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Block Copolymer Electrolytes Synthesized by Atom Transfer Radical Polymerization for Solid-State, Thin-Film Lithium Batteries

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Block copolymer electrolytes of poly[(oxyethylene)₉ methacrylate]-*b*-poly(butyl methacrylate) (POEM-*b*-PBMA) (60:40 by mass) synthesized for the first time by atom transfer radical polymerization (ATRP) exhibited mechanical and electrical properties indistinguishable from those of materials made by the more difficult anionic polymerization method. ATRP offers distinct processing advantages as it is easily scalable and almost solvent-free. Solid-state, thin-film batteries comprised of a metallic lithium anode, a binder-free, additive-free, fully dense vanadium oxide cathode, and an electrolyte of ATRP-synthesized POEM-*b*-PBMA (60:40) doped with LiCF₃SO₃ demonstrate resistance to capacity fade during extended cycling at a discharge rate of C/2, and perform comparably to otherwise identical batteries operated with the liquid electrolyte 1 M LiPF₆ in ethylene carbonate:dimethyl carbonate (1:1 by mass).

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The ideal electrolyte material for a solid-state battery would have the ionic conductivity of a liquid, the mechanical properties of a solid, and the formability of a commodity thermoplastic. To satisfy these rigorous performance requirements researchers have explored the design of solid electrolytes from block copolymers,¹⁻¹¹ which are materials that consist of two chemically dissimilar polymers covalently bonded end-to-end. Under appropriate conditions, a net repulsion between the polymer blocks induces their local segregation, or microphase separation, into periodically spaced, nanoscale domains. When a lithium-salt-solvating polymer is chosen as one block component, continuous, nanoscopic, ion-conducting pathways can form. The ordered morphology meanwhile confers global mechanical rigidity to the material. Thus, by separating the length scales that govern electrical and mechanical performance, films with mechanical properties similar to those of a cross-linked rubber can be obtained without sacrificing the high local chain mobility required for Li⁺ conductivity. Because microphase separation is thermodynamically reversible with the addition of a common solvent, block copolymers can be readily processed by conventional polymer coating methods.¹

Block copolymers traditionally have been synthesized by living anionic polymerization, a laborious procedure that requires rigorous purification of all reagents and solvents and isolation from H₂O, O₂, and CO₂ during the reaction.¹² These strict requirements along with limitations in the monomer chemistries readily amenable to anionic routes have limited the industrial application of this technique and the number of block copolymers that are commercially available. As low manufacturing cost and availability are equally important attributes of any material to be deployed successfully in solid-state lithium batteries, the purpose of this study was to investigate the feasibility of producing block copolymer electrolytes by atom transfer radical polymerization (ATRP), a synthesis route that avoids many of the shortcomings of anionic polymerization.¹³⁻¹⁵ Most notably, ATRP requires little purification, is easily scalable, and is nearly solvent-free. The main disadvantage of ATRP is that the product contains vestiges of catalyst, which in this instance results in the presence of copper in the block copolymer. While extraction, ion exchange,¹⁶ and other techniques¹⁷ have been used to remove the copper from ATRP-prepared polymers, in this paper we show that the performance of as-prepared ATRP material in thin-film batteries

is comparable not only to that of purer material produced by anionic polymerization but also to that of conventional liquid electrolytes.

Experimental

Poly[(oxyethylene)₉ methacrylate]-*b*-poly(butyl methacrylate), POEM-*b*-PBMA, having a POEM:PBMA ratio of 60:40 by weight was synthesized by ATRP techniques for this study. The synthesis was performed in two steps. Initially, as-received butyl methacrylate monomer (Aldrich) was combined with the transition metal catalyst and ligand pair of copper(I) chloride and 1,1,4,7,10,10 hexamethyltriethylenetetramine (Aldrich). Fluctuations in the amount of the latter ingredients have been shown to have little impact on the outcome of the synthesis,¹⁵ but here 0.08 mol % of the hexaamine and 0.32 mol % of the copper chloride were used with respect to the monomer. The system was purged for 30 min with argon, and then the initiator, methyl-2-bromopropionate (Aldrich), was injected with a monomer:initiator ratio of 400:1 on a molar basis. The synthesis was conducted at 90°C. After the reaction, the polymer was dissolved in tetrahydrofuran (THF) and precipitated in methanol. The PBMA was then dissolved in a minimal amount of dimethylformamide and the polyethylene glycol methyl ether methacrylate [herein known as (oxyethylene)₉ methacrylate, Mw = 475 g/mol] macromonomer was added to the reactor. The (EO)₉ chains of the resulting POEM block are small enough to prevent crystallization but long enough to solvate a lithium salt like LiCF₃SO₃. Finally, the copper chloride and hexaamine were added as before, the system was purged, and the reaction was again carried out at 90°C. The resulting block copolymer was precipitated in petroleum ether. With ATRP the rate of the reaction is strongly dependent on both temperature and freshness of reagents. The above reactions took approximately 40 min each at 90°C and starting with new chemicals.

