Polymer Electrolytes Based on Unsaturated Ethylene Oxide-Segmented Polymers

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Polymer electrolytes were prepared from $LiClO_4$ and high molecular weight unsaturated ethylene oxide-segmented polymers with the generic formula $-[(CH_2)_xCH{=}CH(CH_2)_xO(CH_2CH_2O)_y]_n-$ ($\mathbf{[C_x\pi C_xEO_y]_n}$). Synthesized by metathesis polymerization of α,ω-dienes that contain oligomeric poly(ethylene oxide) cores, these polymers are tacky, adhere well to glass and metal surfaces, and have glass transition temperatures between −70 and −80 °C. Polymers that contain relatively long alkyl or polyether segments are crystalline below room temperature, but adding $LiClO_4$ to the polymers converts them to amorphous polymer electrolytes with room-temperature conductivities (20 °C) of $\approx 2 \times 10^{-5}$ S/cm. The T_gs of the materials can be fit by a simple model based on the Fox equation, and an analysis of the results indicates that the Li^+:monomer repeat unit stoichiometry is 1:1 for polymers with long block lengths, and decreases to 1:2 for polymers with poly(ethylene oxide) segments with less than 4 repeat units.

Introduction

A long-standing goal in battery research has been the preparation of polymer electrolytes that combine the processability and physical properties of conventional thermoplastics with the high ionic conductivities needed in applications such as solid-state lithium ion batteries.[1] One design rule for the synthesis of polymer electrolytes is that high conductivity is correlated with materials that have a low glass transition temperature (T_g). Thus, polymers with backbones that contain flexible units should yield polymer salt complexes with the highest ionic conductivities.

The most widely studied electrolyte systems are based on poly(ethylene oxide) (PEO). The T_g of PEO is low, ≈ -65 °C, but PEO and PEO/salt complexes readily crystallize to form a poorly conducting crystalline phase that raises the T_g of the PEO matrix.[2] A variety of synthetic approaches have been used to reduce the crystalline content of PEO/Li^+ salt complexes, with the most successful approaches being those that disrupt the regularity of the PEO backbone and thus inhibit polymer crystallization. Of particular relevance to the work described in this paper are those schemes where relatively short PEO segments are linked to give amorphous linear polymers with good mechanical properties. The types of linkers used to join PEO segments include methylenes,[3−6] siloxanes,[7] esters,[8] urethanes,[9] carbonates,[10,11] and inorganic linkers such as phosphates[12] and aluminates.[13] Many of these polymers can be described as $(AB)_n$ block copolymers, where A represents the linking segment and B corresponds to an oligomeric segment of ethylene oxide. Electrolytes prepared from such materials generally have room-temperature ionic conductivities between 10^{-4} and 10^{-5} S/cm.

One of the most extensively studied PEO block copolymer systems is oxymethylene-linked PEO, where PEO oligomers are linked through OCH_2 groups. Booth et al.[4] showed that the best conductivities were obtained when the PEO block was PEG400, a mixture of PEO oligomers with an average molecular weight of 400 g/mol. Both a distribution in chain lengths for the glycol and the oxymethylene links that join the PEO segments inhibit crystallization, and the resulting polymer melts at 15 °C. Because of the low T_g of the polymer, −66 °C, and its lack of crystallinity, polymer/salt complexes of

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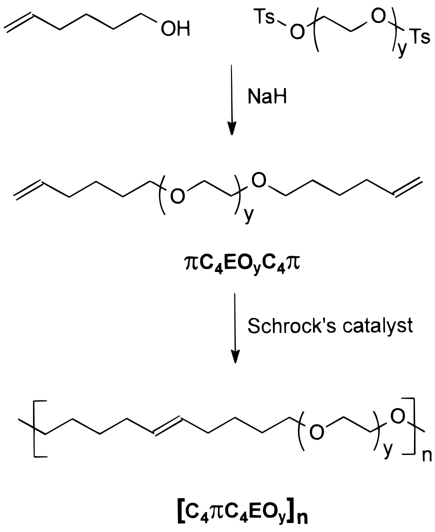

Figure 1. Synthetic scheme for the preparation of $(AB)_n$ polymers with $x = 4$.

