

# Blends of POSS–PEO( $n=4$ )<sub>8</sub> and High Molecular Weight Poly(ethylene oxide) as Solid Polymer Electrolytes for Lithium Batteries

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Solid polymer electrolyte blends were prepared with POSS–PEO( $n=4$ )<sub>8</sub> (3K), poly(ethylene oxide) (PEO–(600K)), and LiClO<sub>4</sub> at different salt concentrations (O/Li = 8/1, 12/1, and 16/1). POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> is amorphous at all O/Li investigated, whereas PEO(600K) is amorphous only for O/Li = 8/1 and semicrystalline for O/Li = 12/1 and 16/1. The tendency of PEO(600K) to crystallize limited the amount of POSS–PEO( $n=4$ )<sub>8</sub> that could be incorporated into the blends, so that the greatest incorporation of POSS–PEO( $n=4$ )<sub>8</sub> occurred for O/Li = 8/1. Blends of POSS–PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> (O/Li = 8/1 and 12/1) microphase separated into two amorphous phases, a low  $T_g$  phase of composition 85% POSS–PEO( $n=4$ )<sub>8</sub>/15% PEO(600K) and a high  $T_g$  phase of composition 29% POSS–PEO( $n=4$ )<sub>8</sub>/71% PEO(600K). For O/Li = 16/1, the blends contained crystalline (pure PEO(600K)), and two amorphous phases, one rich in POSS–PEO( $n=4$ )<sub>8</sub> and one rich in PEO(600K). Microphase, rather than macrophase separation was believed to occur as a result of Li<sup>+</sup>/ether oxygen cross-link sites. The conductivity of the blends depended on their composition. As expected, crystallinity decreased the conductivity of the blends. For the amorphous blends, when the low  $T_g$  (80/20) phase was the continuous phase, the conductivity was intermediate between that of pure PEO(600K) and POSS–PEO( $n=4$ )<sub>8</sub>. When the high  $T_g$  (70/30, 50/50, 30/70, and 20/80) phase was the continuous phase, the conductivity of the blend and PEO(600K) were identical, and lower than that for the POSS–PEO( $n=4$ )<sub>8</sub> over the whole temperature range (10–90 °C). This suggests that the motions of the POSS–PEO( $n=4$ )<sub>8</sub> were slowed down by the dynamics of the long chain PEO(600K) and that the minor, low  $T_g$  phase was not interconnected and thus did not contribute to enhanced conductivity. At temperatures above  $T_m$  of PEO(600K), addition of the POSS–PEO( $n=4$ )<sub>8</sub> did not result in conductivity improvement. The highest RT conductivity,  $8 \times 10^{-6}$  S/cm, was obtained for a 60% POSS–PEO( $n=4$ )<sub>8</sub>/40% PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1) blend.

## 1. Introduction

Dry, or solvent-free, polymer electrolytes provide advantages such as improved mechanical strength, formability, lack of solvent leakage,<sup>1</sup> decreased dendritic growth, and reduced interfacial reactions<sup>2,3</sup> compared with electrolytes based on solvents or gels in lithium metal or lithium ion batteries. However, the decreased ionic conductivity compared with solvent or gel-based systems has motivated interest in developing methods to increase the ionic conductivity in all solid electrolytes. The most common solid polymer electrolyte is based on derivatives of poly(ethylene oxide) (PEO) and a lithium salt, LiX.<sup>4,5</sup> PEO/LiX complexes, formed by the dissolution of a LiX salt in a PEO matrix, with or without the addition of inorganic components, have been extensively investigated for this purpose. PEO solvates the Li cations, whose motions are coupled to the free volume/local segmental mobility of the PEO chains. Branched or dendritic PEOs with increased numbers of chain ends, and thus increase free volume, may therefore provide enhanced conductivities compared with linear chains of the same molecular weight.

Blends of high molecular weight polymers and lower molecular weight branched oligomers can result in the formation

of true solid-state electrolytes. Several systems based on this approach have been investigated. Low molecular weight ( $2.5 \times 10^4$ ) hyperbranched poly[bis(triethylene glycol)benzoate] blended with PEO decreased crystallinity, but raised  $T_g$ , and increased ionic conductivity only at 10 wt %.<sup>6</sup> PEG–borate esters (MW 528–1688 g/mol) and boroxine rings functionalized with three ethylene oxide side chains (MW = 437–1123 g/mol) were shown to be compatible with poly(ethylene glycol) methacrylate/LiTFSI<sup>7</sup> and poly(methyl methacrylate)/LiSO<sub>3</sub>CF<sub>3</sub> or propylene oxide–ethylene oxide copolymers/LiSO<sub>3</sub>CF<sub>3</sub>, respectively. Conductivities of these polymer/oligomer blends resulted in increased conductivities compared with the neat polymers.<sup>8</sup>

Another low molecular weight dendritic PEO system is based on PEO-functionalized polyoctahedral silsesquioxanes (POSS),<sup>9</sup> in which the eight Si–H groups of the SiO<sub>1.5</sub> POSS cage are functionalized with ethylene glycol monomethyl ethers to form POSS–PEO( $n$ )<sub>8</sub>, where  $n$  is the number of ethylene oxide units.<sup>9</sup> We have previously shown that POSS–PEO( $n$ )<sub>8</sub> forms viscous electrolyte solutions upon addition of lithium salts.<sup>10–13</sup> Preliminary studies indicated that solid self-standing films can be prepared when the POSS–PEO( $n$ )<sub>8</sub> are blended with methyl cellulose or high molecular weight PEO,<sup>13</sup> with improvements in room (RT) and low-temperature conductivity compared with high molecular weight PEO.<sup>14</sup> The use of nonvolatile POSS–PEO( $n$ )<sub>8</sub> for this purpose may offer advantages compared with

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the addition of volatile, reactive low molecular weight poly(ethylene glycol) dimethyl ethers,<sup>3</sup> e.g., PEG(500), and plasticizers.<sup>3,15</sup>

In the current work, we have investigated the conductivity and phase transitions of blends of POSS-PEO( $n=4$ )<sub>8</sub>, high molecular weight poly(ethylene oxide), PEO(600K), and LiClO<sub>4</sub>. The salt concentration was varied using O/Li ratios of 8/1, 12/1, and 16/1. The results indicated that the POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> was not compatible with the PEO(600K)/LiClO<sub>4</sub>, resulting in microphase separation. Amorphous biphasic structures formed in which the low  $T_g$ , higher conductivity phase was the majority phase only at high POSS-PEO( $n=4$ )<sub>8</sub> concentrations. The POSS-PEO( $n=4$ )<sub>8</sub> also improved the low-temperature conductivity of PEO(600K) by suppressing the crystallization of the latter, since in PEO-based electrolytes, ion conduction occurs in the amorphous phase of semicrystalline PEO.<sup>16</sup> However, it did not contribute to conductivity increases at high temperatures.

## 2. Experimental Section

**2.1. Materials.** Octakis(hydridodimethylsiloxy)octasilsesquioxanes (Q<sub>8</sub>M<sub>8</sub><sup>H</sup> = POSS<sub>8</sub>) was obtained from Gelest. Tetra(ethylene glycol) monomethyl ether (98% purity) and acetonitrile (extra dry CH<sub>3</sub>CN) were obtained from Acros Organics. High molecular weight poly(ethylene oxide), PEO(600K), with average  $M_v$  ca. 600000, lithium perchlorate, 99.99% LiClO<sub>4</sub>, allyl bromide, and Karstedt's catalyst, were obtained from Aldrich Chemicals. Toluene was obtained from Acros/Fisher. Before use, toluene was run through two columns packed with neutral alumina and a copper(II) oxide oxygen scavenger in order to remove water.

