

# Ionic Conductivity in Physical Networks of Polyethylene–Polyether–Polyethylene Triblock Copolymers

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Received January 11, 2002. Revised Manuscript Received March 11, 2002

A self-assembling ABA triblock copolymer complexed with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) salt showed ion conductivities ( $\sigma$ ) approaching  $10^{-5}$  S/cm at 20 °C. The block copolymer had endblocks of polyethylene (PE) and midblocks of poly(ethylene oxide-co-propylene oxide) (PEOPO) and formed physical networks with PEOPO chains interconnected by crystalline PE domains. Thermal analysis showed a PEOPO glass transition at –68 °C and a PE melting point at 100 °C. When the melting region of the PE phase was reached,  $\sigma$  of the electrolytes was found to increase sharply to attain the same level as the corresponding electrolyte based on the neat PEOPO precursor block. Furthermore, the level of  $\sigma$  of the block copolymer electrolytes was found to be strongly dependent on the thermal history of the samples, and they showed a hysteresis behavior where  $\sigma$  increased by a factor of  $\approx 3$  after annealing above 110 °C. This may be explained by a reduction of the chain constraints of the PEOPO blocks in the physical network after annealing. The electrolytes behaved essentially like thermoplastics and were soft, tacky, self-supporting materials at room temperature.

## Introduction

An important aim in electrolyte research is to develop lithium ion conducting solid polymer electrolytes which combine high mechanical strength with the high ionic conductivity needed for application in, for example, solid-state lithium (ion) polymer batteries.<sup>1–3</sup> Given the generally clear relationship between ionic conductivity and polymer chain mobility, this research has been directed toward the synthesis of polymer electrolytes with low glass transition temperatures ( $T_g$ ). The most widely studied polymer electrolyte systems in this respect are those based on poly(ethylene oxide) (PEO). Although linear PEO is highly conductive at temperatures above  $\approx 65$  °C, these electrolytes rapidly lose their conductivity at lower temperatures because of crystallization of the PEO–salt complexes. In addition, electrolytes based on linear PEO lack the mechanical strength necessary to safely separate the electrodes in a battery cell. Both these limitations have successfully been avoided by employing polymer network electrolytes composed of chemically cross-linked ethylene oxide copolymers containing a lithium salt. Especially two types of ethylene oxide copolymers have recently been studied in this context, namely, those with propylene oxide<sup>4–10</sup> and those with 2-[2-(methoxyethoxy)ethoxy]-

ethylglycidyl ether<sup>5,11–13</sup> as comonomer. Some of the electrolytes based on these polymer networks and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) salt have been reported to reach ion conductivities of  $10^{-4}$  S/cm at 30 °C.<sup>11,12</sup>

Another, and in many aspects a more attractive, approach is to prepare physically cross-linked polymer network electrolytes, where the physical properties and processability of thermoplastics are exploited.<sup>14</sup> This kind of polymer electrolyte can effectively be prepared using self-assembling block copolymers which consist of at least two chemically dissimilar polymer chains, or blocks, covalently joined at the ends. Typically at low temperatures, the dissimilar polymer blocks phase-separate to form periodic structures at the nano level. Thus, a suitable block copolymer to form polymer network electrolytes should consist of one block which

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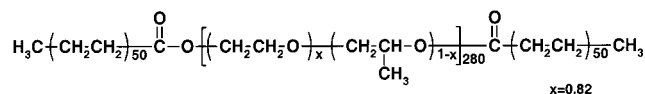
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### Scheme 1. Molecular Structure of the Triblock Copolymer



is ionophilic and able to facilitate the transport of ions and a second block which is ionophobic and well-segregated from the ionophilic block. The architecture of ABA triblock copolymers, in which the B block is ionophilic and constitutes the major part, is especially attractive because the B blocks will be interconnected by the dispersed phase domains formed by the ionophobic A blocks.

The concept of block copolymer electrolytes, as outlined above, has been shown to be successful in systems where ionophilic PEO blocks have been combined with an amorphous ionophobic block having a high or a low  $T_g$ . The former category includes block copolymer electrolytes having ionophobic blocks of polystyrene,<sup>15–18</sup> poly(4-vinylpyridine),<sup>19</sup> and poly(methyl methacrylate),<sup>14</sup> and the latter category includes block copolymer electrolytes having ionophobic blocks of poly(lauryl methacrylate)<sup>14</sup> and more recently also polyphosphazene.<sup>20</sup> An obvious third category of block copolymer electrolytes is based on block copolymers in which the ionophilic block is combined with a crystalline ionophobic block having a melting point ( $T_m$ ) well above the use temperature of the electrolyte. Such a copolymer would ideally show the same behavior as semicrystalline thermoplastics, with a high macroscopic solidlike viscosity below and a low macroscopic liquidlike viscosity above the  $T_m$  of the ionophobic blocks. This means that the electrolyte can be applied as a liquid at high temperature to form films, which then solidify when cooled.

