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Investigations of a Siloxane-Based Polymer Electrolyte Employing ^{13}C, ^{29}Si, ^{7}Li, and ^{23}Na Solid-State NMR Spectroscopy

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Abstract: Magic angle spinning (MAS) high power dipolar decoupling (DD) solid state NMR has been used to characterize a polyether-substituted, siloxane-based polymer electrolyte. Upfield chemical shifts were observed for several of the polyether carbons which is dependent on the concentration of $Li[SO_3CF_3]$. Values of the nuclear Overhauser enhancement, NOE, range from 2.6 to 1.5 depending on the position of the carbon along the polyether chain and the concentration of $Li[SO_3CF_3]$. Both ^{13}C NMR line widths and T_1 values vary as a function of temperature and salt concentration, and both measurements can be correlated to T_g. The ^{7}Li NMR line widths of the $Li[SO_3CF_3]$ complexes also correlate with T_g. The $Na[SO_3CF_3]$ salt complexes exhibit both temperature- and concentration-dependent chemical shifts that suggest a significant degree of ion–ion interaction is present in the polymer–salt complexes.

Solid solvent-free polymer electrolytes have been intensively investigated over the last 10 years.[1] Both the potential technological application of polymer electrolytes in solid-state devices such as batteries and electrochromic displays and a desire to understand how charge is transported in polymer electrolytes have spurred interest in the field. Recently, we have found that polymer electrolytes composed of a flexible inorganic backbone with pendent short-chain polyether moieties have many desirable properties.[2] We have explored polyphosphazene[2] and along with other workers siloxane-based[3] polymer electrolytes. Although much has been learned about polymer electrolytes, the details of charge-transport mechanisms and ion–ion interactions are still unclear.

Nuclear magnetic resonance, NMR, has been very useful for the characterization of polymer electrolytes. In an early NMR study, Berthier and co-workers found that charge transport occurs exclusively in the amorphous domain of semicrystalline poly(ethylene oxide) salt complexes.[4] The pulsed field gradient method has been employed to measure diffusion coefficients of the polyether chains, as well as diffusion coefficients for lithium and fluorine (in $SO_3CF_3^-$) of poly(ethylene glycol) $Li[SO_3CF_3]$ complexes.[5] Also, ^{23}Na NMR data for a dimethylsiloxane–ethylene oxide polymer salt complex indicate the presence of both bound and mobile cations.[3b]

Many workers have shown that NMR is an excellent probe of aqueous and nonaqueous electrolytes,[6] and in recent years characterization of solid polymers by high-resolution solid-state NMR has been a fruitful and growing area of study.[7] For these reasons, high-resolution NMR studies of solvent-free polymer electrolytes should prove to be illuminating. In this paper we will discuss the solid-state NMR characterization of a siloxane-based polymer electrolyte by ^{13}C, ^{29}Si, ^{7}Li, and ^{23}Na NMR.

Experimental Section

The cross-linked comb polymer used in the following study is called siloxane(30) to denote that it is a siloxane-based electrolyte in which 30% of the repeat units are cross-linked. The synthesis and characterization of siloxane(30) has been described previously,[3a] so only an abbreviated discussion of the reaction conditions employed in the synthesis will be given here. Siloxane(30) was made from the reaction of poly(methylhydrosiloxane), PMHS (MW = 4500–5000), with monomethyl ether poly(ethylene glycol), MePEG (av MW = 350), and poly(ethylene glycol), PEG (av MW = 300), in the presence of a $Zn(octoate)_2$ catalyst. The reaction was run in xylene for ca. 4 h at 130 °C, which was followed by removal of the solvent under vacuum and then reheating the reaction mixture to 130 °C until a clear rubbery material forms. The polymer was purified by dichloromethane extraction and then dried under vacuum (2–3 days, 50 °C, 10^{-5} Torr). A similar non-cross-linked polymer, siloxane(0), was prepared in an equivalent manner except PEG was not employed in the synthesis and the material was not extracted with CH_2Cl_2.

The polymer–salt complexes were prepared from weighed amounts of the dried polymer and salt under dry, inert conditions. Acetonitrile (dried over CaH_2 and distilled under a flow of $N_2(g)$) was added to the polymer and salt mixture. The cross-linked polymer was swollen by CH_3CN and the salt entered the polymer because of the strong interaction between the alkali metal cations and the polyether chains of siloxane(30). Complete incorporation of $Na[SO_3CF_3]$ required heating of the polymer/salt/solvent system for 2 days at 50 °C. The solvent was then removed under vacuum followed by drying of the polymer salt complex under vacuum (60 °C, 10^{-2} Torr, 2–3 days). The polymer salt complexes were stored in a dry, inert atmosphere.

The complex impedance methods used for measurement of ionic conductivity have been described previously.[3a] Differential scanning calorimetry experiments were performed on a Perkin-Elmer DSC-2 employing liquid nitrogen for cooling. Values of T_g were taken at the midpoint of the transition while cold crystallization exotherms and melting endotherms were measured at the peak of the transition.

The NMR measurements were made on a Varian VXR-300 spectrometer with a multinuclear MAS solid-state NMR probe (Doty Scientific). The spectra were recorded at 75.4 MHz (^{13}C), 59.6 MHz (^{29}Si), 116.6 MHz (^{7}Li), and 79.3 MHz (^{23}Na). Variable-temperature measurements were made by passing the bearing gas supply ($N_2(g)$) through a dewar of $N_2(l)$ and then regulating the temperature of this gas by a temperature controller and heating element. The rotor (Doty Scientific) has a body of sapphire and O-ring sealed endcaps made of Macor. All

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Table I. DSC Data for Siloxane(30) and Its Salt Complexes

polymer	0:M	$T_g \pm 2$ (K)	$T_{cc} \pm 3$ (K)	$T_m \pm 3$ (K)
siloxane(30)		204	205, 221	261
siloxane(30) Li[SO_3CF_3] 5%	52:1	210	230	264
siloxane(30) Li[SO_3CF_3] 10%	25:1	215		
siloxane(30) Li[SO_3CF_3] 15%	16:1	220		
siloxane(30) Li[SO_3CF_3] 20%	11:1	231		
siloxane(30) Li[SO_3CF_3] 25%	8:1	235		
siloxane(30) Na[SO_3CF_3] 5.5%[a]	52:1	206	231	265
siloxane(30) Na[SO_3CF_3] 11.0%[a]	25:1	216		
siloxane(30) Na[SO_3CF_3] 16.5%[a]	16:1	222		
siloxane(30) Na[SO_3CF_3] 22%[a]	11:1	234		

[a] These salt complexes have the same concentration of salt on a mole basis as is found in the Li[SO_3CF_3] 5, 10, 15, and 20% complexes, respectively.

