



Nanostructured Block Copolymer Dry Electrolyte

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We report on the synthesis and characterization of a solid-state polymer electrolyte with enhanced lithium transport based on a self-assembled diblock copolymer. The diblock copolymer consists of a poly(ethylene oxide) (PEO) block and a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi). Lithium bis(oxalato)borate, LiBC₄O₈ (LiBOB) was used as salt in the dry electrolyte. Impedance and temperature studies were carried out to characterize the conductivity performance of the electrolyte. The diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] with added LiBOB (in the molar ratio ethylene oxide:LiBOB = 3:1) was used to form flexible translucent films, which exhibited an average ionic conductivity value of $1.26 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature (21 °C). Transmission electron microscopy was performed to characterize the morphology of the polymer, and differential scanning calorimetry was carried out to study the thermal properties of the electrolyte.

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In recent years, interest in polymeric batteries has increased dramatically. Current configurations have a liquid or gel electrolyte along with a separator between the anode and cathode. This leads to problems with electrolyte loss and decreased performance over time. The highly reactive nature of such electrolytes necessitates the use of protective enclosures, which add to the size and bulk of the battery. The goal of this study is to investigate nanoscale polymer electrolyte flexible thin films based on the self-assembly of block copolymers. Polymer electrolytes are more compliant than conventional inorganic glass or ceramic electrolytes. Lightweight, shape-conforming, polymer electrolyte-based battery systems, could find widespread application as energy sources in miniature medical devices, such as pacemakers, wireless endoscopes, implantable pumps, treatment probes, and untethered robotic mobile manipulators.

The complex forming capability of poly(ethylene oxide) (PEO) with alkali metal salts, introduced by Fenton et al.¹ has been the starting point for an abundance of published work on polymer electrolytes for use in batteries. A semicrystalline polymer, PEO, has been a focal component in the design of numerous dry solvent-free electrolytes involving: blends,² block copolymers,³⁻⁶ branched networks,⁷ ceramic fillers,⁸⁻¹¹ room-temperature ionic liquids,^{12,13} and specialized salts,^{14,15} to name a few. It is important to carefully tailor the polymer electrolyte matrix to attain appreciable levels of conductivity in a solid-state medium. In this work, we have investigated a nanostructured thin-film battery electrolyte based on a diblock copolymer composed of a PEO block and a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi). The diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] (Fig. 1) with lithium bis(oxalato)borate, LiBC₄O₈ (LiBOB) as the added lithium salt was used to create the dry, solid-state electrolyte films.

We selected a PEO-based diblock copolymer because of its ability to solvate alkali metal salts. The second block, which consists of a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi), was chosen for its ability to incorporate lithium ions within the microphase separated spherical domains of the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] (Fig. 2), creating a secondary lithium source. The primary focus of this work is the electrolyte performance at room temperature, and the experimental results display the role of polymer and salt selection toward this objective.

Experimental

The PEO-*b*-PMMA block copolymer with an average molecular weight 3000:500 of PEO to PMMA and polydispersity index of 1.16

was purchased from Polymer Source Inc. (Canada). LiBOB was obtained from Chemetall GmbH (Germany). All other chemicals and solvents were purchased from Aldrich and used as is.

Hydrolysis was carried out using lithium hydroxide monohydrate (LiOH·H₂O) as the base. The block copolymer (PEO-*b*-PMMA) and LiOH·H₂O were dissolved in a solvent mixture with a molar ratio of 2:1 between LiOH·H₂O and the MMA units of the diblock copolymer. The solvent used was a 2:1 mixture of anhydrous 1,4-dioxane and anhydrous methanol. The hydrolysis process was carried out at 85 °C for 20 h. As a result of the process, the PMMA block was hydrolyzed into a random copolymer of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi). This procedure was adapted from previous work reported by Mikes and Pecka.¹⁶ After the hydrolysis step, the solvent was removed under vacuum using a Schlenk line setup with a liquid nitrogen solvent vapor trap. This dried diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] was then stored in a Mbraun Labmaster 100 argon glove box for further use.

