High Pressure Conductivity and NMR Investigation of Siloxane-Based Polymer Electrolytes

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Variable temperature and pressure conductivity and ^{23}Na nuclear magnetic resonance (NMR) measurements of several siloxane-based polymers complexed with $NaCF_3SO_3$ are reported. The conductivity exhibits V.T.F. behavior of the type commonly observed in amorphous polymer electrolytes, and activation volumes (29.9 cm^3/mol at 313K for one sample) typical of these materials. The NMR linewidths associated with mobile Na$^+$ ions exhibit motional narrowing above T_g in a manner similar to other Na-polymer electrolytes. The pressure dependence of the ^{23}Na linewidth is consistent with a 10–15 K/kbar increase in T_g.

INTRODUCTION

Ionic mobility in polymer electrolytes depends critically on the ability of the host polymer to execute segmental motions. Consequently materials considered for room temperature applications require a relatively low glass transition temperature (T_g). A class of these materials which have recently received considerable attention are those based on copolymers of siloxanes and ethylene oxide.[1,2] The former constituent provides flexibility to the polymer network which, in ad-

dition to enhancing segmental motions, yields desirable mechanical properties. The ethylene oxide (EO) groups provide a polar environment for solvation of the salt.

We have prepared several cross-linked siloxane-EO networks complexed with $NaCF_3SO_3$ which, in turn, have been studied by a combination of differential scanning calorimetry (DSC), complex impedance, and [23]Na nuclear magnetic resonance (NMR) techniques. The effects of hydrostatic pressure on electrical conductivity and NMR linewidth have also been investigated.

EXPERIMENTAL

Two kinds of host polymer were employed. The first was based on commercial (Petrarch) dimethylsiloxane—EO copolymer (hereafter denoted as PDMS-EO), the second was based on a monophenylsiloxane-EO copolymer (PMPS-EO). Both materials were complexed with $NaCF_3SO_3$ with the following EO/Na ratios: 8:1 for PDMS-EO, and both 8:1 and 12:1 for PMPS-EO. The sample preparation details (including cross-linking and synthesis of the PMPS) are described elsewhere.[2,3] A description of the conductivity and NMR measurement techniques is also given elsewhere.[2]

RESULTS AND DISCUSSION

A DSC thermogram for the PDMS-EO complex is shown in Figure 1. A strong glass transition with a "central" T_g of about 205K is observed. This is somewhat lower than the value obtained for 8:1 PMPS-EO (233K). The difference may be attributable, in part, to inhomogeneities in the PDMS-EO material as will be discussed later. As expected the 12:1 PMPS-EO has a lower T_g (225K) than its 8:1 counterpart, although this value is still about 4K higher than T_g for the uncomplexed host polymer.

The temperature dependence of the electrical conductivity of the PDMS-EO complex is displayed on an Arrhenius plot in Figure 2. The curvature commonly observed in amorphous polymers is apparent. The data were first analyzed via the V.T.F. equation[4]

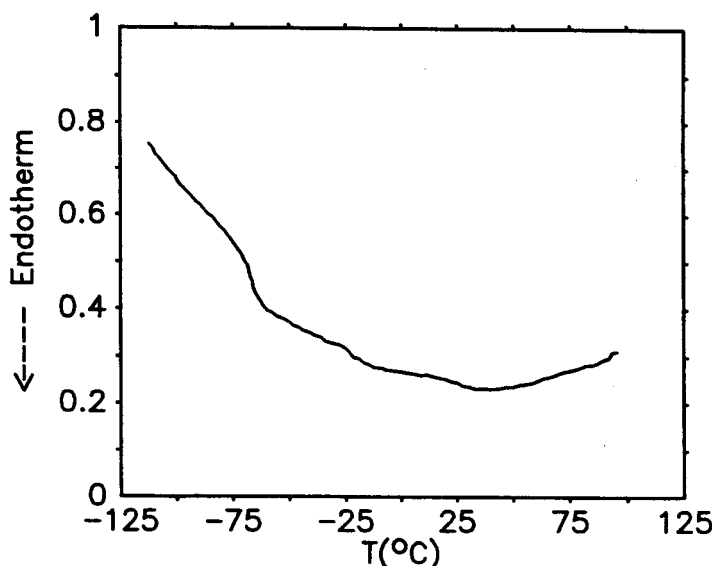$$\sigma = AT^{-1/2} \exp \{-[E_a/k(T - T_o)]\} \qquad (1)$$

FIGURE 1   DSC plot for the PDMS-EO complex showing a central glass transition at about 205K. The data were taken at 10K/min.