samples were loaded under a dry, inert atmosphere. In all experiments, N_2(g) was used for both the spinning and bearing gases in order to prevent contamination of the samples with atmospheric moisture. The magic angle was periodically adjusted by the KBr method. The ^{13}C NMR spectra were externally referenced to the aromatic peak of hexamethylbenzene. The ^{7}Li and ^{23}Na NMR spectra were externally referenced to 0.1 M Li[SO_3CF_3] and Na[SO_3CF_3] solutions, and the single resonance observed in each case was assigned 0 ppm. The ^{29}Si NMR spectra were externally referenced to TMS. The T_1 measurements were obtained with a 180°–τ–90° pulse sequence, and data were analyzed by programs provided by Varian. Typical 90° pulse widths were 7.5 to 8.2 μs for ^{13}C, 18 μs for ^{29}Si, and 20 μs for ^{23}Na. Nuclear Overhauser effect data were obtained by using gated decoupling. The high-power decoupler was not used but instead scalar decoupling was employed. The decoupling power was sufficient to prevent observation of scaler coupling, but the line widths increased 5–30% depending on the salt concentration. A delay time of at least 10 times the longest T_1 was used in all cases.

Results and Discussion

Conductivity of Siloxane(30) Li[SO_3CF_3] and Na[SO_3CF_3] Complexes. In a previous study,[3a] we have shown that the ionic conductivity of the siloxane(30) Li[SO_3CF_3] complexes is dependent on salt concentration with the highest conductivity observed for the siloxane(30) Li[SO_3CF_3] 15% complex (the concentration of salt throughout this paper is expressed in terms of a weight percentage). For the alkali metal salts, M = Li, Na, K, Rb, and Cs in M[SO_3CF_3], the Rb[SO_3CF_3] complex exhibited the largest ionic conductivity at 40 °C.[3a] The glass transition temperature, T_g, of a polymer electrolyte is an important parameter as local segmental motion is believed to be responsible for charge transport.[1] The value of T_g increases linearly as the concentration of salt rises in the siloxane(30) electrolytes (Table I), as other workers have observed for similar siloxane-based electrolytes.[3d] Below 5 wt % salt, a quenched sample of the electrolyte shows a cold crystallization exotherm and a low temperature melting endotherm. The observed curved log σ versus 1000/T plots are characteristic of amorphous polymer electrolytes (Figure 1). The temperature dependence of σ can be described by the Vogel–Tamman–Fulcher equation (VTF), eq 1, which relates to σ to an apparent activation energy, B, and T_0, a parameter which is found to be ca. 50° below T_g. The VTF equation

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

can be derived from free volume[8] or excess entropy[9] models. The nature of the conducting species is not well defined, but because of the low permittivity of the siloxane(30) polymer significant ion aggregation is likely to occur.

^{13}C and ^{29}Si NMR Spectra of Siloxane(30) and Its Salt Complexes. Although standard high-resolution NMR techniques can be applied to the investigation of completely amorphous polymers[10,11] and to the amorphous regions of semicrystalline polymers,[12] dipolar decoupling, DD, and magic angle spinning, MAS, provide better resolved spectra (Figure 2) and were therefore applied throughout this work.

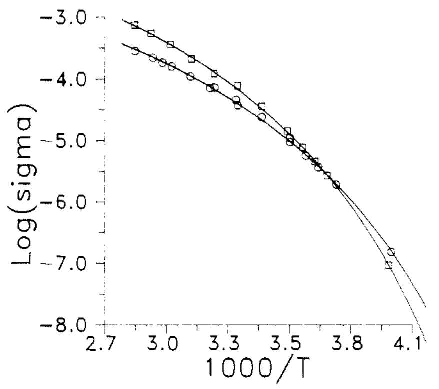

Figure 1. Temperature-dependent ionic conductivity of siloxane(30) Li[SO_3CF_3] 15% (○) and siloxane(30) Na[SO_3CF_3] 16.5% (□). The lines through the data points were calculated from the best-fit parameters obtained from the VTF equation, eq 1.

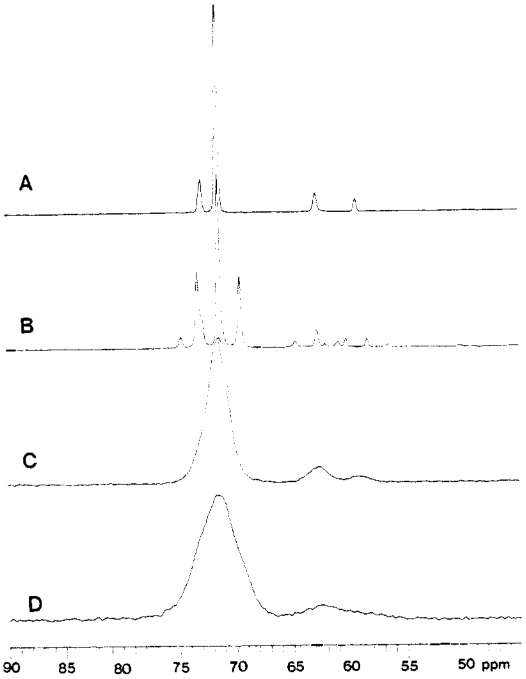

Figure 2. Solid-state ^{13}C NMR spectra of siloxane(30) employing (A) MAS (spinning rate = 1400 Hz) and DD, (B) static and DD, (C) MAS, and (D) static.

Because the spin–lattice relaxation times were not greater than 5 s for siloxane(30) or its salt complexes, ^{13}C–^{1}H cross polarization was not used in these studies. As is typical for amorphous polymers above T_g, Bloch decays were more efficient than cross polarization because the static dipolar interaction which is necessary for cross polarization has been reduced or eliminated by segmental motion.[13]

Figure 2A shows the ambient temperature ^{13}C NMR spectrum of siloxane(30) employing MAS and DD. The line widths are about 30 Hz for all the carbons irrespective of spinning rate (1300–4000 Hz). Due to the extensive molecular motion present in siloxane(30), it is possible to obtain a J-resolved spectrum by removing the high-power decoupling field (Figure 2B). The values of $^{1}J_{CH}$ found for siloxane(30) match well with those observed for monomethyl ether poly(ethylene glycol), MePEG, and poly(ethylene glycol), PEG. The values of $^{1}J_{CH}$ will be used in the next section to aid in the assignment of the siloxane(30) spectrum. Similar experimental techniques have led to a J-resolved spectrum