The present study was aimed at investigating the phase behavior and ion transport properties of solid polymer network electrolytes based on a self-organizing ABA triblock copolymer with a ionophilic and cation coordinating B block and crystalline ionophobic A blocks. More specifically, a copolymer of ethylene oxide and propylene oxide with  $T_g = -68^\circ\text{C}$  was used as the mid(B)block, and a polyethylene with  $T_m = 100^\circ\text{C}$  was used as the end(A)blocks. The electrolytes were prepared by complexing the polyether midblock with LiTFSI salt. The phase behavior of the electrolytes was subsequently studied by calorimetry and the ion conductivity was evaluated by impedance spectroscopy.

## Experimental Section

**Block Copolymer Synthesis.** A triblock copolymer with the chemical structure shown in Scheme 1 was prepared by linking chain-end functional (telechelic) polymers. First, the poly(ethylene oxide-co-propylene oxide) (PEOPO) midblock was

prepared by anionic copolymerization of ethylene oxide (EO) and propylene oxide (PO), and then the polyethylene (PE) blocks were attached to the two chain ends of the PEOPO molecules through an esterification reaction.

A pressure-sustaining reactor was charged with 76 mg of diethylene glycol (99%, Aldrich) in 60 mL of 2-ethoxyethyl ether (99+%, Aldrich) and 7 mg of NaH (60% dispersion in mineral oil, Aldrich) and then carefully degassed. An amount of 10 g of a mixture of 25 wt % PO (99+%, Aldrich) in EO ( $\geq 99.8\%$ , Fluka) was charged to the reactor, and anionic copolymerization was allowed to proceed at  $80^\circ\text{C}$  until all the monomers had been consumed. The product was purified by precipitation in cold diethyl ether (p.a. grade, Merck). The PEOPO precursor block was found by  $^1\text{H}$  NMR spectroscopy to contain 77 wt % EO and by size exclusion chromatography (SEC) to have  $M_n = 13000$  g/mol and  $M_w/M_n = 1.2$ . SEC analyses were run with THF as eluent on Waters ultra-Styrigel columns ( $10^4$ ,  $10^3$ , 500, and  $100\text{ \AA}$ ) using PEO standards (Polysciences) for calibration.

In the esterification reaction, 7.00 g of PEOPO, 0.83 g of mono-carboxylic acid functional PE ( $M = 700$  g/mol, Aldrich), 4 mg of *p*-toluenesulfonic acid monohydrate (98.5%, Aldrich), and 100 mL of toluene (Merck, p.a. grade) were charged to a three-necked glass reactor fitted with a condenser, a nitrogen gas inlet/outlet, and a thermometer. Portions of the toluene were distilled off under reflux at  $110\text{--}120^\circ\text{C}$ , and the progress of the esterification was followed by IR spectroscopy (see below) by observation of the appearance and growth of the ester carbonyl peak at  $1735\text{ cm}^{-1}$ . During cooling of the reaction mixture, a physical gel was formed as the PE endblocks crystallized. The *p*-toluenesulfonic acid and the toluene were carefully extracted from the gel by successive immersions in dry THF (anhydrous, 99.9%, Aldrich). After drying in a vacuum, the material was immersed in isooctane (99+%, Aldrich) to remove the excess of the PE precursor. The removal of the PE precursor was confirmed by IR spectroscopy by the absence of any carboxylic acid peak at  $1710\text{ cm}^{-1}$ .

**Electrolyte Preparation.** Solid polymer electrolytes were prepared by complexing lithium bis(trifluoromethylsulfonyl)imide salt (LiTFSI, battery grade, kindly supplied by the 3M Co.) with the triblock copolymer and the PEOPO precursor block under a dry Ar atmosphere in a glovebox. The polymers were first dried at  $60^\circ\text{C}$  under vacuum for 3 days. Then, precise amounts of a solution of LiTFSI in dimethyl carbonate (Merck, Selectipur, Battery Grade) were added to glass ampules containing 300 mg of polymer to obtain electrolytes with the desired salt concentrations. The dimethyl carbonate was allowed to evaporate under Ar for 2 days at ambient temperature before the samples were transferred to a glass oven where the residual solvent was removed under vacuum at  $60^\circ\text{C}$  for 3 days. Salt concentrations were defined using the  $[\text{Li}]/[\text{O}]$  ratio, that is, the number of lithium ions per coordinating PEOPO oxygen.

