5714 *Macromolecules* **2005,** *38,* 5714−5720

Network-Type Ionic Conductors Based on Oligoethyleneoxy-Functionalized Pentamethylcyclopentasiloxanes

Zhengcheng Zhang,[†] Leslie J. Lyons,[‡] Khalil Amine,[§] and Robert West*,[†]

Organosilicon Research Center, Department of Chemistry, University of Wisconsin—Madison, Wisconsin 53706; Department of Chemistry, Grinnell College, Grinnell, Iowa 50112; and Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

Received January 12, 2005; Revised Manuscript Received May 2, 2005

ABSTRACT: Network-type solid polymer electrolytes (NSPEs) were synthesized containing oligoethylene oxide chains, $CH_3(OCH_2CH_2)_3(CH_2)_3-$, within the network structures. Hydrosilylation reactions of precursors **1** and **2** (oligoethyleneoxy partially substituted pentamethylccyclopentasiloxanes (D_5^H)) with an α,ω-diallyloligo(ethylene glycol) were employed for the formation of the cross-linked networks. The conductivities of the network polymer/LiX complexes with variable EO/Li ratios were measured by impedance experiments. NSPE-**2**, with 36.0% cross-linking density, exhibited higher conductivity than NSPE-**1**, with 43.8%. The optimum conductivity ($\sigma = 9.24 \times 10^{-5}$ S/cm at 25 °C, 2.11×10^{-4} S/cm at 37 °C) was found for NSPE-**2** with lithium bis(oxalato)borate (LiBOB). LiBOB-doped polymers exhibited higher conductivity than those doped with LiTFSI at the same salt concentration.

Introduction

Solid polymer electrolytes (SPEs) have been widely investigated because of their overall potential as practical materials for applied electrochemistry,[1,2] and a number of reviews on this field are available.[3−5] Used as both a separator and an electrolyte in a solid-state battery, SPEs have many merits over their liquid counterparts such as good mechanical stability, flexibility in shapes and sizes, and increased safety. The first generation of high molecular weight poly(ethylene oxide) (PEO) polymers were generally poor conductors ($\sigma < 10^{-7}$ S cm^{-1}) due to the high degree of crystallinity. Reasonable conductivity in PEO−salt polymer electrolytes can be achieved at around 100 °C; however, the mechanical properties of the polymer are quite poor.[1] Better results are obtained for polymers with highly flexible backbones, bearing oligo(ethylene oxide) (EO) as side chains. Polyphosphazenes[6−12] of this type have been studied extensively in form of comb polymers, block copolymers, and cross-linked network polymers. In recent years, oligo(ethylene glycol)-substituted polysiloxanes as ionically conductive polymer hosts have been widely investigated by Smid,[13−15] Shriver,[16−18] Acosta,[19] and West and co-workers.[20−23] The remarkable improvement in the ionic conductivity for these polymers was ascribed to the highly flexible inorganic backbone which produced a totally amorphous polymer host with a very low glass transition temperature. Plasticized and gel polymer electrolytes[24] were synthesized aiming to obtain desirable conductivities.

In our laboratory we have focused on the synthesis of cross-linked network conductors that could provide good mechanical strength as well as high ambient conductivity. In a previous paper, we demonstrated that the conductivity of cross-linked linear polysiloxanes[22,23] with pendant oligo(ethylene glycol) chains showed excellent conductive properties, which has driven us to extend our research to network-type cyclic siloxanes. In this article, we describe cross-linked network polymer electrolytes based on cyclosiloxanes, synthesized by hydrosilylation of partially functionalized pentamethylcyclopentasiloxanes (D_5^H) with an α,ω-diallyloligo(ethylene glycol) cross-linker. Impedance and differential scanning calorimetry (DSC) measurements were carried out to characterize the new materials.

Experimental Section

Materials. Pentamethylcyclopentasiloxane (D_5^H) was purchased from Gelest and distilled prior to use. Allyl bromide, Karlstedt's catalyst (platinum divinyltetramethyldisiloxane) (3% in xylene solution), tri(ethylene glycol) methyl ether, and poly(ethylene glycol) with a molecular weight of 600 were supplied by Aldrich and used without purification. Sodium hydride (NaH, 60% dispersion in mineral oil) was obtained from Acros Organics. THF was dried over sodium benzophenone ketyl and was distilled in an atmosphere of dry nitrogen before use. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was a gift from 3M Co. and was dried under vacuum at 120 °C for 24 h prior to use. Lithium bis(oxalato)borate (LiBOB) was supplied by Chemetall and was purified by recrystallization using dried CH_3CN as solvent. NMR grade $CDCl_3$ was stored over 4A molecular sieves.

Tri(ethylene glycol) Allyl Methyl Ether (APEO$_3$M). Tri(ethylene glycol) allyl methyl ether was synthesized as previously reported.[21] A solution of tri(ethylene glycol) methyl ether (MPEO$_3$) (98.4 g, 0.6 mol) in 250 mL of THF was added dropwise to a suspension of NaH (60% dispersion in mineral oil) (28.8 g, 0.72 mol) in THF (250 mL) chilled to 0 °C. This solution was stirred for a further 2 h followed by the dropwise addition of allyl bromide (87.1 g, 0.72 mol). The resulting mixture was stirred overnight and then filtered to remove the NaBr product and excess NaH. All volatile materials were removed by rotary evaporation to yield an orange oil. This oil was dissolved in water, and unreacted MPEO$_3$ was extracted using 3 × 50 mL portions of toluene. The desired product was then extracted into chloroform from the water layer with 3 × 200 mL portions of $CHCl_3$; this was dried with $MgSO_4$, and all volatile materials were removed by rotary evaporation. 110 g (90%) of product was collected by Kugelrohr distillation (80 °C/0.5 Torr): ^{1}H NMR ($CDCl_3$), δ (ppm): 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.45−3.65 (m, 12H), 3.30 (s, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9.