**2.2. Synthesis.** The POSS-PEO( $n=4$ )<sub>8</sub> was prepared as follows. Tetra(ethylene glycol) monomethyl ether of PEO was refluxed with a 5-fold excess of allyl bromide in the presence of sodium hydroxide for 24 h. The reaction mixture was cooled, filtered to remove sodium bromide and excess sodium hydroxide, dried over anhydrous magnesium sulfate, and filtered and excess allyl bromide was removed under reduced pressure. The product was confirmed by <sup>1</sup>H NMR, which showed the presence of the terminal double bonds. The allyl-PEO( $n=4$ ) was then dried in a vacuum oven at 60 °C for 24 h and stored in a desiccator containing P<sub>2</sub>O<sub>5</sub> in a dry argon-purged glovebox (MBRAUN LabMaster 130).

Octafunctionalization of POSS<sub>8</sub> was achieved by means of a hydrosilylation reaction between the surface Si-H groups and allyl-PEO( $n=4$ ) in the presence of Karstedt's catalyst. All glassware was flame-dried. The allyl-PEO and POSS<sub>8</sub> were heated under vacuum at 60 and 110 °C, respectively, for 24 h. The predried reactants were dissolved in a reaction flask in dry toluene, followed by addition of Karstedt's catalyst, in an argon-purged (Braun) glovebox. The reaction flask was removed from the glovebox and subjected to two to four freeze/thaw cycles (liquid N<sub>2</sub> for 12–24 h/thawed until toluene melted/liquid N<sub>2</sub>) using a diffusion pump. The vacuum was broken with Ar, and the reaction mixture was refluxed (100–110 °C) for ~24 h until <sup>1</sup>H NMR confirmed the disappearance of the allyl double bonds. Activated charcoal was added, the mixture was filtered, and the solvent was then removed under reduced pressure. In general, the synthesis was carried out stoichiometrically (8 equiv of allyl-PEO( $n=4$ )/1 equiv of POSS<sub>8</sub>). However, excess allyl-PEO was found to decrease the amount of condensation products, and the excess allyl-PEO( $n=4$ ) could be removed by evacuation at 60 °C for 1–2 days.

**2.3. Preparation of Films.** A composite polymer electrolyte film was prepared by the solvent casting technique: POSS-

PEO( $n=4$ )<sub>8</sub> (predried at 50 °C, 1 day, under vacuum) and/or LiClO<sub>4</sub> (predried at 110 °C, 2 days, under vacuum) was dissolved in acetonitrile, followed by the addition of high molecular weight PEO(600K); the relative amounts of POSS-PEO( $n=4$ )<sub>4</sub> and PEO(600K) are expressed as weight percents, and the amount of LiClO<sub>4</sub> is given as the O/Li based only on the amount of ethylene oxide in the POSS-PEO( $n=4$ )<sub>8</sub> and PEO(600K). The mixture was stirred for 24 h to form a viscous solution that was cast on a Teflon sheet in an argon-purged glovebox and left undisturbed for 1–2 days until a thin film was achieved. The electrolyte films were further dried under vacuum at 60 °C for 24 h to remove acetonitrile residue and then annealed under vacuum at 110 °C for 48 h.

**2.4. Calorimetric Data.** Calorimetric transitions of the electrolytes were determined by differential scanning calorimetry (DSC) runs of 5–10 mg samples measured in the range of –150 to 100 °C, in hermetically sealed aluminum pans. The DSC runs were cycled two to four times. The melting and crystallization temperatures,  $T_m$  and  $T_c$ , respectively, were reported as their peak values during the second heating cycle. Enthalpies of melting,  $\Delta H_m$ , were reported for the second DSC cycle and were normalized for the mass of ethylene oxide units originating either from the high molecular weight PEO(600K) or the ethylene oxide tetramer arms of POSS-PEO( $n=4$ )<sub>8</sub> (and thus not including the salt or SiO<sub>1.5</sub> of the POSS). Glass transition temperatures,  $T_g$ , were determined from the midpoints of the phase-transition temperatures in the DSC scans.

**2.5. Conductivity Data.** Ionic conductivities were measured by ac impedance spectroscopy using a Schlumberger HF frequency response analyzer (model SI 1255) in combination with an EG&G Princeton Applied research (PAR model 273A) potentiostat/galvanostat in the frequency range from 0.01 to 100 kHz. Control of the equipment was through Z-Plot electrochemical software purchased from Scribner Associates, Inc. Temperature-dependent conductivities were obtained by placing the electrochemical cell in the thermostated oven of a gas chromatograph (GC) or using dry ice at below ambient temperatures. The resistance was obtained from the intercept of the slanted line extrapolated to the real axis of plots of the impedance spectra (imaginary ( $Z''$ ) versus real ( $Z'$ )). The specific ionic conductivity,  $\sigma$ , was obtained from  $\sigma = t/AR$ , where  $t$  = thickness of the film (cm),  $A$  = area (1 cm<sup>2</sup>), and  $R$  is the resistance ( $\Omega$ ). The electrochemical cell was placed in the oven of a GC and annealed overnight at 90 °C. Conductivity measurements were made on the cooling cycle until room temperature. The sample was then reheated, and conductivity measurements were obtained. At each temperature above room temperature, the sample was equilibrated for about 30 min, until the resistance measurements responded to small (~1 °C) temperature perturbations. The resistances on the heating and cooling cycles were very close. Below room temperature, a chamber cooled with dry ice was used, and the conductivity data were obtained on the heating cycle.

## 3. Results and Discussion

**3.1. DSC Data.** The calorimetric data for the PEO(600K), POSS-PEO( $n=4$ )<sub>8</sub>, and blend electrolytes prepared with LiClO<sub>4</sub> are presented in Table 1. For all salt concentrations, the POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> was amorphous and had a single  $T_g$  that increased with increasing salt concentration. For PEO(600K)/LiClO<sub>4</sub>, a single  $T_g$  was observed for O/Li = 8/1 and for the semicrystalline O/Li = 16/1, but two  $T_g$  values were observed for the semicrystalline O/Li = 12/1. The  $T_g$  increased with increasing salt concentration (using the higher  $T_g$  value in the

