Melt-Formable Block Copolymer Electrolytes for Lithium Rechargeable Batteries

Anne-Valérie G. Ruzette,[a] Philip P. Soo,*,[b] Donald R. Sadoway,** and Anne M. Mayes[z]

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Massachusetts 02139-4307, USA

Microphase separated block copolymers consisting of an amorphous poly(ethylene oxide) (PEO)-based polymer covalently bound to a second polymer offer a highly attractive avenue to achieving both dimensional stability and high ionic conductivity in polymer electrolytes for solid-state rechargeable lithium batteries. However, due to the strong thermodynamic incompatibility typically found for most polymer pairs, the disordered, liquid state of the copolymer can rarely be achieved without the incorporation of a solvent, which complicates processing. Herein, we report the design of new block copolymer electrolytes based on poly(methyl methacrylate), PMMA, and poly(oligo oxyethylene methacrylate), POEM, which are segmentally mixed at elevated temperatures appropriate for melt processing, while exhibiting a microphase separated (ordered) morphology at ambient temperature. Although pure PMMA-*b*-POEM is segmentally mixed at all temperatures, it is shown that microphase separation in these materials can be induced in a controlled manner by the incorporation of even limited amounts of lithium trifluoromethane sulfonate ($LiCF_3SO_3$), a salt commonly employed to render PEO ionically conductive. Such ''salt-induced'' microphase separation suggests a simple method for designing new solid polymer electrolytes combining high ionic conductivities with excellent dimensional stability and improved processing flexibility.

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Amorphous poly(ethylene oxide) (PEO)-based materials doped with alkali-metal salts are favored candidates for use as electrolytes in solid-state rechargeable lithium batteries. Yet, technical obstacles to their commercialization derive from the inability to satisfy simultaneously the electrical and mechanical performance requirements, while retaining melt processing capability. Among others, a highly attractive avenue to achieving both high ionic conductivity and dimensional stability consists in covalently bonding an amorphous low T_g PEO-based polymer to a second polymer, thereby forming a block copolymer.[1-8] Depending on the degree of thermodynamic compatibility between the two polymer blocks, such a copolymer will either be segmentally mixed (disordered), or microphase separated (ordered) into periodically spaced nanoscale domains of the different blocks, with the covalent junction residing at the interface.[9-12] This tendency of block copolymers to microphase separate or self-assemble into ordered structures, such as lamellar, bicontinuous, cylindrical, or spherical morphologies, is of particular interest for the design of new solid polymer electrolytes due to the unique resistance to flow and mechanical properties that ensue. Indeed, analogous to crystallization or cross-linking, self-assembly of block compolymer chains confers solid-like mechanical properties to the material at the macroscopic scale over extended temperature ranges.[12-14] In contrast to crystallized or cross-linked systems, however, local chain mobility can still be retained through a judicious choice of composition and chain architecture. In this manner, microphase separated block copolymer electrolytes displaying high room temperature conductivity and good mechanical performance have been prepared. Both high T_g[1-8] and low T_g[6,7] nonconductive blocks have been combined with PEO-based amorphous polymers such as poly(oligo oxyethylene methacrylate) (POEM), and the properties of the resulting electrolytes have been measured. One limitation arises, however, from the strong incompatibility of the block components used in these systems and the resulting lack of control over their bulk thermodynamics and rheological properties, in particular the appearance of order/disorder transitions at temperatures appropriate for processing.

Block copolymers are usually ordered (microphase separated) at low temperature due to a net repulsion between the dissimilar block segments. However, when heated to a sufficiently high temperature such that this repulsion is overcome by the entropy of mixing the two segment types, these materials undergo an order/disorder transition, denoted ODT, accompanied by a solid-like/liquid-like rheological transition.[12] The precise temperature of this thermodynamic transition is governed by three parameters: the composition of the block copolymer, its total molecular weight, and the degree of thermodynamic compatibility, or Flory-Huggins interaction parameter, χ,[15] between the two blocks. In practice, the experimental observation of the ODT is often impeded by the strong thermodynamic incompatibility characterizing most high molecular weight polymer pairs. Indeed, this results in ODT temperatures that exceed by far the degradation temperature of the polymer, except for very low molecular weight systems (oligomers) of little commercial interest. From an applications standpoint, this strong incompatibility is beneficial, as it results in remarkably stable and well defined solid-like microphase separated morphologies. However, for melt processing where flow is essential, the ability to access the disordered liquid state at reasonable processing temperatures without the addition of a common solvent is clearly desirable. Therefore, being able to fine tune the degree of compatibility between the two blocks of a block copolymer electrolyte such that the ODT is experimentally accessible would greatly improve its melt formability. Herein, we report the design of such a block copolymer electrolyte displaying tunable levels of interaction, including miscibility at temperatures appropriate for processing (150-200°C) and complete microphase separation at ambient temperature. A schematic representation of the chemistry of this block copolymer, made of a poly(methyl methacrylate) (PMMA) block and a POEM block and denoted PMMA-*b*-POEM, is shown in Fig. 1. The phase behavior and ionic conductivity of PMMA-*b*-POEM doped with various concentrations of lithium trifluoromethane sulfonate ($LiCF_3SO_3$), are analyzed by small angle neutron scattering (SANS), dynamic rheological testing, and impedance spectroscopy.

