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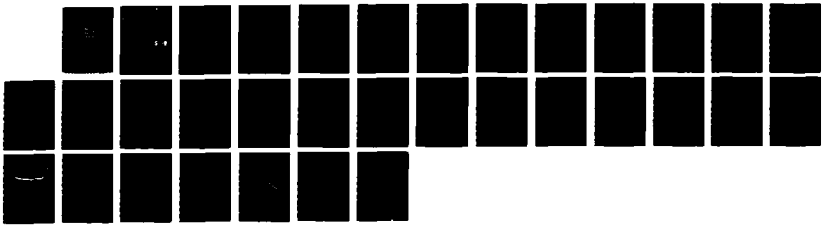

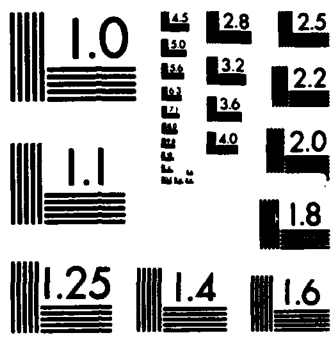

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A crosslinked siloxane-based polymer has been prepared by the reaction of Poly(methylhudrosiloxane), monomethyl ether poly(ethylene glycol), and poly(ethylene glycol). The polymer, which has been structurally characterized by ^{29}Si NMR, forms complexes with $LiSO_3CF_3$ that exhibit good ionic conductivities (~~up to~~ 7.3×10^{-5} Ω^{-1} cm^{-1}, 40 °C for a $LiSO_3CF_3$ 15 wt% complex). The polymer and its salt complexes have been characterized by elemental analysis, ^{29}Si NMR, powder diffraction X-ray powder diffraction,

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20. DSC, and AC complex impedance spectroscopy. The dependence of the ionic conductivity was investigated as a function of temperature, salt concentration (1 wt % to 25 wt %), and alkali metal cation (Li, Na, K, Rb, and Cs).

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Synthesis, NMR Characterization, and Electrical Properties of Siloxane-Based Polymer Electrolytes.

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ABSTRACT

A crosslinked siloxane-based polymer has been prepared by the reaction of poly(methylhydrosiloxane), monomethyl ether poly(ethylene glycol), and poly(ethylene glycol). The polymer, which has been structurally characterized by ^{29}Si NMR, forms complexes with $LiSO_3CF_3$ that exhibit good ionic conductivities (up to $7.3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, 40 °C, for a $LiSO_3CF_3$ 15 wt % complex). The polymer and its salt complexes have been characterized by elemental analysis, ^{29}Si NMR, powder diffraction X-ray powder diffraction, DSC, and AC complex impedance spectroscopy. The dependence of the ionic conductivity was investigated as a function of temperature, salt concentration (1 wt % to 25 wt %), and alkali metal cation (Li, Na, K, Rb, and Cs).

Introduction

As part of a program to elucidate the mechanism of charge transport in solvent-free polymer salt complexes, we have undertaken the synthesis and characterization of new polymer electrolytes. Many different polar polymers have been studied but the electrolytes with the highest ionic conductivities contain ether polar groups.[1-4]

Recently a series of polymers with the highly flexible phosphazene backbone and pendant short-chain polyethers (I) have been shown to form salt complexes that exhibit low values of T_g and high ionic conductivity.[5] The low values of T_g are diagnostic of a high degree of polymer segment motion which is thought to be essential for ion transport.[1-3]

<Structure>

In this report we describe the preparation and characterization of a polyether substituted siloxane host polymer and its salt complexes. We were prompted to prepare these materials because siloxanes typically exhibit low values of T_g. The siloxane polymer was prepared from the reaction of poly(methylhydrosiloxane), PMHS (II), monomethyl ether poly(ethylene glycol), MePEG(III), and poly(ethylene glycol), PEG (IV). Other groups have investigated siloxane-based electrolytes but in most cases the polymer was a block copolymer of dimethylsiloxane and ethylene oxide repeat units.[6] A urethane network formed from poly(dimethylsiloxane-grafted ethylene oxide)

has also been studied .[7] While the work presented in this paper was in progress, other groups reported preliminary results on systems similar to the one reported here.[8]

Experimental

Monomethyl ether poly(ethylene glycol), MePEG (Aldrich, avg. MW = 350), poly(ethylene glycol), PEG (Aldrich, avg. MW = 300), and poly-(methylhydrosiloxane), PMHS (Petrarch, MW = 4,500-5,000), were dried under vacuum at 60 °C for two days, no evidence of H_2O in any of the starting materials was noted by IR spectroscopy. A Zn octoate catalyst (Petrarch, 50 wt.% PDMS) was used as received. The polymer host that we designate as siloxane(30) was prepared by the reaction of a stoichiometric amount of PMHS (2.00g), MePEG (8.15g), PEG (1.50g), and ca. 50 mg of Zn octoate/PDMS in xylene at 130 °C for ca. 4 hours under a flow of Ar. The mixture was then cooled to room temperature and the solvent was removed under vacuum. During the removal of solvent the reaction mixture was slowly reheated to 130 °C. After ca. 2 hours at this temperature, a colorless solid formed. The solid was washed for 1-4 days with CH_2Cl_2 in a Soxhlet extractor to remove unreacted polyethers and the catalyst. Siloxane(30) was dried under vacuum (ca. 2×10^{-5} torr) for more than 48 hours, and stored in a dry, inert atmosphere. Elemental analysis gave a good correlation between the observed and desired composition: found (calculated), C 47.28(47.83), H 8.26(8.46), and Si 7.50(7.16). The undoped siloxane(30) had a conductivity of ca. 4×10^{-8} Ω^{-1} cm^{-1} (40 °C) which is 3 orders of magnitude lower than the conductivity of the salt complexes described here. The conductivity of the parent polymer probably arises from ionic impurities.

The salts used in preparation of the complexes were either obtained from

commercial sources, $LiSO_3CF_3$ and $NaSO_3CF_3$ (Alfa), or synthesized from the reaction of HSO_3CF_3 (Aldrich) with MOH, M = K, Rb, and Cs (Aldrich). In all cases the salts were recrystallized from CH_3CN/C_6H_6 and then dried under vacuum (100 °C, 2 x 10^{-5} torr) for 2-4 days. The salts were stored in a dry, inert atmosphere. Salt complexes were prepared by weighing a stoichiometric quantity of salt and siloxane(30) in a dry, inert atmosphere. Acetonitrile (previously distilled from CaH_2) was added, and the solvent swollen polymer was kept in contact with the solution for one day. Upon removal of the solvent, a separate salt phase was not present. The complexes were dried under vacuum at ca. 60 °C for 2 days and then stored in a dry, inert atmosphere. Throughout this paper, the concentrations of salt are reported as weight percentages, because the more conventional concentration units such as polymer repeat unit per salt formula unit are not well defined for these crosslinked systems. The homogeneous polymer-salt complex was analyzed for sulfur (in $SO_3CF_3^-$) and the results agreed with those calculated for the polymer to salt ratio employed in the preparation: found (calculated), for siloxane(30) $LiSO_3CF_3$ 5%; 0.99(1.03); for siloxane(30) $LiSO_3CF_3$ 10%, 2.05(2.06); for siloxane(30) $LiSO_3CF_3$ 15%, 3.16(3.08); and for siloxane(30) $LiSO_3CF_3$ 20%, 3.73(4.11). As judged by X-ray powder diffraction, no crystalline salt was present in any of the polymer salt complexes.

^{29}Si NMR spectra were obtained on a Varian XL-400 400 MHz spectrometer. $Cr(acac)_3$, ca. 10 mM, was used as a spin relaxant and C_6D_6 was employed for the deuterium lock. NMR spectra of solid siloxane(30) were obtained on the xylene-swollen polymer. Tetramethylsilane was used as an internal standard.