Solutions were prepared by adding varying concentrations of LiBOB salt to the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)]. The solvent used was anhydrous tetrahydrofuran (THF),

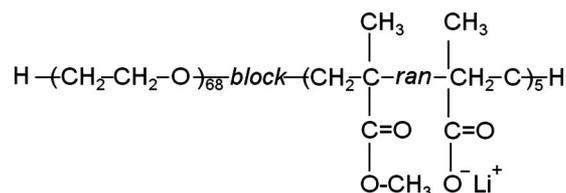


Figure 1. Chemical structure of self-assembled diblock copolymer.

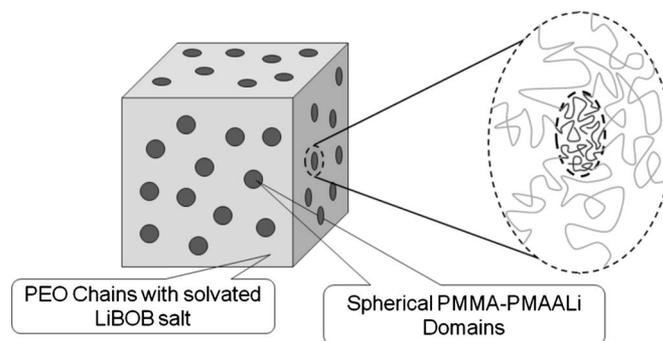


Figure 2. Diblock copolymer electrolyte morphology.

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which was degassed using multiple cycles of a freeze-pump-thaw method. These polymer solutions were then cast into Petri dishes containing molds of fluorinated ethylene propylene coated aluminum sheets. The drying process extended over several days resulting in 200–250 μm thick films. Circular sections of the polymer electrolyte films were cut for conductivity measurements and mounted between two 316 stainless steel blocking electrodes. A poly(tetra fluoroethylene)-based O-ring was placed between the two electrodes to secure the sample thickness and surface area. The test cell assembly was sealed, protecting it from oxygen and humidity, before removal from the glove box for impedance analysis. The ionic conductivity (σ) of the synthesized block copolymer electrolytes was determined from

$$\sigma = \frac{t}{RA} \quad [1]$$

where t , A , and R represent the thickness, surface area, and ionic resistance, respectively, of the electrolyte sample. Our assembled cell samples had a value of t/A of $\sim 0.242 \text{ cm}^{-1}$. The ionic resistance of the dry polymer electrolytes was obtained from impedance studies of the test cells using the Solartron 1287A/55B electrochemical system. The testing parameters were controlled by the associated CorrWare and ZPlot softwares, while the resulting data was analyzed by ZView.

The performance of the electrolyte was studied in the temperature range 0–70°C to characterize its temperature-dependent behavior. Test cells were placed in a waterproof setup, immersed in a temperature-controlled water bath, and allowed 3–4 h to equilibrate at every temperature stage before data collection.

Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Q100 calorimeter. Samples (~ 10 to 14 mg) of PEO and electrolyte films of diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] with added LiBOB salt were sealed in hermetic aluminum pans inside the argon-filled glove box. The PEO homopolymer samples studied were of molecular weights 3.5 k, similar to that of the block copolymer. The measurements were carried out under nitrogen flow at a heating rate of 2.00°C/min and modulation of $\pm 1.27^\circ\text{C}$ every 60 s, in the temperature range 40–120°C. Glass transition temperature (T_g) studies were carried out by melting the samples sealed within the hermetic aluminum pans at 130°C followed by quenching them in liquid nitrogen. The measurements were carried out under nitrogen flow at a heating rate of 5.00°C/min.