The well-known miscibility of PMMA and polyethylene oxide (PEO) in the melt has been extensively studied since it was first predicted[16] and experimentally verified[17-20] 20 years ago. While the molecular origin of this compatibility is not clearly understood, the possibility of weakly attractive secondary interactions between the ether linkages of PEO and the ester groups of PMMA has been advanced by several authors and evidenced experimentally by vibra-

* Electrochemical Society Student Member.
** Electrochemical Society Active Member.
 [a] Present address: Elf-Atochem/CNRS, UMR 167, 92303 Levallois-Perret, France.
 [b] Present address: 3M, 3M Center, St. Paul, MN 55144.
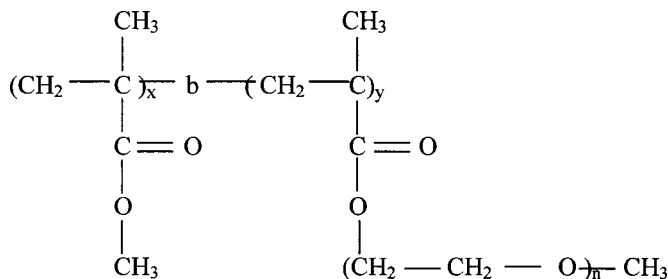 [z] E-mail: amayes@mit.edu

Figure 1. Schematic representation of PMMA-*b*-POEM.

tional spectroscopy.[21] A similar degree of thermodynamic compatibility is naturally found for comb-shaped analogues of PEO such as POEM. As a result, block copolymers of PMMA and POEM are essentially segmentally mixed at all temperatures, as the ODT for this system lies well below the T_g of the mixed (*i.e.*, disordered) phase, and therefore cannot be observed experimentally. Recently, we found, however, that the degree of compatibility between PMMA and POEM can be dramatically affected by even small additions of $LiCF_3SO_3$, one of the alkali metal salts commonly employed to render PEO-based materials ionically conductive. It was indeed expected that the preferential complexation of $LiCF_3SO_3$ with the ether linkages of POEM might lead to a weakening of the segmental interactions responsible for its compatibility with PMMA, thereby raising the ODT of the block copolymer. To better quantify this effect, the phase behavior of PMMA-*b*-POEM was investigated as a function of salt concentration. As reported herein, while pure PMMA-*b*-POEM (80,000 g/mol, 50 wt % POEM) is segmentally mixed (disordered) over the entire experimental temperature range (100-200°C), the addition of $LiCF_3SO_3$ in a molar ratio of 1 per 20 ether linkages ([EO:Li$^+$] = 20:1) results in microphase separation at the same temperatures. Furthermore, for salt concentrations of 30:1 and 25:1, the same block copolymer exhibits an ODT at 130 and 160°C, respectively. Such a tunable ''salt-induced'' microphase separation in doped PMMA-*b*-POEM therefore, suggests a simple method for controlling the bulk thermodynamics and resulting rheological properties of this material, providing a melt-formable electrolyte with significant room temperature ionic conductivity.

Experimental

The anionic synthesis of PMMA-*b*-POEM has been reported elsewhere.[6] In the materials investigated here, the POEM block contained 9 EO units per PEO side chain, sufficiently short to prevent crystallization over the full range of temperatures and salt concentrations investigated. The total block copolymer had a number average molecular weight, M_n, of 80,000 g/mol based on polystyrene standards and contained 50 wt % POEM, as determined by gel permeation chromatography (GPC) and ^{1}H nuclear magnetic resonance (NMR), respectively. In addition, a random copolymer of the same monomers, denoted P(MMA-*r*-OEM), was synthesized by free radical methods as described in Ref. 22. The copolymer had a weight average molecular weight, M_w, of 63,000 g/mol with respect to polystyrene standards, a polydispersity index M_w/M_n of 1.43, and contained 50% POEM. Ionically conductive electrolytes were prepared by dissolving various amounts of $LiCF_3SO_3$ in these polymer hosts, as described previously.[6] Salt concentrations corresponding to [EO]:Li$^+$ ratios ranging from 40:1 to 20:1 were incorporated into PMMA-*b*-POEM and P(MMA-*r*-OEM).

The phase behavior and rheological properties of these electrolytes were determined by a combined use of dynamic rheological testing and SANS. Dynamic rheological measurements were obtained using a Rheometric Scientific ARES rheometer operated in the parallel plate geometry, with 25 mm diam aluminum plates. Previously melt-pressed samples were sandwiched between the

plates and further pressed down to a gap of 0.5 mm. The dynamic storage (G') and loss (G'') moduli of the copolymers were determined isothermally as a function of frequency ($0.1 < \omega < 400$ rad/s), and temperature was varied from 100 to 200°C in 10°C increments. A strain of 0.5% was used, which is in the linear elastic regime for these materials. Whenever possible, the isothermal frequency sweeps obtained at various temperatures were superimposed about a reference temperature of 140°C in order to obtain master plots.[14,23] Data taken at torques lower than 1 g cm (the lower limit of sensitivity of the transducer) were discarded.