**TABLE 1: Calorimetric Data of Electrolyte Materials and Blends**

O/Li	electrolyte composition	$T_g^1, ^\circ\text{C}$	$T_g^2, ^\circ\text{C}$	$\Delta C_p^1 \text{ norm},^a$ J/(g $^\circ\text{C}$ )	$\Delta C_p^2,$ J/(g $^\circ\text{C}$ )	$T_m, ^\circ\text{C}$	$T_c, ^\circ\text{C}$	$\Delta H_m \text{ norm},^a$ J/g	% xtal <sup>b</sup>
8/1	POSS-PEO( $n=4$ ) <sub>8</sub>	-52.7		0.78					
	80% POSS-PEO( $n=4$ ) <sub>8</sub> + 20% PEO(600K)	-43.8	-27.6	0.49	0.23				
	70% POSS-PEO( $n=4$ ) <sub>8</sub> + 30% PEO(600K)	-46.6	-28.1	0.39	0.51				
	50% POSS-PEO( $n=4$ ) <sub>8</sub> + 50% PEO(600K)	-49.5	-29.0	0.21	0.54				
	30% POSS-PEO( $n=4$ ) <sub>8</sub> + 70% PEO(600K)	-46.8	-29.9	0.17	0.57				
	20% POSS-PEO( $n=4$ ) <sub>8</sub> + 80% PEO(600K)	-45.7	-24.8	0.11	0.70				
12/1	PEO(600K)		-20.5		0.65				
	POSS-PEO( $n=4$ ) <sub>8</sub>	-53.3		0.77					
	60% POSS-PEO( $n=4$ ) <sub>8</sub> + 40% PEO(600K)	-75.1	-23.0	0.33	0.28				
	50% POSS-PEO( $n=4$ ) <sub>8</sub> + 50% PEO(600K)	-70.8	-22.7	0.28	0.48				
16/1	PEO(600K)	-27.8	-19.8	0.32	0.18	48.6	13.8	32.3	17
	POSS-PEO( $n=4$ ) <sub>8</sub>	-66.6		0.82					
	30% POSS-PEO( $n=4$ ) <sub>8</sub> + 70% PEO(600K)	-54.4	-15.0	0.09	0.30	52.3	22.0	53.0	28
	20% POSS-PEO( $n=4$ ) <sub>8</sub> + 80% PEO(600K)	-50.8	-18.3	0.07	0.34	54.0	26.2	55.9	30
0	PEO(600K)		-18.3		0.35	56.3	31.4	69.7	37
	POSS-PEO( $n=4$ ) <sub>8</sub>	-85.0		0.9		65.6	44.2	97.6	52

<sup>a</sup>  $\Delta H_m$  and  $\Delta C_p$  were normalized to the amount of ethylene oxide; salt and  $\text{SiO}_{1.5}$  not considered <sup>b</sup> % crystallinity =  $\Delta H_m(\text{normalized})/188 \text{ J/g}$ ;  $\Delta H_m$  for PEO(600K) without salt taken as 188 J/g.

case of O/Li = 12/1). The increase in  $T_g$  with increasing salt concentration for both POSS-PEO( $n=4$ )<sub>8</sub> and PEO(600K) is commonly observed and is attributed to the effect of  $\text{Li}^+$  complexation with PEO, which effectively reduces the chain segmental motion.

In the case of O/Li = 8/1, the PEO(600K)/ $\text{LiClO}_4$ (O/Li = 8/1) was amorphous, as were all the blends. A typical DSC plot is shown in Figure 1 for the 50% PEO(600K)/50% POSS-PEO( $n=4$ )<sub>8</sub>/ $\text{LiClO}_4$ (O/Li = 8/1) blend. The superposition of the repeated scans indicates that the blend morphology is stable. Figure 2 presents selected DSC plots for the samples from Table 1. In the blends, two  $T_g$  values were observed, with values between those of the pure POSS-PEO( $n=4$ )<sub>8</sub> and the neat PEO(600K). The average value of the lower  $T_g$  phase was  $-46.5 ^\circ\text{C}$  (range between  $-44$  and  $-50 ^\circ\text{C}$ ), and the average value of the higher  $T_g$  phase was  $-27.9 ^\circ\text{C}$  (range between  $-28$  and  $-30 ^\circ\text{C}$ ). The  $\Delta C_p^{\text{total}} = \Delta C_p^1 + \Delta C_p^2$  for the blends ( $0.72$ – $0.90 \text{ J/(g } ^\circ\text{C})$ ) is close to that of the PEO(600K)/ $\text{LiClO}_4$  and POSS-PEO( $n=4$ )<sub>8</sub>/ $\text{LiClO}_4$ .

With the Fox equation,<sup>41</sup> the effect of composition on  $T_g$  in a homogeneous phase consisting of components 1 (with weight fraction  $w_1$  and  $T_{g1}$ ) and 2 (with weight fraction  $w_2$  and  $T_{g2}$ ) is

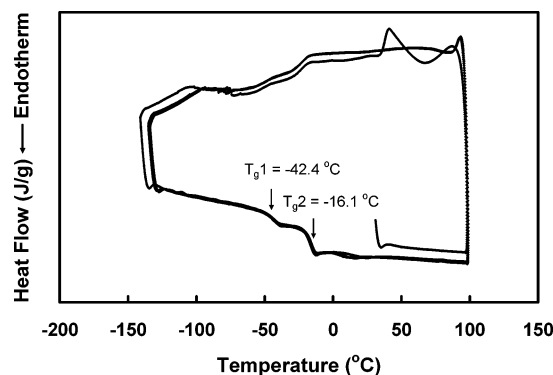
$$1/T_g = w_1/T_{g1} + w_2/T_{g2} \quad (1)$$

Alternatively, with the Couchman<sup>42,43</sup> equation

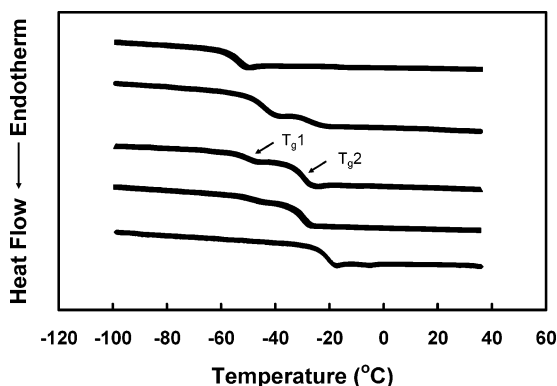
$$\ln T_g = [w_1 \Delta C_{p1} \ln T_{g1} + w_2 \Delta C_{p2} \ln T_{g2}] / [w_1 \Delta C_{p1} + w_2 \Delta C_{p2}] \quad (2)$$

where  $\Delta C_{p1}$  and  $\Delta C_{p2}$  are the heat capacity changes at  $T_{g1}$  and  $T_{g2}$ . By use of the  $T_g$  and  $\Delta C_p$  values of pure POSS-PEO( $n=4$ )<sub>8</sub>/ $\text{LiClO}_4$  (O/Li = 8/1) and PEO(600K)/ $\text{LiClO}_4$  (O/Li = 8/1), and the average values for the lower ( $T_g = -46.5 ^\circ\text{C}$ ) and higher ( $T_g = -27.9 ^\circ\text{C}$ )  $T_g$  phases, the composition of the lower  $T_g$  phase was estimated to be 85% POSS-PEO( $n=4$ )<sub>8</sub>/15% PEO(600K) and that of the higher  $T_g$  phase was estimated to be 29% POSS-PEO( $n=4$ )<sub>8</sub>/71% PEO(600K), using eq 1, or 83% POSS-PEO( $n=4$ )<sub>8</sub>/17% PEO(600K) and 29% POSS-PEO( $n=4$ )<sub>8</sub>/71% PEO(600K) using eq 2.

The results indicate that the blend exhibits a two-phase morphology, in which one of the phases (the lower  $T_g$  phase) is rich in POSS-PEO( $n=4$ )<sub>8</sub> and the other (the higher  $T_g$  phase) is rich in PEO(600K). With increasing PEO(600K), the  $\Delta C_p$  of



**Figure 1.** DSC plot for 50% POSS-PEO( $n=4$ )<sub>8</sub>/50% PEO(600K)/ $\text{LiClO}_4$  (O/Li = 8/1) blend. Three heating and cooling cycles are shown.



