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Synthesis of Polysiloxanes Bearing Cyclic Carbonate Side Chains. Dielectric Properties and Ionic Conductivities of Lithium Triflate Complexes

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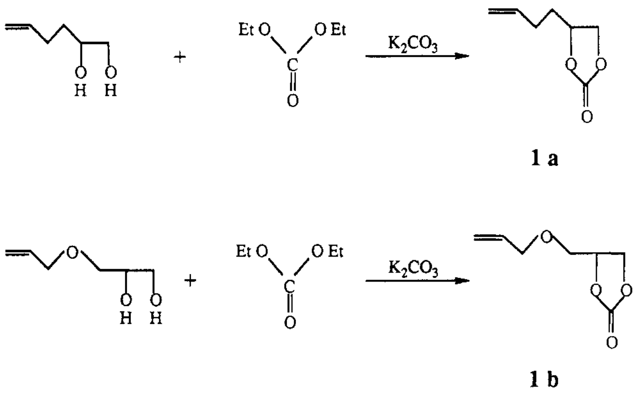
ABSTRACT: Polysiloxanes with cyclic carbonate side chains were prepared by hydrosilation of poly(hydromethylsiloxane) (PHMS) with vinyl-containing cyclic carbonates in acetonitrile using the divinyltetramethyldisiloxane platinum complex as the catalyst. This is initially a heterogeneous reaction since the PHMS is insoluble in acetonitrile, but the polymer eventually becomes soluble as the reaction proceeds. Under these conditions, no gelation due to competitive reactions with the carbonate is observed. The polymers are highly viscous liquids (T_g's of ca. -30 °C) and have dielectric constants ranging from ca. 22 to 44, to our knowledge the largest for any silicones. These polymers can also dissolve large quantities of lithium triflate and represent new polymer electrolytes. The T_g's of the polymer/salt complexes having one Li^+ per 10 cyclic carbonates are ca. -20 °C, accounting in part for the relatively low conductivity of ca. 5×10^{-7} S/cm at 25 °C. Diluents such as acetonitrile can afford substantial increases in conductivity.

Introduction

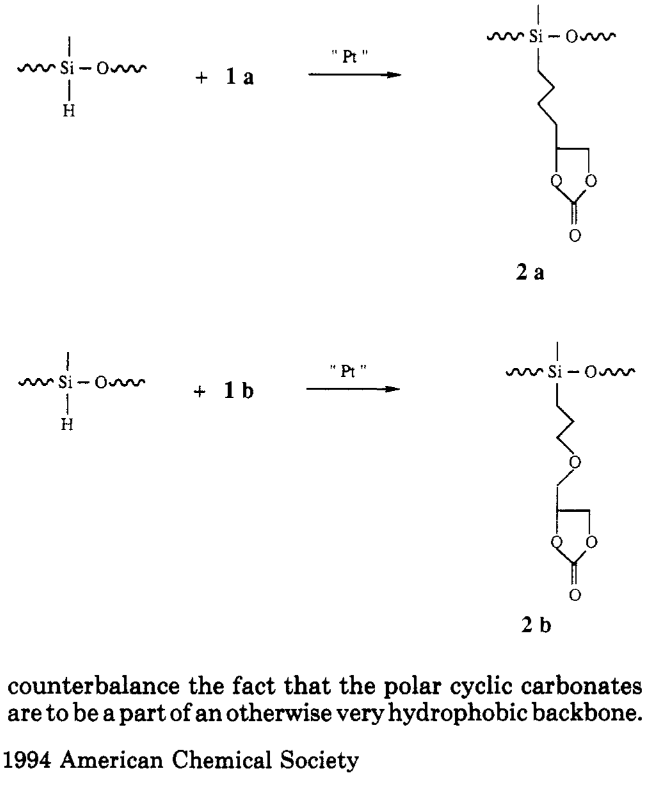
Polymers which can dissolve metal salts and exhibit high conductivity at room temperature are of interest in the development of high-performance batteries and electrochromic displays.[1-5] The principal requirements for high conductivity are an ability to solvate ions (typically alkali-metal ions) and a low glass transition temperature (T_g) affording facile ion transport. The promotion of anion-cation dissociation is desirable as it should lead to enhancement of ionic conductivity via an increase in "free" ion concentration. We sought to prepare polymers with cyclic carbonate side chains in an attempt to encourage ion pair dissociation by virtue of the high dielectric constants associated with these materials. For example, the dielectric constant of propylene carbonate[6] is ca. 65, and it is commonly employed as a solvent in electrochemistry and is a useful plasticizer in so-called gel polymer electrolytes.[7,8] We note that salt complexes of polymers with cyclic carbonates in their main chains have been prepared and their ionic conductivities have been examined with and without crown ether additives.[9]