SAN scattering measurements were obtained at the Cold Neutron Research Facility at the National Institute of Standards and Technology on beamline NG-3. The instrument configuration was $\lambda = 6$ Å, $\Delta\lambda/\lambda = 15\%$ and sample-to-detector distance = 6 m, resulting in values of the wave vector $q = 4\pi \sin\theta/\lambda$ ranging from 0.008 to 0.08 Å^{-1}. Results were corrected for background and detector inhomogeneity in the standard manner and data were scaled to absolute units (cm^{-1}) using a silica standard. Dry polymer samples, previously melt-pressed into disks 15 mm in diam and 0.1 mm thick, where sandwiched between two quartz windows and placed in a brass cell connected to a temperature controller. Temperature was varied by 10 or 20°C increments and sufficient time was provided for thermodynamic equilibration at each temperature. In order to prevent thermal degradation at elevated temperatures, the previously degassed sample chamber was purged by a continuous flow of dry, grade 5.0 nitrogen throughout the experiment. Thermodynamic reversibility of the observed behaviors was verified in each case through temperature cycling.

Conductivities of the block and random copolymer electrolytes were measured by impedance spectroscopy using a Solartron 1260 impedance gain/phase analyzer (Solartron Instruments, Allentown, PA). Dry specimens, previously pressed into small disks of the appropriate size, were loaded between a pair of blocking electrodes made of type 316 stainless steel and separated by a 250 μm gap. The electrode assembly was then placed inside a brass cell equipped with seven hermetically sealed ports. To maintain dry conditions, the sample preparation was carried out in an argon-filled glove box (moisture level measured to be less than 2 ppm). The four electrode lead wires were fitted to BNC connectors at four of these ports. Two ports, equipped with valves, served as inlet and outlet for argon or nitrogen flow. The last port accommodated an O-ring sealed glass tube through which a type-K thermocouple was fed and positioned directly next to one of the stainless steel electrodes. The use of compression fittings rendered the cell cap vacuum tight. The sealed cell was removed from the glove box and annealed at 70°C for 12 h, blanketed by a continuous flow of dry, grade 5.0 nitrogen. Conductivity measurements were carried over a temperature interval spanning 30 to 170°C.

Results and Discussion

Figure 2a and b show the storage (G') and loss (G'') moduli of pure PMMA-*b*-POEM and PMMA-*b*-POEM doped with $LiCF_3SO_3$ ([EO]:Li = 20:1), respectively. Data obtained as a function of frequency at different temperatures have been time/temperature superimposed about a reference temperature of 140°C. As expected, the data obtained for pure PMMA-*b*-POEM (Fig. 2a) indicate that this block copolymer is disordered over the entire temperature range (50-150°C), as evidenced by the low frequency power law behavior. Indeed, G' and G'' scale approximately with frequency as ω^2 and ω, respectively, which is typical for segmentally mixed, homogeneous block copolymer melts.[14,23] When the same material is doped with $LiCF_3SO_3$ in a ratio [EO]:Li$^+$ = 20:1, however, a strikingly different behavior is observed (Fig. 2b). Now, both G' and G'' are found to scale approximately as $\omega^{0.5}$, which is typical for a microphase separated block copolymer.[14,23] This result demonstrates that the incorporation of even limited amounts of $LiCF_3SO_3$ in PMMA-*b*-POEM is sufficient to raise the ODT of this block copolymer from below 50 to above 200°C.
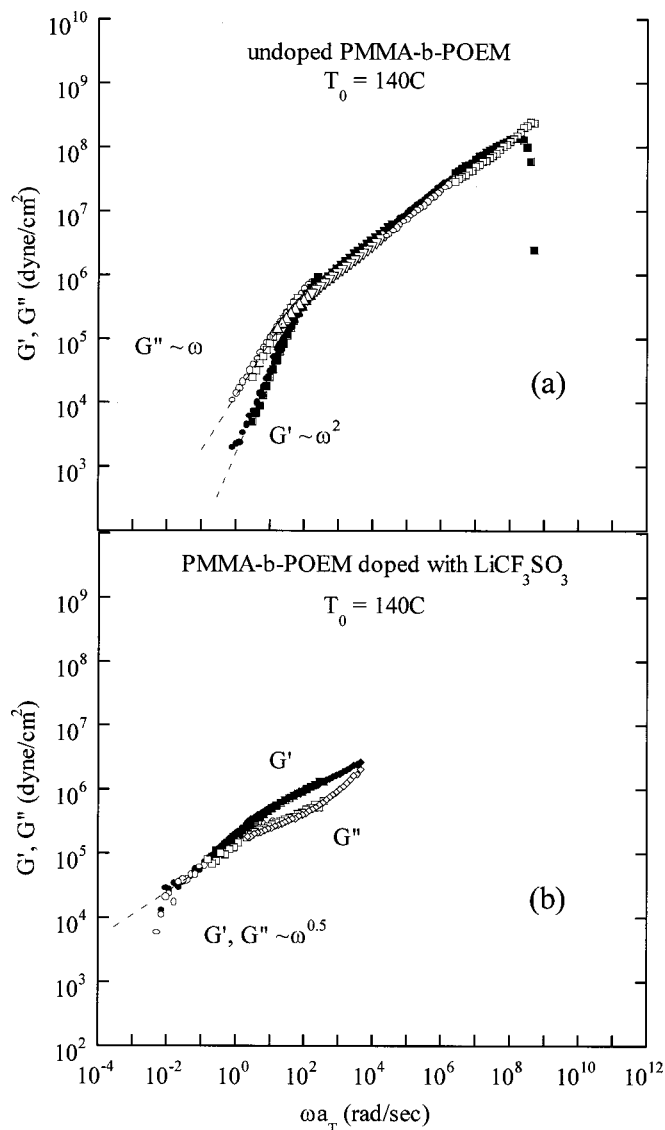
Figure 2. Master plots of G' and G'' obtained about a reference temperature of 140°C for (a) undoped PMMA-*b*-POEM and (b) PMMA-*b*-POEM doped with LiCF$_3$SO$_3$ (EO:Li$^+$ = 20:1).