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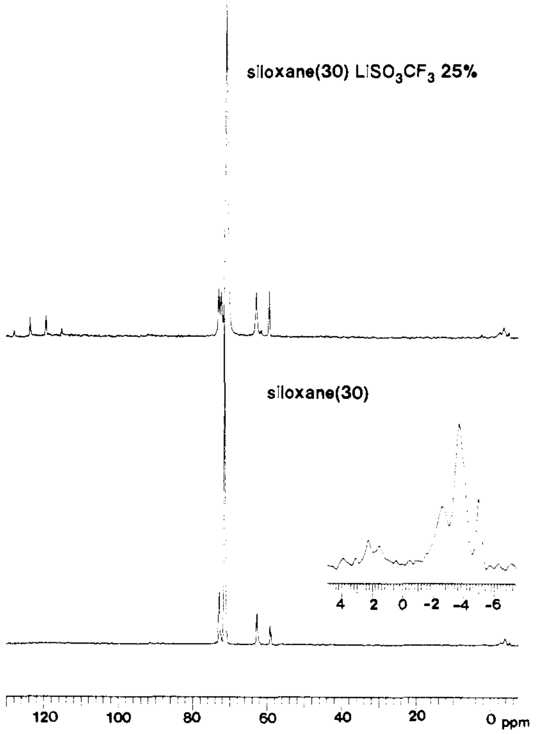
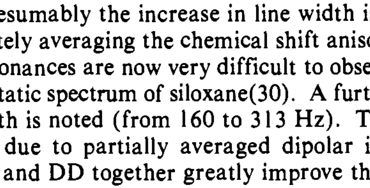


Figure 3. MAS DD ^{13}C NMR spectra of (A) siloxane(30) and (B) siloxane(30) Li[SO_3CF_3] 25%. Inset shows the Si–CH_3 region of the ^{13}C spectrum for siloxane(30).

Chart I



$$\begin{array}{l} \overset{5}{O}\overset{4}{C}H_2CH_2O(\overbrace{CH_2CH_2O}^{3})_x\overset{4}{C}H_2\overset{5}{C}H_2O \\ (SiO)_n \qquad\qquad\qquad\qquad (SiO)_n \\ CH_3 \qquad\qquad\qquad\qquad\quad CH_3 \end{array}$$

$$\begin{array}{l} \overset{5}{O}\overset{4}{C}H_2CH_2O(\overbrace{CH_2CH_2O}^{3})_x\overset{2}{C}H_2CH_2O\overset{1}{C}H_3 \\ (SiO)_n \\ CH_3 \end{array}$$

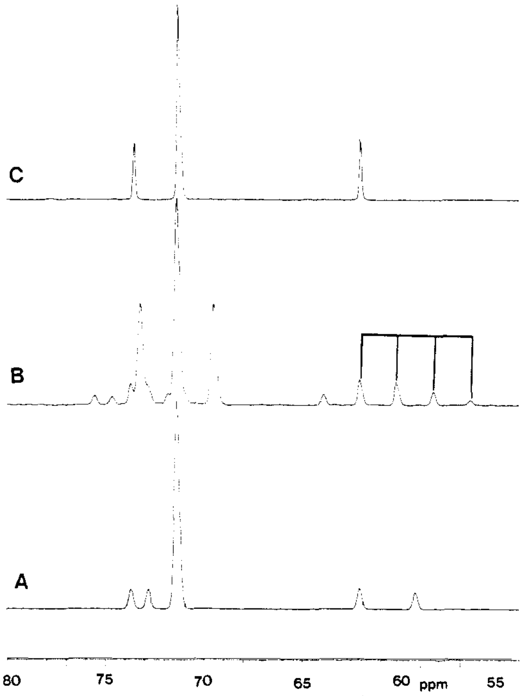


Figure 4. ^{13}C NMR spectra of (A) monomethyl ether poly(ethylene glycol) {^1H}, (B) coupled spectrum of monomethyl ether poly(ethylene glycol), and (C) spectrum of poly(ethylene glycol) {^1H}.

of natural rubber.[14] The static DD spectrum is shown in Figure 2C. The line width of the largest resonance has now increased from 25 to 160 Hz and it is broad enough to obscure the downfield resonance. Presumably the increase in line width is due to the lack of completely averaging the chemical shift anisotropy. The two upfield resonances are now very difficult to observe. Figure 2D shows the static spectrum of siloxane(30). A further increase in the line width is noted (from 160 to 313 Hz). This increase is most likely due to partially averaged dipolar interactions. Clearly, MAS and DD together greatly improve the resolution of the ^{13}C solid-state NMR spectrum of siloxane(30).

Siloxane(30) contains two different types of polyether moieties, cross-linking polyethers, which were derived from PEG, and methyl-capped polyethers, derived from MePEG. A schematic diagram of the two types of ethers in siloxane(30) and the numbering scheme used in this paper is presented in Chart I. The spectrum of siloxane(30) (Figure 3) can be assigned by comparison with spectra for PEG and MePEG (Figure 4). Two resonances, 59.2 and 72.8 ppm, are observed for MePEG but not PEG. The coupled spectrum of MePEG allows identification of the 59.2-ppm resonance as a methyl group (quartet, $^1J_{CH}$ = 140 Hz), we call this carbon C1 (see Chart I). The 72.8-ppm resonance must be associated with a CH_2 group near the methyl end of the MePEG chain since the shifts for CH_2 near the hydroxyl end should resemble those of PEG. Hence the 72.8-ppm resonance is assigned to the carbon α to the methyl group (–CH_2CH_2–OCH_3, C2). The midchain methylene resonances are not resolved in siloxane(30) or in either of the starting polyethers and so the large peak at 71.3 ppm is easily assigned to the C3 carbons. The two remaining resonances (73.7 and 62.1 ppm) in PEG and MePEG are more difficult to assign. They are clearly due to either the methylene α ($HOCH_2CH_2$–) or β ($HOCH_2CH_2$–) to the hydroxyl moiety. Both resonances are shifted (to 72.8 and 62.7 ppm, respectively) in siloxane(30) which supports the idea that these carbons are closest to the siloxane backbone in the polymer. For a structurally similar compound, $(CH_3)_3SiOCH_2CH_2OCH_3$, the resonance at 62.4 ppm has been assigned to the methylene group α to the Si and the signal at 74.28 ppm to the β methylene.[15] By analogy, the resonance at 62.7 ppm is assigned to C5 while the peak at 72.8 ppm is assigned to C4.

The resonances for C2 and C3 are sensitive to the addition of Li[SO_3CF_3] (Figure 3). The feature at 72.8 ppm resolves into two peaks at 72.8 and 72.1 ppm as the salt concentration increases to 25% Li[SO_3CF_3]. We assign the 72.8-ppm peak to C4 and 72.1 ppm to C2. This assignment is consistent with the T_1 data described below.

