

# Electrical conductivity, differential scanning calorimetry and nuclear magnetic resonance studies of amorphous poly(ethylene oxide) complexed with sodium salts

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$^{23}\text{Na}$  nuclear magnetic resonance (n.m.r.), differential scanning calorimetry (d.s.c.) and vacuum and high-pressure electrical conductivity measurements have been carried out on amorphous, oxymethylene-linked poly(ethylene oxide) (PEO) containing various sodium salts. The d.s.c. studies show that the uncomplexed material is semicrystalline. However, all results indicate that the complexed material is completely amorphous. The  $^{23}\text{Na}$  n.m.r. measurements demonstrate the existence of both bound and mobile sodium ions in the complex, and motional line narrowing of the mobile  $^{23}\text{Na}$  resonance above  $T_g$ . The NaI complex contains a substantially higher percentage of bound sodium than the corresponding  $\text{NaCF}_3\text{SO}_3$  material, suggesting the presence of strong cation-anion interactions.

(Keywords: nuclear magnetic resonance; differential scanning calorimetry; electrical conductivity; poly(ethylene oxide); sodium salts)

## INTRODUCTION

Polymer electrolytes based on poly(ethylene oxide) (PEO) have been investigated extensively in recent years<sup>1-3</sup>. However, high-molecular-weight PEO and many of its alkali-metal salt complexes tend to be highly crystalline at room temperature. Since ion transport occurs primarily in the amorphous phase, many studies have been directed towards ethylene oxide copolymers with flexible backbone polymers such as polyphosphazenes<sup>4</sup> and siloxanes<sup>5</sup>. The resulting materials are generally amorphous, with relatively low glass transition temperatures,  $T_g$ . The latter property is particularly important in applications requiring reasonably high ionic conductivity at room temperature. Recently it has been shown that crystallinity can be suppressed in PEO by incorporating evenly (but not regularly) spaced units into the PEO chain<sup>6</sup>. In many cases the resulting materials, when complexed with salts, have been found to have room-temperature conductivity which rivals that of the more complicated polyphosphazene (MEEP) system<sup>7</sup>.

A second important issue in polymer electrolyte science involves the need to quantify and understand the extent of cation-anion interactions in materials of moderately high salt concentration ( $\sim 4$ -20 ether oxygens/cation). Spectroscopic evidence for ion pairing or higher aggregation has been inferred from vibrational studies<sup>8,9</sup>, while systematic conductivity vs. salt concentration

measurements<sup>10,11</sup> have led to similar conclusions.  $^{23}\text{Na}$  nuclear magnetic resonance (n.m.r.) has been shown to be an effective probe of  $\text{Na}^+$  ion mobility<sup>5,12,13</sup>. In most Na-salt-containing polymer electrolytes, the n.m.r. results have demonstrated the presence of both bound and mobile sodium. The bound  $^{23}\text{Na}$  signal has previously been identified with large, relatively immobile clusters of ions, due to its similarity to the spectra of uncomplexed sodium salts<sup>13</sup>.

Amorphous complexes formed between oxymethylene-linked PEO and NaI or  $\text{NaCF}_3\text{SO}_3$  have been investigated by electrical conductivity, differential scanning calorimetry (d.s.c.) and  $^{23}\text{Na}$  n.m.r.

## EXPERIMENTAL

The preparation of oxymethylene-linked PEO has been described by Nicholas and coworkers<sup>6,7</sup>. Two Na salt complexes were prepared, each in the ratio of nine ether oxygens/sodium, by dissolving appropriate quantities of polymer and either iodide or triflate salt in acetonitrile. The resulting solutions were cast onto Teflon dishes and dried in a roughing vacuum to yield thin, flexible films.

The d.s.c. and electrical conductivity techniques are described elsewhere<sup>5</sup>. The n.m.r. measurements were performed at 80.7 MHz utilizing standard pulse techniques. Details regarding the instrumentation and analysis (e.g. subtraction techniques) are given elsewhere<sup>5</sup>.