A non-linear least squares fit (with adjustable parameters A, E_a, and T_o) was performed and the best-fit parameters are listed in Table I. It is generally found that $T_g - T_o$ is about 45–50K.[2] However from Table I (T_o = 187K), it is apparent that $T_g - T_o$ is only 18K. The value of T_o extracted from the data in Figure 2 is believed to be quite reliable due to the wide temperature range over which the data were taken and is further validated by the high pressure conductivity results to be discussed later. The PDMS-EO sample was not heated prior to acquiring the DSC data in Figure 1, whereas the conductivity measurements were obtained after having annealed the sample at 100C (in a roughing vacuum-to drive off residual water) for several hours. It is therefore postulated that the salt concentration in the unannealed sample may have been inhomogeneous, yielding a lower T_g than expected on the basis of the conductivity results.

The high pressure conductivity results are shown in Figure 3. The isothemal (313K) data were fit to the equation

$$\log_{10}\sigma = \log_{10}\sigma_o + aP \tag{2}$$

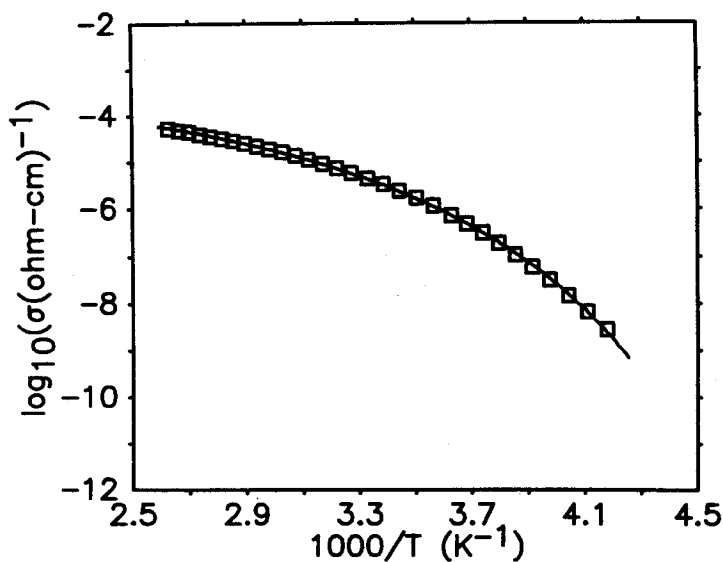and the best-fit parameters are listed in Table I. The activation volume

FIGURE 2 Arrhenius plot of the electrical conductivity data for PDMS-EO. The solid line is the best fit VTF equation utilizing the parameters listed in Table I.

TABLE I

Best fit VTG parameters, WLF parameters, and results of the high pressure electrical conductivity studies.

RMS Deviation	$\log_{10}A$ $(\Omega\text{-cm})^{-1} - \sqrt{K}$			$E_a(eV)$	$T_o(K)$
0.018	-1.31			0.063	187.0
RMS Deviation	$\log_{10}A'$ $(\Omega\text{-cm})^{-1}$			$E'_a(eV)$	$T'_o(K)$
0.020	-2.67			0.060	188.6
	$T_g(K)$	C_1	$C_2(K)$	$\log_{10}\sigma(T_g)$ $(\Omega\text{-cm})^{-1}$	RMS Deviation
Onset	198	32.1	9.4	-34.7	0.020
Central	205	18.3	16.4	-21.0	0.020
End	212	12.8	23.4	-15.5	0.020
T(K)	RMS Deviation	$\log_{10}\sigma_o$ $(\Omega\text{-cm})^{-1}$		$a(GPa)^{-1}$	ΔV^* (cm^3/mol)
313.1	0.0061	-5.08		-5.01	29.9

can be determined from the data in Figure 3 from the relation

$$\Delta V^* = -kT \frac{d(\ln \sigma)}{dP} \tag{3}$$

yielding the result $\Delta V^* = 29.9$ cm^3/mol. This value is close to that obtained for a PDMS-EO sample complexed with $NaCF_3COO$ as opposed to the triflate salt.[2] The similarity in ΔV^* for the two samples (at roughly equal temperatures—that is, for equal values of $T - T_o$) implies that the T_o value in Table I is reliable.