The chemical shifts of C4 and C5 are not influenced by addition of Li[SO_3CF_3]. Presumably the close proximity of C4 and C5 to the siloxane backbone limits the cation affinity of the ether oxygens next to these carbons. By contrast, the ether oxygen next to C2 at the end of the polyether chain can interact strongly with the salt and an upfield shift occurs. It is also reasonable that the midchain ether oxygens have significant cation affinity and in keeping with this expectation an upfield shift is observed for the C3 carbons. Upfield ^{13}C chemical shifts have been correlated to oxygen cation interactions for poly(ethylene oxide)[16] and crown ether[17] salt complexes. The chemical shift change in the present study was smaller for both types of carbons than was observed for PEO in solution (ca. 0.8 ppm versus 1.7 ppm),[16] but the shift still indicates significant interactions of the alkali metal cations with the end and the middle of the polyether chains. It is surprising

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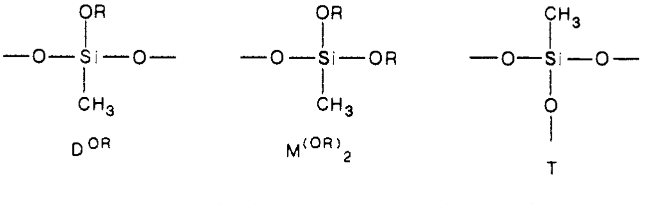
Table II. T_1 Data for Siloxane(30) Salt Complexes (35 °C)[a]

salt complex	C1(s)	C2(s)	C3(s)	C4(s)	C5(s)
0	4.00 (3)	0.65 (4)[b]	0.544 (8)	0.65 (4)[b]	0.384 (8)
5% Li[SO_3CF_3]	3.62 (8)	0.575 (16)[b]	0.473 (6)	0.575 (16)[b]	0.387 (8)
10% Li[SO_3CF_3]	2.50 (8)	0.54 (3)	0.349 (3)	0.350 (8)	0.333 (15)
15% Li[SO_3CF_3]	1.94 (6)	0.429 (15)	0.276 (2)	0.288 (6)	0.285 (3)
20% Li[SO_3CF_3]	1.64 (4)	0.322 (8)	0.223 (1)	0.264 (7)	0.264 (9)
25% Li[SO_3CF_3]	1.42 (4)	0.289 (7)	0.202 (2)	0.233 (8)	0.240 (11)
5.5% Na[SO_3CF_3]	2.53 (15)	0.406 (14)[b]	0.353 (14)	0.406 (14)[b]	0.320 (17)
11% Na[SO_3CF_3]	1.85 (12)	0.314 (5)[b]	0.248 (2)	0.314 (5)[b]	0.251 (8)
16.5% Na[SO_3CF_3]	1.53 (3)	0.279 (16)	0.182 (1)	0.238 (7)	0.219 (9)
22% Na[SO_3CF_3]	1.439 (14)	0.252 (8)	0.166 (2)	0.212 (12)	0.212 (14)

[a] See Chart I for the numbering of the polyether carbons. The error in the T_1 values is given in parentheses. [b] C2 and C4 are not resolved at these salt concentrations.

Chart II



that the chemical shift of the methyl group is not influenced by the addition of salt because a strong alkali metal interaction with the oxygen closest to the methyl group is likely. In addition to the signals from the polymer, a quartet centered at 121 ppm ($^1J_{CF}$ = 318 Hz) grows in as a function of salt concentration. It is assigned to the trifluoromethyl group of $SO_3CF_3^-$.

The backbone of siloxane(30) can be interrogated by both ^{13}C and ^{29}Si NMR spectroscopy. The methyl groups on the siloxane backbone are sensitive to the environment of the silicon atom (inset of Figure 3). Five resonances were observed at 1.4, −2.6, −3.7, −4.0, and −5.0 ppm. The peak at 1.4 ppm is assigned to residual Si–H moieties from the unreacted starting material (PMHS, 1.3 ppm). In previous work, ^{29}Si NMR demonstrated that there are three different types of silicon environments in siloxane(30).[3a] The solid-state ^{29}Si NMR spectrum of siloxane(30) (Figure 5) shows four resonances which have been assigned to $M^{(OR)_2}$ (−49.2 ppm), D^{OR} (−56.5 and −57.2 ppm), and T (−65 ppm) moieties (see Chart II for the nomenclature used to describe the siloxane polymer). Also a resonance due to unreacted starting material is observed (D^H, −35 ppm). The methyl resonance at −2.6 ppm can be assigned to the T moiety since a model compound, $CH_3Si(OSi(CH_3)_3)_3$, displays a resonance at −2.3 ppm. Suitable model compounds were not found for the other groups, but the resonances can tentatively be assigned on the basis of the relative intensities of the ^{29}Si NMR signals. The two methyl resonances at −3.7 and −4.0 ppm have the greatest integrated intensity and therefore, they should correspond to the most prevalent group as judged by ^{29}Si NMR, which is the D^{OR} moiety. The remaining resonance at −5.0 ppm is then assigned to the $M^{(OR)_2}$ moiety.

^{13}C T_1 Studies of Siloxane(30) Li[SO_3CF_3] Salt Complexes. Magic-angle spinning and related solid-state NMR techniques as applied to polymers enables the determination of T_1 values for nuclei in specific chemical environments.[18,19] A goal of the present study was to determine the temperature dependence of T_1 for individual ^{13}C nuclei and to correlate these measurements with T_g and conductivity data.

The chemical shift assignments made above are consistent with the T_1 values (Table II). For the parent siloxane(30), C2 and C4 are not resolved so T_1 appears as a weighted average of the two types of carbons. Upon addition of Li[SO_3CF_3], C2 shifts upfield, and therefore separate values of T_1 can be measured for C2 and C4 in the siloxane(30) Li[SO_3CF_3] 10% complex. For the 10% Li[SO_3CF_3] complex, the larger T_1 is assigned to C2 because numerous studies of organic compounds demonstrate that nuclei situated near the end of a chain exhibit greater T_1 values owing to their enhanced mobility.[20] The relative T_1 values for C1, C3, and C5 are also consistent with this principle.

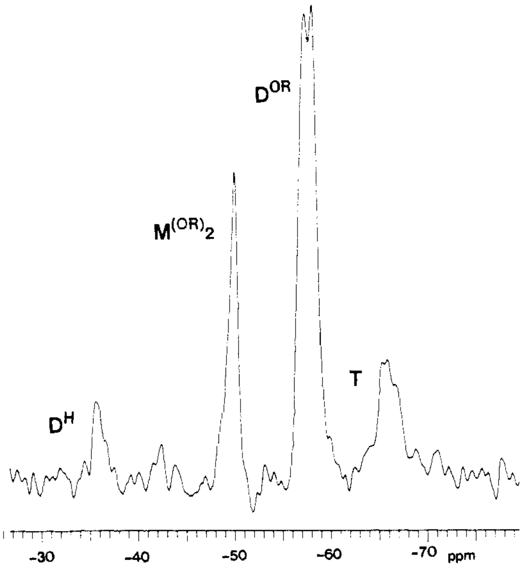


Figure 5. MAS ^{29}Si NMR spectrum of siloxane(30). See Chart II for the nomenclature used here.

