

# Synthesis and Ionic Conductivity of Cyclosiloxanes with Ethyleneoxy-Containing Substituents

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Pentamethylcyclopentasiloxanes ( $D_5H$ ) with oligo(ethylene glycol) substituents,  $D_5N3$  and  $D_5S3$ , and a short-chain siloxane derivative  $MD_6N3M$  were synthesized by  $B(C_6F_5)_3$ -catalyzed dehydrogenative coupling and by platinum-catalyzed hydrosilylation reactions. Conductivities were studied when doped with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI). The oxygen-linked cyclic siloxane  $D_5N3$  exhibits higher conductivity than trimethylene-linked siloxane  $D_5S3$ . The substituted linear oligomeric siloxane  $MD_6N3M$  has a lower  $T_g$  than the  $D_5$  siloxanes, and showed much higher conductivity at the same  $Li^+$  concentration. The curvature of the plot of conductivity vs temperature dependence indicates a free volume mechanism of ion transport.

## Introduction

Solvent-free polymer electrolytes can be formed by the interaction of polar polymers with metal ions. Ion transport in polymer electrolytes has been a topic of extensive study since the first report of high conductivity of a poly(ethylene oxide)/KSCN complex by Wright and co-workers<sup>1</sup> in 1973 and the unique idea of employing these polymer electrolytes in battery applications by Armand et al.<sup>2</sup> shortly afterward. Transport mechanism models developed by Ratner et al.<sup>3</sup> indicated that low  $T_g$  polymers have extremely high free volumes which favor ion transport. Better results are obtained for polymers with highly flexible backbones, bearing oligo(ethylene glycol) (EO) side chains. Polyphosphazenes of this type have been studied extensively in the form of comb polymers, block copolymers, and cross-linked network polymers.<sup>4–9</sup> Interest in polysiloxane-based polymer electrolytes arose early in the 1980s. Poly(ethylene oxide) (PEO)-

substituted polysiloxanes as ionically conductive polymer hosts have been previously investigated.<sup>11–21</sup> Their relatively high ionic conductivity was ascribed to the highly flexible inorganic backbone which produced a totally amorphous polymer host. In recent years, improved battery performance has been observed for systems containing polymer electrolytes, with a  $Li^+$  transference number close to unity.<sup>22</sup> Efforts have also been made to design and synthesize siloxane-based single-ion conductors.<sup>23–27</sup>

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However, the studies of both binary salt and single-ion polysiloxane-based ionic conductors were all focused on a commercially available polymethylhydrosiloxane (PMHS) polymer with an average of 30–35 Si–O repeating units. Little study was made on the oligomeric siloxanes with lower molecular weight. Short-chain siloxane-based polymer electrolytes have been recently reported by us,<sup>28</sup> which showed room-temperature conductivities as high as  $2 \times 10^{-4}$  S/cm. Compared with conventional carbonate electrolytes, (EC/PC), these oligomeric siloxanes are nonvolatile and less flammable, which tremendously decreases the safety issue existing in the lithium battery industry.

Recently, the polymer poly(pentamethylcyclopentasiloxane)<sup>10</sup> (PD5) was reported to have a glass transition temperature,  $T_g$ , of  $-151$  °C, the lowest value ever recorded for a polymer. This led us to study the conductivities of oligoether-substituted cyclopentasiloxanes. In this paper, we have synthesized the oligoether-substituted pentamethylcyclopentasiloxanes and compared their properties with those of a linear oligomeric siloxane, MD<sub>6</sub>N3M. The purpose of this paper is to compare the cyclic and linear siloxanes with similar numbers of backbone repeating units.

## Experimental Section

**Nomenclature.** For convenience and simplicity, a code with a combination of letters and numbers was assigned to each siloxane and their derivatives with specific meanings. D<sub>5</sub>S3 represents the derivative of cyclopentasiloxane D<sub>5</sub><sup>H</sup>, which contains a  $-(CH_2)_3-$  spacer between Si and the oligoether chain. The number “3” stands for the number of repeating units ( $CH_2CH_2O$ ) of the oligoether chain. Accordingly, D<sub>5</sub>N3 refers to nonspacer derivative of pentamethylcyclopentasiloxane D<sub>5</sub><sup>H</sup> (“N” stands for nonspacer, Si is directly attached to the oxygen atom of the oligoether chain). MD<sub>6</sub><sup>H</sup>M and MD<sub>6</sub>N3M represent the linear oligomeric siloxane and its derivative, respectively, with the same definition as their cyclic analogues except that M stands for trimethylsilyl  $[(CH_3)_3Si-]$ .