oxymethylene-linked PEO have room-temperature conductivities of 3×10^{-5} S/cm.[4] Polymers prepared from exact length glycols had higher melting points. For example, an oxymethylene-linked PEO prepared from tetraethylene glycol melted at 33 °C.[4]

In this report, we describe the properties and ionic conductivities for an $(AB)_n$ block copolymer system with the generic formula $-[(CH_2)_xCH{=}CH(CH_2)_xO(CH_2CH_2O)_y]_n-$ (**$[C_x\pi C_xEO_y]_n$**). (The abbreviations used for the monomers and polymers are derived from the well-established shorthand names for a series of structurally related nonionic surfactants.) The expected T_g for such a polymer should be low, between that of PEO (−65 °C) and polyethylene (−130 °C), and because of their low T_g's, these high molecular weight polymers should have room-temperature conductivities comparable to oxymethylene-linked PEO and poly(methoxyethoxy ethoxyphophazene) (MEEP),[14] and other highly conductive polymers based on PEO.

Experimental Section

Unless otherwise specified, ACS reagent grade starting materials and solvents were used as received from commercial suppliers without further purification. Monomers and polymers were prepared as shown for the $x = 4$ series in Figure 1. Synthetic details are provided elsewhere.[15] All manipulations of the polymers and electrolytes were carried out in a helium-filled drybox. Polymer salt complexes were prepared by combining acetonitrile solutions of the polymer and $LiClO_4$, evaporating the solvent to dryness, and drying under vacuum at 50° overnight. Differential scanning calorimetry (DSC) analyses of the polymers and polymer salt complexes were performed under a helium atmosphere at a heating rate of 10 °C/min on a Perkin-Elmer DSC 7, with the temperature calibrated using an indium standard. The reported DSC curves are taken after quenching the samples to −100 °C. All samples have melting points below room temperature and thus are initially amorphous. Samples were also examined using polarized optical microscopy to confirm morphology and melting transition assignments. Ionic conductivities were measured using an HP 4192 Impedance Analyzer from 5 Hz to 10 MHz at temperatures ranging from 20 to 100 °C. Samples were sandwiched between two stainless steel disks separated by a Teflon spacer.

Table 1. Properties of Polymers Used in This Study[a]

$$-\!\!\left[(CH_2)_x-CH{=}CH-(CH_2)_x-O(CH_2CH_2O)_y\right]_n\!\!-$$

polymer	x,y	M_n	PDI	T_g	T_m
$[C_3\pi C_3EO_2]_n$	3,2	93 900	2.29	−79	*b*
$[C_3\pi C_3EO_3]_n$	3,3	55 000	2.57	−77	*b*
$[C_3\pi C_3EO_4]_n$	3,4	66 400	2.24	−75	−14
$[C_4\pi C_4EO_3]_n$	4,3	32 200	2.12	−79	4
$[C_4\pi C_4EO_4]_n$	4,4	28 100	2.16	−77	−5
$[C_4\pi C_4EO_5]_n$	4,5	31 500	2.01	−74	7

[a] Temperatures reported in degrees Celsius. [b] None detected.

Results

Polymers Synthesis and Properties. Recent advances in metathesis polymerization provide a generic route to $(AB)_n$ polymers where A is an alkenyl segment and B is an oligomeric segment that can contain a broad range of functional groups. Our synthetic approach follows that of Wagener,[16] who has shown that α,ω dienes can be linked in a step-growth process to give polymers that retain one double bond per repeat unit. Termed Acyclic Diene METathesis (ADMET), this polymerization method has been applied to the synthesis of ethers,[17] thioethers,[18] esters,[19] carbonates,[20] and many other $(AB)_n$ polymer structures. As shown in Figure 1, we found that the same chemistry can be applied to α,ω-dienes that contain ethylene oxide cores. Polymerization using Schrock's catalyst[21−24] yields high molecular weight polymers that retain one double bond per repeat unit. Because the double bonds formed during the ADMET process can have either a *Z* or *E* geometry, the polymer should have limited crystallinity and have the low T_g characteristic of synthetic rubbers. If desired, the basic polymer structure can be hydrogenated to give polyethylene/poly(ethylene oxide) $(AB)_n$ polymers, or alternatively, the double bond can be used for cross-linking or as a site for introducing chain branching.