DSC traces were obtained on a Perkin Elmer DSC-2 equipped with liquid nitrogen cooling. Values of T_g were determined at the midpoint of the

inflection. Cold crystallization exotherms and melting endotherms were measured at the peak of the transition. The temperature scale was calibrated using five standards (In, naphthalene, Ga, Hg, and heptane). All transitions were obtained at three heating rates (usually 80, 40 and 20 °/min) and the reported transitions were found by extrapolating to a 0 °/min heating rate. X-ray powder diffraction traces were obtained on a Rigaku automated powder diffractometer, at room temperature, using CuKα radiation.

Samples for AC impedance analysis were pressed into pellets inside air-tight conductivity cells. The manipulation of all samples was performed under a dry, inert, and nitrogen-free atmosphere. Pt (Goldsmith) or Li (ribbon, Foote Mineral Co.) electrodes were used in these measurements. The frequency-dependent impedance of the samples was measured on a HP 4192A impedance analyzer (5 MHz to 5 Hz) or a Solartron 1250 Frequency Response Analyzer/1286 potentiostat system (1 KHz to 10^{-3} Hz). Good agreement was found in the region where data from the two different instruments overlap. The sample cell was placed in a regulated air-bath (± 0.1K) for the temperature-dependent conductivity measurements. In the temperature range from 30 to -5 °C, $CO_{2(s)}$ was placed in the oven cavity to maintain the temperature. The -23 °C data was obtained by placing the sealed conductivity cell in a CCl_4 slush bath. The temperature dependent conductivity was fit to the VTF equation, Equation 8, by a linear least squares program where the parameter T_o was varied until the best fit was obtained as judged by $\chi^2 = \Sigma\ (1/Di)^2\ (\sigma_i^{calc} - \sigma_i^{exp})^2$. D_i is the deviation in the experimental conductivity data, σ_i^{calc} is the calculated value of the conductivity, Equation 8, and σ_i^{exp} is the experimental value of the conductivity. The best fit was obtained when $\chi^2 = 1$.

Results and Discussion

Synthesis and Characterization of the Polymer Host. Equation 1 shows the general reaction used to prepare a polyether substituted siloxane polymer.

$$\begin{array}{c} H \\ | \\ (SiO)_x \\ | \\ CH_3 \end{array} \quad + \quad ROH \quad \xrightarrow{\text{catalyst}} \quad \begin{array}{c} OR \\ | \\ (SiO)_x \\ | \\ CH_3 \end{array} \quad + \quad H_{2(g)} \qquad (1)$$

A study of the literature reveals that a wide variety of catalyst have been employed to promote the reaction of silanes with alcohol including $ZnCl_2$, $SnCl_2$, NEt_3, and Na_2CO_3.[9] Scheme 1 summarizes the procedure used in the polymer preparation. A stoichiometric mixture of PMHS, MePEG, and PEG were

Scheme 1

PMHS x	xylene	vacuum	Soxhlet	vacuum	
+ 2 PEG	------->	------->	------->	------->	siloxane(30)
	130 °C	130 °C	CH_2Cl_2	60 °C	
+ 1-x MePEG	4 hrs	2 hrs		48 hrs	

allowed to react together in xylene. PEG was employed as a crosslinking reagent, since the commercially available PMHS is a viscous liquid of ca. 5000 MW. A crosslinking density of 30% (x = 0.3) was found to give the best combination of high ionic conductivity and good mechanical properties.

^{29}Si NMR was an excellent probe of the structure of siloxane(30), because of the wide chemical shift range, distinctive chemical shift values, and the availability of extensive chemical shift information for both molecular[10] and polymeric systems.[11] Figure 1 shows the ^{29}Si NMR spectrum of solid siloxane(30) after impurities had been extracted from it with CH_2Cl_2 and volatiles removed under vacuum. Three signals are observed at -49.8, -57.8, and -65 ppm as well as a very broad resonance centered at ca. -115 ppm, which

is due to the glass NMR tube. By comparison with NMR data for both molecular silanes[10] and polymeric siloxanes[11] we can assign the peaks as follows: $M^{(OR)2}$ (-49.8 ppm), D^{OR} (-57.8 ppm), and T (-65 ppm). The notation used here is explained in Fig. 1. The reaction appears to have gone to completion as judged by the absence of signals due to free Si-H (D^{H}, -33.8 ppm) moieties. Attempts to limit the formation of $M^{(OR)2}$ and T groups by lowering the reaction temperature, decreasing the concentration of the catalyst or changing the catalyst from Zn(octoate)$_2$ to $ZnCl_2$, $SnCl_2$, and K_2CO_3 had only a slight effect on the product distribution. Addition of up to 5% H_2O (based on PMHS) to the reaction mixture resulted in no significant change in the observed products. The synthetic procedure of Smid and coworkers[8b] was also employed but the spectrum for the product indicated a distribution of structures similar to that found for our original product.

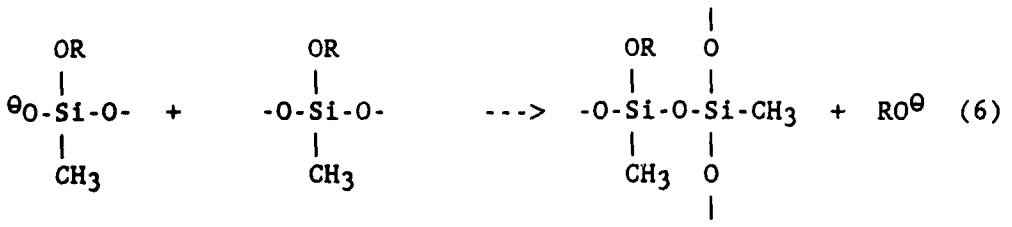
A mechanism for the formation of siloxane(30) is proposed in Equation 2-6. We believe that the formation of the monoalkoxy substituted siloxane moiety (D^{OR}) is catalyzed by an alkoxide, Equation 4.

$$Zn^{+2} \xrightarrow{\text{PMHS}} Zn^{0} \qquad (2)$$

$$2\ ROH + Zn^{0} \longrightarrow Zn(OR)_2 + H_{2(g)} \qquad (3)$$

$$ROH + \text{-O-Si(H)(CH}_3\text{)-O-} \xrightarrow{RO^{\ominus}} \text{-O-Si(OR)(CH}_3\text{)-O-} + H_{2(g)} \qquad (4)$$

$$RO^{\ominus} + \text{-O-Si(OR)(CH}_3\text{)-O-Si(OR)(CH}_3\text{)-O-} \longrightarrow \text{-O-Si(OR)(OR)-} + {}^{\ominus}\text{O-Si(OR)(CH}_3\text{)-O-} \qquad (5)$$



The preparation of alkoxy substituted silanes has been carefully studied[12] and a number of workers have shown that the alkoxide attacks the silane center in a S_N2 fashion to liberate the hydride, Equation 7. The hydride is not a good leaving group but its displacement is assisted by reacting with a proton from

$$HSiR_3 + R'OH \xrightarrow{R'O^{\ominus}} R'OSiR_3 + H_{2(g)} \qquad (7)$$

the alcohol to form $H_{2(g)}$. This last step regenerates the catalytic alkoxide. In the synthesis of siloxane(30), the alkoxide catalyst is formed in two steps, Equations 2 and 3. First Zn^{+2} is reduced by PMHS to finely divided zinc metal which is then followed by the reaction of the polyethers with Zn^0 to form the alkoxide. The reduction of Zn^{+2} to Zn^0 is reasonable as PMHS is known to be a fairly strong reducing agent.[13] Even more compelling evidence for this interpretation is the observation that if insufficient polyether is used during the synthesis of siloxane(30) zinc metal is observed to form. The formation of the $M^{(OR)}2$ and T moieties appears to be associated with the presence of base Equations 5 and 6. The effect of base on the Si-O-Si linkage has been well documented.[14] An example of this reaction is shown in Equation 8 where base cleaves the Si-O-Si bond in disiloxane to form siloxides.[15]

$$[(CH_3)_3Si]_2O + 2NaOH \rightleftharpoons 2\,(CH_3)_3SiONa + H_2O \qquad (8)$$