**Materials.** Pentamethylcyclopentasiloxane (D<sub>5</sub><sup>H</sup>) and hexamethyldisiloxane (MM) were supplied by Gelest and purified by distillation prior to use. Allyl bromide, tri(ethylene glycol) methyl ether, Karlstedt’s catalyst (platinum divinyltetramethyldisiloxane) (3% in xylene solution), and tris(pentafluorophenyl) borane ( $B(C_6F_5)_3$ ) were purchased from Aldrich. Sodium hydride (NaH, 60% dispersion in mineral oil) was from Acros Organics. Fuming sulfuric acid was from Fisher Scientific. THF and toluene were dried over sodium benzophenone ketyl and distilled in an atmosphere of dry nitrogen before use. NMR grade  $CDCl_3$  was stored over 4 Å molecular sieves. Lithium bis(trifluoromethylsulfonyl)imide ( $LiN(SO_2CF_3)_2$ ) was a gift from 3M and was dried under vacuum at 120 °C for 24 h prior to use.

**Synthesis. Tri(ethylene glycol) Allyl Methyl Ether.** This compound was synthesized using the method described previously.<sup>19b</sup> The product was purified by vacuum distillation (80 °C/0.5 Torr) (90%). <sup>1</sup>H NMR ( $CDCl_3$ ),  $\delta$  (ppm): 5.85 (m, 1H), 5.15 (dd, 2H), 3.95 (d, 2H), 3.45–3.65 (m, 12H), 3.30 (s, 3H). <sup>13</sup>C NMR ( $CDCl_3$ ),  $\delta$  (ppm): 134.6, 116.8, 72.1, 71.8, 70.3–70.0, 69.2, 58.9.

**1,3,5,7,9-Penta(methoxytri(oxyethylene)propyl)-1,3,5,7,9-pentamethylcyclopentasiloxane (D<sub>5</sub>S3).** To a 250-mL flame-dried flask

was added 1,3,5,7,9-pentamethylcyclopentasiloxane (D<sub>5</sub><sup>H</sup>) (12.0 g, 0.20 mol of Si–H group) and tri(ethylene glycol)allyl methyl ether (48.96 g, 0.24 mol, 20% excess) under a nitrogen atmosphere. The heterogeneous mixture was stirred vigorously, and 20  $\mu$ L of platinum divinyltetramethyldisiloxane Pt(dvs) (3% solution in xylene) was injected into the mixture by a syringe and the temperature was gradually raised to 70–75 °C. The reaction mixture was continuously stirred at this temperature for about 24 h until no Si–H signal (4.7 ppm) was detected in the <sup>1</sup>H NMR spectrum. After the excess tri(ethylene glycol)allyl methyl ether and its isomer were removed by Kugelrohr distillation at about 120 °C under vacuum, the liquid was measured by FT-IR which showed no Si–H or monomer peaks. The viscous polymer was then decolorized by refluxing in toluene with activated carbon for 12 h. After removal of toluene, a colorless liquid polymer was obtained, 47.5 g (90%). <sup>1</sup>H NMR ( $CDCl_3$ ),  $\delta$  (ppm): 3.65–3.45 ( $CH_2CH_2O$ ), 3.32 ( $OCH_3$ ), 1.55 ( $CH_2CSi$ ), 0.46 ( $SiCH_3$ ), 0–0.2 ( $Si-CH_3$ ). <sup>13</sup>C NMR ( $CDCl_3$ ),  $\delta$  (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. <sup>29</sup>Si NMR ( $CDCl_3$ ),  $\delta$  (ppm): –22.2–24.1.