[†] University of Wisconsin—Madison.

[‡] Grinnell College.

[§] Argonne National Laboratory.

10.1021/ma050066k CCC: $30.25

Cross-Linker: α,ω-Diallyloligo(ethylene glycol). The diallyl-terminated oligo(ethylene glycol) was prepared using the method described previously.[22] The following reagents and quantities were used: NaH (9.6 g, 0.24 mol of a 60 wt % solution in mineral oil), THF (100 mL), PEG (M_w 600, 60.0 g, 0.10 mol), THF (150 mL), allyl bromide (31.46 g, 0.26 mol). The crude product was purified by passing through a silica gel column. Final product: 62.5 g, 92% yield. ^{1}H NMR ($CDCl_3$), δ (ppm): 5.85 (m, 2H), 5.15 (dd, 4H), 3.95 (d, 4H), 3.45−3.65 (m, 40H), 3.30 (s, 6H). ^{13}C NMR ($CDCl_3$), δ (ppm): 134.6, 116.8, 72.1, 71.8, 70.3−70.0, 69.2, 58.9.

Partially Substituted Pentamethylcyclopentasiloxanes (1). The cross-linkable cyclic precursors were synthesized by platinum-catalyzed hydrosilylation of D_5^H with $APEO_3M$. Into a vacuum flame-dried 100 mL round-bottom flask was charged pentamethylcyclopentasiloxane (5.0 g, 16.6 mmol) and $APEO_3M$ (10.2 g, 50.0 mmol) through a syringe under an argon atmosphere. Then 40 μL (100 ppm relative to −Si−H bond) of Karlstedt's catalyst was syringed into the flask through the septum with stirring. The flask was heated to 65 °C for 12 h, after which Kugelrohr distillation was employed to remove the low boiling point byproducts. The viscous polymer was then decolorized by refluxing in toluene with activated charcoal for 12 h. After removal of toluene, a colorless liquid polymer was obtained, 12.9 g (85%).

^{1}H NMR ($CDCl_3$), δ (ppm): 4.62 (Si−H), 3.65−3.45 (CH_2CH_2O), 3.32 (OCH_3), 1.55 (CH_2CSi), 0.46 ($SiCH_2$), 0−0.2 (Si−CH_3). ^{13}C NMR ($CDCl_3$), δ (ppm): 73.9, 72.0, 70.6−70.7, 70.1, 59.1, 23.0−23.1, 13.0−13.2, 1.16, 1.15, −0.63, −0.96. ^{29}Si NMR ($CDCl_3$), δ (ppm): −20.2 to −24.1, −35.5 to −38.7.

Partially Substituted Pentamethylcyclopentasiloxanes (2). Precursor **2** was synthesized using the same procedure as described for precursor **1**. The following reagents and quantities were used: D_5^H (6.25 g, 20.8 mmol); $APEO_3M$ (15.3 g, 75.0 mmol); Karlstedt's catalyst (50 μL). After treatment with charcoal, the final cyclic precursor was a colorless liquid, 17.88 g (83%). ^{1}H NMR ($CDCl_3$), δ (ppm): 4.62 (Si−H), 3.65−3.45 (CH_2CH_2O), 3.32 (OCH_3), 1.55 (CH_2CSi), 0.46 ($SiCH_2$), 0−0.2 (Si−CH_3). ^{13}C NMR ($CDCl_3$), δ (ppm): 73.9, 72.0, 70.6−70.7, 70.1, 59.1, 23.0−23.1, 13.0−13.2, 1.16, 1.15, −0.63, −0.96. ^{29}Si NMR ($CDCl_3$), δ (ppm): −20.2 to −24.1, −35.5 to −38.7.

Network Polymer Electrolyte Films Formation. A representative procedure for NSPE-**1** was as follows: The stoichiometric amounts of precursor **1** (0.5 g), α,ω-diallyloligo(ethylene glycol) cross-linker (0.334 g, 0.49 mmol), $LiN(CF_3SO_2)_2$ (4.38 mL, 0.1547 M THF solution), and Karstedt's catalyst (3 μL, 3% xylene solution) were injected into a flame-dried Schlenk flask. The homogeneous solution was then evacuated for 12 h on a standard Schlenk line and then further evacuated on a high-vacuum line (∼10^{-5} Torr) to make the mixture fully dry. The flask was transferred into a glovebox, where the dry liquid electrolyte was loaded into the O-ring of a conductivity measurement cell. The liquid mixture was cured into a solid by heating at 75 °C for 48 h to ensure that the cross-linking reaction was as complete as possible. Light yellowish self-standing films with thickness of 2.0 mm were obtained, which were subjected to impedance experiments.

Measurements. The ac impedance measurements were performed under computer control using a Princeton Applied Research model 273A potentiostat/galvanostat, a Princeton Applied Research model 1025 frequency response analyzer for frequency control (75 Hz−100 kHz), and Princeton Applied Research PowerSine impedance software for data acquisition. Subsequently, the data obtained were analyzed on a PC with Microsoft Excel. Room temperature conductivity measurements were at 23 ± 1 °C while variable-temperature measurements (25−70 °C) were made by placing the electrochemical cell (Figure 1) in a jacketed holder and circulating ethylene glycol/water from a Lauda RMT6 circulating bath. Actual temperatures were determined via an Omega thermocouple attached directly to the cell.