Also basic catalysts are important in the ring opening polymerization of cyclic siloxanes to produce linear siloxane polymers.[16] In the synthesis of siloxane(30), the alkoxide breaks the Si-O-Si bond to give the $M^{(OR)}2$ moiety

and a siloxide, Equation 5. The siloxide can then react with a D^{OR} group to form the T moiety as is shown in Equation 6. A similar reaction has been used to prepare a monomeric analogue of the T groups, Equation 9.[17]

$$4\ (CH_3)SiOH + (EtO)_3SiCH_3 \xrightarrow{NaOSi(CH_3)_3} [(CH_3)_3SiO]_3SiCH_3 + 4EtOH \quad (9)$$

Characterization of the Polymer Salt Complexes The thermal properties of siloxane(30) and its salt complexes, which were investigated by differential scanning calorimetry (DSC), are listed in Table I. A single glass transition temperature was observed at 204 K in DSC scans for siloxane(30), that were conducted over the temperature range 110 to 400 K. As siloxane(30) is heated past T_g, an exothermic cold crystallization is observed followed by an endothermic melting transition. The cold crystallization is observed when the sample is quenched at rates greater than 10°/min, as the sample forms a metastable glassy state. At slower cooling rates the polymer crystallizes and the exothermic transition is not seen. The similarity of the cold crystallization and melting temperatures between siloxane(30), MePEG, and PEG leads us to suggest that the polyether sidegroups crystallize but the siloxane backbone does not. The selective crystallization of side groups has been observed for other comb polymers.[18]

The presence of salt affects the ability of siloxane(30) to form an ordered crystalline phase. At salt concentrations greater than 5 wt. % $LiSO_3CF_3$ (O:Li = 53:1) no crystalline phases are observed. Other alkali metal salts influence T_g but not the cold crystallization or melting transitions (Table 1). Ion-dipole interactions effectively crosslink the polymer chains and therefore, T_g increases as the concentration of salt increases.

Impedance measurements on the polymer-salt complexes were acquired as a

function of frequency (5 MHz to 10^{-3} Hz) in order to separate response of the bulk polymer electrolyte from polarization at the electrode.[19] Figure 2a shows a characteristic complex impedance plot for the siloxane(30) LiTf 15% complex sandwiched between ion-blocking Pt electrodes. The high frequency semicircle is associated with the bulk properties of the polymer electrolyte. The low frequency spur in the impedance plot arises from double layer capacitance at the electrode-electrolyte interface. This assignment is confirmed by data obtained with cation-reversible lithium electrodes which yield impedance spectra which contain the high frequency semicircle but have a small semicircle in place of the low frequency spur, Figure 2b. The low frequency semicircle is attributed to resistance and capacitance associated with the transfer of lithium cations between the electrolyte and the electrode. The stability of siloxane(30) electrolytes toward Li electrodes was qualitatively investigated by complex impedance measurements. At a given temperature no changes were noted were noted in the impedance spectra when the sample was cycled between 40 and 80 °C over a two day period. Since the electrical properties of the lithium-polymer interface do not change we assume that decomposition of the electrolyte is not occurring at the interface under these conditions. Hall and coworkers[8a] report that their "comb-like" siloxane electrolyte is not stable to Li electrodes. Smid and coworkers[8b] did not report the stability of their electrolyte to lithium electrodes. It is our impression that many reports of polymer electrolyte instability toward lithium may actually originate from the reaction of impurities such as moisture, oxygen, or nitrogen with the lithium electrode.

The effect of salt concentration on ionic conductivity can be broken down into two temperature regions. For the conductivity data collected in the

temperature range 10 to 80 °C, a maximum in the conductivity is observed at 15% $LiSO_3CF_3$ (O:Li = 16.1), Figure 3. Similar behavior has been observed for both semi-crystalline[4a,20] and amorphous polymer electrolytes.[5,21,22,23] At temperatures below 10 °C the maximum in the conductivity is shifted to lower salt concentrations as is shown in Figure 4 for the data collected at -23 °C. To aid our understanding of the concentration dependence of the ionic conductivity we employ Equation 7 which relates the conductivity (σ) to the concentration of charge carriers (n_i), the charge of the carriers (q_i), and their ionic mobility (μ_i).

$$\sigma = \Sigma n_i q_i \mu_i \qquad (7)$$

As the concentration of salt in the electrolyte is increased, the number of charge carriers should also increase, although the increase in charge carriers may not be a linear function of salt concentration if ion pair or multiplet formation is significant. According to the excess entropy model,[24] ionic mobility is strongly influenced by T_g. Therefore it is instructive to look for an explanation of the maximum in the conductivity in terms of variations in T_g as has been discussed by previous workers.[5a,25]

Figure 3 shows that T_g increases in a linear fashion with a slope of 1.3 K/ wt. % $LiSO_3CF_3$. For data collected in the temperature range 10 to 80 °C the conductivity increases with increasing salt concentration up to 15 wt. % $LiSO_3CF_3$, apparently due to an increase in the number of charge carriers. As the $LiSO_3CF_3$ concentration increases beyond 15% the conductivity decreases. This decrease in conductivity can be explained by the excess entropy model for ion transport, Equation 8. The T_o term in that expression is closely related to T_g. As T_g increases T_o also increases which lowers the ionic conductivity for polymer salt complexes which contain greater than 15% $LiSO_3CF_3$.

Interestingly the linear polyether substituted phosphazene electrolytes exhibit a maximum in the conductivity at approximately the same ratio of ether oxygens to formula units of $LiSO_3CF_3$ (16:1) as found in the siloxane(30) salt complexes.[21] Even though the molecular structure of the siloxane(30) electrolyte is more complex than the phosphazene-based electrolytes, the concentration dependence, temperature dependence, and magnitude of the conductivity are comparable for the two electrolytes. The liquid electrolyte prepared by Smid and coworkers[8b] exhibits a maximum in the conductivity at an ether oxygen to lithium cation ratio of 25:1.

As we have previously stated, when the ionic conductivity is measured at lower temperatures the maximum in the conductivity shifts to lower salt concentrations for the $LiSO_3CF_3$-siloxane(30) system, Figure 4. For example, at -23 °C the maximum is observed at 5% $LiSO_3CF_3$. The basis for this shift is apparent in Equation 8 because of the closer proximity of T to T_o when the conductivity is measured at reduced temperatures.

In addition to the influence of polymer segmental motion on conductivity ion-ion interactions may influence the concentration-dependence of the ionic conductivity. The concentration of charge carriers in a low dielectric medium such as polymer electrolytes is probably strongly influenced by the formation of ion pairs and multiplet ions. In the concentration range of salts used in the present studies (ca. 0.1 to 2M), a significant degree of ion pair formation has been found in low dielectric constant solvents.[26] Also evidence for ion-pair formation has been obtained by Raman spectroscopy for PEO-$LiNO_3$ complexes,[27] and multiplet ion formation has been inferred for polyurethane salt complexes.[25] Recent work on low molecular weight polyethers has shown that the conducting species in polymer electrolytes are most likely triplets

and other higher order aggregates.[28] Further work needs to be done to probe the significance of ion-pair formation on conductivity in polymer electrolytes.