**1,3,5,7,9-Penta(methoxytri(oxyethylene))-1,3,5,7,9-pentamethylcyclopentasiloxane (D<sub>5</sub>N3).** To a 500-mL flame-dried flask was added D<sub>5</sub><sup>H</sup> (11.13 g, 0.185 mol of Si–H), tri(ethyleneglycol) monomethyl ether (36.41 g, 0.222 mol), and toluene (100 mL). Tris(pentafluorophenyl)borane ( $B(C_6F_5)_3$ ) (0.047 g, 0.092 mmol) in THF was syringed into the flask, which was then heated to 80 °C with vigorous magnetic stirring. The formation of H<sub>2</sub> was simultaneously observed. The reaction was followed by FT-IR by frequent sample measurements. When no Si–H absorbance was detected at 2160  $cm^{-1}$ , the excess alcohol was removed by Kugelrohr distillation (yield 95%). The structure of the product was analyzed by FTIR (no –OH absorption at  $\sim 3400$   $cm^{-1}$  or –Si–H at 2160  $cm^{-1}$ ). <sup>1</sup>H NMR ( $CDCl_3$ ),  $\delta$  (ppm): 3.73–3.34 ( $CH_2CH_2O$ ), 3.17 ( $OCH_3$ ), 0.10–0.20 ( $Si-CH_3$ ). <sup>13</sup>C NMR ( $CDCl_3$ ),  $\delta$  (ppm): 73.9, 72.0, 70.6–70.7, 70.1, 59.1, 23.0–23.1, –0.63, –0.96. <sup>29</sup>Si NMR ( $CDCl_3$ ),  $\delta$  (ppm): –50.1, –57.5, –66.3.

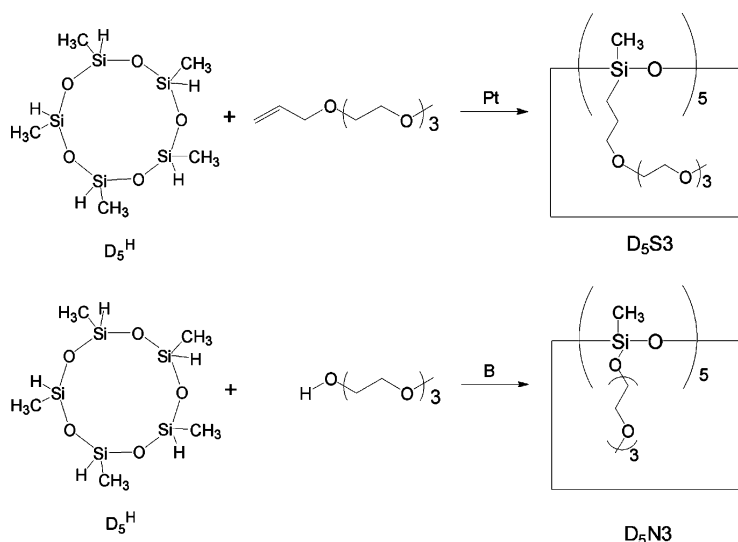
**Oligomeric Siloxane (MD<sub>6</sub><sup>H</sup>M).** An acid-catalyzed equilibrium polymerization was employed to synthesize the oligomeric siloxane. To a 100-mL flame-dried flask was added 16.24 g (0.10 mol) of chain end-blocker hexamethyldisiloxane and 48.10 g (0.20 mol) of D<sub>4</sub><sup>H</sup>. The flask was sealed with a rubber stopper and 1.61 g (2.5 wt %) of fuming sulfuric acid was slowly dropped into the flask as a cationic initiator. The mixture was heated to 60 °C and kept at this temperature for 24 h. The resulting mixture was then allowed to cool and dissolved in diethyl ether. The ether solution was then washed with 10%  $NaHCO_3$  (3  $\times$  15 mL) aqueous solution and deionized water (6  $\times$  10 mL). The washed ether solution was dried over  $Na_2SO_4$  for 48 h. After filtration, the ether was removed by rotovap, and the residue was kept under vacuum at 70 °C overnight to remove any volatile materials (yield 85%). The average  $CH_3-SiHO-$  repeating unit (DP) of 6 was determined by the integration ratio of Si–H at 4.7 ppm to Si–CH<sub>3</sub> at 0.3 ppm from <sup>1</sup>H NMR measurement ( $n \sim 6$ ). <sup>1</sup>H NMR ( $CDCl_3$ ),  $\delta$  (ppm): 4.60–4.65 (broad, Si–H), 0.12–0.21 (m, Si–CH<sub>3</sub>). <sup>13</sup>C NMR ( $CDCl_3$ ),  $\delta$  (ppm): –1.2, 3.9. <sup>29</sup>Si NMR ( $CDCl_3$ ),  $\delta$  (ppm): 9.55 (–Si(CH<sub>3</sub>)<sub>3</sub>), –35.11 to –35.20 (–Si–H).

