

Discontinuous Changes in Ionic Conductivity of a Block Copolymer Electrolyte through an Order–Disorder Transition

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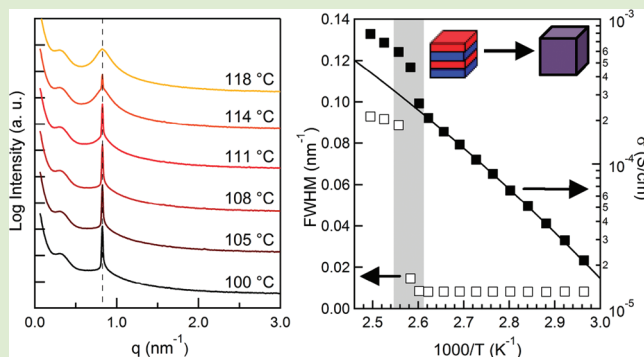
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S Supporting Information

ABSTRACT: The ionic conductivity of a block copolymer electrolyte was measured in an in situ small-angle X-ray scattering experiment as it transitioned from an ordered lamellar structure to a disordered phase. The ionic conductivity increases discontinuously as the electrolyte transitions from order to disorder. A simple framework for quantifying the magnitude of the discontinuity is presented. This study lays the groundwork for understanding the effect of more complex phase transitions such as order–order transitions on ion transport.



Polymer electrolytes have the potential to serve as nonflammable alternatives to traditional organic electrolytes in rechargeable lithium batteries.^{1–3} Nanostructured block copolymer electrolytes with both ionically conducting and hard insulating blocks offer the opportunity of independent control over modulus and ion transport.⁴ At sufficiently high temperatures, the net repulsion between the two blocks driving nanostructure formation is overcome by entropic contributions, resulting in a homogeneous sample. The effect of concentration of diluents such as solvents⁵ and salts⁶ on the temperature at which this order-to-disorder transition occurs, T_{ODT} , provides fundamental insight into the nature of interactions between chemically distinct polymer chains and the diluents. The purpose of this paper is to report on changes in transport of ions through block copolymer electrolytes at the order-to-disorder transition (ODT). Of particular interest is the fact that we observe a discontinuous change in conductivity at the ODT, in contrast to all previous studies wherein continuous changes in conductivity are reported at the ODT.^{7–9} The magnitude of the measured discontinuity is consistent with the predictions of a simple model. These results provide insight into the continuity of phases in the vicinity of the ODT.

Conductivity changes across the ODT of block copolymers have been reported in refs 7, 8, and 9. Majewski et al.⁷ found a plateau in conductivity in the temperatures surrounding the ODT in a poly(ethylene oxide-*b*-6-(4'-cyanobiphenyl-4-yloxy)-hexyl methacrylate) block copolymer with lithium perchlorate (LiClO₄) salt. In contrast, Wanakule et al.⁸ and Ruzette et al.⁹ reported no discontinuity in conductivity through the ODT in polystyrene-*b*-poly(ethylene oxide) (SEO)/lithium bis-(trifluoromethanesulfone)imide (LiTFSI) and poly(methyl

methacrylate)-*block*-poly(oligo oxyethylene methacrylate)/lithium trifluoromethanesulfonate (LiCF₃SO₃) mixtures.

