Effect of Counter Ion Placement on Conductivity in Single-Ion Conducting Block Copolymer Electrolytes

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Single-ion conducting block copolymer electrolytes were prepared in which counter ions were tethered to the polymer backbone to achieve a lithium transference number of unity. Through tailored anionic synthesis, the influence of counter ion placement on conductivity was investigated. Incorporating the anions outside the ion-conducting (poly(ethylene oxide)-based) block, such as in poly[(lauryl methacrylate)-block-poly(lithium methacrylate)]-block-poly[oxyethylene]x methacrylate], known as PLMA-b-PLMA-b-POEM, and P(LiMA-r-LiMA)-b-POEM, caused lithium ions to dissociate from the carboxylate counter ions upon microphase separation of the POEM and PLMA blocks, yielding conductivities of 10−1 S/cm at 70°C. In contrast, incorporating anions into the conducting block, as in PLMA-b-PLMA-r-POEM, rendered the majority of lithium ions immobile, resulting in conductivities one to two orders of magnitude lower over the range of temperatures studied for equivalent stoichiometries.

Converting the carboxylate anion to one that effectively delocalized charge through complexation with the Lewis acid BF3 raised the conductivity of the latter system to values comparable to those of the other electrolyte architectures. Ion dissociation could therefore be equivalently achieved by using a low charge density counter ion (COOBF3)− or by spatially isolating the counter ion from the ion-conducting domains by microphase separation.

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Experimental

Anionic methods were used to prepare single-ion conducting BCEs containing lithium methacrylate (LiMA), lauryl methacrylate (LMA) and (oxyethylene)x methacrylate (OEM) in different molecular architectures. All reagents used in this study were purchased from Aldrich. Tetrahydrofuran (THF) was rigorously purified by refluxing over sodium/benzophenone for 48 h, and then distilled in a nitrogen atmosphere just prior to use. Both n-Butyllithium (n-BuLi), trimethylsilylchloride [([CH3]3Si)Cl], sodium iodide (NaI), chloroform, acetonitrile, and methanol were used as received. 1,1-Diphenylethylene (DPE) was vacuum distilled in the presence of n-ButLi (3 mol %). Lithium chloride (LiCl) was dried under vacuum at 200°C for 48 h.

The anionic block copolymerization was carried out by sequential addition of monomers to a sealed glass reactor fitted with a silicone rubber septa. LiCl (5 times excess to initiator), DPE (1.2 times...
excess to initiator), and THF were introduced into the reactor and submitted to several nitrogen/vacuum pump-purge cycles. After cooling to −78°C, a few drops of s-BuLi were added via syringe until the solution became pale orange. The calculated amount of s-BuLi was then introduced and stirred for 30 min. The purified first monomer was then added to the initiator solution, prompting the solution to change color from red to pale yellow. An aliquot of monomer was then added to the initiator solution, prompting the purification of the first monomer, and the solution was allowed to stir for 3 h. For the triblock copolymers, these procedures were repeated for the addition of the third block. The polymerization was then terminated with methanol, and the solution was poured into a large excess of hexane to precipitate the polymer. To remove residual LiCl, the polymer was dissolved in benzene and passed through an alumina column, then freeze-dried for 8 h. The Mn values were determined by proton nuclear magnetic resonance (1H NMR, Bruker DPX model 1260 frequency response analyzer, Solartron Analytical, Houston, TX) controlled by a personal computer running commercialized software (Z60, Scribner Associates, Inc., Southern Pines, NC). The test fixture consisted of two blocking electrodes made of stainless steel and attached to a micrometer that measured the electrode separation and, hence, the thickness of the polymer specimen, which was kept under an atmosphere of flowing argon gas.