The molecular weight of the resulting polymer was characterized by gel permeation chromatography (GPC) using THF as a solvent. The POEM-*b*-PBMA (60:40) material had a molecular weight of 41.7 kg/mol referenced against polystyrene and a narrow polydispersity of 1.22. Small-angle neutron scattering (SANS) experiments were carried out at room temperature on the NG-7 30 m instrument of the Cold Neutron Research Facility at NIST to ascertain the block copolymer microstructure. Sample-to-detector distances of 1.3, 8.0, and 13.1 m with monochromated neutron wavelengths of 5 Å for the 1.3 and 8.0 m experiments and 10 Å for the 13.1 m experiment and a wavelength spread ($\Delta\lambda/\lambda$) of 0.15 were used to cover scattering wave vectors in the range of $0.002 < Q < 0.6 \text{ \AA}^{-1}$. A second POEM-*b*-PBMA (63:37) system of molecular weight 52.4 kg/mol was synthesized by anionic methods as described previously.¹

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To demonstrate the dimensional stability needed for solid-state battery applications, the dynamic properties of the copolymer were probed using a strain-controlled rheometer (ARES, Rheometrics). The rheometer was operated in the parallel-plate oscillatory shear mode with a 0.6 mm gap. The sample was molded on the 25 mm diam test fixture by pressing the material to the measurement gap width at 85°C. The measurements were performed at four different temperatures (85, 65, 45, and 25°C); the temperature was regulated to within $\pm 1^\circ\text{C}$ using a thermally controlled nitrogen purge. The frequency dependences of the dynamic storage and loss moduli (G' and G'' , respectively) were recorded for the frequency range from 250 to 0.1 rad/s at a relatively small strain amplitude of 1.5%. All the data documented were reproducible within an error limit of 5%.

The electrical conductivity was 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. The block copolymer was made an electrolyte by doping with LiCF_3SO_3 to obtain a $\text{Li}^+:\text{[EO]}$ ratio of 1:20.

Thin-film batteries were assembled to compare the performance of the ATRP-prepared material with that made by anionic synthesis and with a conventional liquid electrolyte. The test cell was comprised of a cathode of vanadium oxide on aluminum foil and an anode of lithium on a copper current collector. Vanadium oxide films were prepared by ion-assisted, electron-beam evaporation of vanadium metal in an atmosphere of controlled oxygen potential at a chamber temperature of 320°C. Following deposition, films were annealed at 250°C for 2 h. Oxide film thickness was measured by profilometry and determined to be $\sim 0.2 \mu\text{m}$. X-ray diffraction studies using $\text{Cu K}\alpha$ radiation (Rigaku RTP500RC) showed the oxide films to be amorphous. By Auger electron spectroscopy the vanadium concentration of the oxide films was measured as $39 \pm 2\%$ on an atomic basis, which puts the stoichiometry between V_2O_3 and V_2O_4 ; accordingly, we refer to the films simply as VO_x , where $1.5 < x < 2$. The electrolyte, measuring about 20 μm thick, consisted of the ATRP-prepared POEM-*b*-PBMA (60:40) doped with LiCF_3SO_3 ($[\text{EO}:\text{Li}^+] = 20:1$) and was formed by solution casting from anhydrous THF directly onto the lithium anode. Cycle testing was conducted at 25°C with a Maccor series 4000 automated test system. Voltage limits were set at 4.0 and 1.5 V with discharge and charge rates of $C/2$, where the $C/1$ rate is defined as a current density of 400 mA/g cathode mass. As controls, two other cells were constructed. One was fitted with an anionically prepared POEM-*b*-PBMA (63:37) electrolyte film of comparable thickness. The other was fitted with the liquid electrolyte, 1 M LiPF_6 in ethylene carbonate (EC): dimethyl carbonate (DMC) (1:1 by mass). The latter cell also used a separator of porous polypropylene (Celgard 2300, Celgard, Inc., Charlotte, NC).