Figure 3. Scattering intensity profile for salt-doped PMMA-*b*-POEM at 160°C and indicated salt concentrations.

critical temperature T_{ODT} below which the block copolymer is microphase separated (ordered). This is illustrated in Fig. 4 for an EO: salt ratio of 30:1. The precipitous decrease in scattering peak intensity with increasing temperature indicates that the material is undergoing a transition from the ordered to the disordered state. In fact, a fully reversible ODT is observed at about 130°C for this particular salt concentration (30:1), as evidenced by the discontinuous change in peak width between 130 and 140°C (see inset in Fig. 4).[12] This abrupt increase in peak width signals the destruction of the periodic arrangement of the block copolymer chains in the microphase separated state. However, in contrast to what is typically observed in pure (undoped) block copolymers, the peak position q^*, which is inversely proportional to R_g, the radius of gyration of the block copolymer chain, is found to decrease as temperature increases and the system moves away from the order/disorder transition. The coil expansion is far more pronounced than what could be explained by

Keeping this in mind, we investigated the phase behavior of a series of PMMA-*b*-POEM block copolymer electrolytes doped with LiCF$_3$SO$_3$ concentrations corresponding to EO:Li$^+$ ratios ranging from 100:1 to 20:1. The scattering intensity profiles obtained from SANS as a function of wave vector $q = 4\pi$ (sin θ/λ) are shown in Fig. 3 for four [EO]:Li$^+$ ratios and at a fixed temperature of 160°C. At this temperature and for salt concentrations corresponding to [EO]:Li$^+$ ratios of 20:1 and 25:1, a narrow, intense scattering maximum is observed. This sharp peak corresponds to the first order Bragg reflection characteristic of the ordered (microphase separated) state. For [EO]:Li$^+$ ratios of 30:1 and higher, by contrast, the block copolymer remains segmentally mixed, as evidenced by the broader, low intensity scattering maximum observed at a wave vector q^* of ~ 0.018 Å^{-1}. Such ''correlation hole'' (broad) scattering is a well-known signature of the segmentally mixed state of block copolymers.[24] Hence, at 160°C, a critical salt concentration ϕ_c is reached, corresponding to a [EO]:Li$^+$ ratio in the range between 25:1 and 30:1. For salt concentrations above ϕ_c, the two blocks become incompatible and the copolymer undergoes microphase separation. Likewise, for a given salt concentration, there exists a
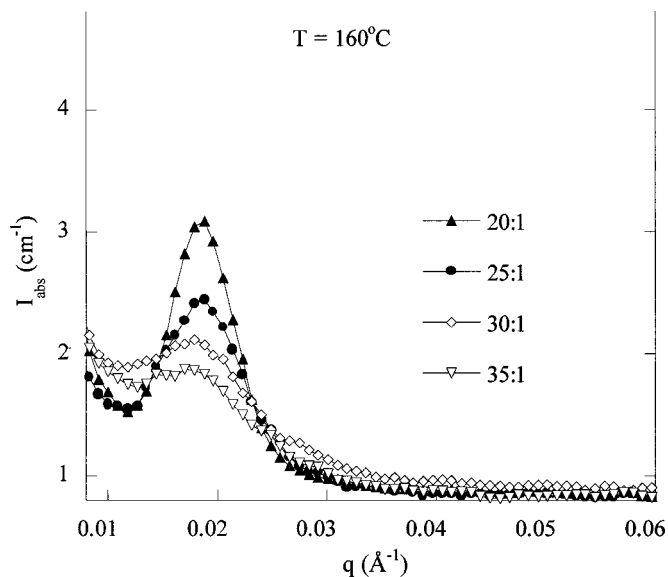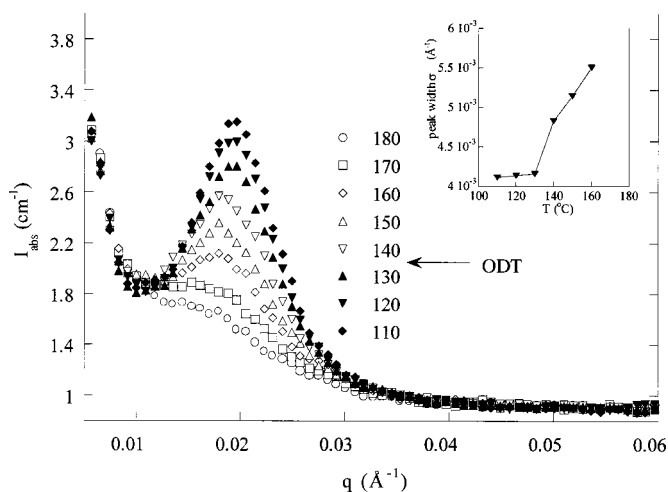