For completeness, the conductivity data were also analyzed according to a modified V.T.F. equation[2]

$$\sigma = A' \exp \{-[E_a'/k(T - T_o')]\} \tag{4}$$

and the W.L.F. equation[5]

$$\log_{10} \left[\frac{\sigma(T)}{\sigma(T_g)} \right] = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{5}$$

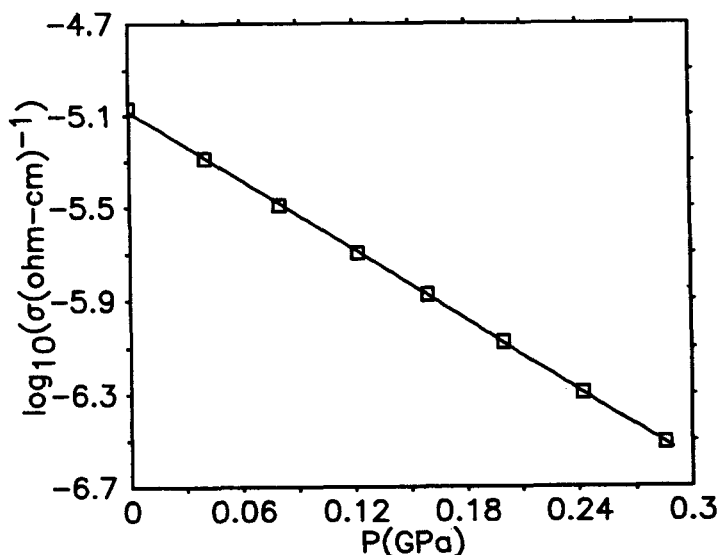The resultant parameters are also listed in Table I.

FIGURE 3   Electrical conductivity pressure dependence at 313K and best-fit straight line.

The PMPS-EO samples were not analyzed as extensively, but were shown to have room temperature conductivities comparable to PDMS-EO.

The ^{23}Na NMR results are similar to those obtained for PDMS-EO complexed with $NaCF_3COO$[2] as well as other polymer electrolytes including PPO:NaI,[6] PPO:NaClO$_4$,[7] and MEEP:NaCF$_3$SO$_3$.[8] In particular, two distinct contributions to the NMR absorption are observed. One component has a spin-lattice relaxation time T_1 on the order of 1 s and a linewidth that doesn't vary appreciably with temperature. The other component has T_1 on the order of 1 ms and exhibits motional line narrowing above T_g. The latter contribution has been identified previously with mobile Na$^+$ ions in the complex,
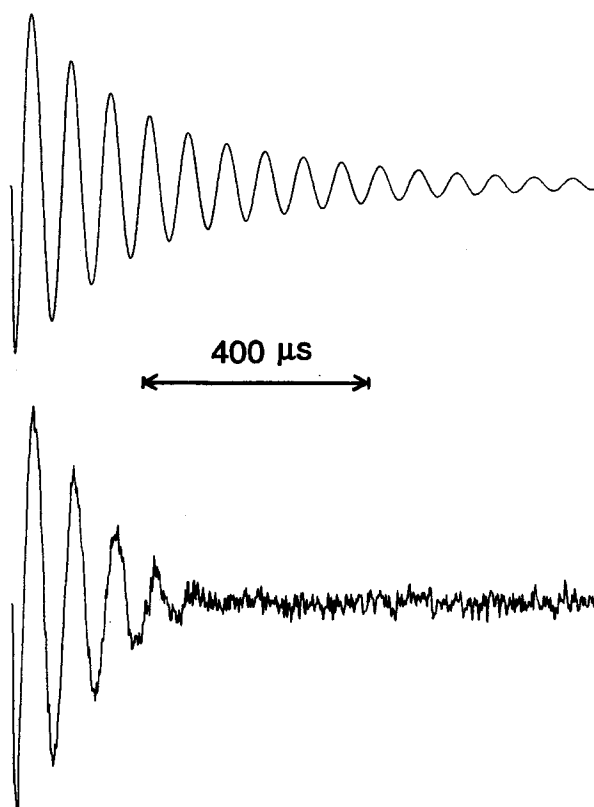