**Figure 2.** DSC plots, from second heating cycle, of from top: 100% POSS-PEO( $n=4$ )<sub>8</sub>; 80% POSS-PEO( $n=4$ )<sub>8</sub>/20% PEO(600K); 50% POSS-PEO( $n=4$ )<sub>8</sub>/50% PEO(600K); 30% POSS-PEO( $n=4$ )<sub>8</sub>/70% PEO(600K); 100% PEO(600K); all with  $\text{LiClO}_4$  O/Li = 8/1.

the higher  $T_g$  phase ( $\Delta C_p^2$ ) increased relative to that of the lower  $T_g$  phase ( $\Delta C_p^1$ ). Assuming that the measured  $\Delta C_p$  values were proportional to the volumes of the two phases, and using mass conservation (adding the amounts of POSS-PEO( $n=4$ )<sub>8</sub> and PEO(600K) in the high and low  $T_g$  phases), the calculated ratios of POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K) were 2.44, 1.40, 1.0, 0.85, and 0.66, compared with the known values of 4, 2.33, 1.0, 0.6, and 0.25 for the 80/10, 70/30, 50/50, 30/70, and 20/80 compositions, respectively. Although not quantitative, these results indicate that the relative amounts of the two phases change with overall composition. As expected, there is a greater



amount of the phase that contains more PEO(600K) (or POSS-PEO( $n=4$ )<sub>8</sub>) as the PEO(600K) (or POSS-PEO( $n=4$ )<sub>8</sub>) increases in the overall composition. However, the calculations underestimate the amount of POSS-PEO( $n=4$ )<sub>8</sub> in the high POSS-PEO( $n=4$ )<sub>8</sub> blends and overestimate the amount of POSS-PEO( $n=4$ )<sub>8</sub> in the low POSS-PEO( $n=4$ )<sub>8</sub> blends. These calculations assumed that the LiClO<sub>4</sub> partitioned equally between the two phases; the observed deviations may be related to unequal partitioning of the salt, as discussed further below.

It is of some interest that two phases exist at all. Previous investigations of electrolyte blends of high molecular weight PEO and linear low molecular weight poly(ethylene glycols) have shown decreased degrees of crystallinity,  $T_m$ , and lower, but single  $T_g$ .<sup>17,18</sup> Crystallization studies of high and low molecular weight fractions of PEO suggest that at low undercoolings the high and low molecular weight fractions crystallize as two distinct crystallite populations, although the phase separation was suggested to occur during the crystallization process itself.<sup>19</sup>

In the case of other linear/(branched, star or ring) polymer blends of similar repeat unit structure, there is mixed evidence for phase separation behavior. Theoretical expressions for the thermodynamic interaction parameter due to architecture for these blends indicate that the size of the interaction increased with increasing number of arms and disparity between the size of the arm length and linear chain.<sup>20</sup> Experimental small angle neutron scattering (SANS) data for amorphous polystyrene (PS) has shown that star/linear blends do not, but comb/linear blends do, phase separate.<sup>21</sup> Blends of highly branched and linear amorphous polyolefins,<sup>22</sup> polymethacrylate (PMMA),<sup>23,24</sup> and polybutadiene (PB)<sup>23</sup> phase separated when the molecular weight of the linear chain was high. SANS data on blends of linear and branched polyethylenes have shown that phase separation occurs at high branch content,<sup>25</sup> and indirect evidence (two crystalline species after cooling) of liquid-liquid phase separation in linear and lightly branched polyethylene (LPE) has been observed.<sup>26</sup>

In the case of POSS-PEO( $n=4$ )<sub>8</sub>, the branches are of the same chemical composition as for the PEO(600K), although the core, SiO<sub>1.5</sub>, is dissimilar, and the arm length is too short to be covered by Gaussian field theory treatments.<sup>20</sup> However, in the limit of a large number of short arms or for large linear polymers, the analytic expression by Fredrickson suggests that the modified Flory interaction parameter,  $\chi$ , should increase with the number of arms in the star, with decreasing arm length, and with a decrease in star concentration and be independent of linear chain length. These trends may help to explain the observed phase separation in the POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> (O/Li = 8/1). The phase separation observed in the current investigation is manifest by two  $T_g$  values and not by the more subtle differences in  $\chi$  observed for PS, PMMA, and PB blends using SANS. The separation of diluent into microdomains that exhibit separate low  $T_g$  features as well as high  $T_g$  solvated domains has been observed in the case of glassy polymer/diluent systems.<sup>27</sup>

In the case of O/Li = 12/1, the PEO(600K)/LiClO<sub>4</sub> was semicrystalline, with a  $T_m$  lower than that for neat PEO(600K) and a lower percent crystallinity. Since  $T_m$  was lowered to 48.6 (from  $T_m$  = 65.6 for neat PEO(600K)), and there was only a single melt peak, the crystalline phase could either be attributed to disordered crystals or to a eutectic composition of a PEO/LiClO<sub>4</sub> compound, as has been observed in low molecular weight PEO(4000)/LiClO<sub>4</sub>,<sup>28</sup> where  $T_m$  = 70 °C for the 6/1 composition and  $T_m$  = 50 °C for the eutectic composition.

Addition of 50% and 60% POSS-PEO( $n=4$ )<sub>8</sub> resulted in completely amorphous materials, in which macrophase separation did not occur either at room temperature or at 90 °C. It was not possible to add more than 60% POSS-PEO( $n=4$ )<sub>8</sub> at room temperature without the occurrence of macroscopic phase separation; this resulted in films in which a liquid layer of POSS-PEO( $n=4$ )<sub>8</sub> could be observed. The morphology at 90 °C was not investigated, although phase separation is expected to be temperature dependent. In previous investigations of a low molecular weight poly(propylene glycol) electrolyte, PPG4000-NaClO<sub>4</sub>, macroscopic two-layer phase separation was observed at room temperature, which reversibly transformed into a microscopic separation upon heating above 40–50 °C.<sup>29</sup>

The semicrystalline PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1) itself has two  $T_g$  values, both higher than the reported  $T_g$  (–55 °C) of PEO(600K) without salt. This may be due to domains with differing salt concentrations, although liquid-liquid phase separation was not observed in supercooled PEO/LiX.<sup>29,30</sup> In the case of the 50/50 or 60/40 blends (O/Li = 12/1), two  $T_g$  values are also observed, indicating that there is microscopic phase separation: repeated DSC scans give the same phase transition temperatures. One  $T_g$  is quite low (–70.8, –75.1 °C), lower than that of POSS-PEO( $n=4$ )/LiClO<sub>4</sub> with O/Li = 12/1 but above that of neat (without salt) POSS-PEO( $n=4$ )<sub>8</sub> (–85 °C). The other (–23 °C) is between the two  $T_g$  values observed for the PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1). The  $\Delta C_p$  for the semicrystalline PEO(600K)/LiClO<sub>4</sub> is less ( $\Delta C_p = \Delta C_p^1 + \Delta C_p^2 = 0.5$ ) than that for the completely amorphous POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> or POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> ( $\Delta C_p \sim 0.61$ – $0.76$ ), as expected. The values for the blends are similar to the amorphous blends prepared with O/Li = 8/1.

These results again suggest that there is a two-phase morphology in the blends in which the low  $T_g$  phase contains more POSS-PEO( $n=4$ )<sub>8</sub>, and the high  $T_g$  phase contains more PEO(600K). However, there also must be unequal partition of the LiClO<sub>4</sub> in the two phases. The low  $T_g$  phase must contain less LiClO<sub>4</sub> than would be contributed by the O/Li = 12/1 in order to account for a  $T_g$  below that of the POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 12/1). The phase with the higher  $T_g$  must therefore contain a higher proportion of both LiClO<sub>4</sub> and PEO(600K).