Figure 4. Scattering intensity profile as a function of temperature for PMMA-*b*-POEM doped with LiCF$_3$SO$_3$ (EO:Li$^+$ = 30:1). The inset shows the change in peak width with temperature. Background subtracted intensity was fit to the Gaussian form $I(q) = I_{max} \exp[-(q - q^*)^2/2\sigma^2]$ to extract q^* and σ.
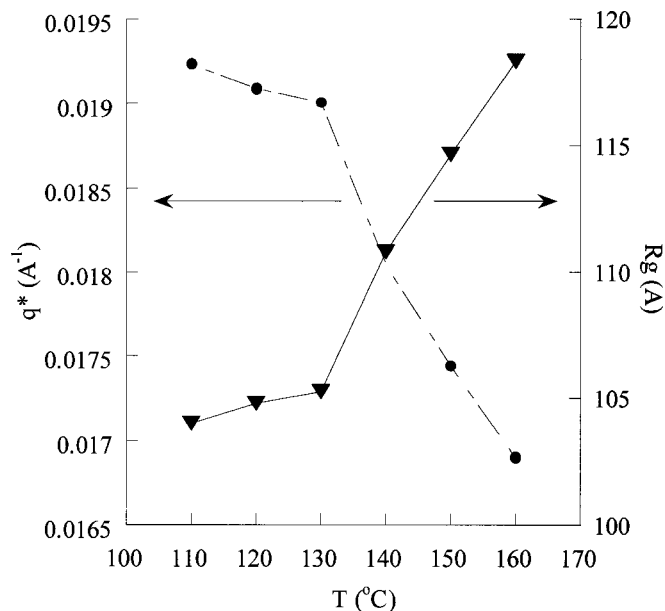
Figure 5. Temperature-dependence of the scattering peak position q^* and radius of gyration R_g for salt-doped PMMA-*b*-POEM (EO:Li$^+$ = 30:1).

Figure 6. Order/disorder transition temperature, T_{ODT}, of salt-doped PMMA-*b*-POEM as a function of salt concentration.

thermal expansion effects, which would yield a <1% increase in R_g over the temperature range 130-160°C ($\alpha \sim 6 \times 10^{-4}$ K^{-1}). This is illustrated in Fig. 5 where q^* and R_g are plotted as a function of temperature for the 30:1 sample. Generally, in fact, the opposite trend is observed for block copolymers, namely, q^* increases (R_g decreases) upon heating due to the more random coil configuration of the block copolymer chains as the two blocks become segmentally mixed.[12,25] The unexpected increase in coil dimensions observed here upon disordering suggests that the chain conformation is modified upon segmental mixing of the PMMA and POEM segments. It has been suggested previously that the interaction of LiCF$_3$SO$_3$ with PEO chains promotes their helical conformation,[26] while upon blending with PMMA, the more opened planar zigzag conformation of the PEO chain is preferred.[21] Provided similar conclusions apply to the ethylene oxide side chains of POEM, this might account for the observed expansion of the polymer coil upon disordering.

Similar scattering profiles with ODTs at ~110 and ~150°C were obtained for PMMA-*b*-POEM doped with [EO]:Li$^+$ ratios of 35:1 and 25:1, respectively. For the higher salt concentration of 20:1, however, a sharp reflection was observed at all temperatures, confirming the ordered state apparent from dynamic rheological measurements on this sample. These results are summarized in Table I and Fig. 6, where the phase behavior and transition temperatures as obtained from SANS are given as a function of salt concentration. From these data, a very rough estimate of the zero salt concentration ODT can be obtained by linear extrapolation. This yields a transition temperature of approximately 10°C for the block copolymer inves-
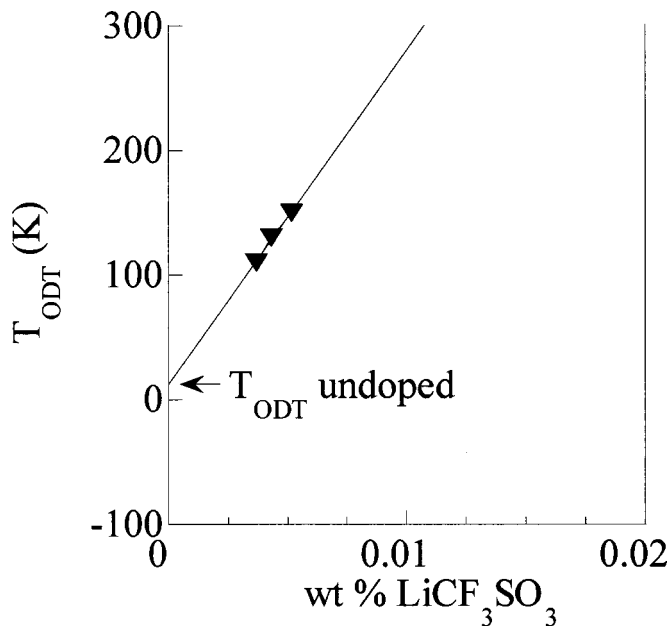
tigated here, consistent with the observation of a segmentally mixed state at temperatures of 50°C and higher (see Fig. 2a).