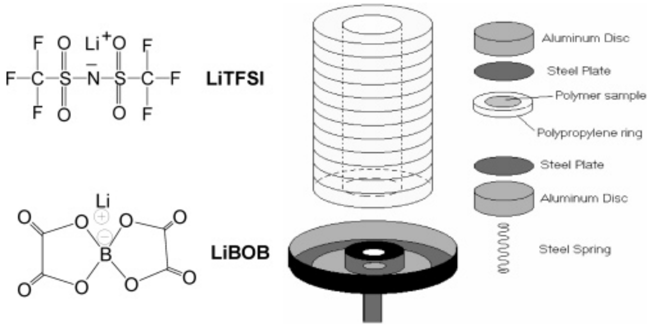


Figure 1. Lithium salts (LiTFSI and LiBOB) structure and diagram of conductivity measurement cell.

Thermal measurements were recorded on a Perkin-Elmer Pyris Diamond DSC operated under computer control. Low temperatures were achieved by using the TA Instruments liquid nitrogen cooling accessory. Samples of preformed gels were loaded in hermetically sealed aluminum pans. Duplicates of all samples were measured. Glass transition temperatures are reported as the onset of the inflection in the heating curve from −150 to 80 °C at a heating rate of 10 °C/min.

FT-IR spectra were recorded on a Nicolet Nexus 670 spectrometer as cross-linked films placed on the Avatar multibounce HATR accessory.

All NMR chemical shifts are reported in parts per million (δ ppm); downfield shifts are reported as positive values from tetramethylsilane (TMS) as the standard at 0.00 ppm. The ^{1}H and ^{13}C chemical shifts are reported relative to the NMR solvent as an internal standard, and the ^{29}Si chemical shifts are reported relative to an external TMS standard. NMR spectra were recorded using samples dissolved in $CDCl_3$, unless otherwise stated, on the following instrumentation. Carbon-13 NMR was recorded as proton-decoupled spectra, and ^{29}Si was recorded using an inverse gate pulse sequence with a relaxation delay of 30 s.

Results and Discussion

Synthesis. $APEO_3M$ and α,ω-diallyloligo(ethylene glycol) were prepared in a one-pot synthesis from tri(ethylene glycol) monomethyl ether and oligo(ethylene glycol) by reacting alkoxides of the reagents with allyl bromide. Precursors with variable amount of −Si−H functionalities were accomplished by altering the relative feeding ratios of D_5^H and $APEO_3M$, as depicted in Scheme 1. The formation of platinum colloids[25,26] was indicated by a yellow color of the solution during the hydrosilylation which changes to dark brown[27,28]at the end of the reaction. The extent of hydrosilylation reaction (disappearance of $CH_2{=}CH{-}CH_2{-}OR$ proton signals) and the purification (disappearance of *cis*- and *trans*-$CH_3CH{=}CH_2{-}OR$) were monitored by ^{1}H NMR. The cyclic oligomer solutions were decolorized with activated charcoal, passed through a silica gel column, and evaporated. The structure and composition (Si−R and Si−H ratios) of the purified precursors were analyzed and summarized in Table 1. Representative spectra of ^{1}H and ^{29}Si NMR are shown in Figure 2.

Scheme 2 outlines the strategy used for the production of NSPEs by hydrosilylation cross-linking reactions in the presence of lithium salt. The precursor, cross-linker, and LiTFSI were dissolved in THF. The complete removal of THF was then achieved by evacuating to pressure <5 × 10^{-5} Torr, after which the viscous mixture was loaded into an electrochemical cell with stainless steel ion blocking electrodes and sealed with O-rings. The dry liquid was cross-linked into a solid membrane upon heating. Interestingly, our gelation test demonstrated that precursors with Si−H molar content lower than 30% (precursors **3** and **4**) could not be made