400 μs

FIGURE 4   Free induction decays for the mobile (top) and bound (bottom) Na$^+$ in the 8:1 PMPS-EO complex at 273K. The vertical gain in the bottom figure is a factor of ten higher than in the top.

while the former component was associated with bound Na.[2,6,7] The bound Na in PPO_8 NaI appeared to reflect the presence of either small amounts of uncomplexed salt (but too small to be detected by powder X-ray diffraction) or clusters of ~10 or more ions.[6] Due to the relative complexity of the present materials, it is possible that interactions between Na^+ ions and the siloxane chain could lead to additional quantities of bound Na. [23]Na free induction decays (FID's) of both lineshape components for 8:1 PMPS-EO (at 273K) obtained by selective saturation and subtraction, are shown in Figure 4. The top FID corresponds to the mobile Na^+ ions and is clearly motionally narrowed (in the frequency domain) with respect to the bound Na response (bottom).

The integrated intensities of the FID's in Figure 4 can be utilized to compute the ratio of mobile to bound Na (M/B). A plot of M/B vs. T is displayed in Figure 5, for both 8:1 and 12:1 PMPS-EO. It is
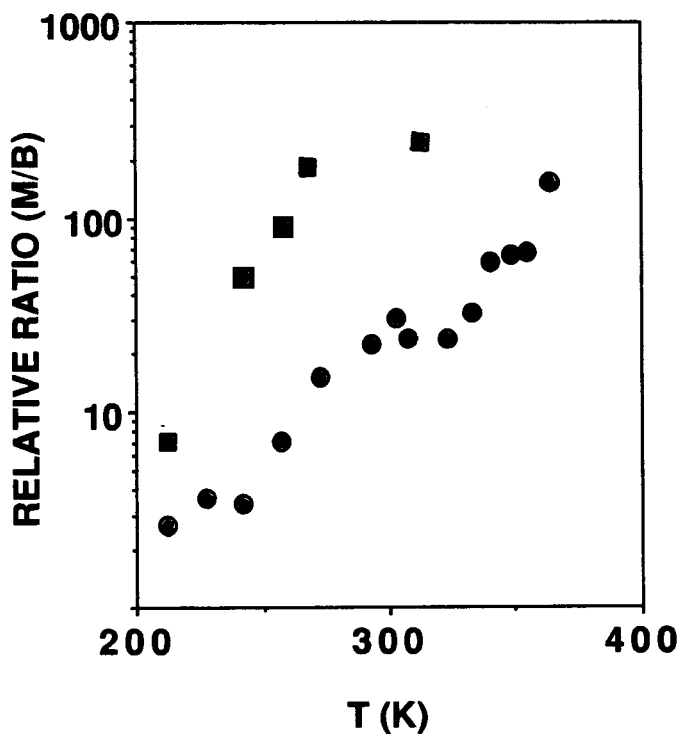

FIGURE 5   Mobile to bound (M/B) Na^+ ratios of both 8:1 and 12:1 PMPS-EO complexes as a function of temperature.

clear from the data that increasing T tends to dissociate the bound Na. As expected, the 12:1 concentration exhibits a higher degree of dissociation than 8:1, in that less than 1% of the Na remains bound above room temperature in the 12:1 sample. It should be noted however that even for the 8:1 material at 212K, which is below T_g, about 60% of the Na is in the mobile phase. Therefore the additional 40% of carriers generated up to 360K has only a minor effect on the conductivity which increases by 4–5 orders of magnitude over the same temperature range.