**Impedance Spectroscopy.** The ion conductivity ( $\sigma$ ) of the electrolytes was evaluated by measuring the temperature dependence of impedance spectra in the region  $-40$  to  $140^\circ\text{C}$ . Samples with a diameter of 18 mm and a thickness of  $90\text{ }\mu\text{m}$  were sandwiched between two gold-plated stainless steel blocking electrodes spaced by a PTFE ring. The measurements were carried out using a computer-controlled Novocontrol BDC40 high-resolution dielectric analyzer equipped with a Novocool cryostat unit. Samples were analyzed in the frequency range  $10^{-1}\text{--}10^7$  Hz at 100-mV ac amplitude, and the conductivities were subsequently evaluated using the Novocontrol software WinDeta.

**FT-IR Spectroscopy.** Infrared spectra were recorded with a Bruker IFS 66 FTIR spectrometer. Samples were extracted directly from the reaction mixture with a syringe during the esterification and placed on KBr crystals. The toluene was then allowed to evaporate at room temperature before analysis. The neat PE and PEOPO precursors were analyzed in the form of films cast from toluene on top of KBr crystals. The spectral resolution was set to  $2\text{ cm}^{-1}$ .

**Calorimetry.** The thermal properties of the neat polymer and the electrolytes were analyzed with a Mettler TA 3000

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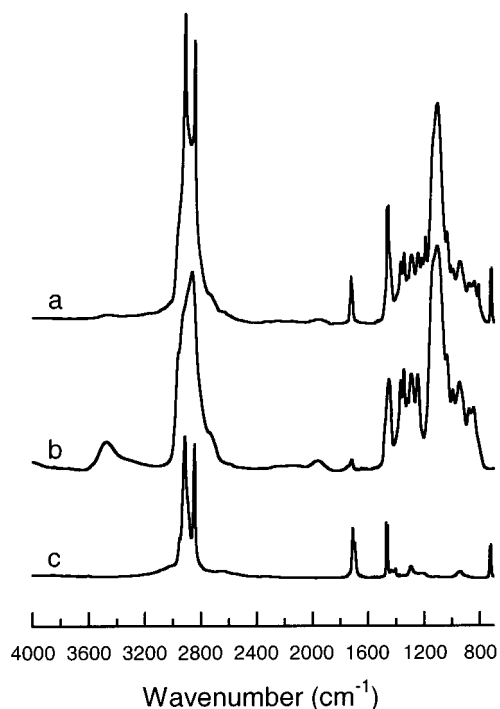
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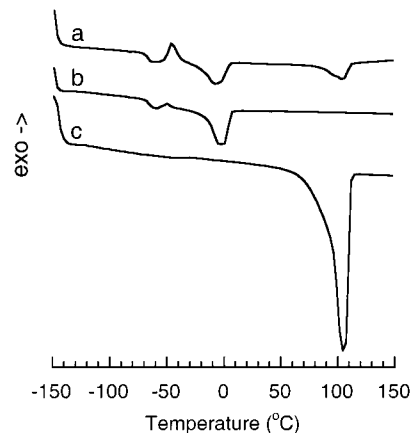
**Figure 1.** IR spectra of the neat triblock copolymer (a) and the precursor PEOPO (b) and PE (c).

DSC system under  $N_2$  purge. Samples were placed in aluminum containers, which were sealed under an Ar atmosphere. The samples were first annealed at 150 °C for 5 min before being cooled down to -150 °C and then finally heated to 150 °C again. The heating and cooling rates were 10 °C/min. Glass transition temperatures ( $T_g$ ), melt temperatures ( $T_m$ ), and heats of fusion ( $\Delta H_m$ ) were evaluated from the heating scan.