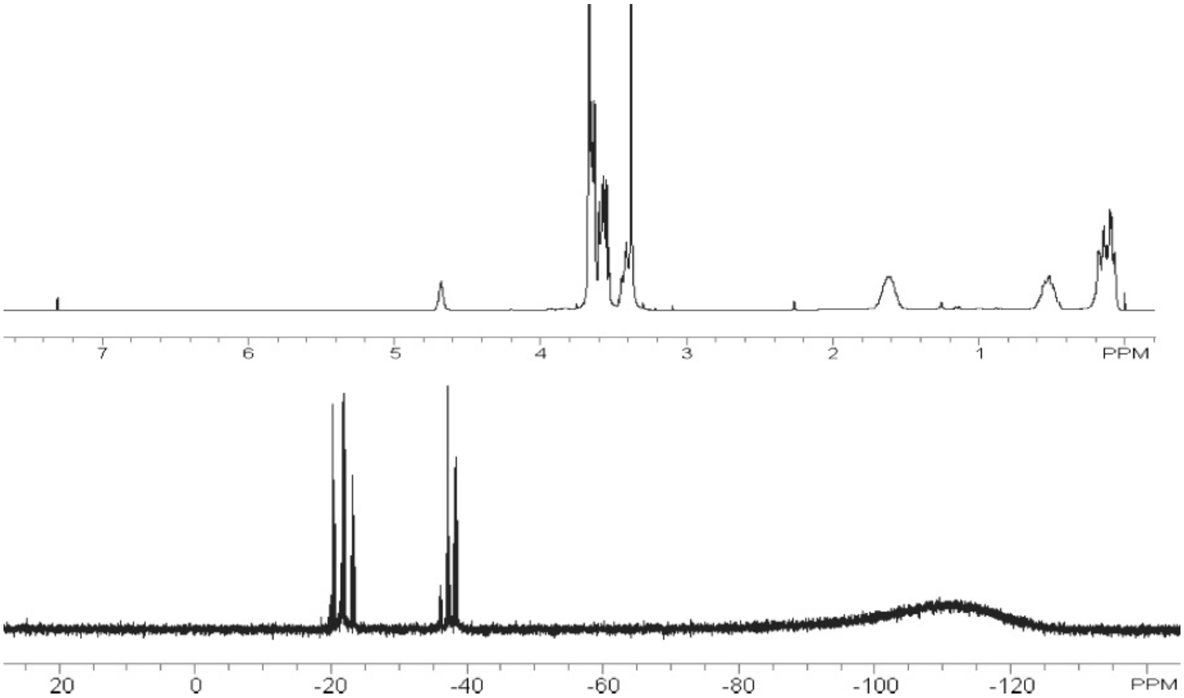


Figure 2. Representative NMR spectra of precursor **2**: ^{1}H NMR (top); ^{29}Si NMR (bottom).

Scheme 1. Synthesis of Monomer, Cross-Linker, and Cyclic Siloxane Precursors 0−4

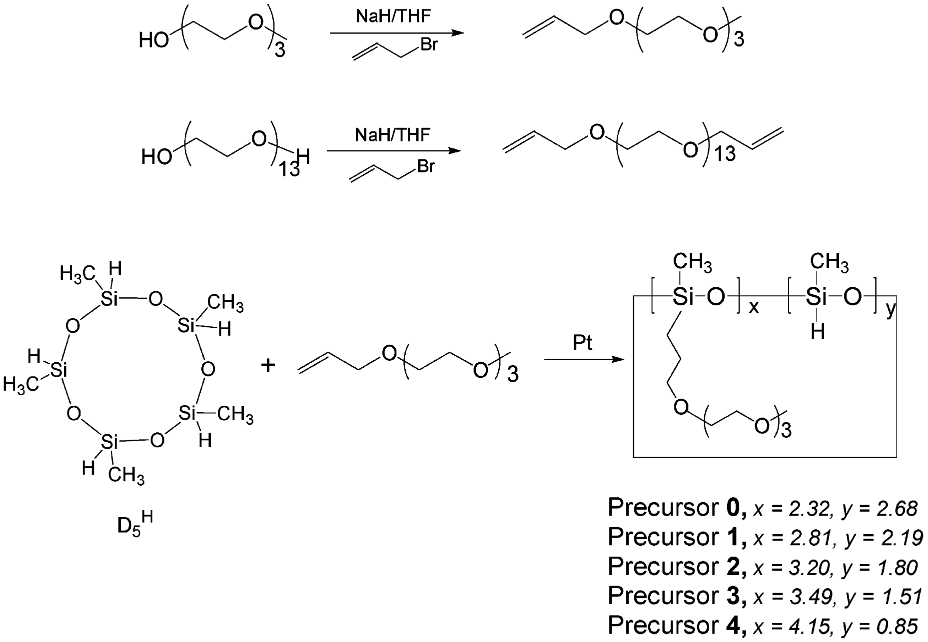


Table 1. Cross-Linking Test Results

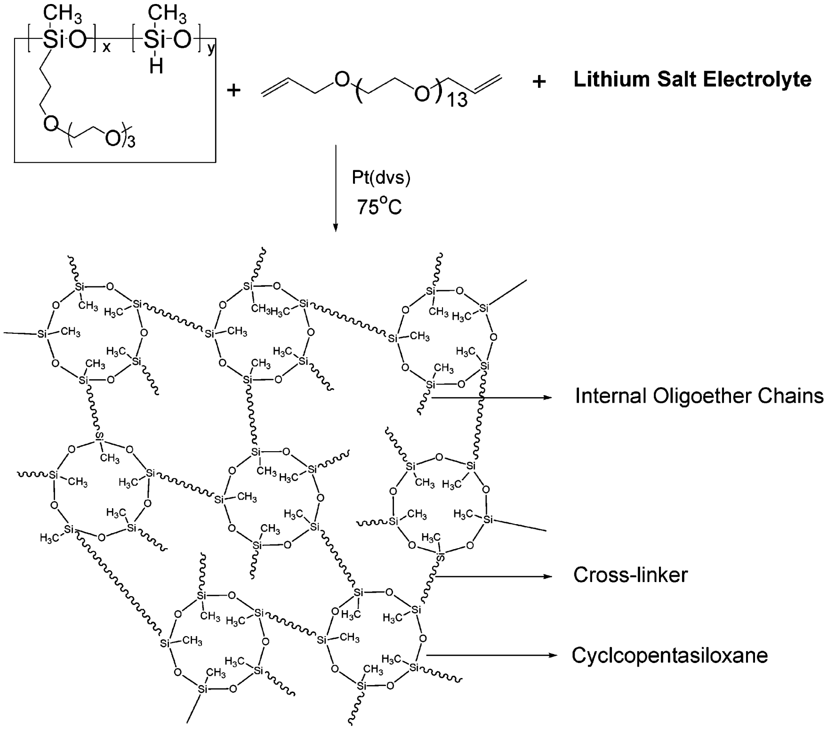
precursor	*x*	*y*	Si−H content (%)	film consistency
0	2.32	2.68	53.6	rigid film
1	2.81	2.19	43.8	rigid film
2	3.20	1.80	36.0	soft film
3	3.49	1.51	30.2	very viscous liquid
4	4.15	0.85	17.0	liquid

into solid films, and the precursor with 20% Si−H only resulted in viscous liquid (Table 1), presumably due to the deficient cross-linking sites. Two NSPEs were produced from precursors **1** (43.8% Si−H) and **2** (36.0% Si−H); both films did not dissolve but were swollen by the deuterated solvents. No Si−H resonance at 4.67 ppm or CH_2=CH− resonances at 5.1 and 5.9 ppm were observed in ^{1}H NMR spectra, nor Si−H stretching absorption at 2160 cm^{-1} in FT-IR spectra (Figure 3), indicating the completion of network formation.