In similar systems, for example in completely amorphous poly(propylene glycol) (PPG) or oxide (PPO)/MX,<sup>29–33</sup> albeit consisting of a single polymer and salt, the existence of microphase separated biphasic structures with liquid-liquid domains, comprised of microdomains of high salt content embedded in a low salt (or no salt) matrix, has been observed. However, liquid-liquid phase separation has not been observed in supercooled PEO/LiX.<sup>29,30</sup> This absence was attributed to the dominant cation-oxygen interactions that favor salt dispersion, since PEO has a higher density of ether oxygens than PPO. A biphasic structure (in which one domain is salt-rich and the other salt-depleted) was suggested to be more stable than a single homogeneous phase when the dominant factor was the Coulombic energy liberated through the ion condensation process associated with the formation of the high  $T_g$  microphase.<sup>29,30</sup> Molecular dynamic simulations (MD) of low molecular weight PEO/LiI (O/Li = 48/1, 15/1, and 5/1) indicated that phase separation between salt-rich and polymer-rich regimes occurred only for the dilute solutions (O/Li > 15/1).<sup>34</sup> Thus, for POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1), which is close to the 15/1 composition, there may be unequal partitioning of the salt into the PEO(600K)-rich phase, as observed. In the present study, the high salt phase appears to be the one that

also contains a greater amount of high molecular weight PEO, perhaps suggesting that it is better at solvating the lithium ions than is POSS-PEO( $n=4$ )<sub>8</sub>.

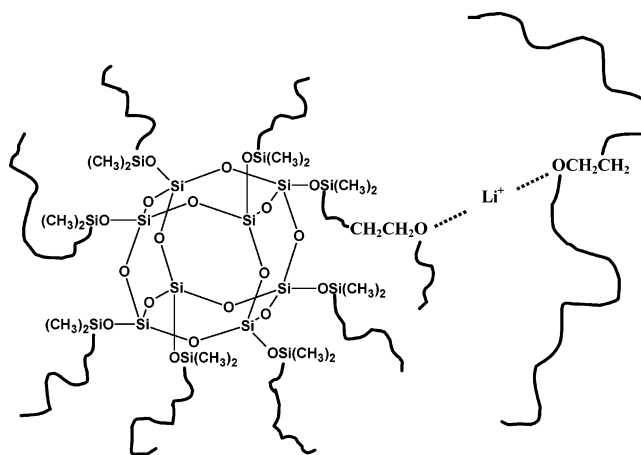
In the case of O/Li = 16/1, PEO(600K)/LiClO<sub>4</sub> was also semicrystalline, with  $T_m$  and a percent crystallinity greater than that of the O/Li = 12/1 sample, and less than that for the PEO(600K) without salt, as expected. It was not possible to prepare blends with more than 30% POSS-PEO( $n=4$ )<sub>8</sub> that did not macrophase separate; even at 35% POSS-PEO( $n=4$ )<sub>8</sub>/65% PEO(600K)/LiClO<sub>4</sub> (O/Li = 16/1) a liquid exuded from the films. For the 30% POSS-PEO( $n=4$ )<sub>8</sub>/70% PEO(600K)/LiClO<sub>4</sub> (O/Li = 16/1) and 20% POSS-PEO( $n=4$ )<sub>8</sub>/80% PEO(600K)/LiClO<sub>4</sub> (O/Li = 16/1) blends, the addition of the POSS-PEO( $n=4$ )<sub>8</sub> resulted in semicrystalline materials, which exhibited two  $T_g$  values. There was thus a three-phase morphology in these blends, consisting of crystalline regions and two amorphous phases, one rich in POSS-PEO( $n=4$ )<sub>8</sub> with a lower  $T_g$  and the other rich in PEO(600K) with a higher  $T_g$ . On the basis of the ratio of the heat capacities ( $\Delta C_p^2/\Delta C_p^1$ ), there was three to five times as much of the PEO(600K)-rich phase, with values of  $T_g$  comparable to PEO(600K)/LiClO<sub>4</sub>. This suggests most of the POSS-PEO( $n=4$ )<sub>8</sub> was incorporated into the PEO(600K) phase, and since the  $T_g$  of this phase was similar to that of PEO(600K), the chain dynamics of the PEO units are very similar to that of the high molecular weight chain.

The addition of POSS-PEO( $n=4$ )<sub>8</sub> reduces  $T_m$  of PEO(600K) and decreases the percent crystallinity PEO(600K)/LiClO<sub>4</sub> (O/Li = 16/1) by 20%. Thus addition of POSS-PEO( $n=4$ )<sub>8</sub> swells the already amorphous regions of PEO(600K)/LiClO<sub>4</sub> (O/Li = 16/1) and increases the amorphous fraction of the PEO(600K). However, the effect is not large.  $\Delta C_p^{\text{total}} = \Delta C_p^1 + \Delta C_p^2$  for the blends is  $\sim 0.4$ , only slightly larger than that for  $\Delta C_p = 0.34$  for PEO(600K). This can be attributed to the large thermodynamic driving force toward crystallization of PEO(600K), which excludes the POSS-PEO( $n=4$ )<sub>8</sub>.

Comparison of the blends prepared at different salt concentrations shows that POSS-PEO( $n=4$ )<sub>8</sub> and PEO(600K) are not compatible at any of the salt concentrations investigated, although the extremes in component compositions (either very high POSS-PEO( $n=4$ )<sub>8</sub> or PEO(600K)) were not prepared; determining phase behavior using weak  $T_g$  thermograms is difficult. Microphase separation or PEO crystallization plus microphase separation was observed for all of the samples. In the absence of salt, mixtures of POSS-PEO( $n=4$ )<sub>8</sub> and PEO(600K) are also not compatible, and both macrophase separation (at high POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K) ratios) and microphase separation (when only small amounts of POSS-PEO( $n=4$ )<sub>8</sub> are incorporated into the PEO(600K) matrix) are observed.

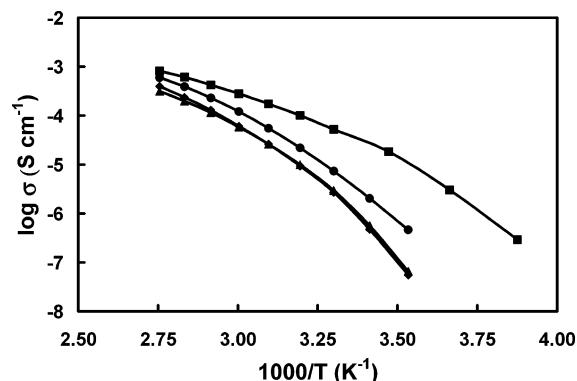
Microphase separation is usually observed in block copolymers where macrophase separation is prohibited due to the chemical binding of the two blocks. In the current investigation, macrophase separation increased with decreasing salt concentration and with increased crystallinity of the blends. It occurred at  $\sim 80\%$  POSS-PEO( $n=4$ )<sub>8</sub> for the completely amorphous O/Li = 8/1 system (where both components were separately amorphous), at  $\sim 60\%$  POSS-PEO( $n=4$ )<sub>8</sub> for O/Li = 12/1, at  $\sim 35\%$  POSS-PEO( $n=4$ )<sub>8</sub> for O/Li = 16/1, and  $<20\%$  for POSS-PEO( $n=4$ )<sub>8</sub> without added salt. Thus, greater amounts of POSS-PEO( $n=4$ )<sub>8</sub> could be added as the degree of crystallinity of the blends decreased; the decreased crystallinity resulted from the suppression of crystallization of the PEO(600K) with added salt. Two effects can account for these trends. One is the strong tendency of PEO to crystallize, promoting macrophase separation, and the other is the presence of the salt, as illustrated