The temperature dependence of the ionic conductivity is shown in Figure 5 for siloxane(30) $LiSO_3CF_3$ 15% and siloxane(30) $LiSO_3CF_3$ 5%. For both complexes the plots are curved over the temperature range studied (80 to -23 °C). Curved log(σ) versus 1000/T plots are characteristic of amorphous electrolytes,[22a,26] although linear or close to linear plots are also observed.[23] The Vogel-Tamman-Fulcher (VTF), Equation 8, has been used to model the temperature-dependent conductivity of amorphous polymer electrolytes.[6b,22a,26]

$$\sigma = AT^{-1/2} \; e(-B/T-To) \qquad (8)$$

Both configurational entropy[24] and free volume[29] models have been used to derive the VTF equation. The significant parameters are B, the apparent activation energy, and T_o, a parameter which is normally found to be 30 to 60 °C below T_g. Table II lists the values of T_o and B obtained by fitting Equation 8 to the temperature dependent conductivity data obtained for the siloxane(30) salt complexes. The pre-exponential factor, apparent activation energy, and T_o all increase as the concentration of salt in the polymer increases. The T_o values were found to be 40 to 50 °C below Tg. The nearly linear nature of the log(σ) versus 1000/T plot over the temperature range of 10 to 80 °C permits the use of the Arrhenius, Equation 9, to determine activation energies.

$$\sigma = AT^{-1} \; e^{-(E/RT)} \qquad (9)$$

These activation energies are listed in Table II and Figure 6 shows a plot of E versus the concentration of LiTf. The activation energies increase linearly

as a function of concentration which mirrors the behavior of T_g, Figure 3. This result suggests that T_g and the activation energy for charge transport are correlated.

Figure 7 exhibits the cation dependence of ionic conductivity for the alkali metal trifluoromethane sulfonate salts (MSO_3CF_3; M = Li, Na, K, Rb, and Cs). In these experiments the concentration of MSO_3CF_3 was constant for each complex and equivalent to the concentration of MSO_3CF_3 found in siloxane(30) $LiSO_3CF_3$ 5%. All the values of T_g for the siloxane(30) MSO_3CF_3 complexes are within 3 K of one another so T_g should not appreciably influence the conductivity values we discuss in this section. The trend observed here is that conductivity increases with increasing radius of the cation from Li through Rb. Similar behavior has previously been observed in both aqueous and nonaqueous solution electrolytes,[30] and also in poly(propylene oxide) network complexes with MSCN(M = Li, Na, and K).[31] The correlation between ionic radius and conductivity does not hold for $CsSO_3CF_3$ which has a lower total ionic conductivity than the $RbSO_3CF_3$ complex. In nonaqueous electrolytes size limitations on ionic mobilities have only been found for the larger NR_4^+ (R = alkyl) cations,[32] but for polymer electrolytes, the more constrained nature of the solvent may hinder the mobility of the larger Cs^+ cation.

Conclusions.

A crosslinked polymer electrolyte based on a siloxane backbone has been synthesized. NMR data indicate that the structure of this polymer, siloxane(30), is complicated by the presence of Si-O-Si crosslinks as well as the intended polyether crosslinks. The electrolytes formed by incorporating alkali metal salts into siloxane(30) display ionic conductivity that is as good as those observed for the structurally simpler polyphosphazene

electrolytes. The cation dependence of the ionic conductivity for the siloxane(30) polymer electrolytes is similar to that for solution electrolytes.

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

Polymer	Tg(K)±2K	Tcc(K)±3K	Tm(K)±3K
PMHS	133	----	----
PEG	194	213	255
MePEG	178	205, 221	246, 266
siloxane(30)	204	218	264
siloxane(30) $LiSO_3CF_3$ 1%	204	205, 221	261
siloxane(30) $LiSO_3CF_3$ 2.5%	207	217	263
siloxane(30) $LiSO_3CF_3$ 5.0%*	210	230	264
siloxane(30) $LiSO_3CF_3$ 7.5%	213	---	---
siloxane(30) $LiSO_3CF_3$ 10%	215	---	---
siloxane(30) $LiSO_3CF_3$ 12.5%	219	---	---
siloxane(30) $LiSO_3CF_3$ 15.0%	220	---	---
siloxane(30) $LiSO_3CF_3$ 17.5%	226	---	---
siloxane(30) $LiSO_3CF_3$ 20.0%	231	---	---
siloxane(30) $LiSO_3CF_3$ 25.0%	235	---	---
siloxane(30) $NaSO_3CF_3$ 5.5%*	209	230	258
siloxane(30) KSO_3CF_3 6.0%*	206	232	259
siloxane(30) $RbSO_3CF_3$ 7.5%*	206	225	257
siloxane(30) $CsSO_3CF_3$ 9.0%*	206	232	257

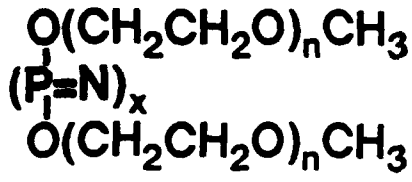
* These complexes all contain the same number of moles of cations to moles of polymer repeat units.

Table II. VTF and Arrhenius Parameters

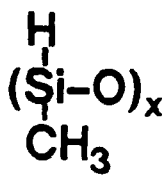
sample	A*	B(eV)*	T_o(K)*	T_g-T_o(K)	E(eV)**
siloxane(30)$LiSO_3CF_3$ 2.5%	0.045	0.062	166	41	0.29
siloxane(30)$LiSO_3CF_3$ 5.0%	0.20	0.068	172	38	0.32
siloxane(30)$LiSO_3CF_3$ 10.0%	0.33	0.072	173	42	0.37
siloxane(30)$LiSO_3CF_3$ 15.0%	0.93	0.075	182	38	0.42
siloxane(30)$LiSO_3CF_3$ 20.0%	1.1	0.081	182	49	0.48

* Equation 8.

** Equation 9.



(I)



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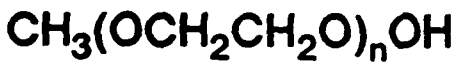

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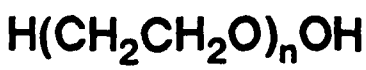


(IV)

Figure Captions

Figure 1. ^{29}Si NMR spectrum of solvent swollen siloxane(30) (top spectrum) and poly(methylhydrosiloxane) (lower spectrum). The broad resonance on the right hand side of the siloxane(30) spectrum is due to the glass of the NMR tube. The siloxane nomenclature used in this paper is shown at the bottom of this figure.

Figure 2. Complex impedance spectra of siloxane(30) $LiSO_3CF_3$ 15% with ion-blocking Pt electrodes (A), and cation reversible Li electrodes (B). The different scales on the two plots are due to the different geometric factors of the polymer electrolytes used in these two experiments.