## Results and Discussion

**The Block Copolymer.** The linking of the precursor PE and PEOPO blocks by esterification to form the block copolymer was conveniently monitored by IR spectroscopy. Spectra of the triblock copolymer and the precursor blocks are shown in Figure 1. An excess of the monocarboxylic acid PE was charged in the reaction and, consequently, after completion of the reaction, the ester peak at 1735  $cm^{-1}$  was observed together with a small peak at 1710  $cm^{-1}$  arising from carboxylic acid dimers (not shown). After purification, only the former peak was present, indicating the removal of the excess PE precursor. Furthermore, the peak arising from the terminal hydroxyl groups of the PEOPO precursor, seen at  $\approx 3480$   $cm^{-1}$  in Figure 1b, was absent in the spectrum of the triblock copolymer.

The block copolymer most probably self-assembled into a physical network where the PEOPO chains were interconnected by crystalline PE domains. A simple experiment was performed where a sample of the copolymer was applied onto a glass slide which was then stored in a vertical position. No signs of flow could be observed after 2 months of storage at room temperature. However, when the same glass slide was put in a vertical position in an oven at 110 °C, the block copolymer started to flow almost immediately. Thus, the copolymer showed the characteristic behavior of semicrystalline thermoplastics. It was also interesting to note that the copolymer formed a thermoreversible gel in toluene during cooling of the reaction vessel after the



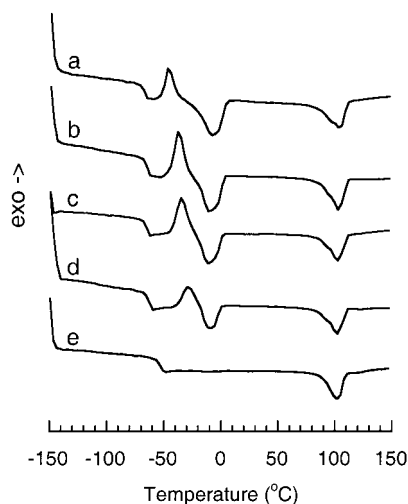
**Figure 2.** DSC heating traces showing the thermal transitions of the neat triblock copolymer (a) as well as the precursor PEOPO (b) and PE (c). The samples were cooled from 25 °C down to -150 °C prior to the heating scan. Scan rate: 10 °C/min.

esterification step. Because of the interconnecting crystalline PE domains, the triblock copolymer was dissolved by very few solvents, but was swelled by many. It was found to dissolve readily in hot toluene and xylene, which are good solvents for semicrystalline low-density PE.

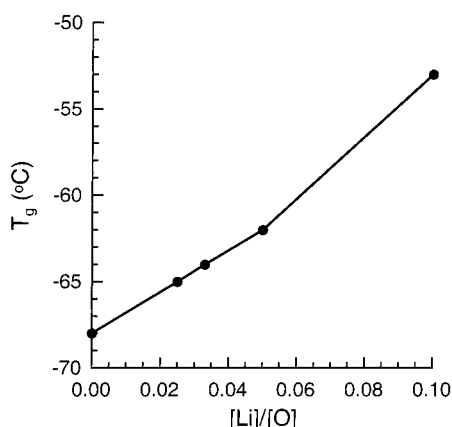
Figure 2 shows the DSC traces of the precursor blocks and the neat triblock copolymer. The PE precursor showed only a large melt endotherm at 105 °C, while the PEOPO precursor showed a glass transition at -65 °C, a small crystallization exotherm at -50 °C, and finally a melt endotherm at 5 °C. The thermogram of the triblock copolymer showed, as expected, features from both blocks with a PEOPO glass transition at -65 °C, a PEOPO "cold" crystallization exotherm at -45 °C, a PEOPO melt endotherm at -10 °C, and a PE melt endotherm at 100 °C. It was noted that the  $T_g$  of the PEOPO phase did not seem to be significantly influenced by being chemically linked to the PE phase. Furthermore, the  $T_m$  of the PE endblocks was almost the same as that for the PE precursor, with the heat of fusion of the PE phase of the triblock copolymer at 10% of that of the PE precursor. In conclusion, the results clearly indicated that the PE and PEOPO blocks of the copolymer were strongly segregated, at least up to the  $T_m$  of the PE blocks.