Ionic Conductivity. The impedance spectra were determined in an equivalent circuit of a parallel capacitance and resistance. The magnitude of the resistance was calculated at the points where the phase angle in the impedance data was closest to zero using the equation $R = Z\cos(\theta)$, where R is the resistance, Z the impedance, and θ the phase angle. The conductivity, σ, was calculated from the relationship $\sigma = 1/R \times l/A$, where l/A values were typically 0.2 cm^{-1}.

The room temperature conductivities were slightly lower than those of cross-linked linear polysiloxane electrolytes as reported by us previously.[22,23] Conductivity data of NSPE-**1** and NSPE-**2** are summarized in Table 2. These NSPEs show typical behavior as ionic

Scheme 2. Formation and Network Structure of Cross-Linked Polymer Electrolytes



conductors: the conductivities increase to an optimum value as the salt content increases, with the conductivity dropping off at higher salt levels, as illustrated in Figure 4. This phenomenon is most likely due to the smaller number of free ions present at lower salt concentration and formation of anchored bulky ion clusters at higher salt level, which hindered the conductivity.

The variable-temperature ionic conductivities for the solid polymer electrolytes are shown in Figures 5 and 6. NSPE-**1** and NSPE-**2** showed typical increased conductivity with increasing temperature, as observed for many other polymer systems.[7−14,16,19,21−23] The type of ion transport suggested by all the plots can be described by the WLF equation or the Vogel−Tamman−Fulcher[3,29−31] equation, $\sigma = AT^{-1/2}\exp(-B/(T - T_0))$, producing parameters for the activation energy (E_a) and empirical glass transition temperature (T_0), as listed in Table 2.

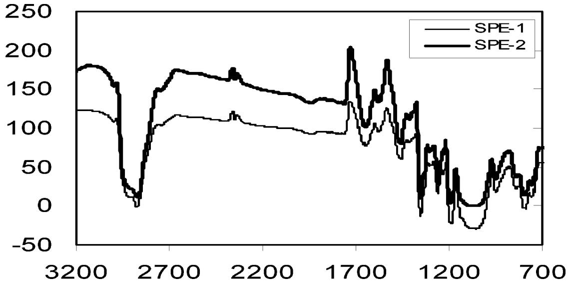


Figure 3. Representative FT-IR spectra of network polymer electrolytes: NSPE-**1**-2, EO/Li = 20 (top); NSPE-**2**-2, EO/Li = 20 (bottom).

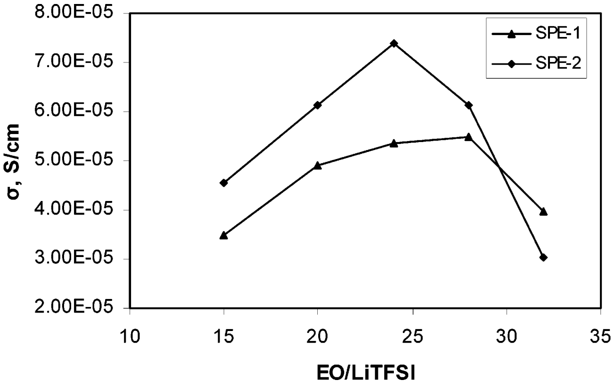


Figure 4. Plots of ambient conductivities of NSPE-**1** and **2** at various EO/LiTFSI.

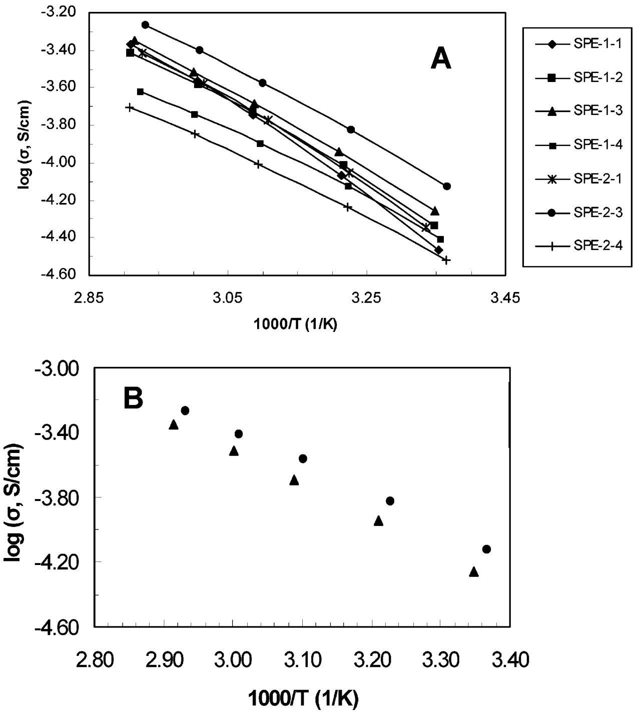


Figure 5. Temperature-dependent ionic conductivities of cross-linked networks: (A) NSPE-**1** and **NSPE-2**; (B) comparison of maximum conductivity for NSPE-**1** (▲) and NSPE-**2** (●).