Wagener has shown that ADMET can give high molecular weight polymers, with the maximum molecular weight mainly limited by the purity of the monomer.[16,18−20,25−29] For our work, we used a sequence of rigorous monomer purification steps that enabled us to obtain polymers with molecular weights approaching 100 000 g/mol (Table 1). At room temperature, the polymers are tacky solids that strongly adhere to glass and metals, not surprising given their low T_gs. All of the measured T_gs fall below that of poly(ethylene oxide), implying that these polymers should exhibit good ionic

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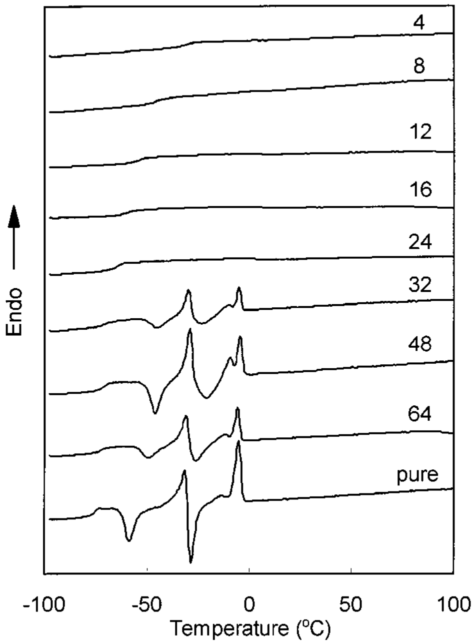

Figure 2. DSC second heating scans for polymer **[C$_4\pi$C$_4$EO$_4$]$_n$**/ lithium perchlorate salt complexes. The number next to each trace is the O:Li ratio of the sample.

conductivities. The thermal analysis data also show a linear relationship of T_g with poly(ethylene oxide) content, with single T_gs detected for each sample, good evidence that in the amorphous phase, the ethylene and ethylene oxide segments do not phase separate.

Some polymers are crystalline at low temperatures, with the melting points dependent on the lengths of the alkenyl and ethylene oxide segments. The data for **[C$_4\pi$C$_4$EO$_4$]$_n$** is representative for this class of polymers. Shown in the bottom trace of Figure 2 are the low-temperature DSC results for **[C$_4\pi$C$_4$EO$_4$]$_n$** obtained after flash quenching the sample from 100 to −100 °C. The sample, initially amorphous, shows a glass transition at −77 °C followed by two crystallization (exotherm)/melting (endotherm) events. Similar combinations of crystallization and melting are seen for all of the polymers except **[C$_3\pi$C$_3$EO$_2$]$_n$** and **[C$_3\pi$C$_3$EO$_3$]$_n$**, which presumably have block lengths too short to support crystallization.

Similar DSC data has been reported for the crystallization of PEO oligomers, and has been related to the crystallization and melting of lamellar crystals of different characteristic thicknesses.[30] X-ray,[31−34] Raman,[35] and optical studies[36] have shown that depending on the crystallization conditions, PEO can crystallize into thick high melting lamellae containing extended chains, or thin lower melting crystals assembled from folded chains. We believe the sequence of melting/crystallization phenomena that occurs in the (AB)$_n$ polymers has a similar origin. Low-temperature crystallization favors chain folded crystals with low melting points, while crystallization at higher temperatures allows formation of the more stable chain extended crystals. The DSC data for polymers with $x = 4$ also show that the crystallization and melting transitions, taken as the onset in the DSC scan for the highest melting phase, show an interesting odd−even effect that depends on the length of the ethylene oxide segments. Thus, polymers with blocks that contain an even number of ethylene oxide units generally have lower melting points than polymers with odd numbers of ethylene oxide units. The source of this effect will be discussed in detail elsewhere.[15]