The T_1 values for siloxane(30) depend strongly on the concentration of Li[SO_3CF_3] (Table II). This is not surprising as T_1 reflects the local segmental motion of the polyether chain which will be influenced by cation binding. Furthermore, previous determinations of T_1 for nonaqueous solutions containing PEO and alkali metal salts show a strong reduction in T_1 as the salt concentration increases.[16a,21]

Table II shows that T_1 values for C4 and C5 are influenced the least as the Li[SO_3CF_3] concentration increases. The T_1 for C5 decreases 27% and for C4 T_1 decreases 34% as the Li[SO_3CF_3] concentration changes from 10 to 25%. For the same change in salt concentration T_1 for C1, C2, and C3 decrease 43, 44, and 42%, respectively. The previous assertion that the ether oxygens close to the siloxane backbone are unlikely to bind Li^+ is corroborated by the moderate lowering of T_1 values for C4 and C5. The segmental motion of the whole polyether chain is decreased by coordination of the alkali metal cation and so T_1 values for C4 and C5 are expected to decrease slightly even if adjacent oxygens are not involved in coordination of the salt. The larger reduction in T_1 for C1, C2, and C3 implies that these carbons are in close proximity to the oxygens coordinated to Li^+.

The influence of the macroscopic viscosity on T_1 was probed by investigating a siloxane electrolyte with no polyether cross-links,

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Table III. Values of NOE for Siloxane(30) $Li[SO_3CF_3]$ Complexes[a]

% salt	C1	C2	C3	C4	C5
0	2.6	2.4[b]	2.4	2.4[b]	2.3
5	2.0	2.1[b]	2.2	2.1[b]	2.1
10	1.9	1.8	2.1	2.0	1.9
15	2.0	1.9	2.2	2.1	2.0
20	1.6	1.6	2.0	2.0	2.2
25	1.5	1.5	1.8	1.9	2.1

[a] Estimated error in the NOE measurements is ±10%. [b] C2 and C4 are not resolvable at these salt concentrations.

siloxane(0). Siloxane(0) is free flowing liquid in contrast to the elastomeric nature of siloxane(30). The ^{13}C NMR spectra of siloxane(0) and siloxane(0) $Li[SO_3CF_3]$ 15% were equivalent to those obtained for siloxane(30) and its 15% $Li[SO_3CF_3]$ salt complex, except for the inclusion of small amounts of unreacted polyethers. Within experimental error the values of T_1 obtained for the cross-linked and un-cross-linked electrolytes were comparable. Apparently local segmental motion of the polyether chains is not limited by the introduction of polyether cross-links but the bulk properties, such as macroscopic viscosity and conductivity, are influenced greatly.

For concentrated polymer solutions and solid polymers, the extreme narrowing condition is rarely met, i.e., $T_1 = T_2$, so the correlation time cannot be described by a simple single exponential model.[22] A reduced nuclear Overhauser enhancement, NOE, is obtained for the polyether carbons of siloxane(30) and its $Li[SO_3CF_3]$ complexes (Table III). An NOE measurement yields the intensity of the $^{13}C-^{1}H$ dipolar interaction. An NOE value of 2.98 is expected if the dipole–dipole mechanism is exclusively responsible for the relaxation of the ^{13}C nuclei. Even for the case in which a dipole–dipole relaxation mechanism is likely to be dominant, solid polymers and concentrated polymer solutions show reduced NOE values.[22] The reduced values of NOE can be described by a distribution of correlation times.[22b] In this model only a limited number of carbons have correlation coefficients which satisfy the extreme narrowing condition and hence their values of NOE will be lower than the theoretical limit. Since the NOE and T_1 measurements were made at only one field strength, we cannot prove that a distribution of correlation times is operative for siloxane(30) and its salt complexes. Siloxane(30) shows reduced values of NOE which within experimental error are equivalent for all the carbons. By increasing the concentration of $Li[SO_3CF_3]$, the NOE values of C1, C2, C3, and C4 decrease whereas those for C5 are approximately constant over the whole concentration range. The reduction of the NOE values may reflect the increasing T_g as the salt concentration increases. In this connection, the NOE values decrease for poly(isobutylene) as the measuring temperatures decrease toward T_g.[23] There is also a possibility that the quadrupole moment of the lithium cation provides another path for relaxation, but the small quadrupole moment of ^7Li makes this unlikely.

As expected from previous studies on samples ranging from small molecules to semicrystalline polymers,[18,23-26] T_1 values for siloxane(30) and its salt complexes are also sensitive to temperature. Figure 6 shows the temperature dependence of T_1 for C3 as a function of both salt concentration and temperature. The T_1 values decrease from 75 to 25 °C and then level off at lower temperatures. As noted earlier, increasing the concentration of salt lowers T_1 at all the temperatures studied. Below 0 °C, the resonances for many of the carbons broaden significantly with a resulting reduction in the accuracy of the T_1 values. The C2, C4, and C5 carbons all show a temperature dependence of T_1 similar to that of C3. The methyl group, C1, exhibits a linear decrease in T_1 versus temperature from 75 to −40 °C. A T_1 minimum is not observed in the temperature range of our experiment presumably because of the low barrier to methyl group rotation.

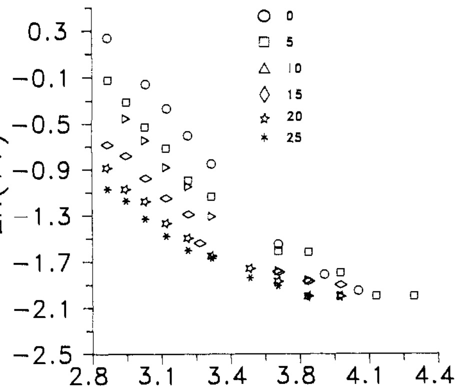

Figure 6. T_1 values for C3 as a function of temperature and $Li[SO_3CF_3]$ concentration.

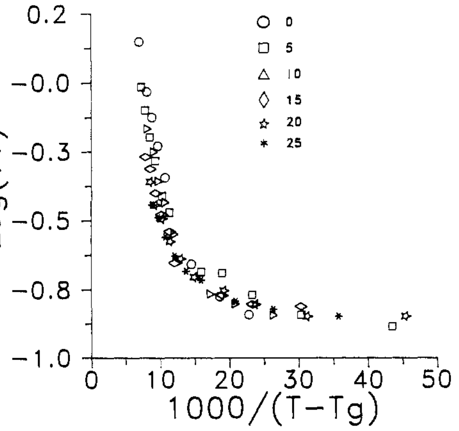

Figure 7. Plot of log (T_1) versus $1000/(T - T_g)$ for C3 as a function of $Li[SO_3CF_3]$.