0.1% solutions of the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] were prepared in THF and cast on transmission electron microscopy (TEM) grids. The grids were placed in a THF-saturated dessicator to prolong the casting over a period of three days. No form of staining was used, with the image contrast coming from lithium. TEM was performed with a JOEL 2100F field emission scanning electron microscope operating at 100 kV.

Results and Discussion

Polymer selection and design is a critical consideration in the development of a solvent-free conductive electrolyte matrix. PEO has been the material of choice because of its ability to form stable complexes with lithium salts and due to its possession of a higher conductivity than any other group of solvating polymers in the absence of organic solvents. In order to suppress PEO crystallinity and to enhance its conductivity, a low-molecular-weight block copolymer was chosen, consisting of PEO as the first block and a random copolymer of poly(methyl methacrylate) and lithium salt of poly(methacrylic acid) (PMMA-*ran*-PMAALi) as the second block. The nanostructured thin-film battery electrolyte does not contain major proportions of nonconducting blocks that are frequently used to enhance the mechanical properties of the material, but do not contribute in any way to the ion transport of the conducting segments. This was also the rationale behind the selection of PMMA ($-\text{CO}_2\text{CH}_3$) in comparison to a diblock copolymer system containing lauryl ester

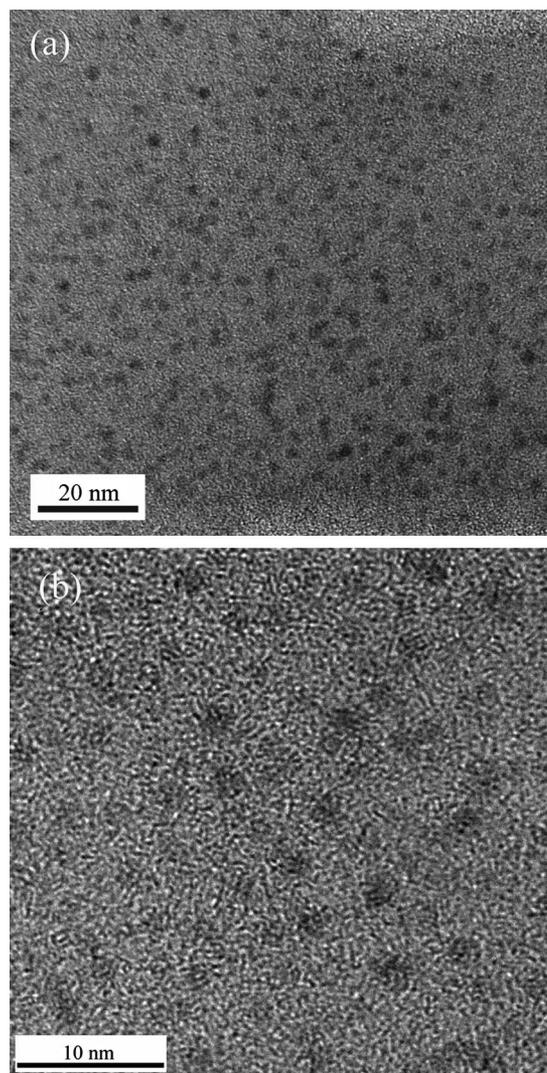


Figure 3. (a) TEM micrograph of PEO-*b*-(PMMA-*ran*-PMAALi) diblock copolymer and (b) higher magnification image showing lithium domains of ~ 2 nm in size.

($-\text{CO}_2\text{C}_{12}\text{H}_{25}$) groups.¹⁷ The longer nonoxygenated side chain of the lauryl ester would work better as a means to provide more free volume if used in a gel electrolyte system. For a dry electrolyte system as is the one in this work, the larger side chain, which contains only carbon and hydrogen atoms, would not aid in providing any additional conductive pathways for Li^+ transport.