Polymer Salt Complexes. At room temperature, polymer salt complexes prepared from lithium perchlorate and the (AB)$_n$ copolymers are homogeneous. As shown in the lower traces in Figure 2, electrolytes prepared from **[C$_4\pi$C$_4$EO$_4$]$_n$** with low Li$^+$ concentrations show partial crystallinity below room temperature. Since the pattern of crystalline transitions is identical to that of the pure homopolymer, the data simply reflect a steady decrease of the crystalline homopolymer phase as the proportion of the salt-containing phase increases. For higher levels of added salt, the crystallinity was completely lost, and polarized optical microscopy confirmed that the samples were amorphous. While a lack of crystallinity might seem unusual for PEO/salt complexes with high Li$^+$ concentrations, the results are consistent with studies of electrolytes based on oxymethylene-linked PEO. Crystalline oxymethylene-linked PEO/salt phases are seen only when the molecular weight of the PEO segments exceeds 5000 g/mol.[37] Obviously the short PEO sequences in the (AB)$_n$ copolymers limit formation of crystalline polymer salt complexes. As the crystallinity is lost in the polymers, the glass transitions for the series of samples increase monotonically with the salt concentrations (Figure 3). The relationship between T_g and the molar salt content is linear at least to O:Li ratios of 8.

Plotted in Figure 4 are typical conductivity data obtained for electrolytes prepared from the (AB)$_n$ polymers. The ionic conductivities for **[C$_3\pi$C$_3$EO$_4$]$_n$**/LiClO$_4$ complexes show a characteristic rise with increasing salt content, reaching a maximum at O:Li = 32. With increasing temperatures, the peak conductivity moves to higher values and shifts slightly to higher salt contents. For comparison, literature data for amorphous PEO[38] are plotted in the same figure. The data show that while the overall shapes of the conductivity curves are similar, the **[C$_3\pi$C$_3$EO$_4$]$_n$** data appear shifted to higher salt contents relative to PEO. This shift can be understood in terms of the lower polyether volume fraction in the copolymers compared to PEO. As shown

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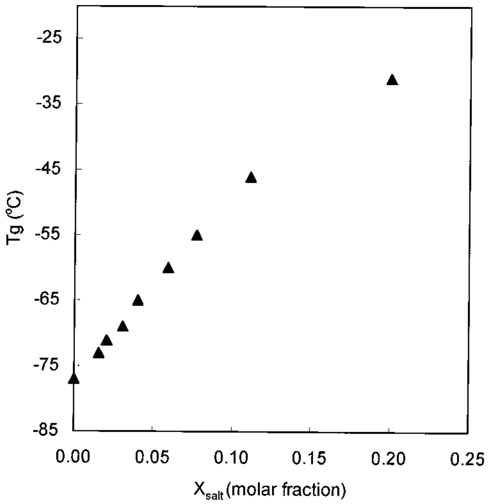

Figure 3. Salt-dependent T_g for polymer $\mathbf{[C_4\pi C_4EO_4]_n}$/LiClO$_4$ complexes.

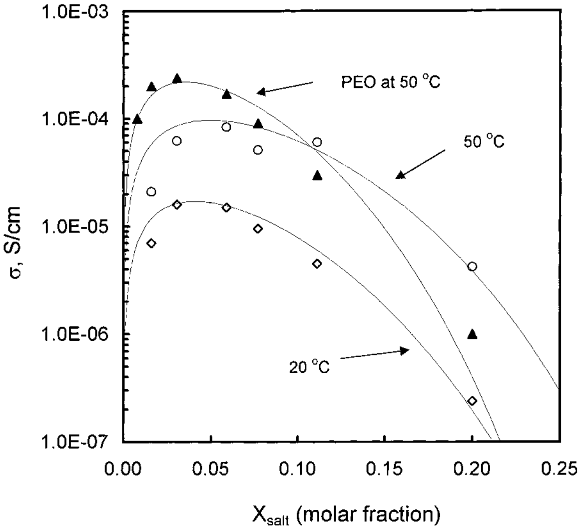

Figure 4. Ionic conductivity of $\mathbf{[C_3\pi C_3EO_4]_n}$ as a function of LiClO$_4$ concentration. The diamonds and circles are data taken at 20 and 50 °C, respectively. The solid triangles are data for a PEO sample with $M_n = 4400$ and are replotted from Vachon et al.[38] The lines are fits based on the equation $\sigma = A'x \exp[-K\sigma/(T - cx - T_0]$, as described in ref 42.

in Figure 5, normalizing the $\mathbf{[C_3\pi C_3EO_4]_n}$ conductivity data for PEO content shows that the peak conductivities of $\mathbf{[C_3\pi C_3EO_4]_n}$ and PEO occur at the same composition. Table 2 lists the peak conductivities for the other $(AB)_n$-based electrolytes.