**The Triblock Copolymer Electrolytes.** Electrolytes were prepared by complexing the PEOPO blocks of the triblock copolymer as well as the neat PEOPO precursor with LiTFSI salt. All electrolytes were transparent and self-supporting at room temperature. Figure 3 shows the DSC thermograms of the electrolytes with different salt concentrations when heated from -150 to 150 °C. The  $T_g$  of the PEOPO block, as evaluated from these thermograms, is plotted in Figure 4. As expected, the  $T_g$  of the PEOPO block increased as the salt concentration was increased. The reason for this behavior is the formation of transient cross-links because of intra- and intermolecular coordination of PEOPO ether oxygens with lithium ions.<sup>1</sup> As seen in Figure 3, the propensity for crystallization of the PEOPO blocks decreased with increasing salt concentration, and no crystallization was observed at  $[Li]/[O] = 0.100$ . The peak position of the "cold" PEOPO crystallization exo-





**Figure 3.** DSC heating traces of solid triblock copolymer sample having  $[\text{Li}]/[\text{O}] = 0$  (a), 0.025 (b), 0.033 (c), 0.050 (d), and 0.100 (e). The samples were cooled from 25 °C down to -150 °C prior to the heating scan. Scan rate: 10 °C/min.



**Figure 4.** Variation of  $T_g$  with the concentration of LiTFSI salt for the solid triblock copolymer electrolytes.

therm increased with increased salt concentration, from -45 °C at  $[\text{Li}]/[\text{O}] = 0$  to -27 °C at  $[\text{Li}]/[\text{O}] = 0.050$ , while the  $T_m$  of PEOPO remained at -10 °C. The increase in the "cold" crystallization temperature was at least partly a result of the increase in  $T_g$ , leading to a decreased mobility in the PEOPO phase. It was finally noted that the salt concentration did not seem to influence the  $T_m$  and  $\Delta H_m$  of the PE phase. This is not surprising when one considers that the PE phase crystallized at 90 °C during the cooling scans (not shown), which is at least 120 °C above the  $T_g$  of the PEOPO phase. Thus, the high mobility in the electrolytes at 90 °C ensured effective crystallization of the PE phase regardless of the salt concentration.

The temperature dependence of the ion conductivity ( $\sigma$ ) of the electrolytes having  $[\text{Li}]/[\text{O}] = 0.025$ , 0.050, and 0.100 was evaluated by impedance spectroscopy. During the measurements, the samples were first heated from -40 to 140 °C, then cooled to -40 °C, and finally heated a second time to 140 °C. Figure 5a-c shows the results in Arrhenius plots for the three polymer electrolytes. There are several interesting features of the curves in the figure. During heating, all the electrolytes showed a sharp, stepwise increase in  $\sigma$  at approximately 80-110 °C. Correspondingly, during cooling, a sharp stepwise decrease in conductivity was noted immediately

after 110 °C. If one considers the results obtained during the first heating (open circles in Figure 5),  $\sigma$  increased by a factor of 30, 15, and 26 for the electrolytes with  $[\text{Li}]/[\text{O}] = 0.025$ , 0.050, and 0.100, respectively, when heating from 90 to 110 °C. The stepwise increase and decrease in  $\sigma$  were clearly a result of the melting and crystallization of the PE domains, respectively, which occur in this temperature region. For example, the DSC results in Figure 3 show that the melting of the PE phase starts at  $\approx 85$  °C and is complete at 110 °C. The rigid crystalline PE phase domains keep the physical PEOPO networks together by forming the nodes of the network below the melting point. Consequently, it is easy to envisage that when the PE phase domains melt in a quite small temperature range, the segmental mobility of the PEOPO blocks, and thereby also  $\sigma$ , will increase sharply. Thus, the PE phase domains seemed to work as thermoreversible physical cross-links in the block copolymer electrolytes. It is however at this point unclear if the PE blocks remained segregated from the PEOPO blocks above  $T_m$  of the PE phase.