The Vogel–Tamman–Fulcher (eq 1) and the Williams–Landel–Ferry (eq 2) relationships have been employed to model the temperature dependence of the ionic conductivity for amorphous polymer electrolytes.[27] Both of these models stress that T_g is an

$$\log a_T = -C_1(T - T_g)/(C_2 + T - T_g) \qquad (2)$$

important reference point for many experimental variables. For several amorphous and semicrystalline polymers T_1 has been found to obey the WLF equation.[23] The coefficients in eq 2 were not determined since we did not measure values of T_1 at T_g. But the dependence of T_1 values on T_g is clearly shown in Figure 7 where log (T_1) is plotted versus $1000/(T - T_g)$. By anchoring the temperature scale to T_g all the curves fall close to one another. These results suggest that the segmental motion of the polyether chains depends on $T - T_g$ in the same manner as the ionic conductivity depends on $T - T_g$.

^{13}C Line Width Studies. The ^{13}C line widths have been found to be sensitive to both the concentration of salt in the polymer electrolyte and the temperature. This is shown clearly in Figure 8 where the ^{13}C NMR spectra of siloxane(30) and siloxane(30) $Li[SO_3CF_3]$ 25% is plotted as a function of temperature. All the polyether resonances for siloxane(30) are ca. 30 Hz wide (fwhm)

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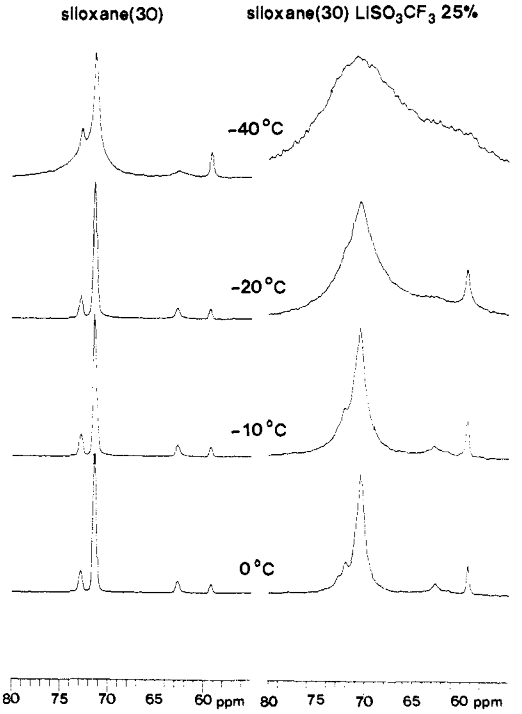

Figure 8. ^{13}C NMR spectra of siloxane(30), left, and siloxane(30) Li[SO$_3$CF$_3$] 25%, right, as a function of temperature.

from −20 to 75 °C. Lowering the temperature below −20 °C causes the methylene resonances to broaden, in fact at −30 °C, it is very difficult to observe a signal for C5. As C5 is closest to the inorganic backbone, its mobility is greatly reduced compared to other carbons in the polyether chain. By −40 °C, the line width of C3 has increased enough to obscure C2 and C4. Increasing the concentration of Li[SO$_3$CF$_3$] increases the line width of all the resonances (Figure 8). For siloxane(30) Li[SO$_3$CF$_3$] 25% the line width of C3 widens to 55 Hz at 25 °C compared to 30 Hz for siloxane(30). The increasing line width can be correlated to T_g. As T_g rises, i.e., concentration of salt increases, local segmental motion is dampened which causes an enhanced dipolar broadening of the resonances. The line width of C3 is 110 Hz at −10 °C which is so broad as to obscure C4 or C2. Also C5 is almost too broad to observe. Only a broad hump (ca. 1130 Hz fwhm) is seen at −40 °C.

For amorphous and semicrystalline polymers, the ^{13}C NMR line width changes as a function of temperature especially as T_g is approached. At some temperature, T_c, the spectrum becomes too broad to be easily observed. This phenomenon, known as spectral collapse, can be used as a high-frequency indication of T_g.[23] The value of T_c is generally greater than T_g and the ratio of T_c to T_g ranges from 1.2 to 1.4.[23] In this study, as in a previous study,[28] the temperature at which the line width equals 400 Hz will define T_c. Values of T_c are dependent on experimental parameters;[10] this makes comparisons of data obtained on different spectrometers difficult but measurements made on the same spectrometer with a consistent set of conditions should be comparable. A plot of log (line width) versus 1000/T was used to determine T_c (see Figure 9 for a representative plot). Values of T_c were only determined for C3 because it was the easiest resonance to observe and direct interaction of the salt occurs at C3. Both T_c and T_g increase with the concentration of Li[SO$_3$CF$_3$] and T_c/T_g is ca. 1.1 (Table IV).

Effect of Salt on the Polymer Backbone. For these comb-polymer electrolytes a siloxane backbone was chosen over more rigid hydrocarbon backbones so as to maximize the thermal motion of the pendant polyether moieties. In an attempt to probe the motion of the backbone, T_1 data were collected by ^{29}Si NMR of the siloxane backbone. In addition T_1 data were collected for ^{13}C NMR of the methyl groups attached to the backbone. The T_1 values obtained for the D^{OR} moiety and its pendant methyl group are given in Table V. The T_1 values for ^{29}Si NMR are substantially larger than those observed by ^{13}C NMR. For silicon compounds lacking Si–H bonds, inter- or intramolecular dipole–dipole or spin rotation relaxation mechanisms dominate ^{29}Si T_1 measurements.[29] Spin rotation relaxation is unlikely to make a contribution to the ^{29}Si relaxation of D^{OR} groups because the bulk of the attached polyether groups prevents facile rotation. For the siloxane(30) salt complexes, the ^{29}Si T_1 values increase as the concentration of Li[SO$_3$CF$_3$] increases. The ^{13}C T_1 values for the methyl group of the D^{OR} moiety follow the same trend as is seen for the ^{29}Si T_1 values. This is the reverse of the situation observed for the carbons of the polyether chain where T_1 decreases as the concentration of salt increases. The relative increases in T_1 for both the Si D^{OR} and CH$_3$ groups suggest that the relaxation of the methyl group and the attached silicon atom is correlated. A similar interaction between the quaternary carbon and methyl group of poly(n-butyl methacrylate) has been shown by employing a heteronuclear 2-D NOE (HOESY) experiment.[30] The strength of the intramolecular dipole–dipole interaction may be even stronger for a silicon atom due to its larger radius. It does not seem reasonable to conclude that the backbone motion is increased upon coordination of the polyether side chains to the salt. Instead, it is more likely that the ^{29}Si relaxation is dominated by the methyl

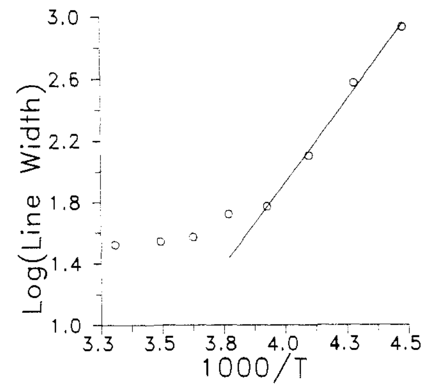

Figure 9. Plot of log (line width) versus 1000/T for siloxane(30) Li[SO$_3$CF$_3$] 10%. The line widths of C3 was used in this figure.