The polymer used in this study was SEO(1.7–1.4) where 1.7 and 1.4 are the molecular weights of the polystyrene and poly(ethylene oxide) (PEO) blocks in kg mol⁻¹, respectively. This study was conducted on a mixture of SEO(1.7–1.4) and LiTFSI with a salt concentration of $r = 0.085$, where r is the molar ratio of Li⁺ ions to ethylene oxide monomers in the sample. A schematic of the in situ small-angle X-ray scattering (SAXS) experiment is presented in Figure 1. Figure 2 shows the results of the simultaneous SAXS and ionic conductivity experiments. Figure 2a shows the SAXS profiles of the sample at selected temperatures. At 100 °C, the sample exhibits a sharp primary scattering peak at $q^* = 0.825$ nm⁻¹. Figure S1 of the Supporting Information shows the same sample in a regular air-free sample holder with Kapton windows, where sharp diffraction peaks at $q/q^* = 1, 2, \text{ and } 3$ are seen, confirming a well-ordered lamellar morphology at 100 °C. We attribute the lack of higher order peaks in Figure 2a to a loss of resolution due to the additional necessary layers of material through which the beam must pass for the in situ experiment. The appearance of an additional broad peak at $q = 0.3$ nm⁻¹ is due to scattering from the inert polymer coating on the pouch material. It is clear from Figure 2a that the sample undergoes an ODT as temperature is increased, indicated by the sudden broadening of the scattering peak in the vicinity of 118 °C. Figure 2b shows the full width half-maximum (fwhm) of the primary scattering

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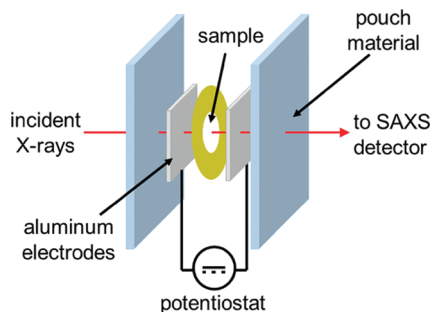


Figure 1. Schematic of the in situ SAXS and conductivity experiment. Symmetric Al/block copolymer electrolyte/Al cells are sealed inside a pouch and connected to an external potentiostat for ac impedance spectroscopy. Incident X-rays pass through the entire cell assembly.

peak as a function of inverse temperature. The abrupt increase in the fwhm indicates a transition from order to disorder. The sample is fully ordered at 111 °C and fully disordered at 118 °C (Figure 2a). The SAXS profile at 114 °C is a superposition of sharp and broad peaks indicating the coexistence of ordered and disordered phases. This coexistence is required by the Gibbs phase rule. We thus report the T_{ODT} of our sample to be 114 ± 4 °C, marked by the gray bar in Figure 2b. The domain spacing remains unchanged over the entire temperature range at 7.7 nm. The right axis of Figure 2b shows the ionic conductivity of the sample obtained concurrently with the SAXS profiles. Conductivity is a sensitive function of temperature in polymer electrolytes, and it is necessary to differentiate expected temperature-dependent changes in conductivity from those arising from changes in the morphology of the polymer. The solid black line in Figure 2b shows the fit of the conductivity to the Vogel–Tammann–Fulcher (VTF) relation¹ in the $T < T_{\text{ODT}}$ regime. The VTF relation is an empirical expression often used to describe the temperature dependence of conductivity in amorphous solid polymer electrolytes:

$$\sigma_{\text{VTF}}(T) = AT^{-1/2} \exp\left(\frac{-E_a}{(T - T_0)}\right) \quad (1)$$

In this expression, σ_{VTF} is the fitted ionic conductivity, A is a constant proportional to the number of charge carriers, E_a is the apparent activation energy for ion motion, and T_0 is a reference temperature typically associated with the glass transition temperature of the polymer. The curve in Figure 1b corresponds to $A = 39.4 \text{ S cm}^{-1} \text{ K}^{-1/2}$, $E_a = 1.99 \times 10^3 \text{ kJ mol}^{-1}$, and $T_0 = 165 \text{ K}$. At $T = T_{\text{ODT}}$, the conductivity exhibits a marked discontinuity, a fundamentally different result from all previous studies of conductivity in the vicinity of the ODT.^{7–9}

The fitted curve in Figure 2b represents the expected increase in conductivity with increasing temperature in the absence of a phase transition. The positive difference between the disordered phase conductivity data in Figure 2b and the fitted curve indicates that the transformation from an ordered lamellar phase to a disordered morphology leads to an increase in conductivity. This result may at first seem counterintuitive, since well-defined ion-transporting channels disappear above T_{ODT} . To focus on the effect of the ODT on conductivity, the temperature dependence of the measured conductivity normalized by the VTF fit, $\sigma/\sigma_{\text{VTF}}$, is plotted in Figure 3. The error bars in Figure 3 reflect the standard deviation of $\sigma/\sigma_{\text{VTF}}$ obtained from five independent samples. The normalized conductivity at 114 °C is intermediate between the ordered and the disordered values. Thus both the conductivity and SAXS indicate the existence of a region of coexistence (110–118 °C) between the ordered and the disordered phases.