Figure 6 shows the temperature-dependent ionic conductivity for a series of $(AB)_n$ polymers ($x = 4$, $y = 2, 3, 4$) at a constant O:Li ratio of 32. The three data sets form nearly parallel lines, with the conductivity increasing with y, the number of ethylene oxide units in the repeat unit. Identical slopes for the three data sets imply that the conductivity mechanism is the same for each sample. We note that the increase in conductivity in going from $y = 3$ to $y = 4$ is relatively large, but the conductivity increase from $y = 4$ to $y = 5$ is modest.

Discussion

Despite the fact that our $(AB)_n$ polymers have roughly a 50% PEO content, their polymer salt complexes have surprisingly good conductivities. By examining the relationship between the T_g and the lithium salt content, we can extract information about the polymer–lithium coordination chemistry in these alternating

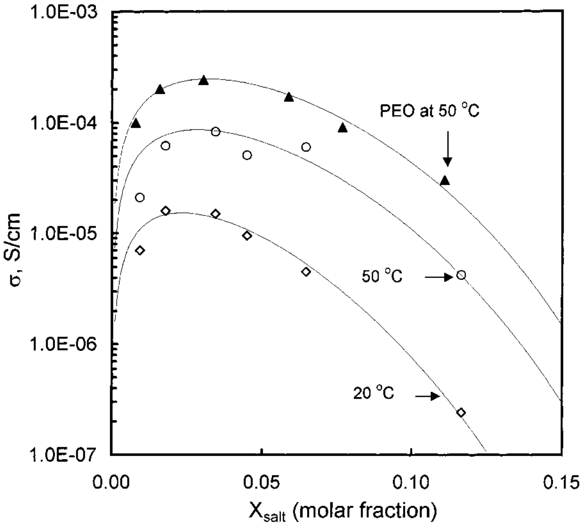

Figure 5. Ionic conductivity of $\mathbf{[C_3\pi C_3EO_4]_n}$ as a function of LiClO$_4$ concentration. The open diamonds and circles are the $\mathbf{[C_3\pi C_3EO_4]_n}$ data from Figure 4, normalized to reflect the lower polyether volume fraction (0.583) in the $\mathbf{[C_3\pi C_3EO_4]_n}$ copolymers.

Table 2. Conductivities of Polymer·LiClO$_4$ Salt Complexes

$-\!\!\left[(CH_2)_x\text{-}CH{=}CH\text{-}(CH_2)_x\text{-}O(CH_2CH_2O)_y\right]_n\!\!-$

polymer	$\sigma_{max} \times 10^5$ (S/cm) 20 °C	50 °C	100 °C
$[C_3\pi C_3EO_2]_n$	0.79 (12)[a]	3.5 (12)	17 (12)
$[C_3\pi C_3EO_3]_n$	2.0 (12)	7.9 (12)	41 (12)
$[C_3\pi C_3EO_4]_n$	1.6 (32)	8.3 (16)	b
$[C_4\pi C_4EO_3]_n$	1.0 (16)	3.9 (12)	23 (8)
$[C_4\pi C_4EO_4]_n$	2.1 (12)	10 (16)	57 (8)
$[C_4\pi C_4EO_5]_n$	2.3 (32)	12 (16)	49 (8)

[a] Numbers in parentheses are the O:Li ratio at the measured σ_{max}. [b] Not measured.

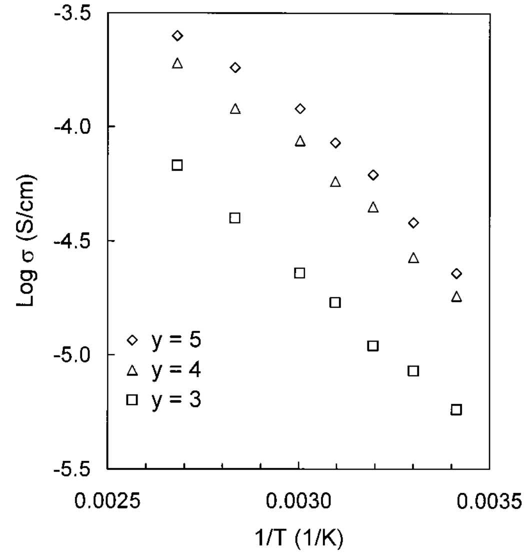

Figure 6. Temperature-dependent ionic conductivity of $\mathbf{[C_4\pi C_4EO_3]_n}$, $\mathbf{[C_4\pi C_4EO_4]_n}$, and $\mathbf{[C_4\pi C_4EO_5]_n}$. The O:Li ratio for each sample is 32.