**CHART 1: Cross-Link Site between PEO(600K) and POSS-PEO( $n=4$ )<sub>8</sub>**



in Chart 1, where EO-Li<sup>+</sup>-EO bridges form cross-link points between the PEO(600K) and POSS-PEO( $n=4$ )<sub>8</sub>, as has been observed in poly(propylene oxide)-LiClO<sub>4</sub> electrolytes,<sup>35</sup> thus promoting microphase separation. With decreasing salt concentration, there is increased tendency of PEO(600K) to crystallize, excluding incorporation of POSS-PEO( $n=4$ )<sub>8</sub>, and decreased solubility limits (as measured by the presence of macrophase separation) between the amorphous PEO(600K) and POSS-PEO( $n=4$ )<sub>8</sub>. The latter arises from the decreased inter-chain interactions between the PEO(600K) and POSS-PEO( $n=4$ )<sub>8</sub> chains that are necessary to promote their mutual solubility.

**3.2. Conductivity Data.** Select conductivity data for electrolytes prepared using LiClO<sub>4</sub> with an O/Li = 8/1 is presented in Figure 3 and Table 2. The conductivity of the POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub>(8/1) is higher than that of PEO(600K) or the POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub>(O/Li = 8/1) blends at all temperatures. We have previously shown that the conductivity of POSS-PEO( $n$ )<sub>8</sub> electrolytes is higher than that of PEO(600K) electrolytes as  $T \rightarrow T_g$  due to the much lower viscosity of the former.<sup>36</sup> At  $T \gg T_g$  the effect of the inert SiO<sub>1.5</sub> core of the POSS-PEO( $n$ )<sub>8</sub> can result in decreased conductivities relative to PEO(600K). However, an additional effect is that conductivity maxima as a function of salt concentration (often observed at O/Li = 8/1 and 6/1) in the semidilute region, which is believed to arise from the competing effects of increased numbers of triple ions and increased viscosities,<sup>37</sup> can occur at different salt concentrations for the POSS-PEO( $n$ ) and PEO(600K). Of more interest is that only one blend composition,



**Figure 3.** Conductivity plots of (i) POSS-PEO( $n=4$ )<sub>8</sub> (■); (ii) PEO(600K) (◆); (iii) blend of 50% POSS-PEO( $n=4$ )<sub>8</sub>/50% PEO(600K) (□); and (iv) blend of 80% POSS-PEO( $n=4$ )<sub>8</sub>/20% PEO(600K) (●); all with LiClO<sub>4</sub> O/Li = 8/1.

**TABLE 2: Ionic Conductivity of POSS–PEO( $n=4$ )<sub>8</sub>, PEO(600K), and POSS–PEO( $n=4$ )<sub>8</sub>/PEO(600K) Blends with LiClO<sub>4</sub>**

electrolytes with LiClO <sub>4</sub>	ionic conductivity, S cm <sup>-1</sup>		
	90 °C	30 °C	10 °C
O/Li = 8/1			
PEO(600K)	$3.95 \times 10^{-4}$	$2.69 \times 10^{-6}$	$5.52 \times 10^{-8}$
POSS–PEO( $n=4$ ) <sub>8</sub>	$8.11 \times 10^{-4}$	$5.21 \times 10^{-5}$	$1.17 \times 10^{-5}$
50% PEO(600K) + 50% POSS–PEO( $n=4$ ) <sub>8</sub>	$3.15 \times 10^{-4}$	$2.95 \times 10^{-6}$	$6.55 \times 10^{-8}$
20% PEO(600K) + 80% POSS–PEO( $n=4$ ) <sub>8</sub>	$5.97 \times 10^{-4}$	$7.35 \times 10^{-6}$	$4.62 \times 10^{-7}$
O/Li = 12/1			
PEO(600K)	$9.33 \times 10^{-4}$	$2.08 \times 10^{-6}$	$1.36 \times 10^{-8}$
POSS–PEO( $n=4$ ) <sub>8</sub>	$3.96 \times 10^{-4}$	$3.23 \times 10^{-5}$	$5.89 \times 10^{-6}$
50% PEO(600K) + 50% POSS–PEO( $n=4$ ) <sub>8</sub>	$2.87 \times 10^{-4}$	$7.12 \times 10^{-6}$	$2.77 \times 10^{-7}$
40% PEO(600K) + 60% POSS–PEO( $n=4$ ) <sub>8</sub>	$4.84 \times 10^{-4}$	$7.86 \times 10^{-6}$	$2.04 \times 10^{-7}$
O/Li = 16/1			
PEO(600K)	$7.94 \times 10^{-4}$	$5.17 \times 10^{-7}$	$1.97 \times 10^{-9}$
POSS–PEO( $n=4$ ) <sub>8</sub>	$5.72 \times 10^{-4}$	$6.81 \times 10^{-5}$	$2.57 \times 10^{-5}$
80% PEO(600K) + 20% POSS–PEO( $n=4$ ) <sub>8</sub>	$4.83 \times 10^{-4}$	$2.16 \times 10^{-6}$	$2.69 \times 10^{-6}$
70% PEO(600K) + 30% POSS–PEO( $n=4$ ) <sub>8</sub>	$5.78 \times 10^{-4}$	$6.26 \times 10^{-6}$	$8.32 \times 10^{-8}$

the 20% PEO(600K)/80% POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1) has conductivities intermediate between the PEO(600K)/LiClO<sub>4</sub> (O/Li = 8/1) and POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1). The other blends, with less than 70% POSS–PEO( $n=4$ )<sub>8</sub>, have almost the same conductivities as the PEO(600K)/LiClO<sub>4</sub> at all temperatures. Data for the 50% PEO(600K)/50% POSS–PEO( $n=4$ )<sub>8</sub> electrolyte is presented. Slight increases in the conductivity of PEO(600K) compared with the blends at high temperatures can be attributed due to the effect of the inert SiO<sub>1.5</sub>.<sup>36</sup>

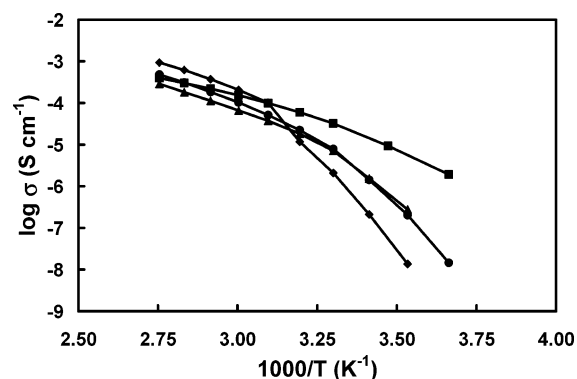
The conductivity data can be understood based on the morphology of the blends, using a model in which the conductivity is determined by the conductivity of the interconnected phase, typically the one in greater abundance. From the DSC results, the morphology of the O/Li = 8/1 electrolyte blends consists of two amorphous phases. From the ratio of the heat capacities, the amount of the lower  $T_g$  phase is less than that of the higher  $T_g$  phase for all the blends except that of the 20% PEO(600K)/80% POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1). Thus, the lower  $T_g$  phase (with more POSS–PEO( $n=4$ )<sub>8</sub>) that might be expected to have higher conductivity at low temperature is the minor phase. The major, interconnected phase, has a higher  $T_g$ , similar to that of pure PEO(600K)/LiClO<sub>4</sub>. The conductivity thus is dominated by the conductivity of this phase, that is, it is similar, even at low temperatures to that of PEO(600K)/LiClO<sub>4</sub>. These results suggest that the PEO segments of the POSS–PEO( $n=4$ )<sub>8</sub> in the high  $T_g$  phase are entangled with the high molecular weight PEO(600K) and are slowed down by the dynamics of the longer chains.