Comparison between batteries is complicated by the variation in capacity of the thin-film VO_x electrodes from sample to sample. To obtain a more direct comparison between the ATRP-prepared electrolyte and the liquid electrolyte, a cell incorporating the solid electrolyte was constructed and run for 301 cycles. Upon completion, the battery was disassembled and the solid electrolyte was removed using THF. The salvaged anode and cathode were then used to construct a new cell, this time incorporating liquid electrolyte and a separator. The battery then was cycled using identical test conditions.

Results and Discussion

Block copolymers of POEM-*b*-PBMA prepared by ATRP exhibited electrical and structural characteristics comparable to the same material prepared by anionic polymerization.¹ Figure 1 shows that

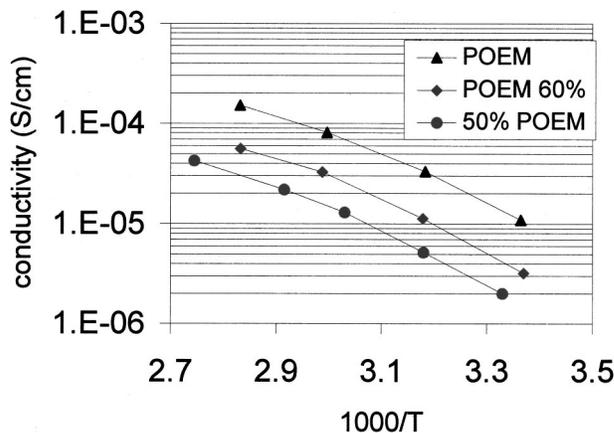


Figure 1. Electrical conductivities measured by impedance spectroscopy for POEM (\blacktriangle), ATRP-prepared POEM-*b*-PBMA (60:40) (\blacklozenge), and ATRP-prepared POEM-*b*-PBMA (50:50) (\bullet).

the temperature dependence of the electrical conductivity for the ATRP-prepared copolymer doped at 20:1 $\text{EO}:\text{Li}^+$ obeys the expected Vogel-Tammann-Fulcher relationship. Also shown in Fig. 1 are data for a POEM homopolymer (liquid over the entire temperature range) and a POEM-*b*-PBMA (50:50) block copolymer prepared by ATRP. It is evident that the conductivity of the block copolymer scales with the POEM fraction, as was observed for block copolymer electrolytes prepared from poly(lauryl methacrylate)-*b*-POEM polymerized by anionic routes.¹ The electrical conductivity of undoped (Li^+ free) POEM-*b*-PBMA (60:40) prepared by ATRP was also tested and was several orders of magnitude lower than that of the salt-doped electrolyte, indicating that residual copper from the ATRP catalyst does not contribute mobile charge carriers to any appreciable extent.

Previously it was demonstrated that the conductivity of POEM-based block copolymer electrolytes scales inversely with the glass transition of the secondary block component.¹ PBMA, with a $T_g \sim 30^\circ\text{C}$, is essentially immobile at room temperature, causing the room temperature conductivity of the POEM-*b*-PBMA block copolymer electrolyte (BCE) to fall below a value that may be conventionally considered suitable for battery applications ($\sigma \sim 3 \times 10^{-6} \text{ S/cm}$). While the conductivity can be enhanced through replacement of lithium triflate by a more conductive imide salt,¹⁸ incorporation of oligomeric PEO,¹ or an increase in the POEM block fraction, the true electrical performance requirements of a solid electrolyte depend strongly on the geometry of the active electrode, as addressed below.

The electrical conductivity measurements provide an indirect indication that the morphology of the block copolymer is microphase separated, as a copolymer in which the two block segments are intermixed would be expected to exhibit significantly lower conductivity.^{1,10} More direct evidence that the BCE is in the ordered state is observed in the SANS data in Fig. 2. A sharp reflection at $\sim 0.019 \text{ \AA}^{-1}$ indicates that the copolymer is microphase separated, with a characteristic period of 34 nm.

The microphase separation of POEM-*b*-PBMA into glassy and rubbery domains results in a material with excellent dimensional stability and rubbery mechanical properties. Figure 3 shows the storage (G') and loss (G'') moduli for the ATRP-prepared POEM-*b*-PBMA (60:40) as functions of reduced frequency, illustrating the solid-like nature of the material. For simplicity, the storage moduli, taken at four different temperatures (85, 65, 45, and 25°C), were brought to overlap using the method known as time-temperature superposition, and the loss moduli were shifted correspondingly. The values used for the horizontal shift (a_i) were 0.00100, 0.0239, 1, and 165 for 85, 65, 45, and 25°C, respectively. Below a scaled