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RESULTS AND DISCUSSION

The d.s.c. thermogram (recorded at 10 K min<sup>-1</sup>) for 'amorphous' PEO is displayed in Figure 1. A relatively weak glass transition at about -60°C is apparent along with a strong endotherm beginning at about 0°C. This implies that the material is actually semicrystalline and is amorphous at room temperature because the crystallites have melted. However, when the PEO is complexed with salts in a 9:1 oxygen:cation ratio, it becomes completely amorphous. This is apparent from the d.s.c. thermograms shown in Figures 2 and 3 where only a strong event characteristic of a glass transition is seen. The 'central' glass transition occurs at about 251 K for PEO<sub>9</sub>NaCF<sub>3</sub>SO<sub>3</sub> and 259 K for PEO<sub>9</sub>NaI. The origin of the d.s.c. feature in the 110–125°C region in Figure 3 is not known at the present time although the possibility that it is attributable to salt precipitation<sup>13</sup> has been ruled out by n.m.r. measurements to be discussed later.

The electrical conductivity results shown in Figure 4 also show that the complexed materials are amorphous in that they exhibit VTF or WLF behaviour<sup>14</sup>. To treat the data quantitatively, the VTF equation<sup>5</sup>:

$$\sigma = AT^{-1/2} \exp[-E_a/k(T - T_0)] \quad (1)$$

was fitted to the data and the best-fit parameters are listed in Table 1. The values of E<sub>a</sub> are significantly larger than

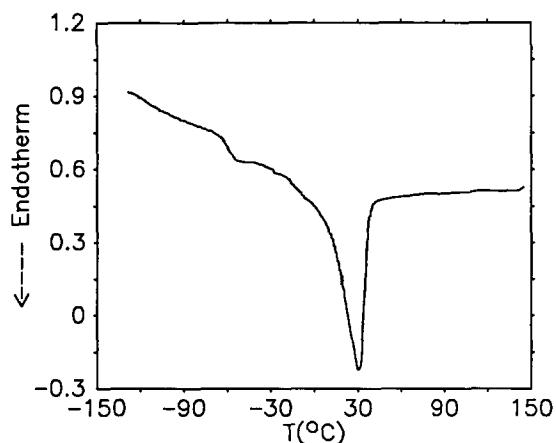


Figure 1 D.s.c. plot for uncomplexed PEO. The data were taken at 10 K min<sup>-1</sup>

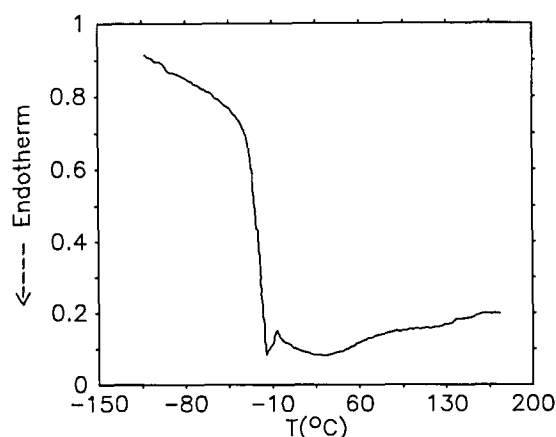


Figure 2 D.s.c. plot for PEO<sub>9</sub>NaCF<sub>3</sub>SO<sub>3</sub>. The data were taken at 10 K min<sup>-1</sup>

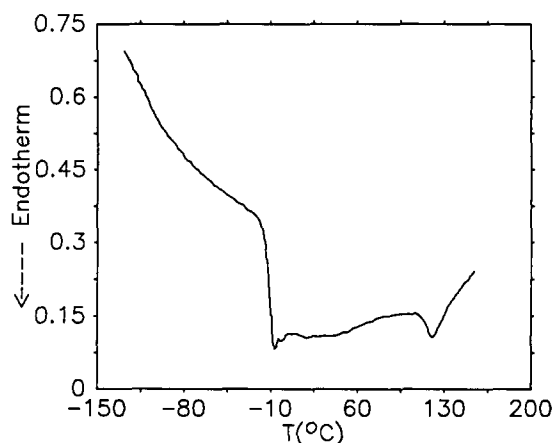


Figure 3 D.s.c. plot for PEO<sub>9</sub>NaI. The data were taken at 10 K min<sup>-1</sup>