We selected polysiloxanes as the carriers for cyclic carbonates for two main reasons. First, siloxane backbones are flexible, offering a low T_g. This is particularly important here because the high polarity of the carbonate group is expected to significantly increase interchain interactions and hence T_g with a concomitant decrease in ion mobility. Second, many derivatives can be readily prepared via hydrosilation of poly(hydromethylsiloxane) (PHMS) with appropriate terminal olefins.[10] While competitive reactions at the carbonate can be problematic,[11] conditions were established such that these are negligible. Two terminal olefins containing cyclic carbonates were prepared from simple starting materials (Scheme 1) and reacted with PHMS to obtain the desired products (Scheme 2). Olefin **1b** with its extra oxygen was selected in order to further encourage salt complex formation and counterbalance the fact that the polar cyclic carbonates are to be a part of an otherwise very hydrophobic backbone.

Scheme 1



Scheme 2



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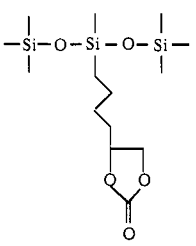
Model compound **3** was prepared to assist in interpretations of spectral data. In this paper, we present the details of the synthesis of these new polymers along with dielectric constant data and ionic conductivities of lithium triflate complexes.



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Experimental Section

Materials. Acetonitrile was dried over molecular sieves prior to use. 5-Hexene-1,2-diol, 3-(allyloxy)-1,2-propanediol, diethyl carbonate, potassium carbonate (all from Aldrich), and platinum divinyltetramethyldisiloxane complex (2–3% platinum concentration in xylene; Petrarch) were used without further purification. Poly(methylhydrosiloxane) (PHMS) was purchased from Petrarch and had a number-average molecular weight of 4500–5000. Bis(trimethylsiloxy)methylsilane (a gift from GE Silicones) was distilled prior to use.

Preparation of Vinyl-Bearing Carbonates. Cyclic (3-butenyl)ethylene Ester Carbonic Acid (1a). To a one-necked, 200-mL, round-bottomed flask fitted with a Dean–Stark trap and a condenser were added 25 g (21.5 mmol) of 5-hexene-1,2-diol, 76 g (64.5 mmol) of diethyl carbonate, and 4 g of K_2CO_3. The flask was heated to 120 °C. The solution was stirred for 24 h, while CH_3CH_2OH was distilled out. The product was filtered and distilled. The distillate having a boiling point of 135 °C was collected under 10 mmHg reduced pressure. ^1H NMR ($CDCl_3$): δ 5.78 (m, 1H, C=CH), 5.08 (m, 2H, CH_2=C), 4.71 (m, 1H, CCH(C)O), 4.52, 4.08 (2m, 2H, CCH_2O), 2.22 (m, 2H, C=CCH_2), 1.88 (m, 2H, CH_2).

Cyclic [(Allyloxy)methyl]ethylene Ester Carbonic Acid (1b). The same procedure as described above was employed, using 3-(allyloxy)-1,2-propanediol instead of 5-hexene-1,2-diol. The distillate having a boiling point of 155 °C was collected under 10 mmHg reduced pressure. ^1H NMR ($CDCl_3$): δ 5.77 (m, 1H, C=CH), 5.25 (m, 2H, CH_2=C), 4.81 (m, 1H, CCH(C)O), 4.43 (m, 2H, CCH_2O), 4.06 (d, 2H, OCH_2C=C), 3.65 (m, 2H, CCH_2O).