**Oligo( $\omega$ -methoxytri(oxyethylene)) Methylsiloxane (MD<sub>6</sub>N3M).** A 250-mL Schlenk flask was flame-dried/N<sub>2</sub> three times, and then 24.0 g of siloxane precursor MD<sub>6</sub><sup>H</sup>M and 62.2 g of tri(ethylene glycol) methyl ether (vacuum-distilled prior to use) were added to the flask by a syringe. Seventy milliliters of dry toluene solvent was injected to make a clear solution. 0.1024 g (0.05 mol % of Si–H) tris(pentafluorophenyl) borane ( $B(C_6F_5)_3$ ) was dissolved in toluene and then injected into the reaction mixture. The flask was

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**Figure 1.** Hydrosilylation and dehydrogenative coupling reactions of  $D_5^H$ .

heated to 80 °C with vigorous magnetic stirring.  $H_2$  bubbles were simultaneously observed. Samples were taken and the process of dehydrogenation was followed by FT-IR measurements. After completion of the reaction, the excess alcohol was removed by Kugelrohr distillation (yield 85%). The structure of the final product was confirmed by FT-IR (no  $-OH$  absorption at  $\sim 3400\text{ cm}^{-1}$  or  $-Si-H$  at  $2160\text{ cm}^{-1}$ ). The product was sealed in a flask under argon.  $^1H$  NMR ( $CDCl_3$ ),  $\delta$  (ppm): 3.70–3.30 ( $CH_2CH_2O$ ), 3.15 ( $OCH_3$ ), 0.05–0.10 ( $Si-CH_3$ );  $^{13}C$  NMR ( $CDCl_3$ ),  $\delta$  (ppm): 73.9, 72.0, 70.6–70.7, 70.1, 59.1, 23.0–23.1,  $-0.63$ ,  $-0.96$ .  $^{29}Si$  NMR ( $CDCl_3$ ),  $\delta$  (ppm): 10.2,  $-50.1$ ,  $-57.5$ ,  $-66.3$ .

**Electrolyte Preparation.** LiTFSI-doped polysiloxanes were prepared by a solution method. The desired amount of substituted siloxane was dissolved in a THF solution of LiTFSI ( $8.05 \times 10^{-2}$  M). All of the polymers formed homogeneous, viscous liquid mixtures with this salt. The homogeneous polymer/lithium salt complex was then evacuated for 12 h on a Schlenk line and then further evacuated on a high-vacuum line ( $\sim 10^{-5}$  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.

**NMR Characterization.**  $^1H$ ,  $^{13}C$  NMR spectra were obtained on a Bruker AC 300 MHz spectrometer;  $^{29}Si$  NMR spectra were recorded on a Varian Unity 500 MHz with grants NIH 1 S10 RRO4981-01 and NIH CHE-9629688.  $^1H$  and  $^{13}C$  chemical shifts are reported relative to TMS as an internal standard, and the  $^{29}Si$  chemical shifts are reported relative to an external TMS standard ( $CDCl_3$  as solvent) using an inverse gate pulse sequence with a relaxation delay of 15 s.

**ac Impedance Measurements.** Impedances were measured under computer control using a Princeton Applied Research model 273A potentiostat/galvanostat, Princeton Applied Research model 1025 frequency response analyzer for frequency control (75 Hz to 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  $23 \pm 1$  °C while variable-temperature measurements (0–70 °C) were made with the electrochemical cell in a jacketed holder surrounded by ethylene glycol/water from a Lauda RMT6 circulating bath. Actual temperatures were determined via an Omega thermocouple attached directly to the cell. The conductivity values ( $\sigma$ ) were calculated from the equation  $\sigma = (1/R_b)(L/A)$ , where  $R_b$  is the bulk electrolyte resistance,  $L$  is the sample thickness, and  $A$  is the area of the sample.