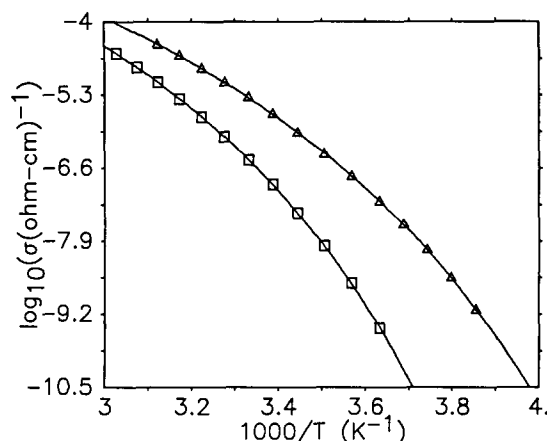


Figure 4 Arrhenius plot of the vacuum electrical conductivity data. The triangles are the data for PEO<sub>9</sub>NaCF<sub>3</sub>SO<sub>3</sub> and the squares are the data for PEO<sub>9</sub>NaI. The full curves are the best-fit VTF equation

those which are found for poly(propylene oxide) (PPO)<sup>15,16</sup>. However, the values of T<sub>0</sub> reflect the trends in the glass transition as it is lower for PEO<sub>9</sub>NaCF<sub>3</sub>SO<sub>3</sub> than for PEO<sub>9</sub>NaI (it is 44 and 57°C lower than the central glass transition for the iodide and triflate complexes, respectively). The observed values of T<sub>g</sub> - T<sub>0</sub> are similar to the results obtained in other materials<sup>5,15</sup>.

For completeness, the WLF equation:

$$\log_{10} \left( \frac{\sigma(T)}{\sigma(T_g)} \right) = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \quad (2)$$

and modified VTF equation:

$$\sigma = A' \exp[-E_a/(T - T_0)] \quad (3)$$

were fitted to the data. The best-fit parameters are given in Tables 1 and 2.

The effect of pressure on the electrical conductivity is shown in Figure 5. A quadratic equation:

$$\log_{10} \sigma = \log_{10} \sigma_0 + aP + bP^2 \quad (4)$$

was fitted to the data and the results are given in Table 3. In addition, an activation volume was calculated via:

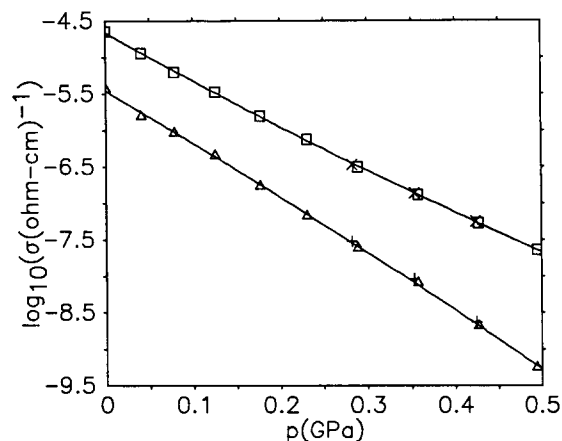
$$\Delta V^* = kT \, d \ln \sigma / dp \quad (5)$$

**Table 1** Best-fit VTF parameters

	VTF equation (1)				Mod. VTF equation (3)			
	R.m.s. deviation	$\log_{10}[A \text{ (S cm}^{-1} \text{ K}^{1/2})]$	$E_a \text{ (eV)}$	$T_0 \text{ (K)}$	R.m.s. deviation	$\log_{10}[A' \text{ (S cm}^{-1})]$	$E'_a \text{ (eV)}$	$T'_0 \text{ (K)}$
PEO <sub>9</sub> NaCF <sub>3</sub> SO <sub>3</sub> Vacuum	0.0048	1.97	0.128	194.0	0.0049	0.615	0.125	194.7
PEO <sub>9</sub> NaI Vacuum	0.067	2.12	0.124	214.6	0.0065	0.768	0.122	215.1