Polymer Synthesis. Poly{[5,6-(carbonyldioxy)hexyl]-methylsiloxane} (2a). To a one-necked, 50-mL, round-bottomed flask fitted with a condenser was added 2.0 g (33.3 mmol) of PHMS, 4.7 g (33.3 mmol) of cyclic (3-butenyl)ethylene ester carbonic acid and 20 mL of acetonitrile. The flask was heated to 60 °C. To this stirred heterogeneous mixture was added 3–4 drops of platinum divinyltetramethyldisiloxane (2–3% platinum concentration in xylene). The mixture turned cloudy and then became clear in a few minutes. The reaction was allowed to proceed for 8–12 h and was followed by monitoring the decrease of the SiH IR band at 2160 cm^{-1}. After rotary evaporating removal of solvent, the polymer was purified by repeated precipitation into a 90/10 (v/v) mixture of hexane and acetone and then dried under vacuum. The dried polymer was analyzed by ^1H, ^{29}Si, and ^{13}C NMR. ^1H NMR (acetone-d_6): δ 4.81 (1H, CCH(C)O), 4.61, 4.17 (2H, CCH_2O), 1.80 (2H, $COCH_2$), 1.51 (4H, CH_2CH_2), 0.69 (2H, $SiCH_2$), 0.18 (3H, $SiCH_3$). ^{29}Si NMR (acetone-d_6): δ −22.4. ^{13}C NMR (DMSO-d_6): δ 154.74, 76.86, 69.07, 32.65, 27.60, 22.27, 16.93, −0.57. Specific assignments are given in Figure 2.

Poly{[3-[2,3-(carbonyldioxy)propoxy]propyl]methylsiloxane} (2b). The same procedure as described above was employed, using cyclic [(allyloxy)methyl]ethylene ester carbonic acid instead of cyclic (3-butenyl)ethylene ester carbonic acid. ^1H NMR (acetone-d_6): δ 4.96 (1H, CCH(C)O), 4.60, 4.37 (2H, CCH_2O), 3.71 (2H, OCH_2CO), 3.51 (2H, OCH_2), 1.70 (2H, CH_2), 0.62 (2H, CH_2Si), 0.19 (3H, $SiCH_3$). ^{29}Si NMR (acetone-d_6): δ −21.8. ^{13}C NMR (DMSO-d_6): δ 154.83, 75.44, 73.24, 69.44, 65.91, 22.59, 12.81, −0.73.

The model compound bis(trimethylsiloxy)[5,6-(carbonyldioxy)hexyl]methylsiloxane (3) was made from bis(trimethylsiloxy)methylsilane and cyclic (3-butenyl)ethylene ester carbonic acid under conditions similar to those outlined for the corresponding polymer. ^1H NMR (acetone-d_6): δ 4.81 (m, 1H, CCH(C)O), 4.61, 4.17 (2m, 2H, CCH_2O), 1.78 (t, 2H, $COCH_2$), 1.44 (m, 4H, CH_2CH_2), 0.54 (m, 2H, CH_2Si), 0.10 (s, 18H, Si(CH_3)$_3$), 0.03 (s, 3H, OSi(CH_3)O). ^{29}Si NMR (acetone-d_6): δ 7.65, −21.95. ^{13}C NMR (DMSO-d_6): δ 154.86, 77.01, 69.24, 32.83, 27.48, 22.48, 17.06, 1.81, −0.30.