Lithium symmetric cells fitted with the polymer electrolytes (300-500 μm thick, −0.1 cm² area) were used to obtain a measure of the lithium transference number. The electrodes were active to lithium ions but blocked the anions; upon application of a stepped potential, the initial current (I₀) reflected both cation and counter ion contributions, whereas the long-term, steady-state value (Iₘ) arose solely from lithium ion motion. The transference number was then taken to be Iₘ/I₀. This simplified method does not take into account the concentration dependence of the lithium diffusion coefficient, but it does correct for any changes in the IR drop across electrode surface films (either due to a variation in current or in film thickness during the course of the test²⁴). However, these added complications have no effect if the transference number is experimentally found to be unity; a constant current response obviates the need for IR corrections and also implies that concentration gradients are absent in the electrolyte. Transference number tests were performed at room temperature.

The electrochemical stability of the materials was investigated by cyclic voltammetry performed at room temperature. The electrolyte was pressed between an oversized counter electrode of lithium and a 0.08 cm² working electrode of platinum to a film thickness of approximately 200 μm. Using a Solartron 1286 electrochemical interface (Solartron Analytical, Houston, TX) controlled by a personal computer running CorrWare (Scribner Associates, Inc., Southern Pines, NC), the potential was scanned from +2.5 to +5.0 V at a sweep rate of 25 mV s⁻¹.

Table 1. Molecular characteristics of block copolymer precursors.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Molecular weight (g/mol)</th>
<th>Polydispersity (M₉/M₈)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLMA-b-PtBMA-b-POEM</td>
<td>28:11:61</td>
<td>30:35:35</td>
</tr>
<tr>
<td>PLMA-b-PtBMA-b-POEM</td>
<td>18:05:77</td>
<td>24:20:56</td>
</tr>
<tr>
<td>PLMA-r-PtBMA-b-POEM</td>
<td>28:10:62</td>
<td>31:33:36</td>
</tr>
<tr>
<td>PLMA-r-PtBMA-b-POEM</td>
<td>11:06:83</td>
<td>15:24:61</td>
</tr>
<tr>
<td>PLMA-b-PtBMA-r-OEM</td>
<td>31:09:60</td>
<td>34:30:36</td>
</tr>
</tbody>
</table>

Atomic force microscopy (AFM) was performed on a Digital Instruments (Santa Barbara, CA) Nanoscope IIIa scanning probe microscope with a TAP300 silicon cantilever (Nano Devices) having a spring constant of ~40 N/m. A film ~200 nm thick of PLMA-r-LiMA-b-POEM was spin-coated from the THF solution onto a cleaned Si substrate. A phase image of the BCE film was recorded in tapping mode.

Fourier transform infrared (FTIR) spectra were measured using a Magna-IR 860 spectrometer (Thermo-Nicolet) with an 80° specular reflectance accessory. Samples were solvent cast onto silicon substrates and placed under vacuum overnight to remove moisture.

Differential scanning calorimetry (DSC) measurements were carried out on a TA Instruments Q1000 at a heating rate of 20°C/min. Samples were solution cast into standard aluminum pans. The samples were thermally cycled until no sign of residual moisture was observed. Glass transition values are reported from the last heating scan.

Electrical conductivities were determined by impedance spectroscopy using a waveform generator/response analyzer (Solartron model 1260 frequency response analyzer, Solartron Analytical, Houston, TX) controlled by a personal computer running commercially available software (Z60, Scribner Associates, Inc., Southern Pines, NC). The test fixture consisted of two blocking electrodes made of stainless steel and attached to a micrometer that measured the electrode separation and, hence, the thickness of the polymer specimen, which was kept under an atmosphere of flowing argon gas.

Results and Discussion

The molecular weight and compositional characteristics of the precursor block copolymers synthesized for this study are presented.
of the tBMA component and subsequent lithiation produced single first block from impurities in the OEM macromonomer. Hydrolysis broad polydispersities mer products ranged from 28,900 to 83,800 g/mol, with somewhat controlled by the feed ratio. Molecular weights of the block copolymerizations were almost quantitative based on gravimetric analysis; addition of LMA, tBMA, and OEM. In all experiments, monomerization of the triblock materials was carried out by sequential addition of LMA, tBMA, and OEM. 20,21 Evidence for microphase separation of the single-ion conducting BCEs was obtained from SANS, AFM, and DSC studies. SANS data from PLMA-b-LiMA-b-POEM, PLMA-r-LiMA)-b-POEM, and PLMA-b-P(LiMA-r-OEM) systems, each with 1:1:1 ratio LMA:LiMA:OEM, are shown in Fig. 1. For the triblock (PLMA-b-PLiMa-b-POEM), an intense first-order reflection is observed at a wavevector $q_1 = 0.0277 \text{ Å}^{-1}$, indicating that this material is ordered (microphase separated), with a characteristic period of $\sim 22.7$ nm.