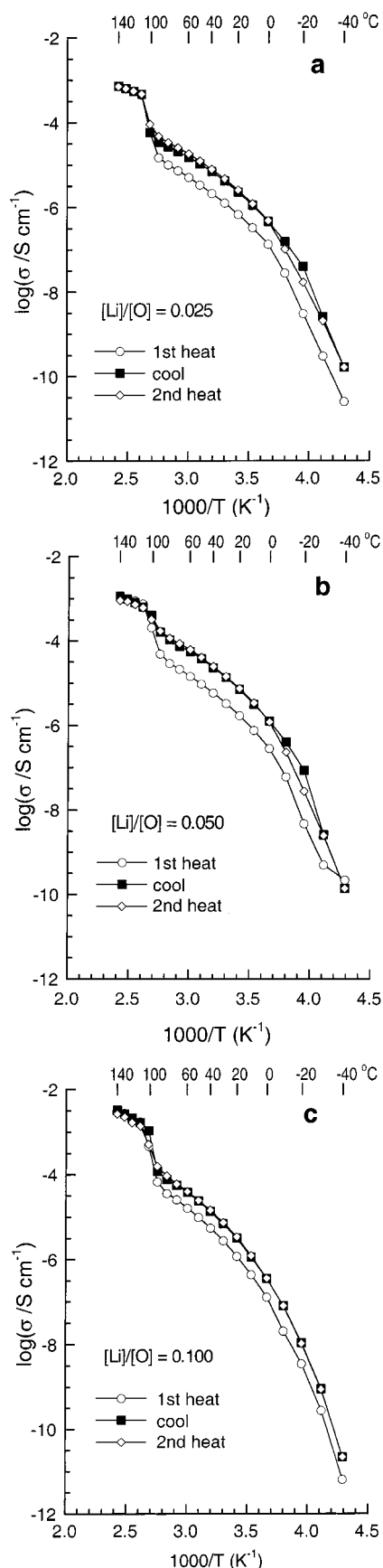
Another distinct feature of the results in Figure 5 was the hysteresis displayed by the electrolytes. Below  $T_m$  of the PE phase, the level of  $\sigma$  was significantly higher during the cooling scan (filled squares), as compared to the first heating scan (open circles). In the second heating scan (open diamonds), the level of  $\sigma$  was the same as that during the cooling scan. The conductivity above the PE melting point was the same during all three scans. It was also noted that in the temperature region -30 to 0 °C, the conductivity during the cooling of the electrolytes having  $[\text{Li}]/[\text{O}] = 0.025$  and 0.050 was slightly higher than that during the second heating scan. This observation may be explained by the crystallization and melting, respectively, of PEOPO. The thermograms of these electrolytes show that melting during heating is complete at 0 °C (Figure 3) and that crystallization started during cooling between -20 and -30 °C (not shown). In the electrolyte with  $[\text{Li}]/[\text{O}] = 0.100$ , no crystallization or melting of PEOPO was observed and, consequently, the conductivity measured during the cooling and second heating scans was the same (Figure 5c).

The convex conductivity curves noted for the electrolytes between  $T_m$  of the PEOPO and  $T_m$  of the PE block agree well with the general temperature dependence observed for amorphous polymer electrolytes, and this may be described by the Vogel-Tammann-Fulcher (VTF) equation:<sup>21</sup>

$$\sigma = A \exp[-B/(T - T_0)] \quad (1)$$

The electrolyte with  $[\text{Li}]/[\text{O}] = 0.100$  showed VTF behavior over the temperature region -40 to 80 °C, while the other two followed the VTF equation between 0 and 80 °C. This shows that in the absence of phase transitions the process of ion conduction was closely linked to the segmental relaxation of the PEOPO side chains. Table 1 shows the results of a two-parameter fit to the VTF equation in the temperature region 0-80 °C. The results show that the main difference between

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**Figure 5.** Arrhenius plots showing thermal hysteresis effects of  $\sigma$  for the solid triblock copolymer electrolyte at  $[\text{Li}]/[\text{O}] = 0.025$  (a),  $0.050$  (b), and  $0.100$  (c). The conductivities were evaluated by impedance spectroscopy during the temperature scan:  $-40 \rightarrow 140 \rightarrow -40 \rightarrow 140$  °C.

**Table 1.** VTF Data<sup>a</sup> for the Solid Polymer Electrolytes Based on the Triblock Copolymer and the PEOPO Precursor Block