**DSC Thermograms.** A Perkin-Elmer Pyris Diamond DSC was used to measure thermal properties. Low temperatures were achieved by using the liquid nitrogen cooling accessory. Polymer samples were loaded in hermetically sealed aluminum pans prepared in the drybox. All samples were measured in duplicate. Glass transition temperatures ( $T_g$ ) 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.

**Viscosity Measurements.** Viscosities were measured on a Brookfield Digital Viscometer DV-I+. Then 6 mL of each polymer/LiTFSI complex liquid was poured into the small sample chamber under nitrogen over several spindle rotation rates according to the manufacturer's specifications. Temperature was controlled by a thermocouple housed in the viscometer sample chamber.

**FTIR Measurements.** IR spectra were recorded on a Nicolet Nexus 670 spectrometer as viscous samples placed on the Avatar multibounce HATR accessory.

## Results and Discussion

The trimethylene ( $-(CH_2)_3-$ ) type oligoether-substituted cyclopentasiloxane polymer ( $D_5S3$ ) was successfully synthesized by platinum-catalyzed hydrosilylation of  $D_5^H$  with allyl oligoethylene oxides (Figure 1). The reaction was monitored by the disappearance of the  $Si-H$  peaks in both  $^1H$  NMR and FT-IR spectra. Isomeric byproducts were observed in the reaction mixture. The formation of olefin isomers can be attributed to the dissociation of the labile divinyltetramethyldisiloxane ligand and the subsequent generation of colloidal Pt species<sup>29,30</sup> leading to the undesired side products and coloration of the product. After removal by Kugelrohr distillation, the product was treated with activated carbon by refluxing in toluene for 24 h, yielding a viscous polymer. The viscosity,  $\eta = 45.6$  cP at  $24.5$  °C, is much lower than that for our previously synthesized, long-chain polysiloxane polymers.<sup>19</sup>

The directly linked ( $-O-$  bridged between Si and oligoether chains)  $D_5^H$  and linear oligomeric siloxane ( $MD_6^H M$ ) with oligoether chains were synthesized by dehydrogenative

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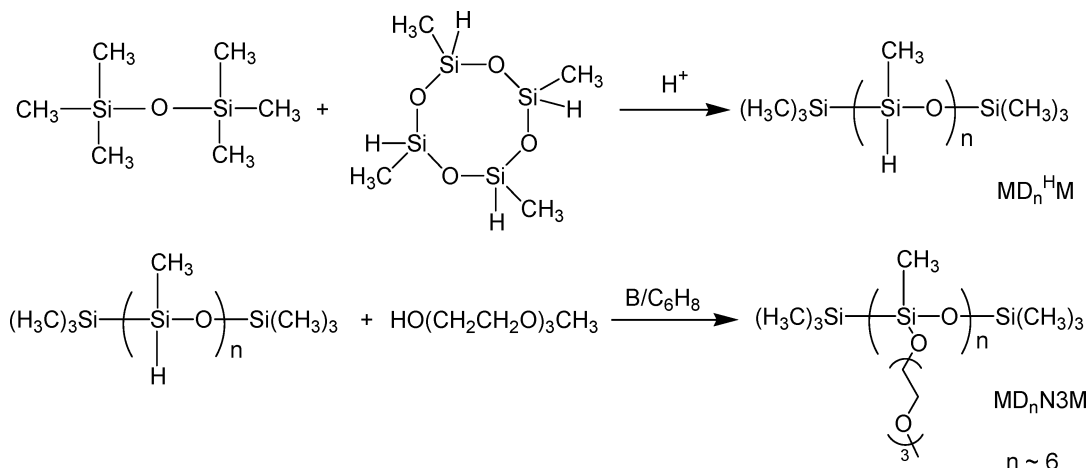


Figure 2. Synthesis of short-chain oligosiloxane (MD<sub>6</sub><sup>HM</sup>) and oligoether-substituted oligomeric siloxane derivatives (MD<sub>6</sub>N3M).