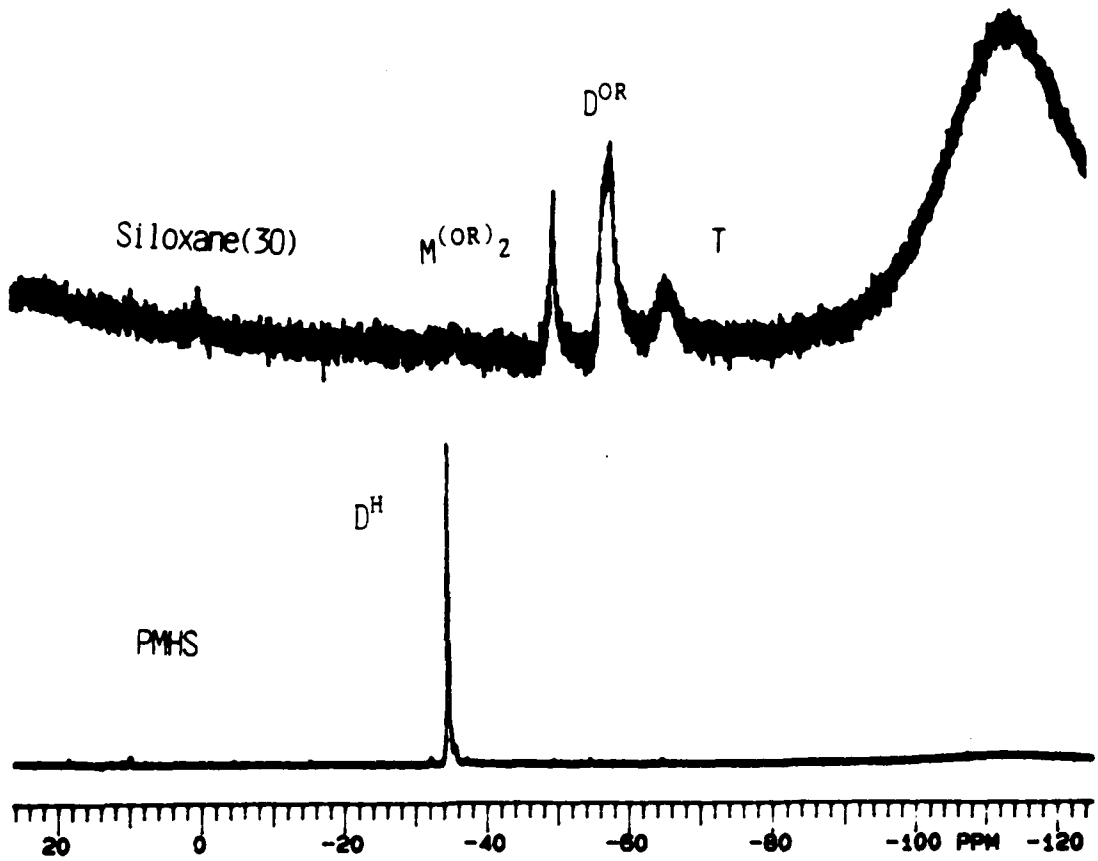
Figure 3. Concentration dependence of the ionic conductivity (left hand axis, circles) and T_g (right hand axis, triangles) for the siloxane(30) $LiSO_3CF_3$ salt complexes at 40 °C.

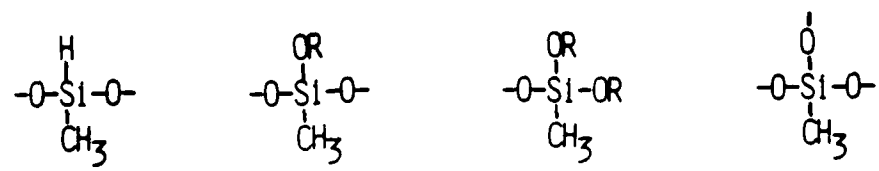
Figure 4. Conductivity of the siloxane(30) $LiSO_3CF_3$ polymer salt complexes as a function of salt concentration at -23 °C.

Figure 5. Temperature dependence of the ionic conductivity for siloxane(30) $LiSO_3CF_3$ 5% (circles) and siloxane(30) $LiSO_3CF_3$ 15% (stars). The lines drawn through the data points were calculated from the best-fit parameters obtained from the VTF equation (Equation 8) for each complex, see Table II for the parameters.

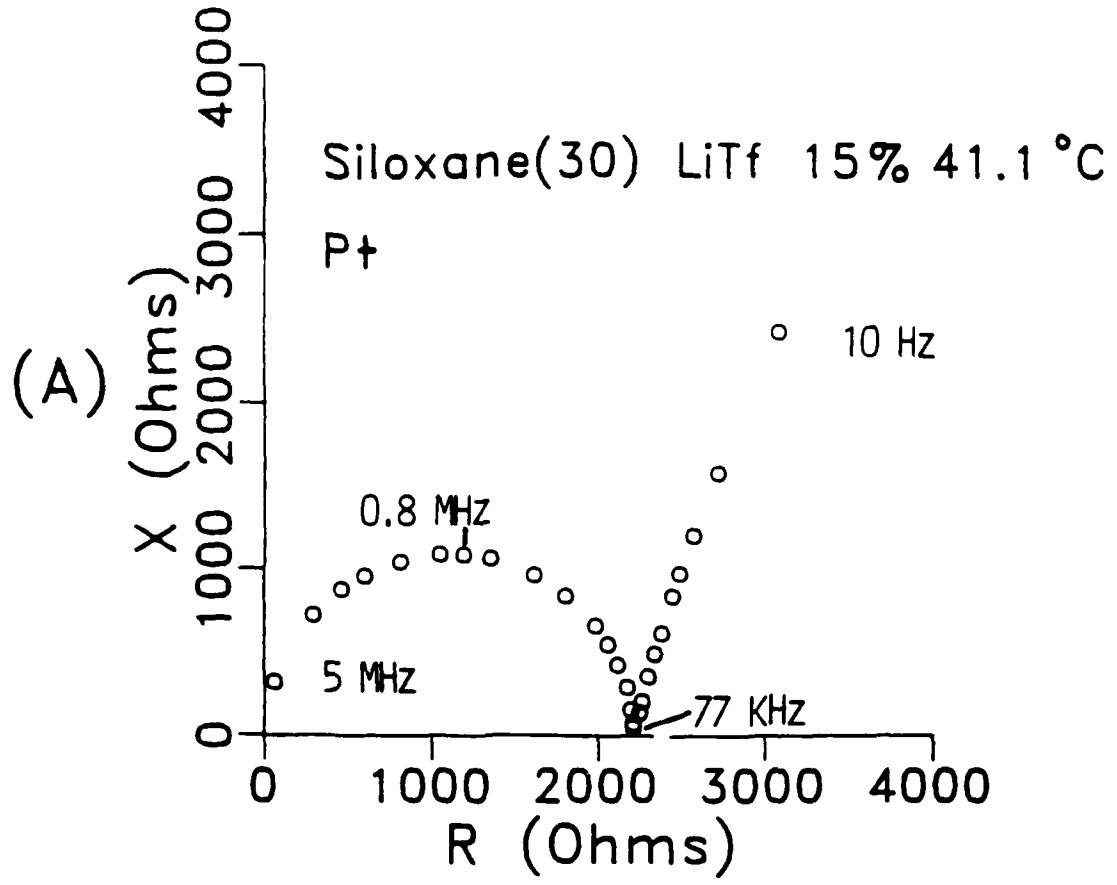
Figure 6. Arrhenius activation energies for siloxane(30) $LiSO_3CF_3$ salt complexes shown as a function of $LiSO_3CF_3$ contained in the electrolyte.