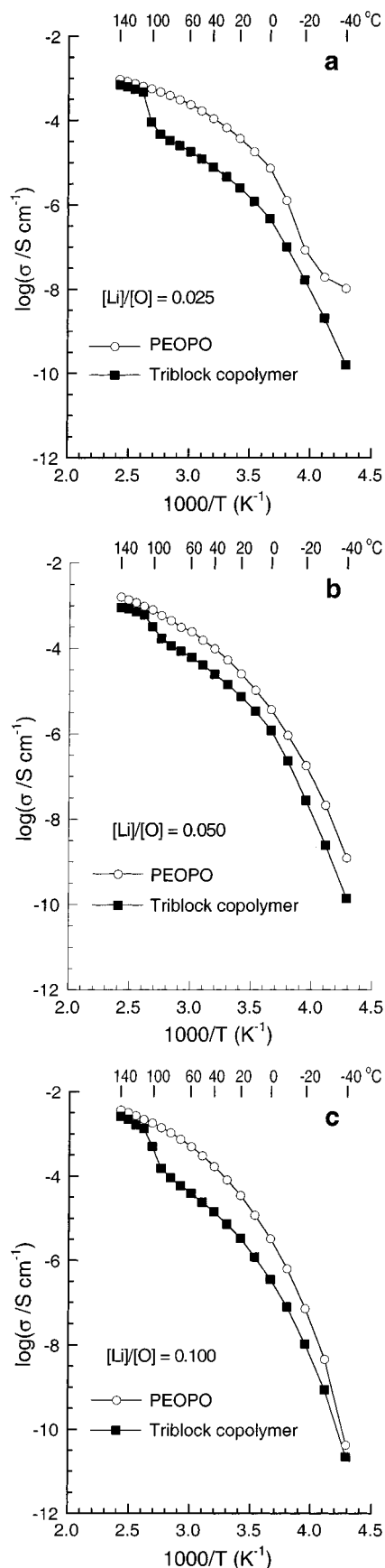
electrolyte	$A$ (S/cm)	$B$ (K)	$T_0$ (K) <sup>b</sup>	$T_g$ (K)
Block Copolymer				
$[\text{Li}]/[\text{O}] = 0.100$				
1st heat	0.027	1240	170	220
2nd heat	0.079	1210	170	220
$[\text{Li}]/[\text{O}] = 0.050$				
1st heat	0.014	1190	160	210
2nd heat	0.041	1130	160	210
$[\text{Li}]/[\text{O}] = 0.025$				
1st heat	0.0041	1170	158	208
2nd heat	0.0097	1100	158	208
PEOPO Precursor				
$[\text{Li}]/[\text{O}] = 0.100$	0.530	1100	175	225
$[\text{Li}]/[\text{O}] = 0.050$	0.120	1050	165	215
$[\text{Li}]/[\text{O}] = 0.025$	0.054	950	159	209

<sup>a</sup> Obtained by two-parameter fits ( $A$  and  $B$ ) in the temperature region  $0$ – $80$  °C. <sup>b</sup>  $T_0$  was set to  $T_g + 50$  K.

the electrolytes was seen in the parameter  $A$ , which denotes the “ultimate conductivity”. For the electrolytes with  $[\text{Li}]/[\text{O}] = 0.025$ ,  $0.050$ , and  $0.100$ , the  $A$  parameter increased by a factor of 2.4, 2.9, and 2.9, respectively, during the second heating scan, as compared to the values measured during the first scan.

The observed hysteresis, reflected in the increase in  $A$  during the second heating scan, was obviously a result of the thermal history of the electrolyte samples and shows that annealing is decisive for the level of  $\sigma$  reached with these materials. The physical explanation of the observed behavior may be that in the unannealed electrolytes, prepared essentially through solvent casting, the triblock copolymer formed constrained physical networks where the block copolymer molecules were interlocked by the crystalline PE phase domains. This would lead to a reduced segmental mobility of the ion-conducting PEOPO midblocks and thus a reduced  $\sigma$ . When the PE endblocks melted at  $\approx 100$  °C, the block copolymer molecules were able to rearrange and form a network in which the PEOPO midblocks were less constrained, leading to an increase in  $\sigma$ . It should be mentioned that no difference in  $T_m$  or  $\Delta H_m$  of the PE phase was noted before and after annealing. Furthermore, when analyzed after 2 months of storage at room temperature, it was found that the  $\sigma$  of the annealed samples had not decreased.

It is interesting to compare the results on the triblock copolymer electrolytes with those obtained with the electrolytes based on the “unblocked” PEOPO precursor block. It should be noted that electrolytes based on the precursor blocks are viscous liquids, which makes them less interesting for battery applications than the self-supporting block copolymer electrolytes. Figure 6a–c shows the results of the conductivity measurements on the electrolytes based on the PEOPO precursor complexed with LiTFSI at  $[\text{Li}]/[\text{O}] = 0.025$ ,  $0.050$ , and  $0.100$ , respectively. For comparison the results on the triblock copolymer electrolytes (second heating scan) are also included in Figure 6. Of course, the electrolytes based on the PEOPO precursor block did not show any stepwise increases or decreases in  $\sigma$  nor any hysteresis behavior at high temperatures. The level of  $\sigma$  of these electrolytes was  $10^{-4.5}$  S/cm at  $20$  °C, which is considerably higher than that for the block copolymer electrolytes. When the VTF data of the block copolymer