block copolymers. It is well-known that the T_gs of polymers increase as the concentration of added salt increases. This effect is often interpreted in terms of the formation of "transient cross-links"[39] that involve lithium ions coordinated to oxygen atoms on adjacent polymer chains that cause an increase in the local viscosity of the polymer.

To interpret our data we constructed a simple model based on the Fox equation:[40]

$$\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}} \qquad (1)$$

an additive relationship useful for the prediction of the T_gs of AB random copolymers. In the Fox equation, T_{g1} and T_{g2} are the glass transition temperatures of pure polymers derived from the two monomers used to form the copolymer, and M_1 and M_2 are the mass fractions of the monomers in the copolymer. Since our DSC data show only single T_gs for the electrolytes, we believe these samples meet the basic requirement of the Fox equation, that the monomers be randomly distributed in an amorphous phase. To adapt the model to our situation, we treat each polymer electrolyte as a random copolymer composed of two different types of monomer units, those coordinated to lithium ions, and those not coordinated. We consider the $LiClO_4$ in the electrolyte as a perturbing influence that modifies the flexibility of the polymer chains, and not as an integral part of the monomer structure. Thus, the two types of monomers in the polymer electrolyte have identical structures and molecular weights, and simply correspond to the monomer repeat units of the polymer. To complete the copolymer model, we assign each monomer unit either the T_g of the pure polymer or the T_g that corresponds to electrolytes with an overall composition of one Li ion per monomer repeat unit. Both of these values are available from our DSC plots. For convenience, we rearranged the Fox equation as shown in eq 2 and plotted the data in terms of x_2, the mole fraction of monomer units bound to Li^+. Similarly, x_1 is defined as the ratio of the number of monomer repeat units not coordinated to Li^+ relative to the total number of monomer units in the sample. Since the molecular weights of the two types of monomer units are identical, expressing the composition in terms of mass fraction (M_2) or mole fraction (x_2) is equivalent.[41]

$$\frac{1}{T_g} = \frac{x_1}{T_{g1}} + \frac{x_2}{T_{g2}} \Rightarrow T_g = \left[\frac{1}{T_{g1}} + \left(\frac{1}{T_{g2}} - \frac{1}{T_{g1}}\right)x_2\right]^{-1} \qquad (2)$$

Shown in Figure 7 are the experimental results for $\mathbf{[C_4\pi C_4EO_5]_n}$ and $\mathbf{[C_4\pi C_4EO_4]_n}$ along with the T_gs calculated using the Fox equation. The fit is excellent over the entire range of salt concentrations studied. The parameters used in the fit, $T_{g1} = -77$ and $T_{g2} = -38$ °C, match well the experimentally determined values for both polymers, −77 °C for the pristine polymers and −31 °C for samples with an O:Li ratio of 4. That both sets of data can be fit using the same parameters is a good indication of the validity of our main assumption, that the polymer−salt interaction in these materials can be described as a single monomer repeat unit coordinated to a single ion. The 1:1 relationship between monomer units and ions implies that the coordination geometry around the Li^+ cation must be similar for both samples, and as shown at the left in Figure 8, we envision a single monomer unit forming a pocket similar to that of a crown ether.

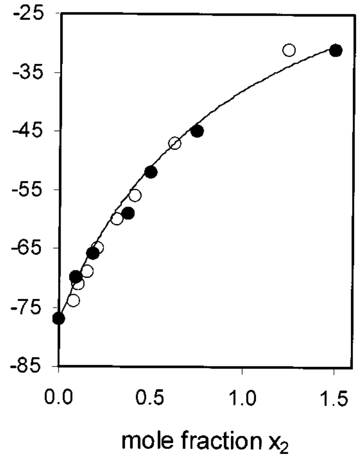

Figure 7. Observed glass transition temperatures for $\mathbf{[C_4\pi C_4EO_5]_n}\cdot LiClO_4$ (filled circles) and $\mathbf{[C_4\pi C_4EO_4]_n}\cdot LiClO_4$ complexes (open circles). The line represents the calculated values obtained from the Fox equation. Parameters: $T_{g1} = -77$ °C; $T_{g2} = -38$ °C.