Measurements. Routine NMR measurements were performed with a Varian XL-200 spectrometer at 200 MHz for ^1H, 50 MHz for ^{13}C, and 40 MHz for ^{29}Si. 2D proton–carbon correlated spectroscopy was performed on a Varian UNITY-500 spectrometer at 500 MHz for ^1H and 125 MHz for ^{13}C. Chemical shifts (in ppm) were referenced to TMS for ^1H and ^{29}Si and to DMSO-d_6 (39.5) for ^{13}C. IR spectra were taken on a Perkin-Elmer Model 1800 Fourier transform infrared spectrometer. Glass transition temperatures (T_g's) were determined using a Perkin-Elmer DSC-4 differential scanning calorimeter with a heating rate of 20 °C min^{-1}. Dielectric constants were measured at room temperature using a Solartron 1260 impedance/gain phase analyzer using a Balsbaugh liquid cell. The measurements on water and acetone at 25 °C afforded dielectric constants of 78.8 and 21.1; the dielectric constants of both are reported to be 78.5 and 20.7 at 25 °C.[12] For measurements of ionic conductivities, the polymers were dissolved in acetone, and then lithium trifluoromethanesulfonate was added with stirring to form a homogeneous solution. After removal of the solvent, the samples were loaded onto the glass slides having a thin aluminum coating with an area of 1.0 × 1.0 cm as the electrodes. Air bubbles were removed by maintaining the sample in a vacuum oven for 4 h at 100 °C. Then a 0.026-cm-thick Teflon spacer was placed on top of these slides followed by another glass slide electrode. This sandwich-type cell was placed in an oven, and the measurements were carried out on the 1260 impedance/gain phase analyzer. This cell was also employed for measurements of dielectric constants at elevated temperature. The resulting data are likely to be less accurate compared with those from a Balsbaugh cell, but they are still reasonable. For comparison, the dielectric constant of **2b** was 50.6 using a Balsbaugh cell and 44.1 using a sandwich-type slide cell at room temperature. Sample preparation, conductivity measurements, and dielectric measurements were carried out under dry argon.

Results and Discussion

Polymer Synthesis. Two terminal olefins containing cyclic carbonates (**1a** and **1b**) were easily prepared by transesterification. The subsequent hydrosilation of these with PHMS was quantitative as suggested by the complete disappearance of the SiH IR absorption around 2160 cm^{-1} and its ^1H NMR peak around 4.60 ppm. Our first experiments utilized THF as solvent at 50–60 °C, and we found that the reaction mixture gelled rather quickly, presumably due to competitive reactions between SiH and the carbonate. Indeed, it has been observed that hydrosilation with allyl phenyl carbonate (in toluene) leads to significant decomposition of the carbonate functionality.[11] However, we found that solvents other than THF allow the reaction to reach high conversion without gelation. For example, no gelation was observed in reactions run in acetone, although spectral data suggested that hydrosilation of the carbonyl of acetone occurred to a small degree. Acetonitrile turns out to be an excellent solvent in which to carry out the reaction, despite the fact that PMHS is insoluble in it. However, the initially heterogeneous mixture became homogeneous after about 20% conversion to the carbonate-containing siloxane. Nearly quantitative conversion to polymers **2a** and **2b** could be achieved after about 12 h at 60 °C. The ^1H NMR spectra of polymers **2a** and **2b**, the product of the model

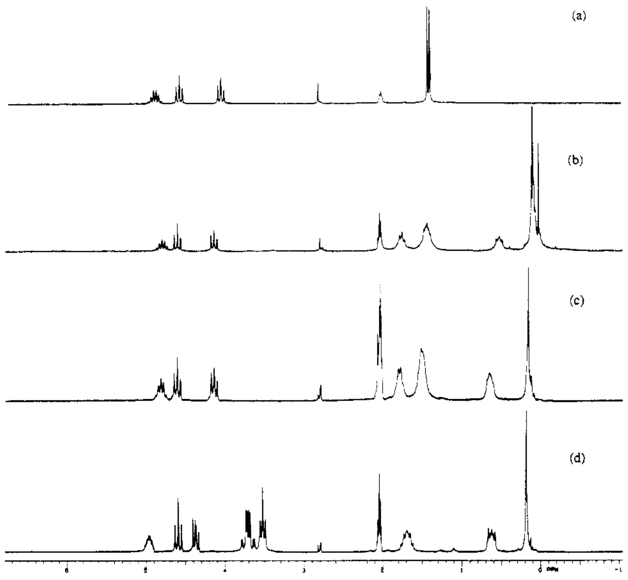

Figure 1. 200-MHz ^{1}H NMR spectra: (a) propylene carbonate; (b) model compound **3**; (c) **2a**; (d) **2b**. (Solvent: acetone-d_6.)