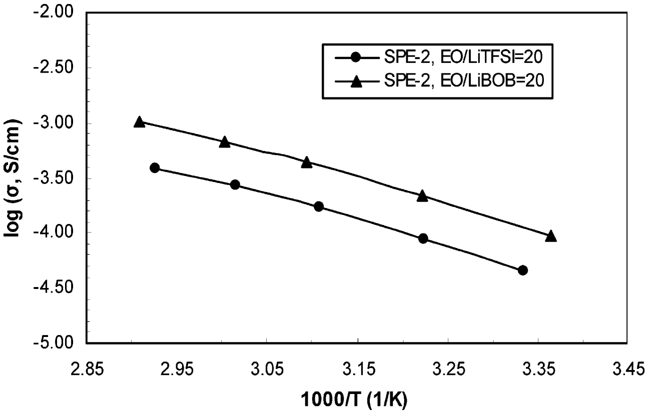


Figure 6. Variable temperature conductivities for NSPE-**2** with LiTFSI and LiBOB at salt concentration (EO/Li = 20).

The conductivity behavior was influenced by the cross-linking density. For NSPE-**1** ($x = 2.81$, $y = 2.19$) and NSPE-**2** ($x = 3.20$, $y = 1.80$), the maximum conductivities and their temperature dependence are shown in Table 2 and Figure 5B. Within the temperature measurement range, the optimum conductivities for NSPE-**2** were 35% higher than those for NSPE-**1**, as expected because this system has lower cross-linking density which allows more flexible chain motion within the network structure.

The type of anion in the metal salt also influenced the conductivity. Larger ions induce better ion-pair separation, in addition to generating a larger free volume.[32] Thus, lithium ions become more mobile resulting in increased conductivity. This effect was detected for NSPE-**2** by doping with lithium bis(oxalato)borate) (LiBOB)[33] and $\mathrm{LiN(CF_3SO_2)_2}$ (LiTFSI), which are widely investigated electrolyte salts. Data in Table 2 reveal that with same doping level of 20/1 the polymer/LiBOB complex displayed higher conductivity than the LiTFSI-doped material both at room temperature and at elevated temperatures (Figure 6). The superior conductivity associated with LiBOB is presumably due to the electron-withdrawing boron providing a very weakly basic bulky anion,[34,35] leading to the easy dissociation into free ions.