An understanding of the effect of the ODT on conductivity begins with a simple expression for ionic conductivity in composite electrolytes, σ_{comp} :

$$\sigma_{\text{comp}}(T) = f\phi_c\sigma_c(T) \quad (2)$$

where $\sigma_c(T)$ is the intrinsic conductivity of the conducting phase (the only term that is a strong function of temperature), ϕ_c is the volume fraction of the conducting phase, and f is a morphology factor that accounts for constraints imposed by the geometry of the conducting phase. The volume fraction of the

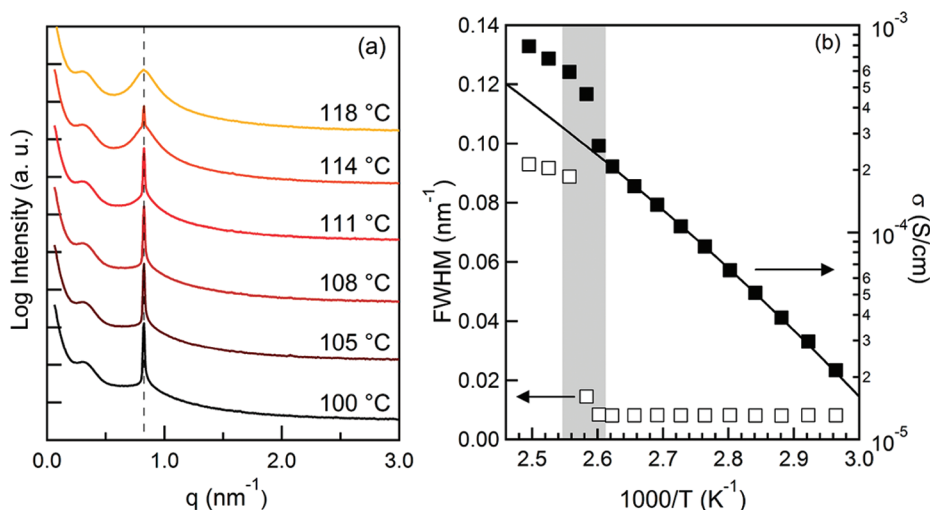


Figure 2. (a) SAXS intensity versus scattering vector, q , for SEO(1.7–1.4)/LiTFSI at $r = 0.085$ in an in situ pouch cell at select temperatures. The dotted vertical line emphasizes the invariance of the domain spacing with temperature. (b) Left axis (empty squares) shows the full-width half-maximum of the primary scattering peak versus inverse temperature. Right axis (full squares) shows ionic conductivity versus inverse temperature. The gray bar indicates the order–disorder transition temperature, T_{ODT} , and the solid line indicates the VTF fit to conductivity data below the T_{ODT} .

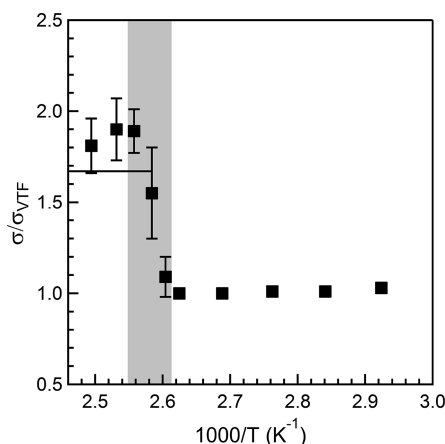


Figure 3. Ionic conductivity normalized by VTF fit versus inverse temperature. The gray bar denotes the ODT. The solid horizontal line denotes the expected increase in conductivity from changes in the morphology factor and vehicular transport.