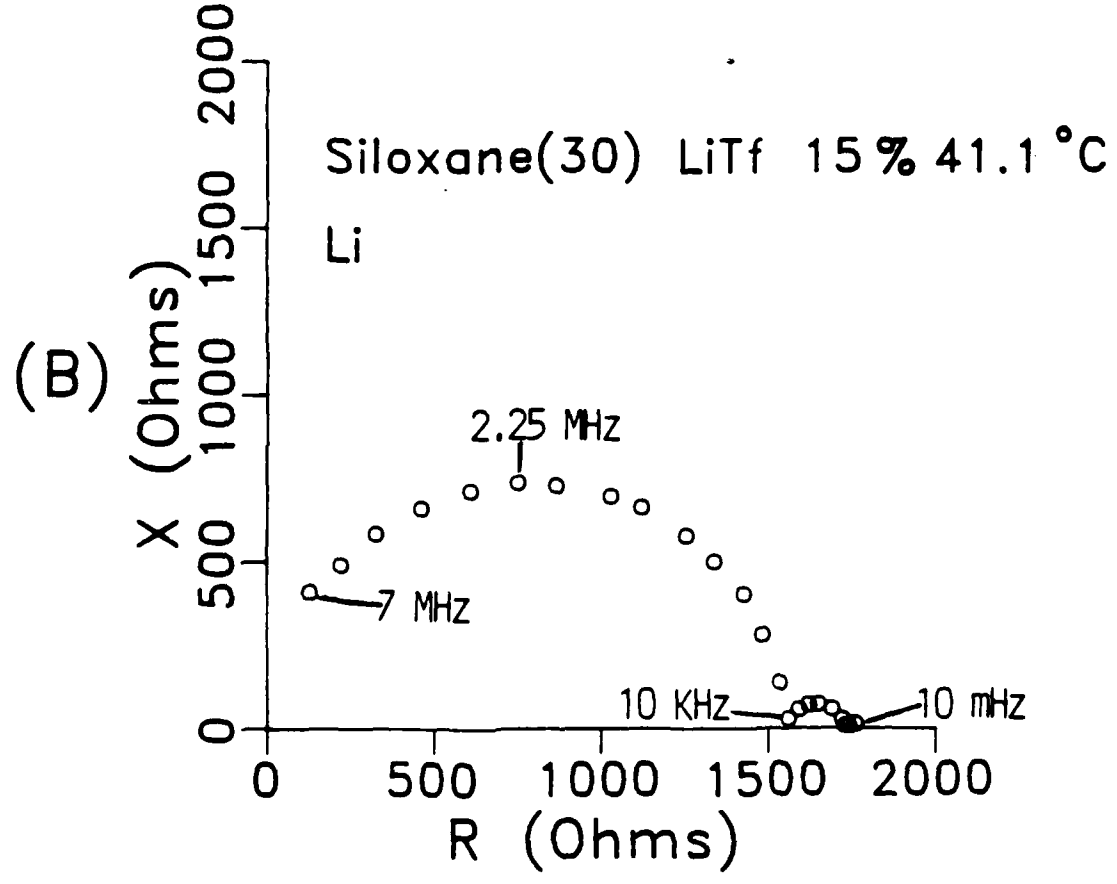
Figure 7. Ionic conductivity as a function of alkali metal cation for the siloxane(30) MSO_3CF_3 (M = Li, Na, K, Rb, and Cs) complexes. Equimolar concentrations of salt were employed in these measurements. The ionic conductivity was measured at 40 °C.