**Figure 6.** Arrhenius conductivity plots for solid polymer electrolytes based on the precursor PEOPO (circles) and the triblock copolymer (squares) at  $[\text{Li}]/[\text{O}] = 0.025$  (a),  $0.050$  (b), and  $0.100$  (c). The conductivities were evaluated by impedance spectroscopy during heating of annealed samples from  $-40$  to  $140$  °C.

electrolytes were compared with those of the PEOPO precursor electrolytes in the temperature region  $0$ – $80$  °C (Table 1), it was seen that the levels of  $B$  and  $T_0$  were approximately the same. This is not surprising since these parameters are linked to the mechanism of conduction and the  $T_g$ . The values of  $A$ , however, were considerably higher for the latter electrolytes. This indicates that the level of chain mobility of PEOPO is considerably lower in the block copolymer electrolytes, as compared to the PEOPO precursor electrolytes. Thus, the unrestrained chain ends of PEOPO in the latter electrolytes lead to higher segmental mobility and thus to higher values of  $\sigma$ . At temperatures above  $T_m$  of the PE phase, however, the  $\sigma$  of the block copolymer electrolytes were almost on the level with those of the PEOPO electrolytes. This indicates that the segmental mobility of the PEOPO chains is approximately the same in the two types of electrolytes when the PE endblocks were in the molten state, indicating that the chain-end mobility was at the same level. Indeed, the short PE endblocks can be expected to have a high mobility above the  $T_m$  because of their low  $T_g$ . At temperatures below  $0$  °C, the electrolytes based on the precursor block with  $[\text{Li}]/[\text{O}] = 0.025$  and  $0.050$  showed signs of PEOPO melting, which was also confirmed by DSC.

As mentioned in the Introduction, different electrolyte systems based on PEOPO copolymers have been studied previously. For example, a study of linear high-molecular-weight PEOPO copolymers complexed with  $\text{LiClO}_4$  salt ( $[\text{Li}]/[\text{O}] = 0.042$ ) have  $\sigma$  equal to  $\approx 10^{-5}$  S/cm at  $25$  °C.<sup>8</sup> In another study, aggregating comb-shaped PEOPO containing LiTFSI ( $[\text{Li}]/[\text{O}] = 0.050$ ) was shown to have  $\sigma = 10^{-4.6}$  S/cm at  $20$  °C.<sup>22</sup> It is especially interesting to compare the level of  $\sigma$  reached in the physically cross-linked triblock copolymer networks with the level of  $\sigma$  reached in chemically cross-linked PEOPO. Hayamizu et al. recently investigated the  $\sigma$  of electrolytes based on a three-armed star-shaped PEOPO copolymer having terminal acrylate groups.<sup>5</sup> The macromonomer, containing  $\approx 80$  wt % EO and having a molecular weight between  $8000$  and  $10000$  g/mol, was doped with LiTFSI, corresponding to  $[\text{Li}]/[\text{O}] = 0.1$ , and then cross-linked by electron irradiation. The  $\sigma$  of this electrolyte was measured to be  $10^{-4.7}$  S/cm at  $30$  °C, which may be compared with  $10^{-5.2}$  S/cm reached by the block copolymer electrolyte at the same salt concentration and temperature. Thus, the chemically cross-linked network has  $\approx 3$  times higher  $\sigma$  than the physically cross-linked network. Although quite small, the difference may be explained by the formation of a more rigid network by the block copolymer, leading to a somewhat lower degree of mobility on the segmental level. The lithium ion transport number in chemically cross-linked PEOPO network electrolytes containing LiTFSI has been determined by pulsed gradient spin-echo NMR to be  $0.12$ .<sup>6</sup> A study by Ismail et al. of the electrochemical stability of PEOPO-based electrolytes in contact with lithium metal electrodes showed that the polymer network played a less significant role in controlling the interfacial property and that the nature of the lithium salt had

a much greater effect on the passivation layer formed.<sup>23</sup> The study further showed that a thin and stable nonresistive layer was formed at the interface between the lithium metal and a PEOPO network electrolyte containing LiTFSI salt. Thus, PEOPO network electrolytes containing LiTFSI seem to be good candidates for use in, for example, lithium polymer batteries.

Future studies of the block copolymer electrolytes will include morphological and rheological investigations of

the solid systems as well as an investigation of gel electrolytes formed by swelling the physical networks with electrolyte solutions.

**Acknowledgment.** I thank the Swedish Foundation for Strategic Environmental Research, MISTRA, for the financial support. The work was done within the framework of the Jungner Centre for batteries and fuel cells.

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CM021103E