It is important to note that the materials investigated here are fully amorphous, and the transitions observed at these relatively low salt concentrations ([EO]:Li$^+$ > 20:1) truly represent reversible thermodynamic transitions induced by the progressive weakening of the interactions between PMMA and POEM upon the addition of LiCF$_3$SO$_3$. The influence of alkali-metal salts on the thermodynamic compatibility of PMMA and semicrystalline PEO was reported previously by Vernugopal *et al.*[27] and Eastmond *et al.*[28] However in those studies, the authors investigated a much higher salt concentration regime ([EO]:Li$^+$ < 5:1), where the salt was found to dominate completely the thermodynamics of the system and reversible phase separation could therefore not be observed. In contrast, for the lower salt concentration regime probed here, a competition takes place between, on one hand, the weak attractive interactions between PMMA and POEM segments and the conformational entropy to be gained upon mixing, and on the other hand, the highly favorable complexation of the PEO side chains of POEM with Li$^+$ cations. Provided the concentration of Li$^+$ remains low, only a small fraction of ether linkages of the PEO side chains forms complexes with the salt, while the remaining units are, in principle, free to interact with PMMA. However, even at low doping levels, this interaction is entropically hampered by loss of configurations of the PEO side chains due to PEO-Li$^+$ complexation. This explains why microphase separation occurs at salt concentrations far below the value at which complete complexation of the PEO segments is expected ([EO]:Li$^+ \sim$ 3.5).[26] The results further illustrate how the degree of interaction between the two blocks of PMMA-*b*-POEM can be controlled via salt doping and how this might be utilized to design new electrolytes that can be easily processed from the melt, while displaying a microphase separated morphology at service temperatures.

By impedence spectroscopy, ionic conductivities of the electrolytes were measured as a function of temperature and for the various salt concentrations discussed above. In order to characterize the effect of the order/disorder transition of the salt-doped block copolymer on its electrical properties, data were taken over an extended temperature range spanning 30 to 170°C. It was indeed expected that the loss of percolating nanoscale POEM domains might result in

Table I. Phase behavior and transition temperatures of salt-doped PMMA-*b*-POEM as a function of LiCF$_3$SO$_3$ concentration.

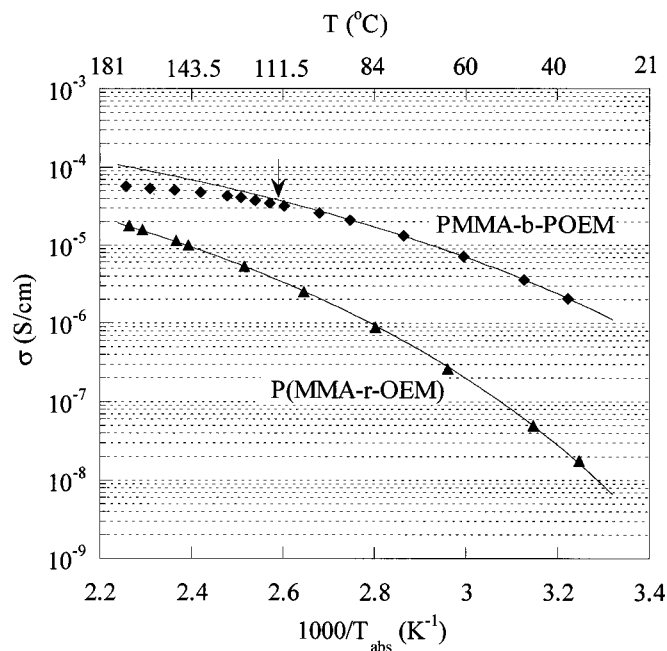| Salt concentration [EO]:Li$^+$	Type of phase behavior	Transition temperature T_{ODT} (°C)
40:1 and lower	always disordered	<80
35:1	ODT	110
30:1	ODT	130
25:1	ODT	150
20:1	always ordered	>200

Figure 7. Ionic conductivity σ of salt-doped PMMA-*b*-POEM (diamonds) and P(MMA-*r*-OEM) (triangles) at a salt concentration of EO:Li$^+$ = 30:1. The full lines represent fits to the experimental data obtained with the VTF equation and using the parameters listed in Table II.

Figure 8. Linear conductivity plots for salt-doped PMMA-*b*-POEM as a function of temperature and at indicated salt concentrations. The full lines represent fits to the experimental data obtained with the VTF equation and using the parameters listed in Table II.

a drop of ionic conductivity in these materials.[6] To better quantify this effect, data were also taken for a random copolymer of the same monomers, denoted P(MMA-*r*-OEM), and containing the same fraction of each component as the block copolymer.

For amorphous solid polymer electrolytes in which there is a coupling between ionic mobility and segmental motion of the polymer host, the observed temperature dependence of the conductivity is generally non-Arrhenius and may be more effectively analyzed by the empirical Vogel-Tammann-Fulcher (VTF) relation[29-31]

$$\sigma(T) = A T^{-1/2} \exp\left(\frac{-E_a}{(T - T_0)}\right) \qquad [1]$$

In this expression, σ is the ionic conductivity, A is a constant proportional to the number of charge carriers, E_a is the apparent energy barrier for ion motion, k is the Boltzmann constant, T is the absolute temperature, and T_0 is a reference temperature usually associated with the ideal glass transition of the matrix polymer.