Peaks are also observed for the diblock materials, but they are less intense and shifted to lower wavevectors. The latter finding is consistent with the lower scattering contrast between the blocks. Observation of a peak at wavevector $q_2 = 0.022 \text{ Å}^{-1} (d = 28.5 \text{ nm})$ is thus good evidence of block demixing in this system. Further support for this conclusion was obtained from AFM investigation of a P(LMA-r-LiMA)-b-POEM (1:1:1) block copolymer film deposited on silicon. Figure 2 shows a phase image of the film surface. The contrast in this case arises from differences in stiffness exhibited across the surface. 23,26 Two distinct phases are seen with a characteristic periodicity of $\sim 25$ nm, which is smaller than, but still consistent with, the value determined by SANS ($\sim 28.5$ nm). In this image, the light phase is interpreted to be the stiffer minority P(LMA-r-LiMA) block domains, whereas the majority POEM phase forms an interconnected network. The larger light domains observed likely contain P(LMA-r-LiMA) copolymer impurities generated by partial termination of this block during the living synthesis. 27 Their inclusion in the block domains would shift the peak of the SANS data to a lower wavevector, accounting for the discrepancy between periodicities determined by SANS and AFM for this system.

DSC was performed on the three (1:1:1) molar ratio single-ion BCEs in the temperature range of $-150$ to $+150^\circ\text{C}$. For the triblock system, two distinct $T_g$ values were observed, at $-53$ and $-20^\circ\text{C}$, thought to correspond to the PLMA and POEM phases, respectively. Thermal signatures for PLiMA should fall outside the temperature range of investigation. 28 The $T_g$ of the POEM block domain ($-20^\circ\text{C}$) is higher than that of POEM homopolymer ($T_g = -60^\circ\text{C}$), a first indication that Li$^+$ from the neighboring PLMA block enters the POEM domains. The DSC trace for PLMA-b-P(LiMA-r-OEM) similarly reveals two $T_g$ values at $-58$ and $-11^\circ\text{C}$, indicative of microphase separation. The P(LMA-r-LiMA)-b-POEM system, by contrast, shows only a single $T_g$ at $-12^\circ\text{C}$. As both SANS and AFM data on this material strongly indicate a microphase-separated structure, the single glass transition may be interpreted as comparable shifts in $T_g$ of the PLMA and POEM domains due to the incorporation of LiMA in the PLMA block, again implying Li$^+$ migration into adjacent POEM domains.

To verify the single-ion nature of the electrolytes, transference number measurements were made in lithium symmetric cells. Figure 3 shows the current response to the application of a stepped potential to a cell fitted with the PLMA-b-PLiMA-b-POEM (1:1:1) electrolyte. The current and voltage waveforms are completely in phase.
with no evident polarization. The slight linear decay in the current can be ascribed to the formation and growth of a passivating film on the lithium electrodes; when the magnitude of the applied potential was abruptly reduced to zero, no current behavior akin to a discharging capacitor was observed. Therefore, the anions were effectively immobile over the time frame of the experiment. Longer stepped-potential tests demonstrated that anions did not migrate even over a period of several hours. All the electrolytes, including those complexed with BF$_3$, exhibited similar behavior in stepped-potential studies, indicating that for all materials the transference number was effectively unity.

Figure 5 shows that P(LMA-$r$-LiMA)-$b$-POEM exhibits excellent electrochemical stability at room temperature, with no sign of breakdown evident up to the 5 V limit. This result is consistent with findings published previously. All single-ion systems investigated (including those with BF$_3$ incorporation) possessed electrochemical stability comparable to that demonstrated in Fig. 5.