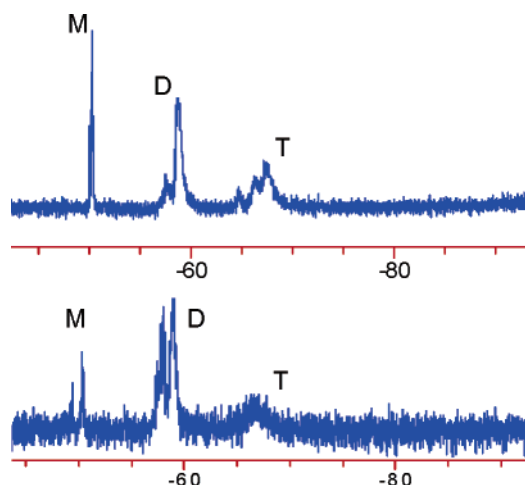


Figure 3. <sup>29</sup>Si NMR spectra of D<sub>5</sub>N3 (above) and MD<sub>6</sub>N3M (bottom).

coupling, catalyzed by B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> ([B]/[Si-H] = 0.05%) at 80 °C in toluene, as shown in Figure 1 and Figure 2. Excess tri(ethylene glycol) monomethyl ether was employed to ensure the complete consumption of Si-H groups. The cyclic product could readily be distinguished from the linear counterparts by <sup>29</sup>Si NMR. However, the <sup>29</sup>Si NMR spectra of nonspacer siloxanes, both cyclosiloxane D<sub>5</sub>N3 and linear MD<sub>6</sub>N3M, are quite similar, as can be seen in Figure 3. The assignments of the respective peaks can be made by comparison with literature data.<sup>31,32</sup> Alkoxy and especially siloxy bound to a Si atom result in large upfield <sup>29</sup>Si NMR shifts. The spectra have a dominant peak at -57.0 ppm, assigned to a Si with two siloxy and one OR substituent (D unit). A relatively strong absorption is found at -66.3 ppm and can be traced to a Si atom with three siloxy substituents (T unit). A redistribution mechanism is proposed in Figure 4, accounting for the appearance of M units (a Si attached by two OR and one siloxy). The combined results suggest that the structure of D<sub>5</sub>N3 is considerably more complex than shown in Figure 1. The ambient viscosities for nonspacer siloxanes are 25.0 cP for D<sub>5</sub>N3 (24.5 °C) and 30.4 cP for MD<sub>6</sub>N3M (25.0 °C), respectively.

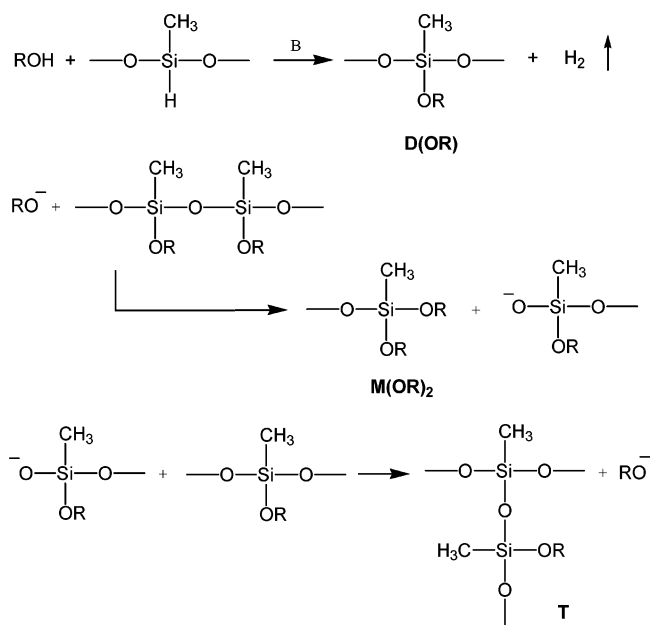


Figure 4. Si-O redistribution mechanism of formation of M, D and T units.