The NMR linewidth is proportional to the reciprocal of the FID time constant $(T_2^*)^{-1}$ which is plotted as a function of T in Figure 6 for both PMPS-EO samples. As observed for all other Na-containing polymer electrolytes,[2,6,7,8] motional narrowing above T_g is clearly indicated. Another universal feature of the ^{23}Na results is that the linewidth reaches a minimum at about 45–55K above T_g and then
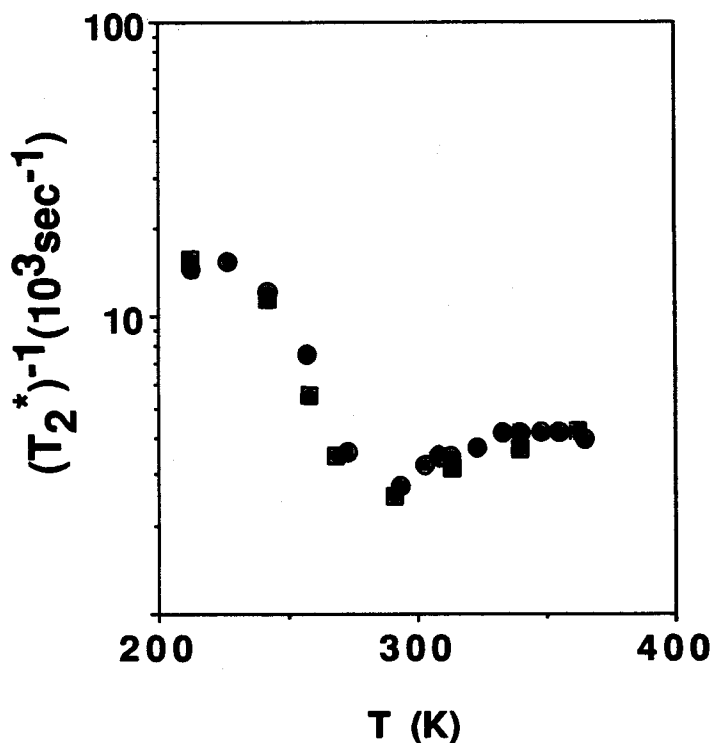

FIGURE 6   Temperature dependence of ^{23}Na linewidth $(T_2^*)^{-1}$ of mobile Na$^+$ in 8:1 and 12:1 PMPS-EO complexes.

broadens somewhat. The high temperature broadening is consistent with the extremely short ($\sim$300 μs) T_1 values measured in this region, although a microscopic model for this unusual behavior (i.e. the linewidth normally levels off in a BPP-type treatment[9]) has not yet been formulated.

The effect of hydrostatic pressure on the linewidth $(T_2^*)^{-1}$ is shown in Figure 7. Only data for PDMS-EO is included in Figure 7. The two data symbols correspond to previously unpressurized and pressure cycled samples. There is clearly a systematic decrease in linewidth with increasing P. This result is in marked contrast to the pressure induced *increase* in linewidth observed in PPO_8NaI,[6] however in the latter material the data were obtained at 313K which corresponds to $T - T_g \approx 35K$. The PDMS-EO measurements were performed at 290K or $T - T_g \approx 85K$. From the data in Figure 6,
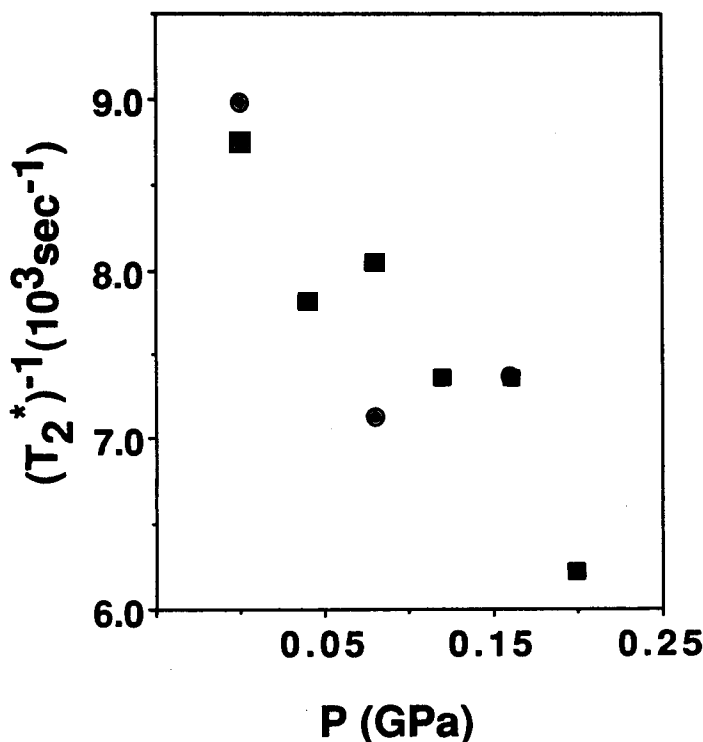