It has been shown that PEO undergoes complexation with carboxylic acid groups.¹⁸ This complexation is driven by the proton-donating nature of poly(methacrylic acid) with PEO being a proton-acceptor. The complexation of PEO chains is a concern, as it would restrict the segmental motion that drives ion transport. In tailoring the electrolyte matrix, a very small fraction of the polymer contains lithium salt of carboxylic acid groups. In addition, the presence of ions from the added lithium salt, acts as an effective screening barrier to subdue the complexation. The low carboxylic acid group content ensures that the block copolymer's microphase separation is not disrupted, as confirmed by the TEM (Fig. 3). The images show lithium domains of approximate size 2 nm, templated by the diblock copolymer [PEO-*b*-(PMMA-*ran*-PMAALi)] morphology. Thus, the diblock copolymer acts as a polymer electrolyte, rather than a poly-electrolyte with ionomer-like ion cluster morphologies.

It is important to use the appropriate lithium salt concentration in order to obtain an optimum performance from the electrolyte. An

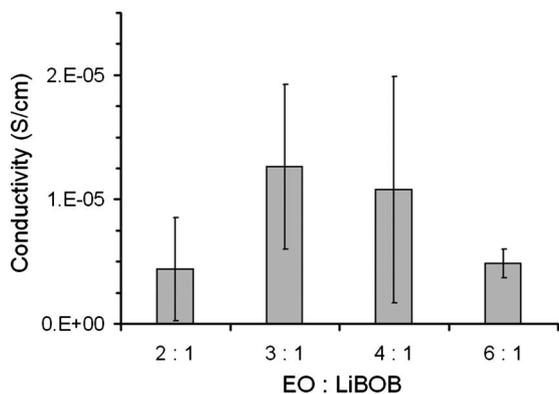


Figure 4. Salt optimization of PEO-*b*-(PMMA-*ran*-PMAALi) diblock copolymer at room temperature (21°C).

ideal electrolyte is a medium that is rich in charge carriers and provides for a rapid transport of charge carriers through it. Too little salt results in poor conductivity. Too much salt not only severely affects the mechanical properties of the polymer, thus negating its inherent advantages, but also results in decreased conductivity.¹⁹ We observed the same behavior with our LiBOB-doped diblock copolymer. Samples were prepared with different salt contents by varying the molar ratio between ethylene oxide (EO) units and LiBOB. Data were taken from a minimum of three different electrolyte test cells with polymers from different hydrolysis batches. A very similar trend in conductivity was observed across the batches, although statistical analysis shows no significant statistical difference between electrolytes containing EO:LiBOB = 3:1 and 4:1 because of their close compositional proximity. Results show that the salt concentration was optimized at EO:LiBOB = 3:1 (Fig. 4) for the best performance based on average conductivity obtained. This diblock copolymer electrolyte exhibited an average ionic conductivity value of $1.26 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature (21°C) as compared to $2.6 \times 10^{-6} \text{ S cm}^{-1}$ measured for a PEO homopolymer of similar molecular weight (3.5 k) and molar composition of LiBOB. The value obtained for the diblock copolymer electrolyte is nearly two orders of magnitude greater than that shown by traditional high molecular weight PEO homopolymer electrolytes, in the absence of ceramic fillers and similar additives.^{9,20}

The electrolyte membranes showed the expected rise in conductivity with temperature (Fig. 5). This is attributed to the increased segmental motion of the chains as PEO approaches its melting point. The optimized electrolyte sample achieved a conductivity of

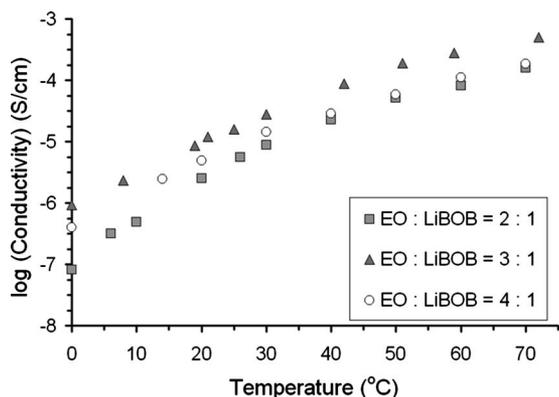


Figure 5. Temperature studies of PEO-*b*-(PMMA-*ran*-PMAALi) diblock copolymer.