Measured values of the ionic conductivities of the block copolymer, PMMA-*b*-POEM, and the random copolymer, P(MMA-*r*-OEM), both doped with LiCF$_3$SO$_3$ at a ratio of 35:1, are shown in Fig. 7. As reported previously, the electrical performance of the random copolymer is very poor compared to that of the block copolymer.[6] For a given salt concentration, the room temperature conductivity of the random copolymer is two orders of magnitude lower than that of the block copolymer (2.18 · 10^{-8} compared to 2.06 · 10^{-6} S/cm). Hence, although the amount of conducting polymer is identical in these two materials, the formation of POEM ionic pathways upon ordering of the block copolymer leads to a higher conductivity compared to that obtained for a homogeneous system. However, as temperature increases and the block copolymer goes through the ODT (~110°C for a EO:Li$^+$ of 35:1), the rate at which conductivity increases with temperature slows down dramatically. This is evidenced by the distinct departure from the low temperature VTF fit at temperatures exceeding 110°C. In fact, at 170°C, a temperature at which the block copolymer is no longer microphase separated for this salt concentration, its conductivity
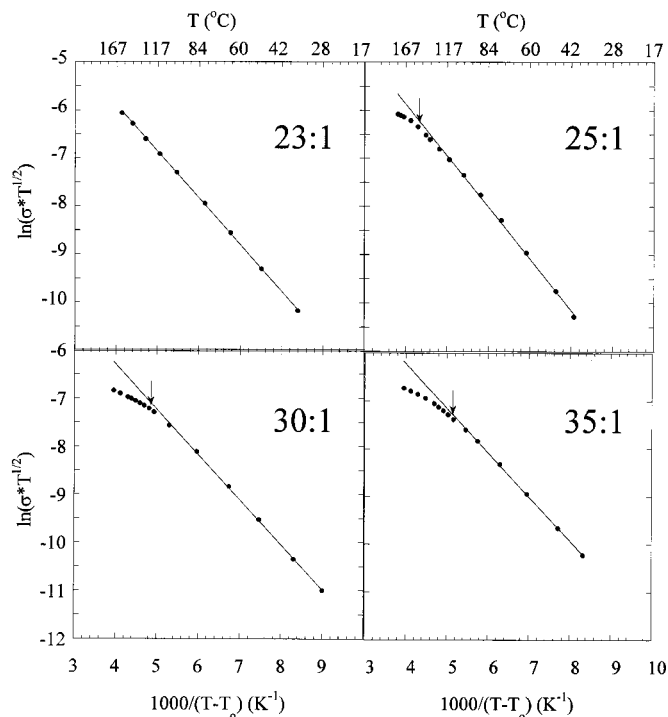
(5.6 · 10^{-5} S/cm) approaches that of the random copolymer (1.8 · 10^{-5} S/cm). This is consistent with the well known resemblance between the macroscopic properties of a segmentally mixed (homogeneous) block copolymer and a random copolymer of the same composition. In general, while the individual properties of each block are preserved in the microphase separated state, disordered block copolymers in which both components are intimately mixed at the molecular level exhibit averaged properties very similar to those resulting from a random sequence of the two segment types. More detailed examination of the data in Fig. 7, however, shows that the conductivity of the block copolymer does not change abruptly upon disordering, but rather progressively deviates from the low temperature trend to approach that of the random copolymer. Such a gradual change in properties indicates that, although temporally homogeneous, the block copolymer still displays large local instant fluctuations in concentration even at temperatures exceeding by far the ODT.

The observed deviation from the low temperature VTF fit accompanying the order/disorder transition is even more apparent in the linear conductivity plots shown in Fig. 8. Indeed, if the ionic conduction follows the VTF equation, a linear relationship between $\ln(\sigma^*T^{1/2})$ and $(T - T_0)$ is expected. Such relationships are shown in Fig. 8 for the various salt concentrations considered in this study. Distinct deviations from linearity are observed at 110, 125, and 150°C for the 35:1, 30:1, and 25:1 samples, respectively. Such deviations are not encountered for pure POEM electrolytes or for block copolymer electrolytes that reside in the ordered state throughout the temperature range of measurement,[6] as shown here for the 23:1 sample. The deviation from linearity evidences a transition in the energetics of local ion motion and a reduction of the effective ion density upon passing into the disordered (mixed-block) state. The results presented in Fig. 8 further illustrate how the addition of LiCF$_3$SO$_3$ to PMMA/POEM based block copolymers can be used to fine tune the rheological and electrical properties of these electrolytes. For any given molecular architecture

Table II. VTF fitting parameters and ionic conductivities as a function of salt concentration for PMMA/POEM block and random copolymer electrolytes.