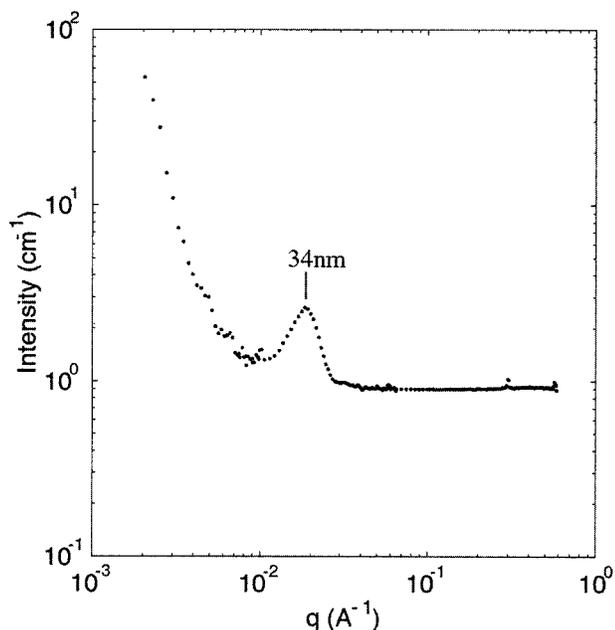


Figure 2. SANS data taken at 20°C on POEM-*b*-PBMA (60:40) prepared by the ATRP method. The intense reflection at 0.019 Å⁻¹ indicates an ordered morphology having a domain periodicity of ~34 nm.

frequency of 5×10^{-3} rad/s, the slopes of both G' and G'' are approximately 0.5, in good agreement with the known behavior of microphase-separated block copolymer systems.¹⁹ Also, the magnitudes of the moduli of the POEM-*b*-PBMA material are quite high, and are expected to be sufficient for use in most battery applications. Further enhancements in mechanical performance could be achieved with little penalty in conductivity by moving to an A-B-A type triblock copolymer in which the A-block is PBMA. Triblock copolymers of polystyrene-*b*-polyisoprene-*b*-polystyrene, for example, show a factor of 2.5 enhancement in modulus over diblocks of the same composition and molecular weight.²⁰ Triblock structures by ATRP have been prepared using sequential polymerization of the three blocks, as well as difunctional initiators.²¹

The good mechanical properties, facile synthesis, and high formability of the ATRP-prepared POEM-*b*-PBMA material are highly desirable features as a candidate solid electrolyte. However, the conductivity of the salt-doped material is questionably sufficient for operating batteries at high cycling rates. Moreover, impurities from the catalyst used in the synthesis may be expected to have a detrimental effect on battery performance. Hence, cycle testing of prototype thin-film cells proves a critical test of the true potential these materials hold as battery electrolytes.

Figure 4 shows cycle test data for representative thin-film VO_x

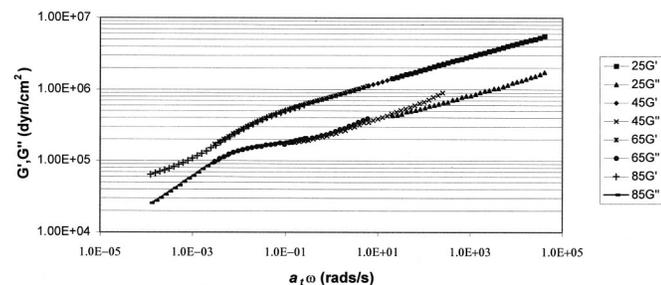


Figure 3. Dynamic frequency sweep testing on POEM-*b*-PBMA (60:40) system with 1.5% strain. Moduli data are shifted to a 45°C reference temperature.

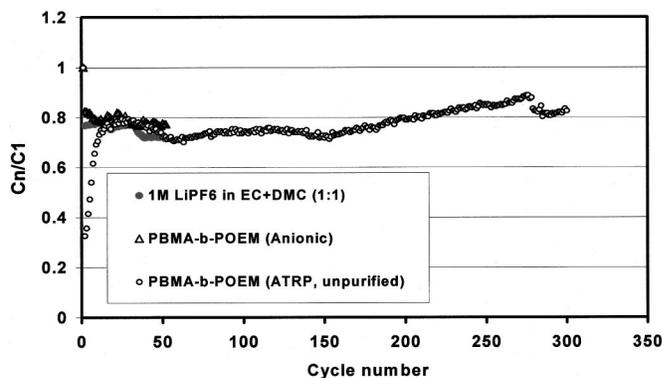


Figure 4. Cycle testing comparison of Li/Li⁺/VO_x cells fitted with different electrolytes: solid electrolyte comprising POEM-*b*-PBMA made by ATRP (○), solid electrolyte comprising POEM-*b*-PBMA prepared by anionic polymerization (△), and 1 M LiPF₆ in 1:1 EC:DMC (●).