PEO/LiTFSI microphase in our sample was estimated to be $\phi_c = 0.502$ based on the approach described in ref 8. In previous work we have argued that f should have a value of $2/3$ for randomly oriented lamellae, and $\sigma_c(T)$ for our system is the conductivity of a mixture of homopolymer PEO and LiTFSI at the same value of salt concentration.⁴ In conventional electrolytes, the motion of ions is coupled to that of the solvation shells that surround the ions. In the case of polymer electrolytes, the connectivity of the chains makes this mode of motion ineffective in the high molecular weight limit. It has thus been recognized that transport facilitated by rapid segmental motion is essential for significant ionic conductivity in the high molecular weight limit.^{10–12} Shi and Vincent first proposed the following expression for the conductivity of homopolymer electrolytes:

$$\sigma_c(T) = \sigma_0(T) + K(T)/M \quad (3)$$

where σ_0 is the ionic conductivity due to segmental motion of the polymer chains (obtained in the limit of infinite polymer molecular weight) and the K/M term accounts for so-called “vehicular” transport, that is, transport of coupled polymer chains and ions.¹⁰ The temperature dependence of σ_0 and K for PEO/LiTFSI mixtures with $r = 0.085$ are given in ref 14. We assume that vehicular motion is not possible in the ordered state because the polymer chains form a structure that is assumed to be static on the time scale of interest. The ionic conductivity of the ordered lamellar state is then given by

$$\sigma_{\text{ord}}(T) = \frac{2}{3}\phi_c\sigma_0(T) \quad (4)$$

The importance of concentration fluctuations in the disordered phase formed by low molecular weight block copolymers was recognized in the pioneering works of Leibler¹⁵ and Fredrickson and Helfand.¹⁶ In ref 16 it was shown that disordered phases of low molecular weight block copolymer melts are characterized by large amplitude concentration fluctuations. The geometric constraints of a lamellar phase are no longer present in the disordered phase, and we thus expect $f = 1$. In addition, SEO molecules are no longer constrained to form a quasi-static ordered phase, and thus both segmental motion and vehicular motion are expected to contribute to the conductivity of the disordered phase. With

these approximations, the conductivity of the disordered phase is given by

$$\sigma_{\text{dis}}(T) = \phi_c[\sigma_0(T) + K(T)/M] \quad (5)$$

and the ratio $\sigma_{\text{dis}}/\sigma_{\text{ord}}$ is given by

$$\frac{\sigma_{\text{dis}}}{\sigma_{\text{ord}}} = \frac{3}{2} \left(1 + \frac{K(T)}{\sigma_0(T)M} \right) \quad (6)$$

Using the total block copolymer molecular weight M of 3.1 kg mol^{-1} and values of $K = 1.4 \times 10^{-3} \text{ S kg mol}^{-1} \text{ cm}^{-1}$ and $\sigma_0 = 3.48 \times 10^{-3} \text{ S cm}^{-1}$ reported in ref 14 at $T = T_{\text{ODT}} = 114 \text{ }^\circ\text{C}$, we obtain $\sigma_{\text{dis}}/\sigma_{\text{ord}} = 1.67$ due to both morphology factor and vehicular transport contributions. The horizontal line in Figure 3 in the $T > T_{\text{ODT}}$ regime shows this prediction. It is evident that the experimental data are in reasonable agreement with this prediction. If the two contributions were separated, $\sigma_{\text{dis}}/\sigma_{\text{ord}}$ would equal 1.50 due exclusively to the increase in morphology factor and only 1.11 due to the enabling of vehicular transport. It is thus clear that, at this molecular weight, the largest increase is a result of the change in morphology factor.