Table 1. Maximum Conductivity (25 and 37 °C), Activation Energy,  $T_o$ , and  $T_g$

sample	EO:Li	$\sigma$ , 25 °C (S/cm)	$\sigma$ , 37 °C (S/cm)	$E_a^{a,b}$ (kJ mol <sup>-1</sup> )	$T_o^a$ (K <sup>-1</sup> )	$T_g^c$ (K <sup>-1</sup> )
D <sub>5</sub> N3	24:1	$1.43 \times 10^{-4}$	$2.72 \times 10^{-4}$	4.12	208.4	190.65
D <sub>5</sub> N3	15:1	$1.16 \times 10^{-4}$	$2.40 \times 10^{-4}$	6.46	188.1	197.81
D <sub>5</sub> S3	24:1	$6.97 \times 10^{-5}$	$1.18 \times 10^{-4}$	7.56	226.8	194.76
D <sub>5</sub> S3	15:1	$5.86 \times 10^{-5}$	$9.35 \times 10^{-4}$	5.21	214.2	198.28
MD <sub>6</sub> N3M	24:1	$2.66 \times 10^{-4}$	$4.58 \times 10^{-4}$	3.07	202.0	187.69
MD <sub>6</sub> N3M	15:1	$2.01 \times 10^{-4}$	$3.08 \times 10^{-4}$	4.37	196.0	190.55

<sup>a</sup> Two-parameter fit, unit of A is S cm<sup>-1</sup> K<sup>1/2</sup>. <sup>b</sup>  $E_a = B^*R$ . <sup>c</sup> DSC measurements.

All polymers formed homogeneous amorphous complexes with LiTFSI salt. The conductivity results we observed are much higher than those reported by Fish et al. for oligo(ethylene oxide)-substituted commercial polymethylhydro-siloxane.<sup>13</sup> The maximum conductivities are summarized in Table 1. Ambient conductivity for D<sub>5</sub>N3/LiTFSI complexes increases from  $6.62 \times 10^{-5}$  to  $1.43 \times 10^{-4}$  S/cm with increasing salt concentration, as shown in Figure 5. As the LiTFSI concentration increases beyond EO/Li = 24:1, the conductivity decreases, becoming  $6.41 \times 10^{-5}$  S/cm at the

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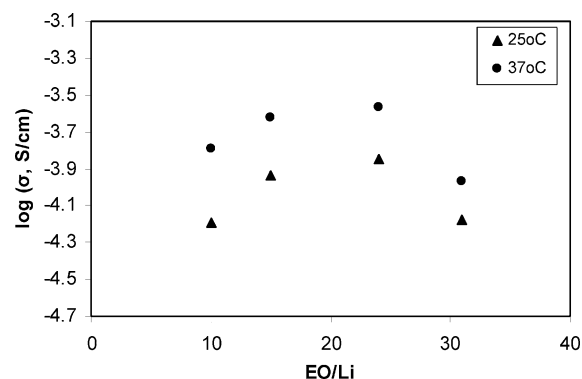


Figure 5. Plots of conductivity vs EO/Li for D<sub>5</sub>N3/LiTFSI complexes.

doping level EO/Li<sup>+</sup>=10/1. The dependence of the ionic conductivity on lithium salt doping concentration can be adequately interpreted by two opposing effects. There is a buildup of charge carriers as the salt concentration is increased, but this is eventually offset by an increase in the viscosity of the polymer electrolyte which will impede the ion migration through the polymer matrix. Compared to D<sub>5</sub>N3, the spacer-type siloxane, D<sub>5</sub>S3, gave much lower ambient conductivity ( $6.97 \times 10^{-5}$ ) at the same doping level of EO/Li = 24/1, the optimum concentration for nonspacer D<sub>5</sub>N3. The lower conductivity for D<sub>5</sub>S3 is probably caused by the presence of  $-(\text{CH}_2)_3-$ , which will decrease polymer polarity and increase its viscosity. An inverse relationship between viscosity and conductivity relationship is well-known.<sup>33–35</sup> Recent studies by Williams et al.<sup>36</sup> and Chagnes et al.<sup>37</sup> have described similar results for a metal complex molten salt and for  $\gamma$ -butyrolactone/LiX (X = BF<sub>4</sub><sup>−</sup>, AsF<sub>6</sub><sup>−</sup>, and N(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub><sup>−</sup> systems.