Table IV. T_c Values Using ^{13}C and ^{7}Li Line Widths

	^{13}C		^{7}Li	
salt complex	T_c (K)	T_c/T_g	T_c (K)	T_c/T_g
0	224	1.10		
5% Li[SO$_3$CF$_3$]	225	1.07	227	1.08
10% Li[SO$_3$CF$_3$]	231	1.08	228	1.06
15% Li[SO$_3$CF$_3$]	240	1.09		
20% Li[SO$_3$CF$_3$]	243	1.05		
25% Li[SO$_3$CF$_3$]	253	1.08	242	1.03

Table V. ^{29}Si T_1 Values for D^{OR} Moiety and ^{13}C T_1 Values for the Si-CH$_3$ Group[a]

salt complex	^{29}Si D^{OR} (s)	^{13}C Si-CH$_3$ (s)
0	10.7 (4), 10.1 (4)	1.16 (10)
15	11.5 (9), 11.6 (8)	1.26 (7)
20	15.0 (9), 16.0 (6)	1.32 (9)
25	20 (3), 19.0 (1.3)	1.67 (12)

[a] The error in the T_1 values is given in parentheses. The ^{13}C T_1 values are for the methyl group pendant to the D^{OR} moiety. The ^{29}Si T_1 measurements were made at ca. 22 °C while the ^{13}C T_1 values were collected at 25 °C.

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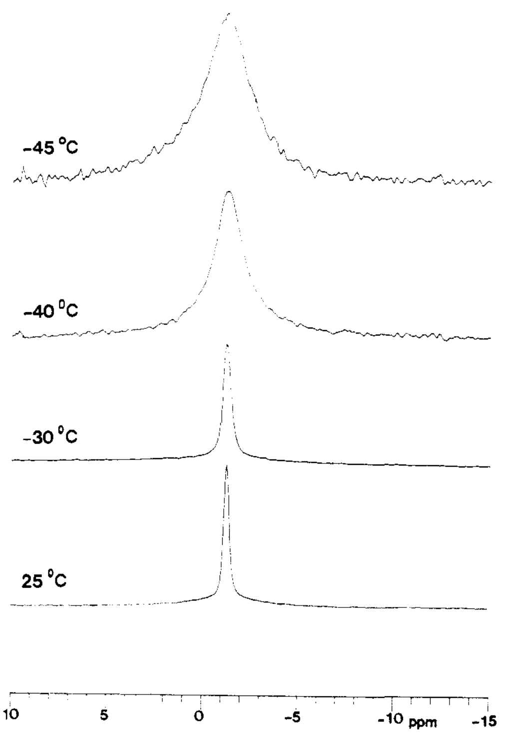

Figure 10. ^{7}Li NMR spectra of siloxane(30) Li[SO_3CF_3] 10% as a function of temperature.

group rotation, which is not strongly influenced by the addition of salt. The reason for the increased mobility of the methyl group is not clear. The larger increase in the ^{29}Si T_1 values compared to the ^{13}C T_1 is not clear.

^{7}Li NMR. In the study of solution electrolytes, alkali metal NMR has proven to be a useful technique since it allows for the direct interrogation of the cation environment.[6] The small chemical shift range (*ca.* 6 ppm) and the low quadrupole moment of ^{7}Li accounts for the reduced sensitivity of lithium to its environment, but still the strong receptivity of ^{7}Li makes it a very attractive nucleus to study.

The ^{7}Li chemical shift of Li[SO_3CF_3] in siloxane(30) was constant at −1.3 ppm irrespective of salt concentration or temperature of the measurement. Concentration-dependent ^{7}Li chemical shifts have been observed for Li[ClO_4] and LiBr in acetonitrile, but the changes were a few tenths of a ppm over a fourfold increase in concentration of salt.[31] The resolution in our experiments is not great enough to observe such small changes.

Even though there is no information from the ^{7}Li chemical shift, the line widths prove to be interesting. The ^{7}Li line widths are sensitive to both the concentration of Li[SO_3CF_3] and also temperature. Figure 10 shows that the line widths broaden as the temperature is lowered. This behavior is similar to that observed for the ^{13}C line widths of siloxane(30) and its Li[SO_3CF_3] complexes. In fact the ^{7}Li line widths can be used as an indicator of T_g. As with the ^{13}C line widths, 400 Hz will be considered a broad line. Values of T_c determined by this method correlate closely to the ones found by ^{13}C NMR over a wide range of Li[SO_3CF_3] concentrations (Table III). Hence the local segmental motion of the polyether chains correlates with the motion of the lithium cation. The weak quadrupole moment of ^{7}Li allows for relaxation mechanisms other than quadrupolar to become significant. For example, it has been shown that up to one-half of the relaxation rate of aqueous LiCl, LiBr, and LiI is mediated through a dipole–dipole mechanism.[32] Asymmetry of the polyether coordination environment will increase the quadrupolar contribution to T_1 of ^{7}Li. Even though we have not elucidated the mechanism of relaxation, the ^{7}Li nucleus is clearly being influenced by the segmental motions of the polyether chains.

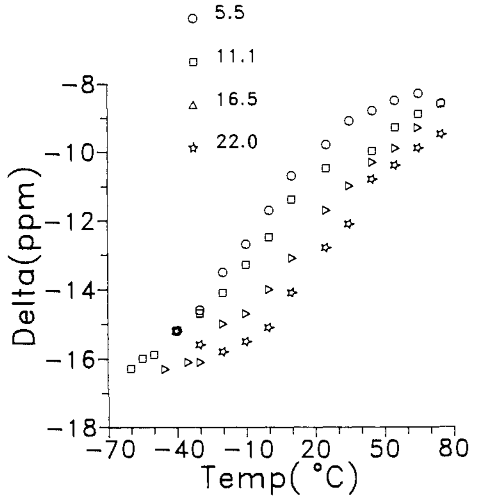

Figure 11. ^{23}Na NMR chemical shifts for the siloxane(30) Na[SO_3CF_3] salt complexes as a function of salt concentration and temperature.