**Table 2** D.s.c. results and best-fit WLF parameters

	$T_g \text{ (K)}$	$C_1$	$C_2 \text{ (K)}$	$\log_{10}[\sigma(T_g) \text{ (S cm}^{-1})]$	R.m.s. deviation
PEO <sub>9</sub> NaCF <sub>3</sub> SO <sub>3</sub>					
Onset	243	13.0	48.3	-12.4	0.0049
Central	251	11.2	56.3	-10.5	0.0049
End	258	9.93	63.3	-9.31	0.0049
PEO <sub>9</sub> NaI					
Onset	253	16.2	37.9	-15.4	0.0065
Central	259	14.0	43.9	-13.2	0.0065
End	265	12.3	49.9	-11.5	0.0065

**Figure 5** Typical data and best-fit quadratics for the pressure dependence of the electrical conductivity. The upper curve ( $\square$ , decreasing pressure;  $\times$ , increasing pressure) are the data for PEO<sub>9</sub>NaCF<sub>3</sub>SO<sub>3</sub> and the lower curve ( $\triangle$ , decreasing pressure;  $+$ , increasing pressure) are data for PEO<sub>9</sub>NaI. The data are at 41°C**Table 3** Best-fit parameters in equation (4) and activation volumes for isothermal data

Maximum pressure (GPa)	$T \text{ (K)}$	R.m.s. deviation	$\log_{10}[\sigma_0 \text{ (S cm}^{-1})]$	$a \text{ (GPa)}^{-1}$	$b \text{ (GPa)}^{-2}$	$\Delta V^* \text{ (cm}^3 \text{ mol}^{-1})$
PEO <sub>9</sub> NaCF <sub>3</sub> SO <sub>3</sub>						
0.50	314.1	0.0134	-4.65	-6.80	+1.59	40.9
0.50	353.3	0.0059	-3.35	-4.37	+1.22	29.6
PEO <sub>9</sub> NaI						
0.50	314.1	0.0386	-5.42	-7.56	-	45.5

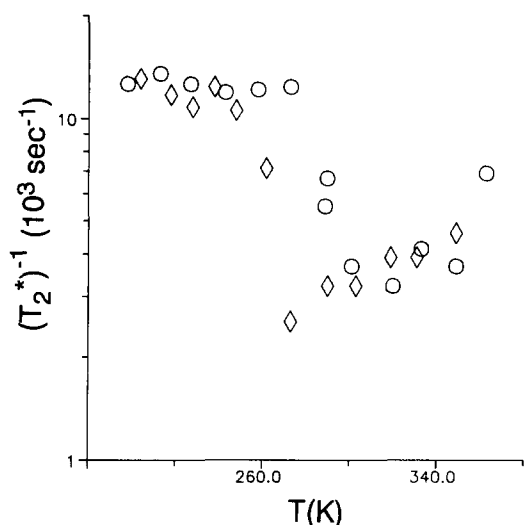
The results are consistent with those obtained previously for PPO in that the activation volume exhibits a strong decrease as temperature is increased. It is also observed that the activation volume for PEO<sub>9</sub>NaI is larger than for PEO<sub>9</sub>NaCF<sub>3</sub>SO<sub>3</sub>. On the basis of the results for PPO<sup>15</sup>, this finding merely reflects the fact that the glass transition temperature for the NaI-complexed material is higher, i.e. the activation volumes will be the same (or nearly so) at the same distance above the glass transition.

Interestingly, the curvature in the conductivity vs. pressure plots in *Figure 5* is found to be positive ( $b > 0$  in equation (4)) for the iodide-complexed material and very small for the triflate complex. This is the same result as that reported previously for PEO<sup>17</sup>, but is opposite to that for amorphous PPO in which it is found<sup>15</sup> that  $b < 0$ . The implications of this result are not clear at the present time.