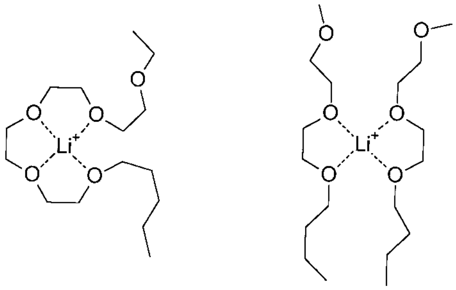

Figure 8. Schematic diagram showing Li^+ complexation to a single monomer unit (left), and complexation involving two adjacent monomer units (right).

For $\mathbf{[C_3\pi C_3EO_2]_n}$ we find that parameters that fit the $\mathbf{[C_4\pi C_4EO_4]_n}$ and $\mathbf{[C_4\pi C_4EO_5]_n}$ data fail to give a reasonable fit to the $\mathbf{[C_3\pi C_3EO_2]_n}$ data (Figure 9). However, if we assume that each ion coordinates to two monomer units in $\mathbf{[C_3\pi C_3EO_2]_n}$, our calculated and experimental data agree. We believe that the ethylene oxide segments in $\mathbf{[C_3\pi C_3EO_2]_n}$ are too short (two ethylene oxide units, three oxygen atoms) to support the coordination geometry found for $\mathbf{[C_4\pi C_4EO_5]_n}$ and $\mathbf{[C_4\pi C_4EO_4]_n}$ and complexation with adjacent chains (Figure 8, at right) is required in order to satisfy the coordination requirements of Li^+. Apparently $\mathbf{[C_4\pi C_4EO_3]_n}$ with three ethylene oxide units represents an intermediate case. As shown in Figure 10, T_g values calculated for a 1:1 monmer:ion stoichiometry fit the experimental data at low x_2 values, while the data for high salt concentrations approach the T_gs calculated for

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[40] Sperling, L. H. *Introduction to Physical Polymer Science*, 2nd ed.; John Wiley & Sons: New York, 1992.

[41] Obviously the model as presented is valid for polymer:salt compositions up to 1:1, or one Li^+ ion per monomer unit. Samples a with higher Li^+ contents are possible, but to treat these samples, eq 1 must be used and the composition must be expressed as the mass fraction.

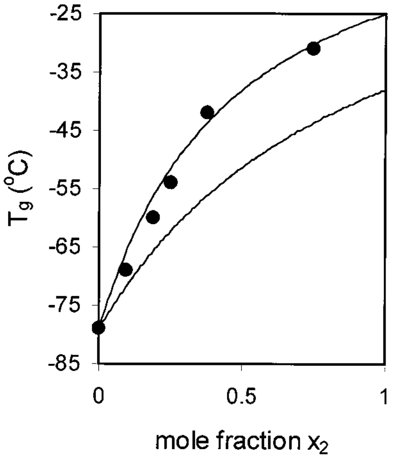

Figure 9. Observed glass transition temperatures for $[C_3\pi\text{-}C_3EO_2]_n\cdot LiClO_4$ complexes. The lines represents the calculated values obtained from the Fox equation assuming 1:1 (bottom line) and 1:2 (top line) stoichiometries for ion:monomer complexation. Parameters: $T_{g1} = -79$ °C; $T_{g2} = -38$ °C.

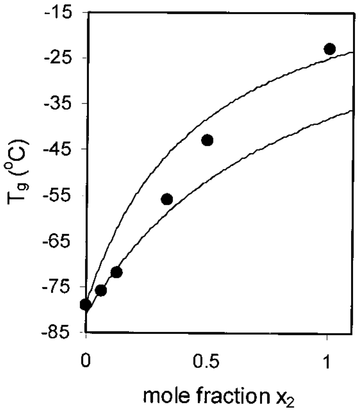

Figure 10. Observed glass transition temperatures for $[C_4\pi C_4EO_3]_n\cdot LiClO_4$ complexes (filled circles). The lines represents the calculated values obtained from the Fox equation assuming 1:1 (bottom line) and 1:2 (top line) stoichiometries for ion:monomer complexation. Parameters: $T_{g1} = -81$ °C; $T_{g2} = -38$ °C.

a 2:1 stoichiometry. The reason for the apparent transition from single- chain coordination to a geometry involving more than one chain in this sample is unclear.