It has previously been observed that supercooled PEO/salt mixtures of low (PEO  $4 \times 10^3$ ) (with a molecular weight only slightly higher than that for POSS–PEO( $n=4$ )<sub>8</sub>) and high (PEO  $4 \times 10^6$ ) molecular weight PEO have nearly identical conductivities (for O/Li = 8/1, 12/1 down to 128/1).<sup>38</sup> Although the number of end groups in the POSS–PEO( $n=4$ )<sub>8</sub> is eight times greater than that for the linear PEO ( $4 \times 10^3$ ), the effect on free volume, and thus conductivity, also appears to be negligible. Thus incorporation of POSS–PEO( $n=4$ )<sub>8</sub> does not appear to increase the free volume of the blend. The  $T_g$  of the phase containing 71% PEO(600K) is about 8 °C lower than that of neat PEO(600K)/LiClO<sub>4</sub> (O/Li = 8/1).

On the basis of heat capacity ratios, the low  $T_g$  phase containing 83–85% POSS–PEO( $n=4$ )<sub>8</sub> is the dominant phase for the blend in which the total composition is 20% PEO(600K)/80% POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1). In this case, the conductivity is intermediate between that of PEO(600K)/LiClO<sub>4</sub> (O/Li = 8/1) and POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1). At

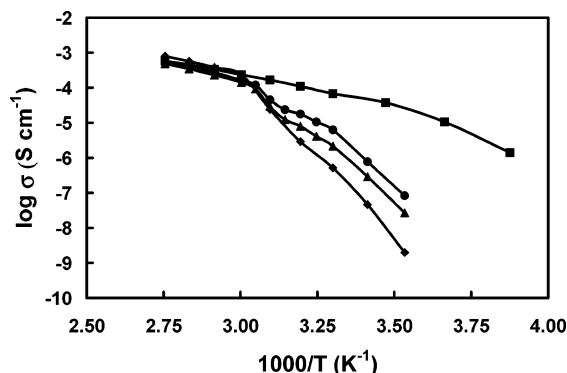
this high concentration of POSS–PEO( $n=4$ )<sub>8</sub>, it is possible that the morphology of the blend may approach that of a gel electrolyte, in which there is translational migration of the POSS–PEO( $n=4$ )<sub>8</sub> complexed with LiClO<sub>4</sub>. The ion conduction would thus contain contributions from diffusion of the ions complexed with the mobile POSS–PEO( $n=4$ )<sub>8</sub>, as well as those associated with PEO backbone dynamics. In polymers such as PEO, conductivity occurs through long-range migration of the lithium ions through an exchange of solvation sites, whereas in solvents conductivity occurs through migration of the ions with their solvation spheres. The increased contribution of the latter may occur when, at high POSS–PEO( $n=4$ )<sub>8</sub> concentrations, there is decreased probability of forming salt bridges between POSS–PEO( $n=4$ )<sub>8</sub> and PEO(600K).

The conductivity data for the O/Li = 12/1 components and blends are presented in Figure 4 and Table 2. The conductivity of POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 12/1) is greater than that of PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1) at low temperature, but lower at high temperature. We have previously attributed the decrease of conductivity of POSS–PEO( $n$ )<sub>8</sub> based electrolytes compared with PEO(600K) electrolytes at high temperature to the effect of the inert SiO<sub>1.5</sub> core of the silsesquioxanes.<sup>36</sup> The increased conductivity of the POSS–PEO( $n$ )<sub>8</sub> based electrolytes at low temperature was attributed to its lower viscosity as well as to the crystallization of the PEO(600K). At  $T \gg T_g$ , the conductivities of the POSS–PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 12/1), and the two blends are similar and slightly lower than that of PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1); this effect can also be attributed to the presence of inert SiO<sub>1.5</sub>.



**Figure 4.** Conductivity plots of (i) POSS–PEO( $n=4$ )<sub>8</sub> (■); (ii) PEO(600K) (◆); (iii) blend of 50% POSS–PEO( $n=4$ )<sub>8</sub>/50% PEO(600K) (□); and (iv) blend of 60% POSS–PEO( $n=4$ )<sub>8</sub>/40% PEO(600K) (●); all with LiClO<sub>4</sub> O/Li = 12/1.





**Figure 5.** Conductivity plots of (i) POSS-PEO( $n=4$ )<sub>8</sub> (■); (ii) PEO(600K) (◆); (iii) blend of 20% POSS-PEO( $n=4$ )<sub>8</sub>/80% PEO(600K) (□); and (iv) blend of 30% POSS-PEO( $n=4$ )<sub>8</sub>/70% PEO(600K) (●); all with LiClO<sub>4</sub> O/Li = 16/1.

At low temperatures,  $T \rightarrow T_g$ , the conductivities of the 50% and 60% POSS-PEO( $n=4$ )<sub>8</sub> blends with PEO(600K) and LiClO<sub>4</sub> (O/Li = 12/1) are similar to each other and between those of the constituents. This can be attributed to the effect of the suppression of crystallinity of the PEO(600K) by the POSS-PEO( $n=4$ )<sub>8</sub>. In many PEO/diluent (e.g., PC, EC, dioctyl sebacate, diethyle phthalate) mixtures, the increase in conductivity at low temperatures is due to the decreased crystallinity of the PEO.<sup>39</sup> Since the conductivity of amorphous PEO(600K)/LiClO<sub>4</sub> (O/Li = 12/1) is not known, it is not possible to compare the conductivity of the blends with that of amorphous PEO(600K) at this salt concentration. However, it has previously been observed that the conductivities of supercooled high molecular weight PEO/salt (O/Li = 12/1) mixtures are similar to those of low molecular weight PEO/salt ( $4 \times 10^3$ ), in which the molecular weight is only slightly higher than that for POSS-PEO( $n=4$ )<sub>8</sub>.<sup>38</sup> In addition, by analogy with the results for PEO(600K)/POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1) blends, the conductivity of amorphous PEO(600K) is expected to be the same as that of the blends, particularly if the high  $T_g$  phase is the majority phase. This is certainly the case for the 50/50 composition, where  $\Delta C_p$  for the high  $T_g$  phase is about twice that for the low  $T_g$  phase. For the 60/40 composition, there are similar amounts (based on a comparison of  $\Delta C_p$  values) of the high and low  $T_g$  phases. However, the conductivities of the blends with 50% and 60% POSS-PEO( $n=4$ )<sub>8</sub> are similar to each other, suggesting that in both cases the majority phase is the high  $T_g$  phase, with a  $T_g$  (and thus a conductivity) similar to that of neat PEO(600K). Although the DSC data indicate the presence of a low  $T_g$  ( $\sim -70$  °C) phase, it exists as the minority, non-interconnected phase, and thus does not increase the conductivity of the blends.