reaction between **1a** and bis(trimethylsiloxy)methylsilane, and propylene carbonate for comparative purposes are shown in Figure 1a–d. The integrity of the cyclic carbonate is confirmed in both the polymer and model trisiloxane derivative. The 2D NMR spectrum of polymer **2a** (Figure 2) confirms our assignments and indicates that the hydrosilation gives exclusively the anti-Markovnikov product. That the siloxane backbone in either **2a** or **2b** does not suffer degradation to cyclic oligomers under our reaction conditions is supported by the observation of a single peak at −22.4 (**2a**) or −21.8 (**2b**) ppm in the ^{29}Si NMR spectrum characteristic of linear polymer. A cyclic tetramer prepared from D4H and **1b** gave a single peak in the ^{29}Si NMR at −19.44 ppm, characteristic of an intact cyclic tetramer.

Table 1. Dielectric Constant Measurement[a]

sample	lit. value	Balsbaugh cell 1 kHz	Balsbaugh cell 10 kHz	Balsbaugh cell 100 kHz	slide cell 1 kHz	slide cell 10 kHz	slide cell 100 kHz
PC	64.4			64.5			
1a				38.9			
2a		30.0	29.5	28.0	24.7	24.1	22.5
1b				68.8			
2b		52.6	52.4	50.6		46.3	44.1

[a] Measurement was carried out on a Solartron 1260 impedance/gain phase analyzer at 25–26 °C.

Polymers **2a** and **2b** are not water-soluble even though compounds **1a** and **1b** are, reflecting a major contribution of the nonpolar silicone backbone to the solubility of the polymers. Only polar solvents like acetone, acetonitrile, DMF, DMSO, and NMP can dissolve the polymers; THF is a relatively poor solvent.

Dielectric Properties. The dielectric constants for polymers **2a** and **2b** as well as compounds **1a**, **1b**, and propylene carbonate are shown in Table 1. A commercial Balsbaugh-type cell was typically employed, although the highly viscous polymers were difficult to load in the sample well. For this reason, we also prepared polymer samples on Al-coated glass slides (see the Experimental Section). Most of our measurements were obtained at 100 kHz to minimize contributions from ionic polarization, although frequency dependencies were examined in some cases. Compounds **1a** and **1b** were found to have dielectric