AC impedance spectroscopy was used to measure the ionic conductivity of the BCEs over a range of temperatures. Figure 6 displays results for the three systems incorporating equimolar ratios of LiMA, OEM, and LMA in three distinct architectures. Remarkably, the conductivities of the electrolytes with the anion bound outside of the ion-conducting POEM block, namely P(LMA-$r$-LiMA)-$b$-POEM and PLMA-$b$-PLiMA-$b$-POEM, are one to two orders of magnitude higher than that of the PLMA-$b$-P(LiMA-$r$-OEM) material over the range of temperatures studied, confirming preliminary findings by this laboratory. Conductivity data could be fit to the Vogel-Tammann-Fulcher (VTF) equation

$$\sigma = AT^{-1/2} \exp\left[-E_a/(kT - T_0)\right]$$

where the pre-exponential term $A$ is proportional to the number of charge carriers in the system, $kT$ is the thermal energy, and $T_0$ is a reference temperature roughly associated with the $T_g$ of the conducting polymer host. $T_0$ usually falls 25-50 K below $T_g$. The activation energy, $E_a$, scales inversely with the ease of motion of the charge carriers. VTF fits (Table III) showed that the variation in conductivity is attributable to vastly different numbers of mobile ions represented by $A$. While the activation energy appears to be lowest for PLMA-$b$-P(LiMA-$r$-OEM), any associated gain in conductivity is more than offset by the five order-of-magnitude difference in the pre-exponential $A$ parameter. The VTF fits support the hypothesis that ion dissociation is induced in the P(LMA-$r$-LiMA)-$b$-POEM and PLMA-$b$-PLiMA-$b$-POEM materials by microphase separation.
of incompatible POEM and PLMA blocks. Upon microphase separation, the anions become spatially isolated from the ion-conducting POEM component, being tethered to the chain backbone. However, the cations are free to migrate into the POEM domains. The recorded conductivities for these systems suggest that the solvating power of PEO for Li$^{+}$ is sufficient to overcome the electrostatic energy penalty to separate Li$^{+}$ and COO$^{-}$ into adjacent nano-domains.

Further evidence to this effect is shown in Fig. 7, which compares the FTIR spectra for the P(LMA-$r$-LiMA)-b-POEM and PLMA-b-(PLMA-$r$-OEM) systems. The asymmetric stretching vibration of the carboxylate ion is observed at $-1600$ cm$^{-1}$ when LiMA is incorporated in the POEM block, as compared to $-1650$ cm$^{-1}$ when incorporated in the PLMA block. This shift to higher frequency can be linked to an enhanced dissociation of Li$^{+}$ and COO$^{-}$. In alkali metal methacrylate homopolymers, this vibration has been reported at $-1560$ cm$^{-1}$. It has further been demonstrated that adding low molecular weight polyethylene glycol (PEG) to random copolymers of methyl methacrylate and LiMA, P(MMA-$r$-LiMA), results in a shift of the COO$^{-}$ stretch to higher wavenumbers due to ion-dipole interactions between the lithium cations and the ether groups of PEG. In the P(LMA-$r$-LiMA)-b-POEM system investigated here, this shift becomes more pronounced, consistent with increased dissociation of Li$^{+}$ and COO$^{-}$, presumably due to Li$^{+}$ migration into the POEM domains.

A more traditional approach to reduce ion pairing in single-ion conducting polymer electrolytes has been to decrease anion charge density, for instance, through the incorporation of a suitable Lewis acid. For example, BF$_3$ has been shown to strongly associate with carboxylate anions, reducing the effective anion charge density and thus ion pairing interactions. When BF$_3$ was added to the PLMA-b-P(OEM-$r$-LiMA) (1:1:1) electrolyte, the conductivity of this material was raised to the level of the other two 1:1:1 systems. The FTIR spectrum of the BF$_3$-complexed material (Fig. 7) shows a corresponding shift of the asymmetric carboxylate stretch to 1657 cm$^{-1}$, comparable to the peak position found for P(LMA-$r$-LiMA)-b-POEM for this vibration. These findings suggest that BF$_3$ incorporation induces ion dissociation with effectiveness similar to counter ion isolation. Interestingly, when BF$_3$ was added to the P(LMA-$r$-LiMA)-b-POEM and PLMA-b-PLMA-b-POEM (1:1:1) electrolytes, no change in conductivity was observed (Fig. 8). These results support the notion that ion dissociation is already substantially achieved in these systems by the spatial isolation of counter ions resulting from block demixing.