Changes in the coordination environment should be manifest in the conductivity data. The ionic conductivity can be modeled as $\sigma = nq\mu$, where n is the number of charge carriers, q is the charge of the carrier, and μ is its mobility. The mobility term contains the details of conductivity mechanism. Because ionic transport in polymer electrolyte systems is believed to follow liquid-like mechanisms, the VTF (eq 3) and similar equations are commonly used to interpret conductivity data.[42]

$$\sigma = AT^{1/2}\exp[-E_a/R(T - T_0)] \tag{3}$$

Figure 6 shows that Arrhenius plots of the conductivity data for the $(AB)_n$ polymers yield a series of nearly parallel lines, implying that the same conduction mechanism holds for each polymer electrolyte. The vertical displacement of the curves can be traced to changes in the $AT^{1/2}$ prefactor in the VTF equation, which in turn is related to n and q of the simple conductivity model. We note that the high-temperature data for $[C_4\pi C_4EO_4]_n$ and $[C_4\pi C_4EO_5]_n$ show some curvature. We believe the nonlinearity results from the differences in the value of T_0 appropriate for each sample. Since T_0 roughly corresponds to T_g, decreases in the sample T_g lead to increases in the value of $(T-T_0)$ and increased curvature. The T_gs for the samples shown in Figure 6 decrease from $[C_4\pi C_4EO_5]_n$ to $[C_4\pi C_4EO_4]_n$ to $[C_4\pi\text{-}C_4EO_3]_n$.

In the absence of ion clustering, the charge of Li^+ is constant and the differences in electrolyte conductivity are related to the number of charge carriers. To understand the conductivity in these materials, it helps to think in terms of the number of coordination sites available per unit volume to support carrier hopping. Thus the slight negative displacement of the $[C_4\pi\text{-}C_4EO_4]_n$ data relative to those from $[C_4\pi C_4EO_5]_n$ can be ascribed to the lower volume fraction (0.58 vs 0.63) of sites in $[C_4\pi C_4EO_4]_n$. As discussed above, our modeling of the T_gs for these electrolytes points to an increase in the monomer:Li^+ stoichiometry from 1:1 ($[C_4\pi\text{-}C_4EO_4]_n$, $[C_4\pi C_4EO_5]_n$) to 2:1 ($[C_3\pi C_3EO_2]_n$). Thus the number of available sites decreases from one per monomer unit to one-half per monomer as the length of the PEO segments decrease. At the same time, the PEO volume fraction decreases further. Thus the change in coordination geometry is the dominant factor in the conductivity decline, while the decrease in PEO volume fraction makes a smaller contribution.

Conclusions

Polymers with the generic formula $-[(CH_2)_xCH{=}CH\text{-}(CH_2)_xO(CH_2CH_2O)_y]_n-$ ($[C_x\pi C_xEO_y]_n$) were prepared by metathesis polymerization of α,ω-dienes that contain a poly(ethylene oxide) core. The polymers are tacky, adhere well to glass and metal surfaces, and have glass transition temperatures between -70 and -80 °C. Polymers with short block lengths ($x = 3$, $y = 2$; $x = 3$, $y = 3$) are amorphous at all temperatures, while all other polymers studied crystallize and melt below room temperature. As $LiClO_4$ is added to the polymers the crystallinity of the polymer steadily decreases and all samples with O:Li ratios $<$ 32 are amorphous. The T_gs of the materials can be fit by a simple model based on the Fox equation, and an analysis of the results indicates that the Li^+:monomer repeat unit stoichiometry is 1:1 for polymers with long block lengths and decreases to 1:2 for polymers with short PEO segments. The conductivities of the electrolytes generally range from 1 to 2 $\times 10^{-5}$ S/cm at 20 °C, rising to $1-5 \times 10^{-4}$ S/cm at 100 °C.

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