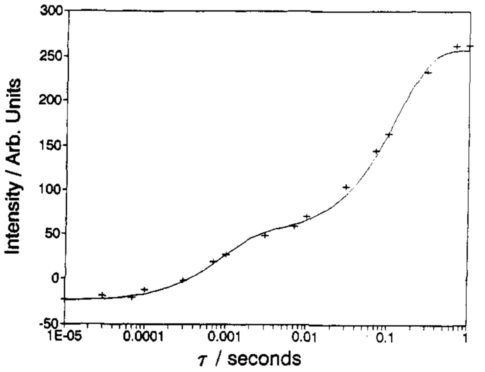

Figure 4. ^{23}Na signal peak intensity vs pulse delay, τ, in inversion–recovery experiments for poly($ME_{8.7}$)$_{25}$NaI at 343 K. The solid line corresponds to the best fit using calculated parameters.

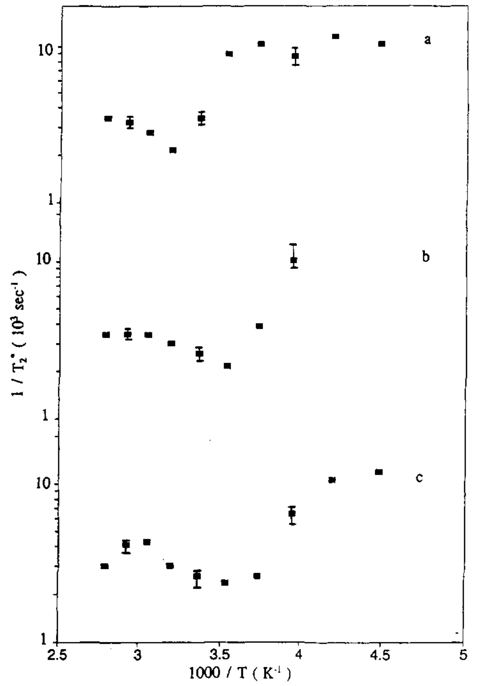

Figure 5. $1/T_2^*$ vs $1000/T$ for the mobile component (Na_A^+) in poly($ME_{8.7}$)$_x$NaI: (a) x = 8; (b) x = 25; (c) x = 50.

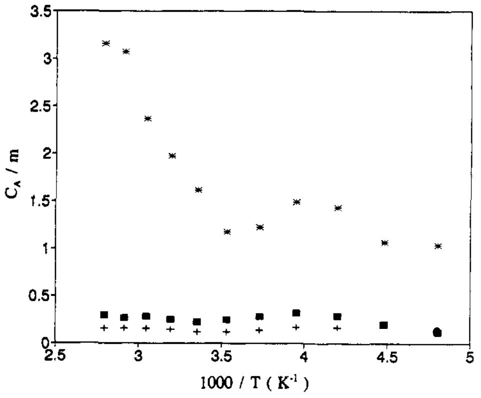

Figure 6. Concentration of Na_A^+ in poly($ME_{8.7}$)$_x$NaI vs $1/T$: (+) x = 50; (■) x = 25; (*) x = 8.

Previous studies have indicated that the relative abundance of Na_A^+ decreases for complexes with softer anions.[8] One possibility is the assignment of Na_B^+ to cross-links of the type $R_2O–Na_B^+–An^-–Na_B^+–OR_2$. There is some evidence for the action of Na_B^+ as a cross-linker: a plot of $1000/T_g$ vs c_B (Figure 8) shows the approximately linear relation expected if c_B is associated with the cross-link density for the complex. An unexpected result, however,

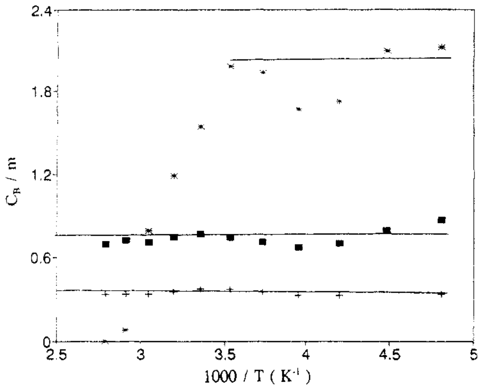

Figure 7. Concentration of Na_B^+ in poly(ME$_{8.7}$)$_x$NaI vs $1/T$: (+) $x = 50$; (■) $x = 25$; (*) $x = 8$. The line drawn through each set indicates the value for c_B in Figure 8.

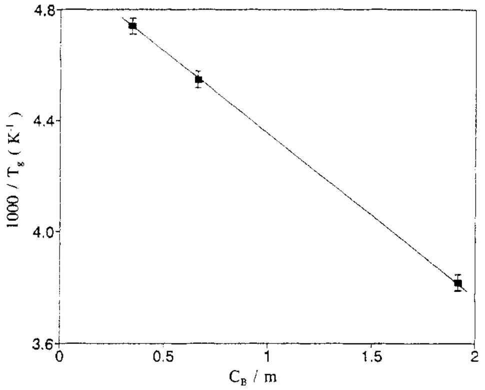

Figure 8. $1000/T_g$ vs c_B for poly(ME$_{8.7}$)$_x$NaI complexes with x = 50, 25, and 8.

is the strong relation of c_B with temperature above T_g for poly(ME$_{8.7}$)$_8$NaI, which indicates a more complicated relation between polymer dynamics and salt concentration than indicated by the VTF model alone.

Acknowledgment. The authors gratefully acknowledge supporting grants from the Petroleum Research Fund (PRF-23923-G3), the National Science Foundation (DMR-9157005), and Allied-Signal Corp.

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