Table III. VTF fit parameters for the single-ion BCE materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$A$ (SK$^{10}$ cm$^{-1}$)</th>
<th>$E_{i}$ (eV)</th>
<th>$T_{o}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P(LMA-$r$-LiMA)-b-POEM</td>
<td>4.52</td>
<td>0.121</td>
<td>206.2</td>
</tr>
<tr>
<td>PLMA-b-PLMA-b-POEM</td>
<td>4.82</td>
<td>0.122</td>
<td>205.5</td>
</tr>
<tr>
<td>PLMA-b-PLMA-$r$-OEM</td>
<td>$7.5 \times 10^{-5}$</td>
<td>0.026</td>
<td>250.2</td>
</tr>
</tbody>
</table>

Although conductivities for the P(LMA-$r$-LiMA)-b-POEM and PLMA-b-PLMA-b-POEM (1:1:1) systems were an order of magnitude or more above that found for PLMA-b-P(LMA-$r$-OEM) (1:1:1), they remain too low for practical application. For these systems, the relatively high EO:Li ratio of $\sim 9:1$ limits the number of unoccupied sites available for Li$^{+}$ diffusion, raises the $T_{g}$ of the polymer, and also possibly induces ion clustering. By diluting the number of charges through a reduction in LiMA content to EO:Li ratios above 20:1, the room temperature conductivity can be appreciably enhanced for both architectures, as shown in Fig. 9. However,
note that having a larger number of charge carriers becomes advantageous at high temperatures, indicating that the optimal architecture for a single-ion conductor depends on the temperature range of the application.

Conclusions

In this work, microphase separation of incompatible PLMA and POEM blocks of single-ion conducting BCEs provided a mechanism to explore the effect of counter ion placement on Li$^+$ conductivity. When the carboxylate anions were spatially separated from the ion-conducting POEM domains, conductivities were 1 to 2 orders of magnitude higher than for stoichiometrically equivalent materials in which the counter ions resided within the POEM domains. From VTF fits and DSC and FTIR studies, the higher conductivities could be linked to enhanced ion dissociation, apparently due to the migration of Li$^+$ into POEM. The results imply that the energy gained by Li$^+$ solvation in POEM is sufficient to outweigh the electrostatic energy penalty for nanoscale separation of Li$^+$ from COO$^-$, by rough approximation

$$E_{Li^+\text{solv}} \approx \frac{e^2}{4\pi \varepsilon_0 r_{Li-O}}$$  \hspace{1cm} [2]$$

where $E_{Li^+\text{solv}}$ is the Li$^+$ solvation energy, $\varepsilon$ is the dielectric constant of PLMA-$r$-LiMA, and $r_{Li-O}$ is the distance between Li$^+$ and O$^-$ in the Li$^+$-COO$^-$ ion pair. Based on the crystal structure of LiMA, the value of $r_{Li-O}$ for associated ions can be estimated as 0.20 nm, while $\varepsilon$ can be conservatively estimated as 2.3 (the value for polyethylene). The required Li$^+$ solvation energy to achieve ion separation can thus be crudely approximated as $\sim 300$ kJ/mol. Recent $ab\ initio$ calculations for Li$^+$-PEO complexes gave Li$^+$ binding energies in the range of 500-600 kJ/mol, depending on EO coordination number (4-6), suggesting that Li$^+$ migration into the POEM domains from PLMA is energetically feasible. This work thus discloses a potential new strategy for enhancing conductivity in single-ion conducting polymer electrolytes by spatial isolation of the counter ion outside of the ion-conducting PEO-based domain.

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