The conductivity data for POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub>, PEO(600K)/LiClO<sub>4</sub> and the 20% and 30% POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> blends at O/Li = 16/1 are presented in Figure 5 and Table 2. In this case, the blends as well as the PEO(600K)/LiClO<sub>4</sub> are semicrystalline. This is apparent in the shape of the conductivity plots, which show abrupt decreases in conductivity at the melt temperatures of the PEO(600K)/LiClO<sub>4</sub> (O/Li = 16/1) or blends, but not for the POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 16/1). At low temperatures, the conductivities increase with increasing amount of POSS-PEO( $n=4$ )<sub>8</sub>. This can be attributed to the decrease in crystallinity of the PEO(600K) induced by the POSS-PEO( $n=4$ )<sub>8</sub> and is consistent with the calorimetric data (Table 1) that show this trend. The O/Li = 16/1 blends exist as three-phase systems consisting of crystalline PEO and two amorphous phases. As with the O/Li

= 8/1 and 12/1, the conductivity at the temperatures measured is determined by the majority high  $T_g$  phase; there is very little (based on  $\Delta C_p$  data) of the low  $T_g$  phase present. At high temperatures,  $T \gg T_g$  and above  $T_m$ , the conductivities of all the samples are similar, with that of the PEO(600K) slightly higher than the rest due to the absence of inert SiO<sub>1.5</sub>.

### 3.3. Qualitative Room Temperature Appearance of Films.

The POSS-PEO( $n=4$ )<sub>8</sub> was a liquid at room temperature for all LiClO<sub>4</sub> salt concentrations. At LiClO<sub>4</sub> salt concentrations of O/Li = 8/1, all the samples (PEO(600K) and blends) were elastomers at room temperature. At LiClO<sub>4</sub> salt concentrations of O/Li = 12/1, the PEO(600K)/LiClO<sub>4</sub> was a strong, free-standing film. Addition of POSS-PEO( $n=4$ )<sub>8</sub> resulted in rubbery films that were stronger than those prepared using O/Li = 8/1, although the films were amorphous (based on the calorimetric data) at room temperature. At LiClO<sub>4</sub> salt concentrations with O/Li = 16/1, the PEO(600K) was a strong, self-supporting film. Addition of POSS-PEO( $n=4$ )<sub>8</sub> resulted in films that were rubbery and stronger than those prepared using O/Li = 12/1.

The blends prepared with O/Li = 16/1 were semicrystalline and contained less POSS-PEO( $n=4$ )<sub>8</sub> than did the blends prepared using O/Li = 12/1. The crystalline domains in the films prepared using LiClO<sub>4</sub> (O/Li = 16/1) can account for their elastomeric properties above  $T_g$ . Although intermediate PEO/LiX crystalline compounds of various stoichiometries have been reported to persist well above the melting point of PEO,<sup>28</sup> which could account for the rubbery mechanical properties of the POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub>, the 6/1 compound formed for PEO/LiClO<sub>4</sub> melts at low ( $\sim 50$  to  $60$  °C) temperature;<sup>28</sup> no melt transitions were observed to  $100$  °C for the systems investigated here. Thus, it is not clear what is the origin of the rubbery properties above  $T_g$  for the amorphous blends with LiClO<sub>4</sub> (O/Li = 8/1 and 12/1). The viscoelastic properties above  $T_g$  may result from the effects of Li<sup>+</sup> bridges that serve as cross-link sites between ether oxygens on neighboring chains. In the case of a low molecular weight ( $4 \times 10^3$  g/mol) PEO sample and LiSCN salt, at O/Li = 8/1, a viscous liquid formed at room temperature, whereas the O/Li = 4/1 resulted in an elastomeric material.<sup>40</sup> Alternatively, the system may behave similarly to diblock copolymers that exhibit lower critical ordering transition temperatures (LCOT) as the result of entropically driven phase separation.<sup>44,45</sup> In these systems the ordered phase results in a rigid material that behaves like a cross-linked rubber, although it is above the  $T_g$  of both blocks. This structure be consistent with the proposed microphase separated morphology of the POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> blends.

## 4. Conclusions

Calorimetric and conductivity data were obtained for blends of POSS-PEO( $n=4$ )<sub>8</sub>, with a nominal molecular weight of 3002 g/mol, and high molecular weight poly(ethylene oxide), PEO(600K), with LiClO<sub>4</sub> at O/Li ratios of 8/1, 12/1, and 16/1. The POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> was a liquid at all LiClO<sub>4</sub> concentrations and PEO(600K)/LiClO<sub>4</sub> was a viscous elastomer for O/Li = 8/1 and a semicrystalline solid for O/Li = 12/1 and 16/1. For O/Li = 8/1, the conductivity of POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1) was greater than that of PEO(600K)/LiClO<sub>4</sub>, but the conductivities of blends with less than 70% POSS-PEO( $n=4$ )<sub>8</sub> were the same as that of the PEO(600K)/LiClO<sub>4</sub> (O/Li = 8/1). The morphology of these blends was a biphasic structure, in which the high  $T_g$  phase was the majority phase. This strongly suggested that the ethylene oxide side chains of POSS-PEO( $n=4$ )<sub>8</sub> were slowed down by the dynam-

ics of the longer PEO chains, so that the Li ions migrated through an exchange of solvation sites in the continuous high molecular weight PEO matrix, in which the POSS-PEO( $n=4$ )<sub>8</sub> was entangled. Only a blend with 20% PEO(600K)/80% POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1) had a conductivity between that of the pure PEO(600K)/LiClO<sub>4</sub> and POSS-PEO( $n=4$ )<sub>8</sub>/LiClO<sub>4</sub> (O/Li = 8/1). In this case, the low  $T_g$  phase was the continuous phase, and the conductivity was suggested to have a additional component due to migration of Li ions solvated by the diffusing POSS-PEO( $n=4$ )<sub>8</sub>. Blends of POSS-PEO( $n=4$ )<sub>8</sub>/PEO(600K)/LiClO<sub>4</sub> with O/Li = 12/1 and O/Li = 16/1 were microphase separated into two amorphous phases, or one crystalline and two amorphous phases, respectively. The maximum amount of POSS-PEO( $n=4$ )<sub>8</sub> that could be incorporated into PEO(600K) was 80%, 60%, and 30% when O/Li = 8/1, 12/1, and 16/1, respectively. For the O/Li = 12/1 blends, incorporation of the POSS-PEO( $n=4$ )<sub>8</sub> completely suppressed the crystallinity of the PEO(600K). For the O/Li = 16/1 blends, incorporation of the POSS-PEO( $n=4$ )<sub>8</sub> resulted only in decreased crystallinity for the PEO(600K). The blends were all viscoelastic, with strengths increasing with decreasing salt concentration, due to increased crystallinity of the lower salt blends. However, even the amorphous blends were viscoelastic. This is a result of the transient salt bridges that act as cross-link sites in these systems. When incorporated in the blends, POSS-PEO( $n=4$ )<sub>8</sub> increased the conductivity at low temperature, but the improvement was limited by the amount of POSS-PEO( $n=4$ )<sub>8</sub> that could be incorporated into the PEO(600K). Improvements in conductivity were not appreciable above  $T_m$ . This was attributed to the dilution effects of the SiO<sub>1.5</sub> core of the POSS-PEO( $n=4$ )<sub>8</sub>.

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## References and Notes

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