The effect of conformation of siloxane backbone on the conductivity is well-illustrated in Table 1. As discussed in the previous section, <sup>29</sup>Si NMR measurements have revealed the complexity of the products. However, by quantitative calculation of the peaks in the spectra, we found the core structure (peak D, 80% for D<sub>5</sub>N3 and 83% for MD<sub>6</sub>N3M) is the predominant fraction in both reaction mixtures; hence, the conductivity results in Table 1 are comparable and meaningful. It is clear that the linear siloxane derivative MD<sub>6</sub>N3M has conductivity almost twice that for cyclic D<sub>5</sub>N3 at the same salt concentration. Thermal analysis revealed that linear oligomeric siloxane derivative exhibits lower  $T_g$  than that of its cyclic counterpart, as shown in Figure 6, indicating a more flexible backbone of the linear siloxane.

The temperature dependence of conductivity for D<sub>5</sub>N3 was also studied. Plots of the conductivity versus temperature are curved, as shown in Figure 7, rather than linear, suggesting that segmental motion aids in the movement of ions among the polymer chains. The experimental conductivity and temperature data fit well to the Vogel-Tamman-Fulcher<sup>38</sup> (VTF) equation,  $\sigma = AT^{-1/2}e^{-B/(T-T_0)}$ , produc-

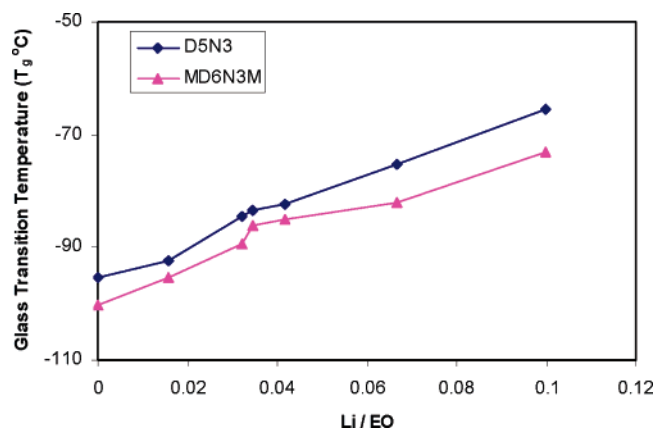


Figure 6. Glass transition temperature ( $T_g$ ) of D<sub>5</sub>N3 and MD<sub>6</sub>N3M with varying EO/Li.

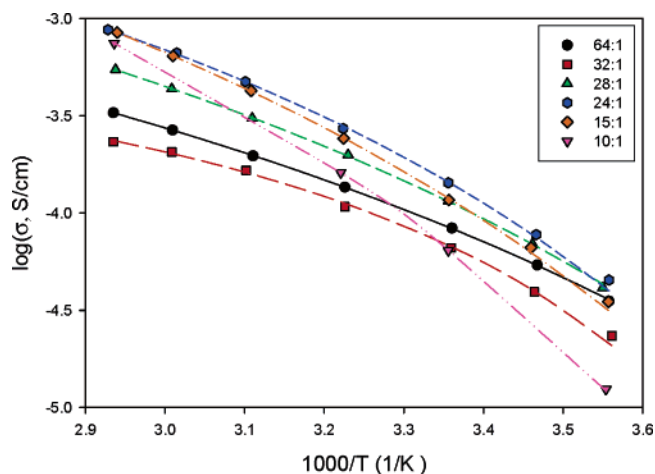


Figure 7. Variable-temperature conductivities for D<sub>5</sub>N3 at various LiTFSI doping levels.

ing the parameters for  $E_a$  ( $B \times 8.31$  J/(mol K)) and the empirical glass transition temperature ( $T_0$ ), which are included in Table 1.

## Conclusions

Cyclopentasiloxanes with oligo(ethylene glycol) substituents, D<sub>5</sub>N3 and D<sub>5</sub>S3, and the oligomeric siloxane derivative MD<sub>6</sub>N3M were synthesized by dehydrogenative coupling and hydrosilylation reactions and their conductivities were investigated after doping with LiTFSI. The oxygen-linked cyclic siloxane D<sub>5</sub>N3 exhibits higher conductivity than trimethylene-linked siloxane D<sub>5</sub>S3 due to its lower viscosity. The substituted linear oligomeric siloxane MD<sub>6</sub>N3M had higher viscosity than D<sub>5</sub>N3, but a lower  $T_g$  and activation energy, and showed a conductivity twice as great as that of D<sub>5</sub>N3. At least in this example, the linear polymer provides higher conductivity than its cyclic counterparts.

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