^{23}Na NMR. Unlike the ^{7}Li NMR studies, ^{23}Na chemical shifts change as a function of both salt concentration and temperature (Figure 11). In general, the resonances shift upfield as the concentration of salt increases or the temperature decreases, although at both the high and the low end of the temperatures studied the chemical shifts appear to approach limiting values. A suggestion for the origin of the upfield shifts is available from ^{23}Na NMR data for solution electrolytes.

Concentration dependence of ^{23}Na chemical shifts have been correlated to cation–anion interactions in both aqueous and nonaqueous electrolytes.[6b,c] Halide anions produce downfield shifts whereas NO_3^- and $SO_3CF_3^-$ cause upfield shifts.[33] In some cases concentration-independent chemical shifts are observed which suggest that only free solvated ions exist. An example of such a case is Na[ClO_4] in formamide where the chemical shift is independent of concentration from 0.01 to 0.5 M.[34] In low-dielectric solvents, significant concentrations of ion pairs and higher order ionic aggregates are present.[35] If cation exchange is fast compared to the NMR time scale, a single resonance is observed with a chemical shift that is a weighted average of the individual components, eq 5, where δ_{obsd} is the observed chemical shift, χ_i is the mole fraction of ionic component i, and δ_i is the chemical

$$\delta_{obsd} = \sum_i \chi_i \delta_i \qquad (3)$$

shift of component i. When the various values of δ_i can be measured, it becomes possible to determine equilibrium constants for the formation of ion pairs, ion triplets, etc.[36]

The low dielectric constant environment of polymer electrolytes presumably is conducive to the formation of ion aggregates. Vibrational studies of PEO $LiNO_3$ complexes[37] and conductivity studies of liquid polyether Li[SO_3CF_3] complexes[38] both point to significant cation–anion interactions in polymer electrolytes. The ^{23}Na NMR data in the present study are also consistent with the formation of ion aggregates. Thus the ^{23}Na chemical shift data indicate that as the concentration of Na[SO_3CF_3] increases

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the degree of anion–cation interaction increases. Similarly, the upfield chemical shift at lower temperatures indicates cation–anion aggregation. The determination of equilibrium constants for ion association is not possible at this point since the limiting δ_i values were not resolved.

Greenbaum and co-workers[3b] have used ^{23}Na NMR measurements to indicate the presence of mobile and bound cations in a siloxane polymer electrolyte. The line width and ^{23}Na T_1 values of the Na[SO$_3$CF$_3$] siloxane(30) complexes correspond closely to their mobile species. No evidence for bound species was obtained in our studies.

Conclusions

These studies have shown that local segmental motion of the polyether chains, as probed by ^{13}C T_1 and line width measurements, is influenced by formation of a polymer salt complex. Both ^{13}C chemical shifts and T_1 values indicate that the ether carbons closest to the siloxane backbone are not involved in coordination of the lithium cations. As many workers have shown, the ionic conductivity of polymer salt complexes is strongly influenced by T_g. A correlation between T_1 and T_g substantiates the role of local segmental motion of the polyether chains in the ion transport process. The ^{23}Na NMR spectra of the siloxane(30)–Na[SO$_3$CF$_3$] complexes indicates extensive ion aggregation in these polymer electrolytes.

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Temperature-Induced Spontaneous Emission of Uranyl Nitrate Hexahydrate

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Abstract: The spectrum of the temperature-induced spontaneous emission (TSE) from uranyl nitrate hexahydrate, UO$_2$(NO$_3$)$_2$·6H$_2$O, has been recorded for the first time. It was observed as brilliant spark-like flashes in the temperature range 100–135 K on slow cooling and warming of its crystals. The TSE, as well as photoluminescence, originates from the first excited electronic state ($^3\Pi_u$) of the uranyl ion. Each TSE pulse is accompanied by a pulsed electric charge generation between two surfaces of a single crystal. The pulsed charge appears with opposite signs for cooling and warming processes, and in good correlation with the TSE pulse. It is suggested that the internal strain formed in a crystal during the cooling and warming processes causes microcracks, which lead to irregular transient pulses of both TSE and charge generation. The mechanism of excitation of TSE is discussed in detail.

I. Introduction

Characteristic flashes of green light observed on immersing a glass tube containing single crystals of uranyl nitrate hexahydrate (UNH), UO$_2$(NO$_3$)$_2$·6H$_2$O, into liquid nitrogen have been reported by several workers.[1] Pant and Bist have suggested that this luminescence is related to development of electric charges in the crystal.[1] We have recently found that the UNH crystal emits light solely by changing its temperature. No external force or irradiation is necessary. In addition, it is observed both for cooling and warming processes in the temperature range 100–130 K. These characteristic features of the temperature-induced spontaneous emission (TSE) are phenomenologically different from analogous phenomena such as triboluminescence (TL), which is the mechanically induced luminescence, or thermoluminescence, which is normally defined as the light emission induced by heating the preirradiated materials containing metastable species.

Triboluminescence has recently attracted renewed attention because of its general importance in materials used for fiber communication and of its possible role in detonations in condensed media.[2-5] Reliable TL spectra of UNH have recently been reported with use of diode array detectors.[3] On the other hand, the spectroscopic features of TSE have never been recorded, obviously due to inherent problems encountered in measuring weak unpredictable flashes of variable intensity during the temperature change.

In the present work, we have measured the TSE spectra of UNH single crystals near 130 K and compared them with the corresponding photoluminescence (PL) spectra. We attempted also to make quantitative measurements on the electric voltage generated across the single crystal for the purpose of finding a correlation with the TSE pulse. On the basis of these results, we discuss the mechanism of the temperature-induced charge separation (pyroelectricity) and its relation to the TSE excitation in some detail.

II. Experimental Section

A single crystal of UNH was grown by slow evaporation of its slightly acidic solution. It was placed in a quartz tube, evacuated, and sealed with a few mTorr of water vapor to prevent possible dehydration. The bottom part of the quartz tube was immersed in liquid nitrogen, and temperature was controlled by adjusting the level of liquid nitrogen. Temperature measurements were carried out with a calibrated chromel-gold(Fe) thermocouple placed inside the tube. The cooling or warming rate of ca. 6 deg/min was found to be appropriate to observe TSE.

The PL was excited with 440 nm (Coumarine 440, ~1 mJ/pulse) radiation from an excimer-pumped dye laser (Lumonics, Models TE-430 and EPD-330) at 10 Hz. The PL or TSE emission was measured with a 0.25-m polychromator (Nikon, model G-250) equipped with a cooled intensified diode array detector (Tracor Northern, Model TN 6132).

To measure the pyroelectric voltage (V_{PyE}) pulses, thin (0.3 mm) gold-plated copper electrodes were attached by silver paint to the crystal surfaces perpendicular to the hexagonal *c* axis. The crystal with elec-

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