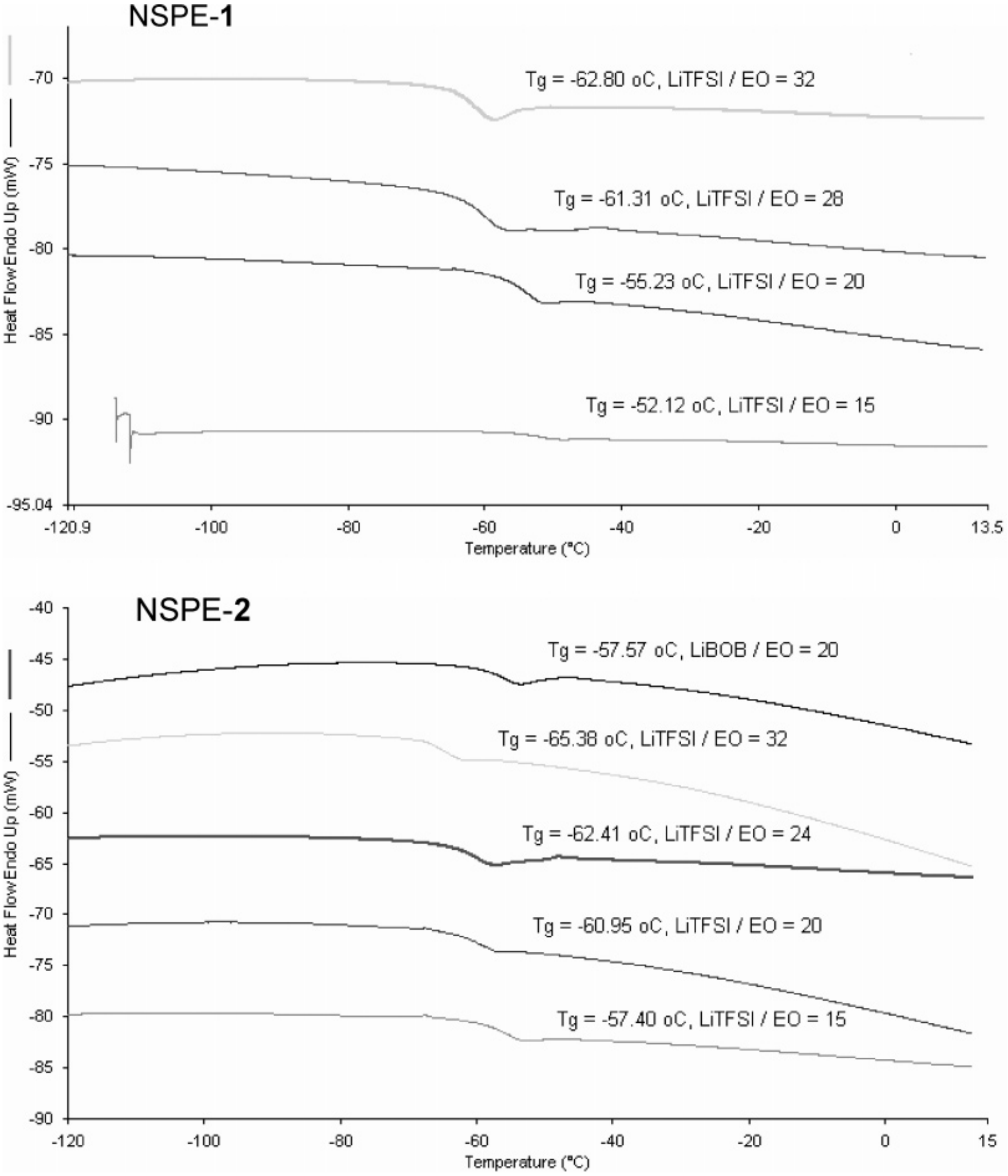


Figure 7. DSC thermograms of NSPE-**1** and NSPE-**2** with various lithium salt concentrations.

Table 2. Conductivity, E_a, and T_0 Values and Thermal Analysis of NSPE-1,2

polymer	EO/Li	conductivity 25 °C (S cm^{-1})	conductivity 37 °C (S cm^{-1})	E_a^{a} (kJ/mol)	T_0^{a} (K)	T_g^{b} (K)
NSPE-**1**-1	15:1	3.48×10^{-5}	8.53×10^{-5}	7.33	192.97	220.88
NSPE-**1**-2	20:1	4.90×10^{-5}	9.30×10^{-5}	5.13	204.81	217.77
NSPE-**1**-3	24:1	5.12×10^{-5}	9.68×10^{-5}	5.48	156.23	213.45
NSPE-**1**-4	28:1	5.48×10^{-5}	1.14×10^{-4}	6.12	150.80	211.69
NSPE-**1**-5	32:1	3.97×10^{-5}	7.46×10^{-5}	5.02	196.86	210.20
NSPE-**2**-1	15:1	4.55×10^{-5}	8.86×10^{-5}	5.15	146.12	215.62
NSPE-**2**-2	20:1	6.12×10^{-5}	9.38×10^{-5}	6.04	153.25	212.05
NSPE-**2**-3	24:1	7.38×10^{-5}	1.92×10^{-4}	3.45	136.78	210.59
NSPE-**2**-4	32:1	3.04×10^{-5}	5.75×10^{-5}	6.70	160.71	207.62
NSPE-**2**-5^c	20:1	9.24×10^{-5}	2.11×10^{-4}	4.24	149.64	215.43
NSPE-**2**-6^c	24:1	6.33×10^{-5}	9.25×10^{-5}	6.56	152.44	212.14

^{a} Two parameters fit of VTF equation. ^{b} Measured by DSC with a scanning rate of 10 °C/min. ^{c} Doped with LiBOB.

The glass transition temperatures, T_g, for cross-linked polymer electrolytes NSPE-**1** and **2** were studied by DSC analysis. The DSC curves of the salt-free as well as the salt-complexed polymers confirmed that these materials are completely amorphous over the temperature range of −150 to 50 °C. As seen in Figure 7, glass transitions ranging from −65.38 to −52.12 °C were observed for each polymer. T_g's of all the polymers are reported in Table 1. These values are well below the room temperature, and the low values reflect the good flexibility of the siloxane segments. Both polymers showed increases in T_g values with increases in LiTFSI salt concentration, presumably due to transient coordinative cross-linkings between the oligoether chains. The T_g values of NSPE-**1**/LiTFSI complexes were higher than those of NSPE-**2** complexes, indicating that NSPE-**2** has higher segmental flexibility, thus facilitating the ion transfer. The result is consistent with the ionic conductivity results discussed earlier.

Conclusions

A new type of solid polymer electrolyte based on cross-linked pentamethylcyclopentasiloxane ($D_5{}^H$) precursors was synthesized and studied. These SPE's, with a unique cross-linked network structure, were synthesized by hydrosilylation of partially oligoethyleneoxy-substituted pentamethylcyclopentasiloxane ($D_5{}^H$) precursors with an α,ω-diallyloligoethyleneoxy cross-linking reagent. NSPE-**2** with 36.0% cross-linking density exhibited higher conductivity than NSPE-**1** with cross-linking density of 43.8%, attributed to the higher flexibility of the network structure of the former. Our preliminary studies of the LiX salt effect on the conductivity showed that samples doped with LiBOB had higher ambient conductivity (9.24×10^{-5} S cm^{-1}) than those doped with LiTFSI (6.12×10^{-5} S cm^{-1}).

Acknowledgment. This work was supported by the U.S. Department of Commerce, National Institute of Standards and Technology, Advanced Technology Program. We thank 3M Co. for the gift of $LiN(CF_3SO_2)_2$. Instrumentation at Grinnell was funded by the NSF-MRI program (Grant 0116159). The NMR instruments in this research were funded by NIH (Grants NIH 1 S10 RRO 8389-01, 1 S10 RRO8389-01, 1 S10 RRO4981-01, and CHE-9629688).