Sample	[EO]:Li$^+$	A (S K$^{0.5}$/cm)	E_a (kJ/mol)	σ_{RT} (S/cm)	σ_{100} S/cm	σ_{170} S/cm
P(MMA-*r*-OEM)[a]	35:1	0.07	10.11	$2.8 \cdot 10^{-8}$	$3.4 \cdot 10^{-6}$	$1.8 \cdot 10^{-5}$
PMMA-*b*-POEM[b]	35:1	0.08	7.69	$2.0 \cdot 10^{-6}$	$2.6 \cdot 10^{-5}$	$5.7 \cdot 10^{-5}$
PMMA-*b*-POEM	30:1	0.08	7.79	$1.8 \cdot 10^{-6}$	$2.7 \cdot 10^{-5}$	$5.1 \cdot 10^{-5}$
PMMA-*b*-POEM	25:1	0.13	7.8	$3.3 \cdot 10^{-6}$	$4.3 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$
PMMA-*b*-POEM	23:1	0.13	8.02	$2.3 \cdot 10^{-6}$	$3.5 \cdot 10^{-5}$	$1.4 \cdot 10^{-4}$

[a] $T_0 = 209$ K.
[b] $T_0 = 190$ K, independent of salt concentration.

(*e.g.*, PMMA-*b*-POEM diblock *vs.* PMMA-*b*-POEM-*b*-PMMA triblock), composition (ϕ_{POEM} = volume fraction of POEM) and total molecular weight M_n, a critical salt concentration exists which can be used to simultaneously optimize room temperature conductivity, dimensional stability, and processibility. For the particular block copolymer studied here (diblock copolymer, $\phi_{POEM} = 50\%$, $M_n \sim 80,000$ g/mol) this concentration corresponds to a [EO]:Li$^+$ ratio of about 25:1.

The values of conductivity at room temperature, 100 and 170°C for each salt concentration are given in Table II, along with the parameters used in the VTF fits. A constant value of $T_0 = 190$ K was utilized for the block copolymer in the microphase separated state, since it has been shown that this parameter does not depend on salt concentration for several PEO-based electrolytes.[32] Due to the alternating sequence of POEM and stiff PMMA units along the backbone of the polymer chain in the random copolymer, a higher value of 209 K was needed to fit the data for this material. This also explains the higher E_a for ionic motion in this material compared to that of the block copolymer doped at the same concentration (35:1). Within experimental error, and for the concentration interval considered here, the E_a, the pre-exponential factor A, and the ionic conductivity σ for the block copolymer are all found to increase with increasing salt concentration.

While the absolute conductivities listed in Table II are below those reported in recent studies, it is important to note that the block copolymer investigated here contains only 50 wt % POEM, *i.e.*, just enough to form a percolating network of the conductive polymer. As has been shown in previous reports,[6,7] the electrical performance of such block copolymer electrolytes can be improved by a factor of two or more by increasing the volume fraction ϕ_{POEM} of the conductive block, while still retaining excellent dimensional stability due to the microphase separated structure. In fact, the unique properties of block copolymers offer great versatility for controlling independently the mechanical and conducting properties of the electrolyte. The results presented here thus demonstrate that, besides molecular architecture, composition and chain length, a fourth parameter, namely, the alkali-metal salt concentration, can be used to extend this principle to the simultaneous optimization of electrical performance, mechanical properties, and processing ease. Finally, toward the goal of highly conductive solid polymer electrolytes, at least two extra handles commonly used but not considered here are available to optimize performance: the nature of the alkali-metal salt and the incorporation of low molecular weight PEO-based additives such as polyethylene glycol dimethyl ether.

Conclusion

In an attempt to identify new melt formable block copolymer electrolytes for solid-state rechargeable Li batteries, the phase behavior and ionic conductivity of a block copolymer of PMMA and POEM, denoted PMMA-*b*-POEM, have been investigated as a function of temperature and concentration of LiCF$_3$SO$_3$. Unlike most diblock copolymers, which remain microphase separated (ordered) over extended ranges of temperature, PMMA-*b*-POEM displays a segmentally mixed (disordered) state, due to a larger thermodynamic compatibility for this monomer pair. It was found, however, that the degree of compatibility between the two blocks can be dramatically affected by the addition of alkali-metal salts such as LiCF$_3$SO$_3$, which form complexes with the EO units of POEM, thereby reducing the strength of segmental interactions between the blocks and the number of available configurations, raising the order/disorder transition. In fact, even limited amounts of salt, corresponding to [EO]:Li$^+$ ratios of 30:1 to 20:1, were found to be sufficient to raise the order/disorder transition of the block copolymer from below room temperature to temperatures ranging from 100 to 200°C, a range quite suitable for melt-processing. This salt concentration regime incidentally also corresponds to that typically reported to lead to optimal electrical performance of PEO-based electrolytes doped with LiCF$_3$SO$_3$. Although the particular PMMA-*b*-POEM (50 wt % POEM) copolymer discussed here only exhibits conductivities of about $3 \cdot 10^{-6}$ S/cm when doped with LiCF$_3$SO$_3$, improved electrical properties for this electrolyte could easily be obtained by increasing the volume fraction of the conducting block, changing the salt dopant, etc. The results presented here thus suggest a simple method for designing new block copolymer electrolytes which exhibit segmental mixing (and flow) at temperatures appropriate for processing, while displaying excellent dimensional stability and good ionic conductivity at room temperature in the microphase separated state. The observation of a tunable salt-induced order/disorder transition in these materials demonstrates the existence of an extended thermodynamic range over which ionic conductivity, dimensional stability, and processing flexibility can be optimized simultaneously through a judicious choice of total molecular weight, chain architecture, and alkali-metal salt concentration.

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