FIGURE 7   Pressure dependence of ^{23}Na linewidth $(T_2^*)^{-1}$ of mobile Na^+ in PDMS-EO at 290K. The squares correspond to the sample subjected to pressure for the first time; the circles represent data taken after several 0–0.2GPa cycles.

which again is more or less representative of all Na polymer electrolytes, it is clear that $T - T_g = 35K$ is within the motional narrowing region while $T - T_g = 85K$ is within the motional *broadening* region. Therefore, the principal effect of pressure appears to be an increase in T_g on the order of 10–15K/kbar. This result is consistent with the conductivity pressure dependence which reflects a similar increase in T_o.[2] The lack of agreement between the room temperature ambient pressure linewidths from Figures 6 and 7 is attributable partly to magnetic field inhomogeneities associated with the high pressure NMR probe and differences between the PMPS-EO (Figure 6) and PDMS-EO (Figure 7) samples.

Finally, the pressure dependence (at 290K) of M/B in PDMS-EO is displayed in Figure 8. Comparison with the data in Figure 5, which clearly shows that M/B decreases as the temperature is lowered toward T_g (a similar result was obtained for PDMS-EO:NaCF$_3$COO[2]), again implies a pressure induced increase in T_g.
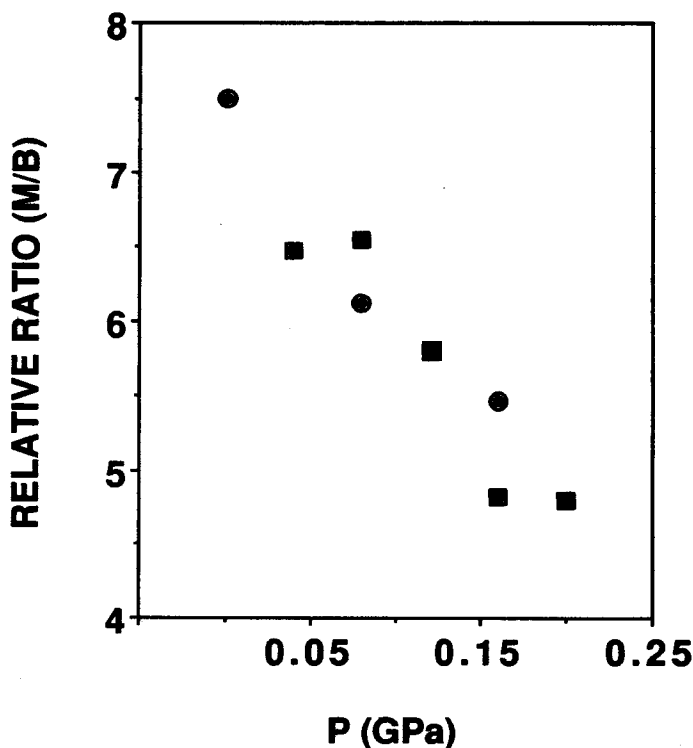

FIGURE 8   Mobile to bound (M/B) Na$^+$ ratio of PDMS-EO as a function of pressure. Circles—pressure cycled sample; Squares—uncycled (first pressure run).

CONCLUSIONS

Several polymer electrolytes consisting of crosslinked siloxane-EO networks complexed with $NaCF_3SO_3$ have been investigated by temperature and pressure dependent conductivity and ^{23}Na NMR. The conductivity exhibits an activation volume and V.T.F. behavior with parameters similar to those reported for PDMS-EO complexed with $NaCF_3COO$.[2] The mobile ion concentration as probed by ^{23}Na NMR has been shown to increase with increasing T and decrease with increasing P. The ^{23}Na linewidth becomes motionally narrowed above T_g, and then broadens due to short T_1 values at higher temperatures. The pressure dependence of the linewidth is consistent with an increase in T_g on the order of 10–15K/kbar.

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