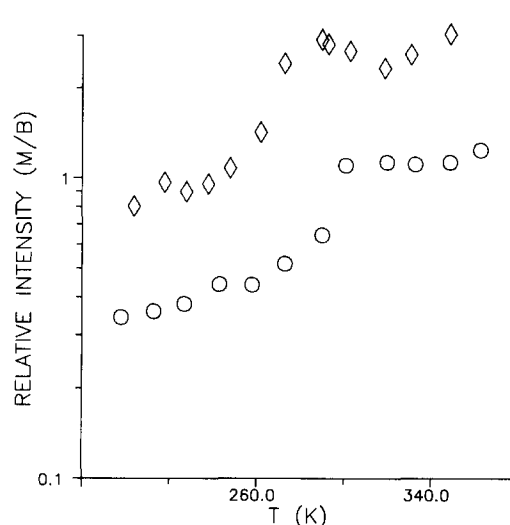
The <sup>23</sup>Na n.m.r. absorption in Na-containing amorphous polymer electrolytes generally consists of two separate spectra corresponding to mobile sodium ions and bound sodium<sup>5,12,13,16</sup>. The mobile response is characterized by spin-lattice relaxation times  $T_1$  of the

order of milliseconds and a strongly temperature-dependent linewidth above  $T_g$ . The bound <sup>23</sup>Na signal exhibits substantially longer  $T_1$  values (of the order of 1 s) and little, if any, temperature dependence of its linewidth. As mentioned previously, the bound spectrum has previously been identified with large relatively immobile clusters of ions<sup>12,13</sup>. *Figure 6* displays the temperature dependence of the mobile sodium reciprocal free induction decay constant,  $(T_2^*)^{-1}$ , which is proportional to the linewidth, for PEO<sub>9</sub>NaI and the corresponding triflate complex. Both spectra undergo significant motional narrowing just above their respective  $T_g$  (about 10 K higher for the iodide complex than the triflate). In both samples, the linewidth reaches a minimum value about 45 K above  $T_g$  and then slowly increases as a result of extremely rapid spin-lattice relaxation ( $T_1 \sim 300 \mu\text{s}$ ).

The mobile:bound Na ratios, obtained by integration of the respective free induction decays, for the triflate and iodide complexes are plotted as a function of temperature in *Figure 7*. Both materials exhibit an increase in mobile Na<sup>+</sup> concentration with increasing  $T$ , with a sharp



**Figure 6** Temperature dependence of reciprocal  $^{23}\text{Na}$  free induction decay constant,  $(T_2^*)^{-1}$ , for  $\text{PEO}_9\text{NaCF}_3\text{SO}_3$  (diamonds) and  $\text{PEO}_9\text{NaI}$  (circles)



**Figure 7** Temperature dependence of ratio of mobile/bound sodium concentration in  $\text{PEO}_9\text{NaCF}_3\text{SO}_3$  (diamonds) and  $\text{PEO}_9\text{NaI}$  (circles)

increase observed in the vicinity of  $T_g$ . The triflate complex, however, displays a consistently higher mobile  $\text{Na}^+$  concentration than the iodide, most probably a result of the greater tendency of  $\text{Na}^+$  and  $\text{I}^-$  to form aggregates in the latter material. Similar effects have been observed in other polymer electrolytes in which the anions have been varied systematically. Finally, it has been observed that the mobile  $\text{Na}^+$  concentration in  $\text{PEO}_9\text{NaI}$  continues to increase slowly with increasing temperature up to  $130^\circ\text{C}$  (data not shown). Therefore the high-temperature d.s.c. feature in *Figure 3* is not attributable to salt precipitation, which has been shown to occur in PPO–Na salt complexes<sup>13,16</sup>.

## SUMMARY

Oxymethylene-linked PEO has been shown to be partially crystalline below  $0^\circ\text{C}$ , although when complexed with either NaI or  $\text{NaCF}_3\text{SO}_3$  in the ratio of nine ether oxygens/sodium the resulting material is completely amorphous. Activation volumes of the complexes computed from variable-pressure conductivity data were shown to have values and temperature dependences comparable to those reported for PPO-based materials.  $^{23}\text{Na}$  n.m.r. measurements demonstrate the presence of bound and mobile sodium ions. The mobile  $^{23}\text{Na}$  resonance undergoes motional line narrowing above  $T_g$  in a manner similar to that reported for other Na-containing polymer electrolytes. The triflate complex was observed to have a substantially higher concentration of mobile  $\text{Na}^+$  ions than the iodide complex, which suggests the presence of strong cation–anion interactions in the latter material.

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