References and Notes

(1) (a) Fenton, D. E.; Parker, J. M.; Wright, P. V. *Polymer* **1973**, *14*, 589. (b) Wright, P. V. *J. Polym. Sci., Phys. Ed.* **1976**, *14*, 955. (c) Wright, P. V. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 955.
(2) (a) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. *Abstracts of Papers,* Second International Meeting on Solid Electrolytes, St. Andrews, Scotland, 1978. (b) Armand, M. B.; Chabagno, J. M.; Duclot, M. J. In *Fast Ion Transport in Solids*; Duclot, M. J., Vashishta, B., Mundy, J. N., Shenoy, G. K., Eds.; North-Holland: Amsterdam, 1979. (c) Berthier, C.; Gorecki, W.; Minier, M.; Armand, M. B.; Chabagno, J. M.; Rigaud, P. *Solid State Ionics* **1983**, *11*, 91.
(3) (a) Ratner, M. A.; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109. (b) Ratner, M. A.; Johansson, P.; Shriver, D. F. *MRS Bull.* **2000**, *8*, 31.
(4) (a) Gray, F. M. *Solid Polymer Electrolytes: Fundamentals and Technological Applications*; VCH Publishers: New York, 1991. (b) *Polymer Electrolytes*; Royal Society of Chemsitry: Cambridge, 1997.
(5) Bruce, P. G.; Vincent, C. A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3187.
(6) Blonsky, P. M.; Shriver, D. F.; Allcock, H. R.; Austin, P. *J. Am. Chem. Soc.* **1984**, *106*, 6854.
(7) Allcock, H. R.; Napierala, M. E.; Cameron, C. G.; O'Connor, S. J. M. *Macromolecules* **1996**, *29*, 1951.
(8) Allcock, H. R.; O'Connor, S. J. M.; Olmeijer, D. L.; Napierala, M. E.; Cameron, C. G. *Macromolecules* **1996**, *29*, 7544.
(9) Allcock, H. R.; Ravikiran, R.; O'Connor, S. J. M. *Macromolecules* **1997**, *30*, 3184.
(10) Allcock, H. R.; Olmeijer, D. L.; O'Connor, S. J. M. *Macromolecules* **1998**, *31*, 753.
(11) Allcock, H. R.; Napierala, M. E.; Olmeijer, D. L.; Best, S. A.; Merz, K. M. *Macromolecules* **1999**, *32*, 732.
(12) Allcock, H. R.; Laredo, W. R.; Kellam, E. C.; Morford, R. V. *Macromolecules* **2001**, *34*, 787.
(13) Khan, I. M.; Yuan, Y.; Fish, D.; Wu, E.; Smid, J. *Macromolecules* **1988**, *21*, 2684.
(14) Zhou, G. B.; Khan, I. M.; Smid, J. *Macromolecules* **1993**, *26*, 2202.
(15) Fish, D.; Khan, I. M.; Wu, E.; Smid, J. *Br. Polym. J.* **1988**, *20*, 281.
(16) Spindler, R.; Shriver, D. F. *Macromolecules* **1988**, *21*, 648.
(17) Spindler, R.; Shriver, D. F. *J. Am. Chem. Soc.* **1988**, *110*, 3036.
(18) Siska, D. P.; Shriver, D. F. *Chem. Mater.* **2001**, *13*, 4698.
(19) Morales, E.; Acosta, J. L. *Electrochim. Acta* **1999**, *45*, 1049.
(20) Hooper, R.; Lyons, L. J.; Moline, D. A.; West, R. *Organometallics* **1999**, *18*, 3249.
(21) Hooper, R.; Lyons, L. J.; Mapes, M. K.; Schumacher, D.; Moline, D. A.; West, R. *Macromolecules* **2001**, *34*, 931.
(22) Zhang, Z. C.; Sherlock, D.; West, R.; Lyons, L. J.; Amine, K.; West, R. *Macromolecules* **2003**, *36*, 9176.
(23) Zhang, Z. C.; Jin, J. J.; Bautista, F.; Lyons, L. J.; Shariatzadeh, N.; Sherlock, D.; Amine, K.; West, R. *Solid State Ionics* **2004**, *170*, 233.
(24) Song, J. Y.; Wang, Y. Y.; Wan, C. C. *J. Power Sources* **1999**, *77*, 183.
(25) Lewis, L. N. *J. Am. Ceram. Soc.* **1990**, *112*, 5998.
(26) Lewis, L. N.; Uriarte, R. J. *Organometallics* **1990**, *9*, 621.
(27) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(28) Marko, I. E.; Sterin, S.; Buisine, O.; Mignani, G.; Branlard, P.; Tinant, B.; Declercq, J.-P. *Science* **2002**, *298*, 204.
(29) Fulcher, G. S. *J. Am. Ceram. Soc.* **1925**, *8*, 339.
(30) Vogel, H. *Phys. Z.* **1921**, *22*, 645.
(31) Tammann, V. G.; Hesse, W. Z. *Anorg. Allg. Chem.* **1926**, *156*, 245.
(32) Xu, K. *Chem. Rev.* **2004**, *104*, 4303.
(33) (a) Lischka, U.; Wietelmann, U.; Wegner, M. DE 19829030 C1, 1999. (b) Xu, K.; Zhang, S. S.; Jow, T. R. *Electrochem. Solid-State Lett.* **2003**, *6*, A117. (c) Xu, K.; Lee, U.; Zhang, S. S.; Wod, M.; Jow, T. R. *Electrochem. Solid-State Lett.* **2003**, *6*, A144.
(34) Videa, M.; Xu, W.; Geil, B.; Marzke, R. L.; Angell, C. A. *J. Electrochem. Soc.* **2001**, *148*, A1352.
(35) Xu, W.; Shusterman, A.; Videa, M.; Velikv, V.; Marzke, R. L.; Angell, C. A. *J. Electrochem. Soc.* **2003**, *150*, E74.

MA050066K