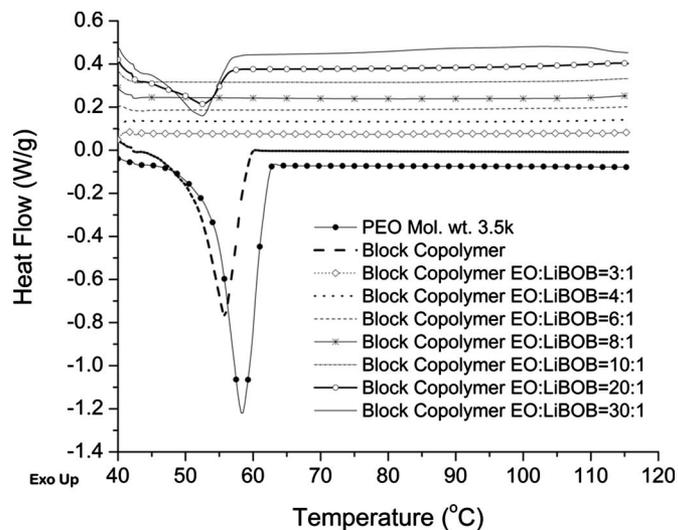


Figure 6. DSC scans of PEO-*b*-(PMMA-*ran*-PMAALi) diblock copolymer with different added compositions of LiBOB compared to native PEO.

$10^{-4} \text{ S cm}^{-1}$ as the sample temperature crossed 40°C. The temperature characterization was halted at 70°C, which is above the melting point of PEO.

The physical appearance of the diblock copolymer electrolyte [PEO-*b*-(PMMA-*ran*-PMAALi)] also differed with varying salt content. Polymer electrolyte films with high salt loading (EO:LiBOB = 2:1) and low salt loading (EO:LiBOB > 10:1) were brittle and opaque, whereas intermediate salt content films were flexible and translucent. The widely accepted view is that conduction of ions in polymer electrolytes occur almost predominantly in the amorphous phase due to the segmental motion of the polymer chain.¹⁹ The flexibility of polymer films is related to the segmental motion of the chains and hence is a characteristic that can be associated with the conductivity potential of the electrolyte. DSC was performed to compare the initial crystallinity content in the polymer electrolytes. Scans of normalized heat flow (in watts per gram) against temperature (in degrees Celsius) were obtained (Fig. 6). The pure block copolymer showed reduced crystallinity as compared to PEO of similar molecular weight. The plasticizing effect of LiBOB salt aided in suppressing the crystallinity of the polymer electrolyte. These materials exhibited a suppressed melting over a broad temperature range. Crystalline domains were again shown to appear in low salt content (EO:LiBOB > 20:1) samples, as the plasticizing presence of LiBOB was reduced. T_g studies were carried out for the diblock copolymer electrolyte [PEO-*b*-(PMMA-*ran*-PMAALi)] with (EO:LiBOB = 3:1) and without salt content and PEO homopolymer of similar molecular weight (3.5 k). No significant shift in T_g was observed between the samples with PEO and PMMA-*ran*-PMAALi blocks showing glass transition temperatures at $-25.9 \pm 1.5^\circ\text{C}$ and $103.5 \pm 1.4^\circ\text{C}$, respectively.

Conclusions

We designed a self-assembled diblock copolymer electrolyte that exhibits higher ion transport at room temperature compared to traditional solid polymer electrolytes. TEM showed structured domains of lithium, templated by the microphase separation of the block copolymer. The improved conductivity was attributed to reduction of crystallinity and introduction of secondary lithium domains in the conductive polymer matrix. The room-temperature conductivity was improved by an order of magnitude compared to similar molecular weight PEO homopolymers.

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