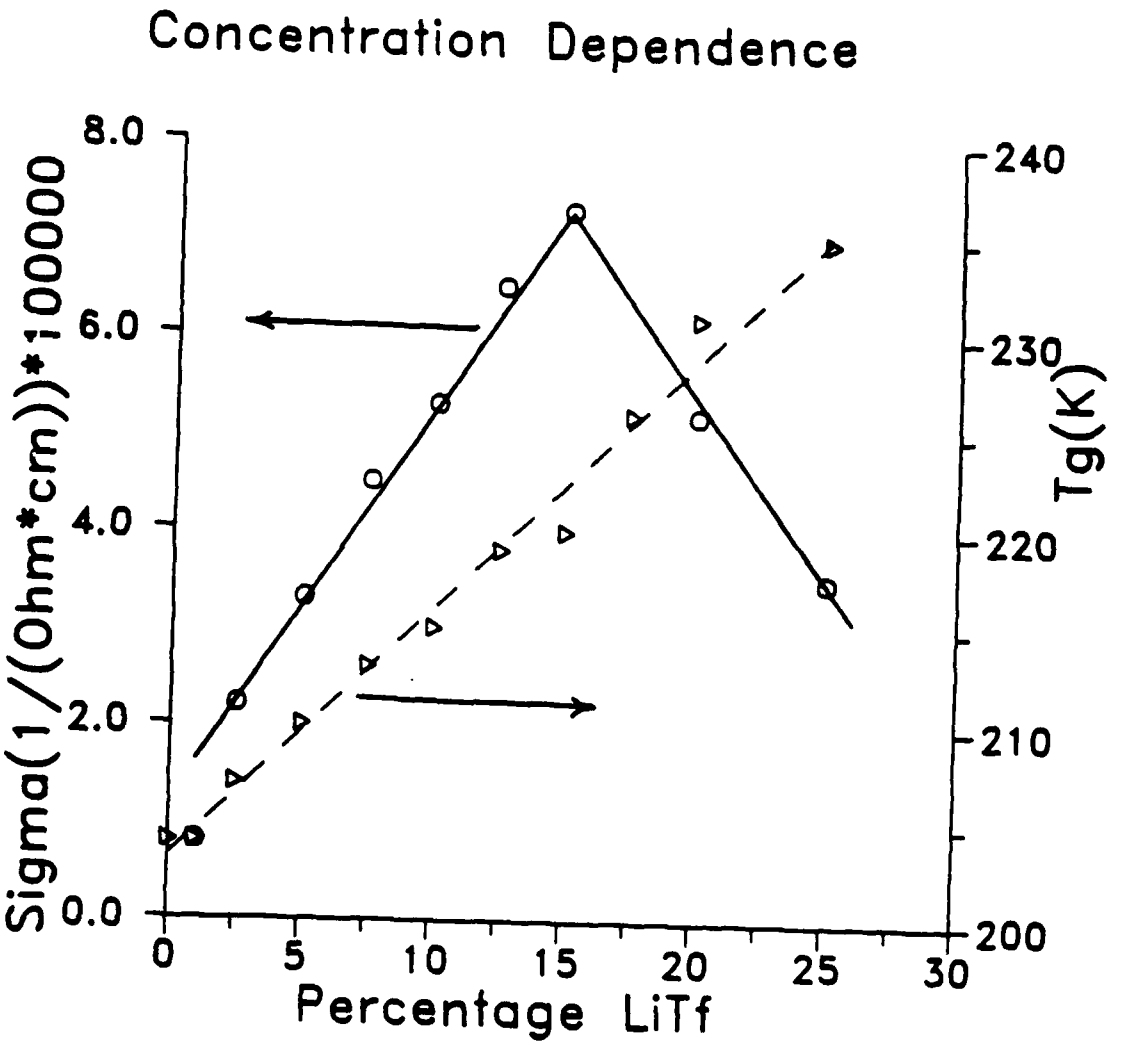

Siloxane(30)
$M^{(OR)_2}$
D^{OR}
T
D^H
PMHS
20
0
-20
-40
-60
-80
-100 PPM
-120

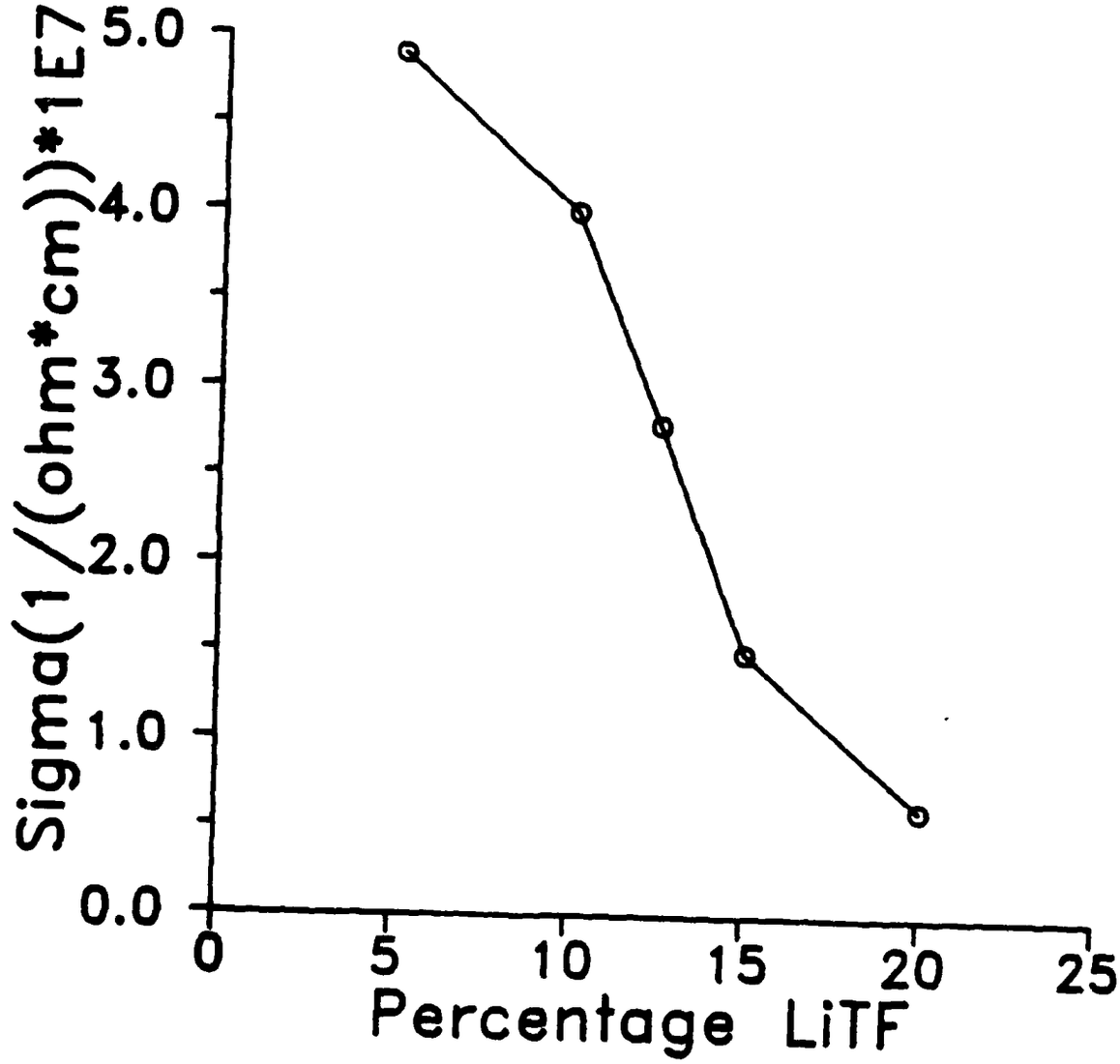

H
-O-Si-O-
CH3
OR
-O-Si-O-
CH3
OR
-O-Si-OR
CH3
O
-O-Si-O-
CH3

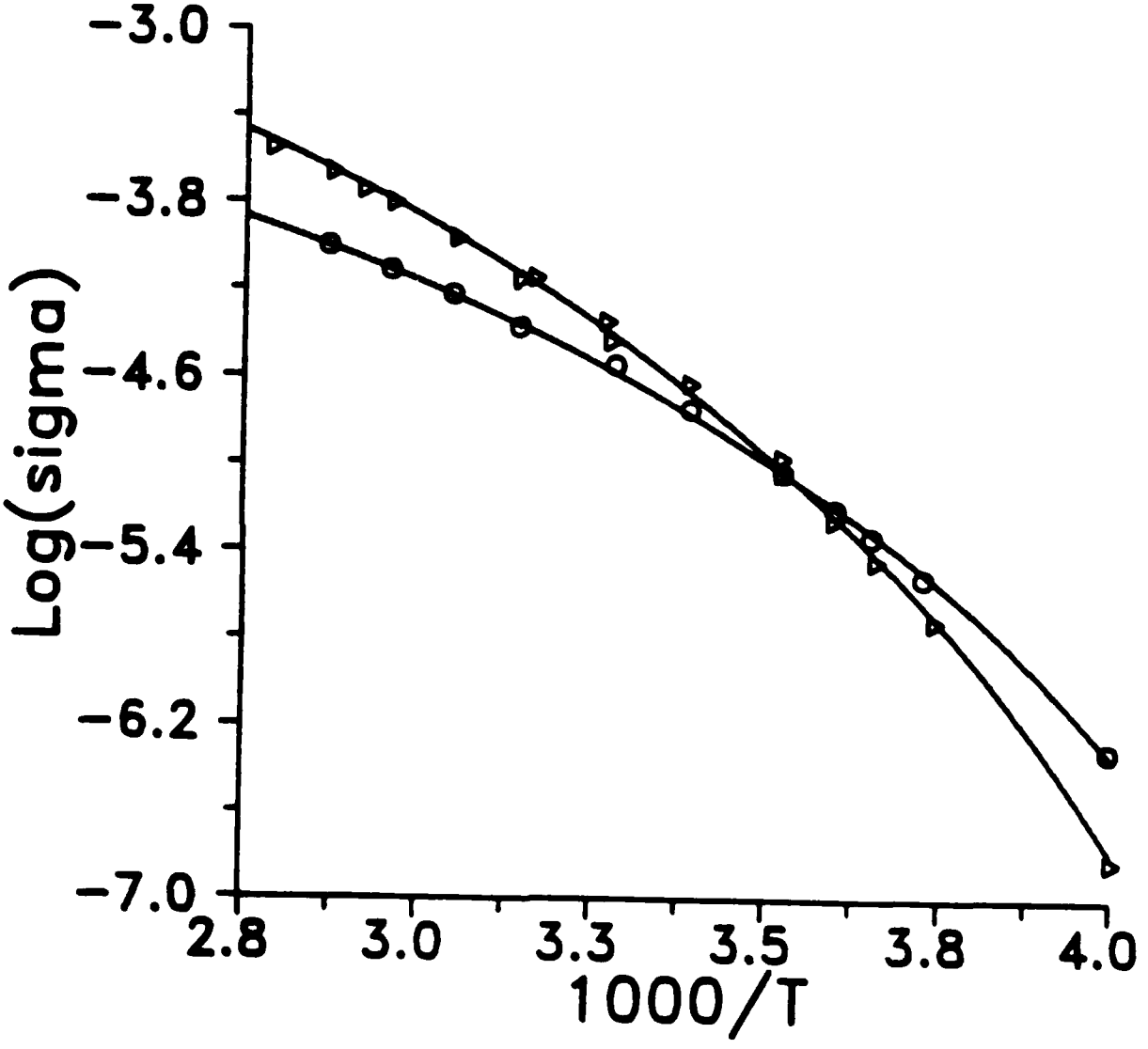
D^H D^{OR} $M^{(OR)_2}$ T

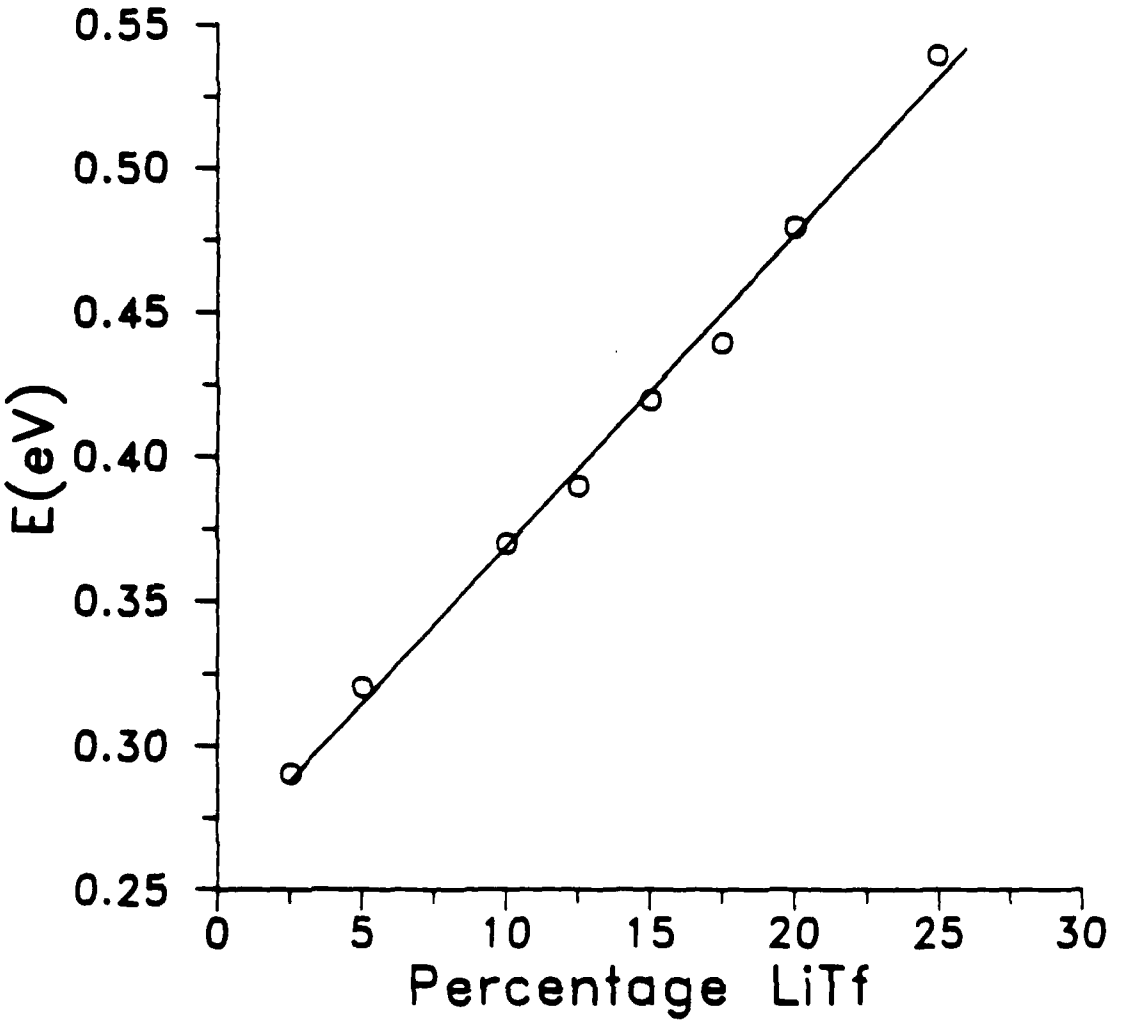

(A)
Siloxane(30) LiTf 15% 41.1 °C
Pt
10 Hz
0.8 MHz
5 MHz
77 KHz
X (Ohms)
R (Ohms)
0
1000
2000
3000
4000

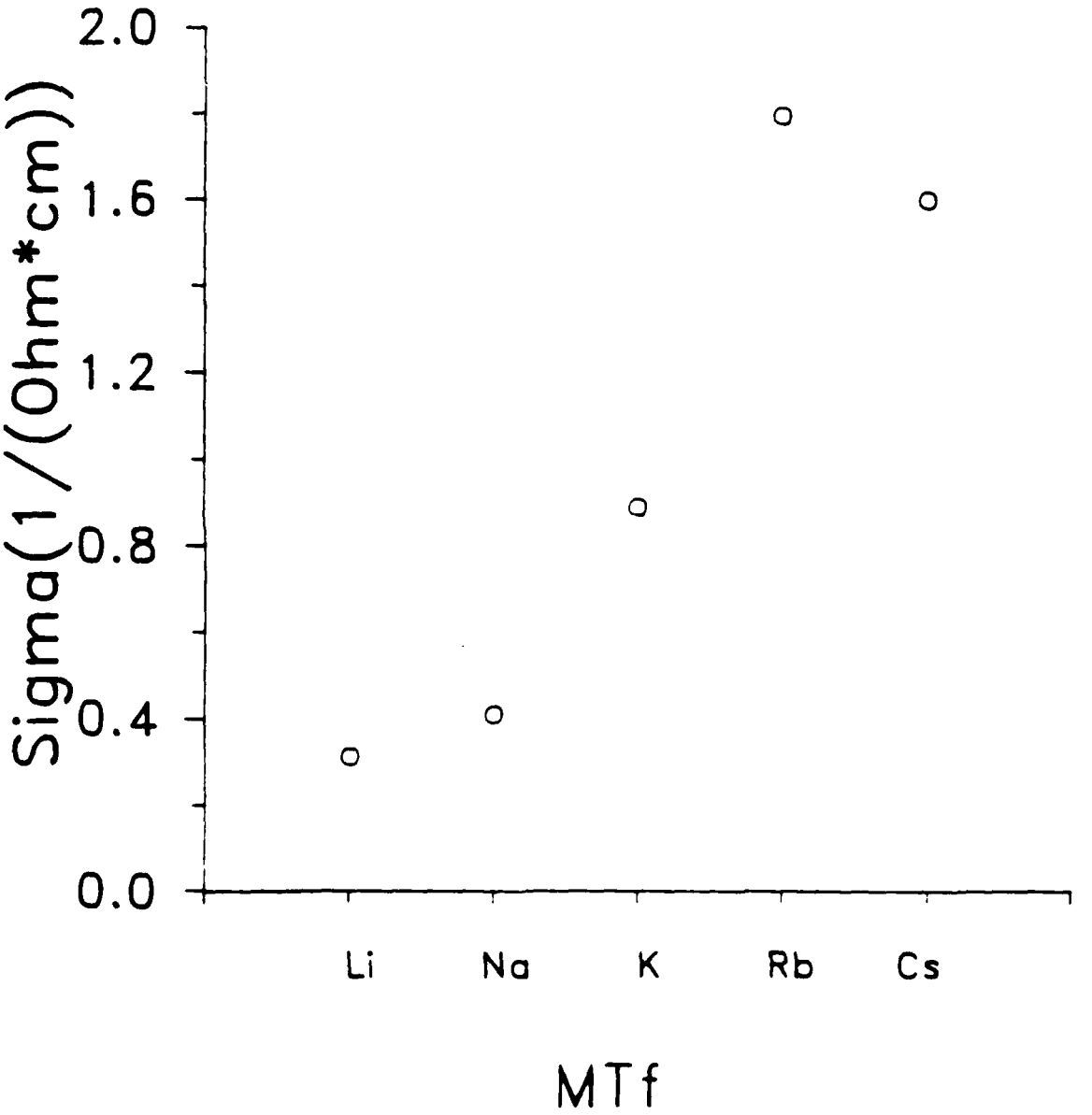

(B)
Siloxane(30) LiTf 15% 41.1 °C
Li
2.25 MHz
7 MHz
10 KHz
10 mHz
X (Ohms)
R (Ohms)
0
500
1000
1500
2000


Concentration Dependence
Sigma(1/(Ohm*cm))*100000
8.0
6.0
4.0
2.0
0.0
Tg(K)
240
230
220
210
200
0
5
10
15
20
25
30
Percentage LiTf


Sigma(1/(ohm*cm))*1E7
5.0
4.0
3.0
2.0
1.0
0.0
0
5
10
15
20
25
Percentage LiTF


-3.0
-3.8
-4.6
-5.4
-6.2
-7.0
Log(sigma)
2.8
3.0
3.3
3.5
3.8
4.0
1000/T


0.55
0.50
0.45
0.40
0.35
0.30
0.25
E(eV)
0
5
10
15
20
25
30
Percentage LiTf


Sigma(1/(Ohm*cm))
2.0
1.6
1.2
0.8
0.4
0.0
Li
Na
K
Rb
Cs
MTf