cells fitted with ATRP-prepared POEM-*b*-PBMA (60:40) electrolyte, anionically prepared POEM-*b*-PBMA (63:37) electrolyte, and a conventional EC:DMC liquid electrolyte, cycling at a rate of C/2. To compensate for differences in instant cathode capacity between specimens, the ordinate plots the capacity as the ratio of the absolute value of the capacity of the n th cycle to that of the first cycle, C_n/C_1 . It is clear from Fig. 4 that battery cycling performance is unaffected by the choice of electrolyte. The two cells fitted with solid polymer electrolytes (one made by anionic polymerization and the other by ATRP) cycled with the same facility as the cell fitted with the liquid electrolyte. (The solid electrolytes used here contained no oligomeric PEO additives, unlike our previously published cycle testing studies of other block copolymer electrolytes.^{1,9}) The capacity of the cell fitted with the ATRP solid electrolyte remains stable at ~80% of its initial capacity beyond 300 cycles, comparable to the two control cells, thereby demonstrating its excellent resistance to capacity fade. Equally important, Fig. 4 shows that the presence of residual copper catalyst in the ATRP material (approximately 0.06% as determined by chemical analysis) seems to have no effect on cell performance, indicating that these materials essentially can be used as synthesized for the preparation of electrolytes, without the need for costly extraction steps.

A comparison of the absolute capacities based on cathode weight (Table I) shows no systematic discrepancies between the different electrolytes for all samples tested. The results are promising, suggesting that if cathode dimensions are suitably reduced, and thus the surface-to-volume ratio is sufficiently high, the electrical properties of the electrolyte do not strongly limit cell performance, even at cycling rates of C/2. However, due to differences in VO_x capacities from film to film, a more direct comparison between the performance of the ATRP-prepared solid electrolyte and liquid electrolyte was sought. To this end, a cell fitted with a POEM-*b*-PBMA electrolyte and run for 301 cycles was disassembled, and then reassembled replacing the solid electrolyte with liquid (Fig. 5). Only a slight enhancement in the capacity (~15%) was observed on the

Table I. Absolute and reduced VO_x capacities for thin-film cells constructed with different electrolytes and cycled at C/2.

Electrolyte	C ₅₀ (mAh/g)	C ₅₀ /C ₁
1 M LiPF ₆ in EC + DMC (1:1)	217	0.723
1 M LiPF ₆ in EC + DMC (1:1)	185	0.725
PBMA- <i>b</i> -POEM (Anionic)	378	0.777
PBMA- <i>b</i> -POEM (Anionic)	175	0.734
PBMA- <i>b</i> -POEM (ATRP, 23% PEDME, unpurified)	163	0.774
PBMA- <i>b</i> -POEM (ATRP, unpurified, no PEGDME) ¹	158	0.723

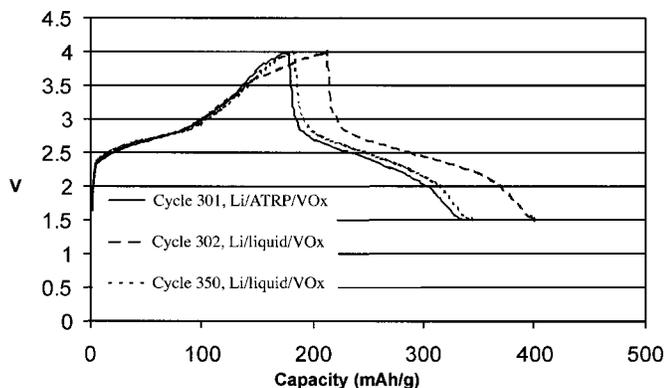


Figure 5. The 301st charge-discharge cycle for the VO_x battery fitted with ATRP-prepared POEM-*b*-PBMA (60:40) electrolyte, along with the 302nd and 350th cycles run with the liquid electrolyte.

302nd cycle with the replacement of the polymer electrolyte, which gradually diminished on further cycling. These results indicate that, even for this high cycling rate, the large amount of interface present between the electrolyte and cathode enables most of the VO_x capacity to be accessed, irrespective of the dramatic difference in electrolyte conductivities. A reduction in solid electrolyte film thickness, necessary to achieve high energy density batteries, might further close the gap between liquid and solid electrolyte performance.

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