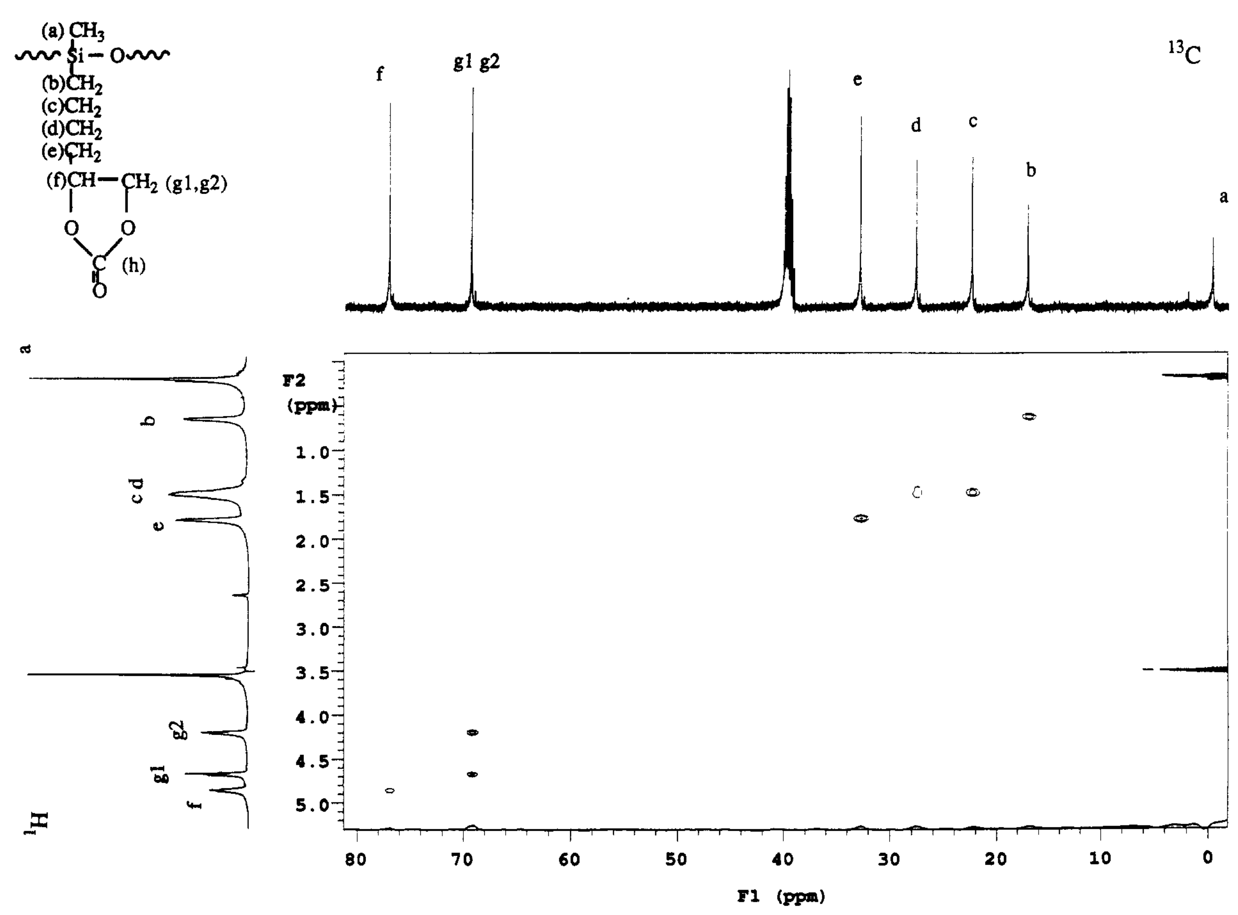

Figure 2. 2D proton–carbon correlated spectroscopy of **2a**. (Solvent: DMSO-d_6.) The broadening of the silylmethyl signals in the 2D spectrum is an artifact.

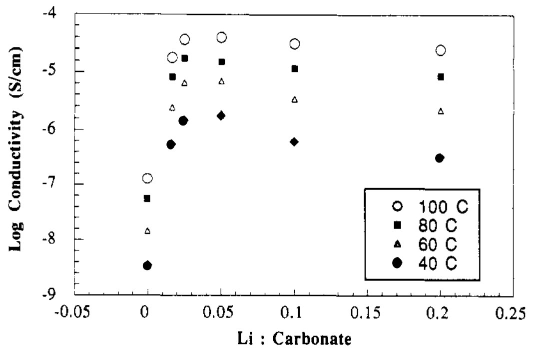

Figure 3. Plots of log conductivity vs carbonate/Li$^+$ for **2b**–lithium triflate complexes at different temperatures.

Table 2. T_g's and Ion Conductivities of Polymers

sample	T_g (°C)	σ (S/cm) at 40 °C
2a	−28	2.3×10^{-9}
2a–Li complex^a	−19	4.0×10^{-7}
2a–Li, 30% CH_3CN^a		8.9×10^{-5}
2b	−32	3.5×10^{-9}
2b–Li complex (carbonate:Li)		
60:1	−22	5.4×10^{-7}
40:1	−22	1.4×10^{-6}
20:1	−19	1.7×10^{-6}
10:1	−19	6.0×10^{-7}
5:1		3.2×10^{-7}
2b–Li, 30% CH_3CN^a		2.5×10^{-4}

[a] Carbonate:Li = 10:1.

constants of ca. 39 and 69, respectively, the latter being even slightly larger than that of propylene carbonate presumably due to the additional contribution of the polar ether adjacent to the carbonate. Polymers **2a** and **2b** have dielectric constants of ca. 22 and 44, respectively. The latter is significantly higher than that of poly(β-cyanoethylmethylsiloxane) which, with a dielectric constant of ca. 18 at 100 kHz,[13] was among the highest previously reported for a polysiloxane.

Ionic Conductivities of Polymer/Salt Complexes. Transparent complexes of polymers **1a** and **2b** with lithium triflate were cast from acetone. The dependence of the conductivity of polymer **2b** as a function of salt concentration (Li$^+$ per cyclic carbonate) is shown in Figure 3. The conductivity of the salt-free polymer is ca. 10^{-9} S/cm at 25 °C. A maximum is reached near 1 Li$^+$ per 20 carbonates, and the drop in conductivity at higher salt concentrations is likely the result of a decrease in ion mobility. Complexation of lithium ions by carbonates on several chains should lead to a T_g elevation and a concomitant decrease in mobility as observed in other systems.

The conductivities of the salt-doped, carbonate-containing siloxanes are rather low near room temperature, most likely because of low ion mobility. Both polymers **2a** and **2b** are highly viscous melts at room temperature. DSC analysis (Table 2) reveals that the T_g of **2a** is −28 °C, while that of **2b** is −32 °C. These are considerably higher than, for example, siloxanes[14] and polyphosphazenes[15] with less polar oligo(ethylene oxide) side chains (T_g's ca. −60 and −85 °C, respectively) and are the result of strong dipole–dipole interactions between the polar cyclic carbonates. Therefore, any gain in ion pair dissociation from the higher dielectric constants of these new polymers is offset by the increase in T_g. The T_g's are further raised by ca. 10–12 °C in complexes of polymers with lithium triflate (1 Li per 60 carbonate), implying weak cross-linking by complexation between a Li$^+$ and carbonates from different chains. We do not observe a further increase in T_g with increasing salt concentration, perhaps because of preferential intramolecular complex formation. It is also not clear to what degree the nonpolar siloxane backbone may be impeding the shuttling of ions among carbonates. The temperature dependencies of the ionic conductivities of polymers **2a** and **2b** (1 Li$^+$ per 10 carbonates) are shown in Figure 4. The conductivities of the two polymers are similar as are their dependencies on temperature, whose curvatures are characteristic of amorphous polymer/salt complexes. Finally, we note that addition of ca. 30 wt % acetonitrile to the complexes decreases their viscosities considerably and affords conductivities of ca. 10^{-4} S/cm at room temperature.

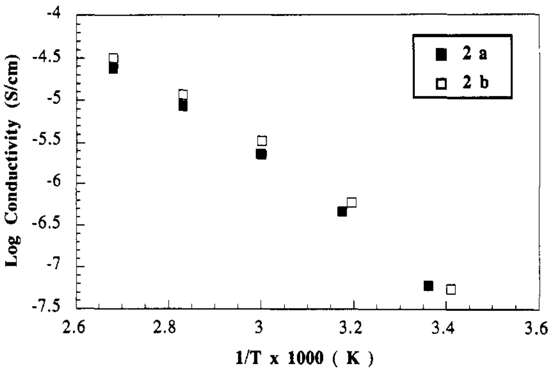

Figure 4. Plots of log conductivity vs reciprocal temperature for **2a** and **2b** with carbonate/Li$^+$ = 10.

Conclusions

We have demonstrated that polysiloxanes containing cyclic carbonates can be cleanly prepared via hydrosilation. Ionic conductivities of lithium triflate complexes are low near room temperature despite the high dielectric constants of these new polymers. While dipole interactions in these polymers are strong, leading to T_g elevation and presumably low ion mobility, they may be useful in studies of electric field effects on polymer blends where the dielectric constant difference between components is a key parameter for morphology modulation.[16] The large dielectric constants in and of themselves may make these materials of interest in capacitor applications.

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