A more stringent test of the proposed framework is conducted by computing a normalized conductivity, σ_n , defined as

$$\sigma_n(T) = \sigma(T)/f\phi_c\sigma_c(T) \quad (7)$$

For $T < T_{\text{ODT}}$ we use $f = 2/3$ and $\sigma_c(T) = \sigma_0(T)$ [eq 4]. For $T > T_{\text{ODT}}$ we use $f = 1$ and $\sigma_c(T) = \sigma_0(T) + K(T)/M$ [eq 5]. Figure 4 shows the dependence of σ_n on temperature. If our framework was exact and the conductive lamellae were

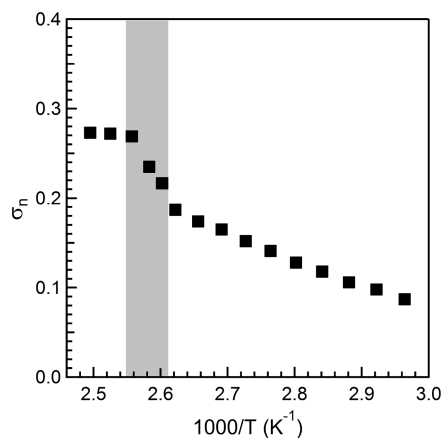


Figure 4. Normalized conductivity (as calculated from eq 7) versus inverse temperature. The gray bar denotes the ODT.

equivalent to pure PEO homopolymer, then σ_n would be unity at all temperatures. Instead we find that the normalized conductivity increases monotonically with increasing temperature in the $T < T_{\text{ODT}}$ regime and is independent of temperature in the $T > T_{\text{ODT}}$ regime. The temperature dependence of σ_n below the ODT indicates that the activation energy for ion conduction in the ordered SEO block copolymer is different from that of PEO homopolymer. The temperature independence of σ_n above the ODT indicates that the activation energy for ion conduction in the disordered SEO block copolymer is identical to that of PEO homopolymer. The fact that σ_n is significantly less than unity in Figure 4 can be either due to the fact that the intrinsic conductivity of the PEO-

rich microphase is affected by the presence of the PS phase or limitations of the proposed framework. In spite of these limitations, it is clear that the proposed framework provides a starting point for understanding the reason for conductivity changes across the order–disorder transition in block copolymer electrolytes.

Our framework can readily be extended to predict conductivity changes through other transitions (e.g., order–order transitions) in block copolymer electrolytes. Majewski et al.⁷ observed a plateau in conductivity in the vicinity of the transition from the cylinder with the minority conducting phase to a disordered phase. Based on the framework presented in this paper, we expected $\sigma/\sigma_{\text{VTF}}$ to be 3 at temperatures above this transition due to an increase of the morphology factor from 1/3 to unity. In contrast, Majewski et al.⁷ observed $\sigma/\sigma_{\text{VTF}}$ values less than unity in the disordered phase. This discrepancy may be the result of discontinuous concentration fluctuations due to the small fraction of conducting phase or the liquid–crystalline nature of the insulating block. Wanakule et al.⁸ report a transition to the disordered phase from both the lamellar phase and the majority conducting cylinder phase, as well as an order–order transition (OOT) from the lamellar phase to the gyroid phase. No discontinuity in conductivity is expected for a transition from a majority conducting cylinder phase to a disordered phase if $f = 1$ and M is sufficiently large so that vehicular ion transport is negligible. The lamellar to gyroid transition reported by Wanakule et al.⁸ occurred over the wide temperature window of 52–106 °C, which may have obscured the expected increase in conductivity as f changes from 2/3 to unity. We offer no explanation for the lack of a discontinuity in conductivity for the lamellar to disorder transition reported by Wanakule et al.⁸ Perhaps improvements in sample preparation and simultaneous morphology characterization and conductivity measurements may have helped elucidate the behavior observed in the present work. Similarly we have no explanation for the lack of discontinuity in conductivity for the ODT reported by Ruzette et al.⁹ Cho et al.¹⁷ reported an order of magnitude increase in conductivity as a PEO-based dendrimer–linear chain diblock copolymer underwent an OOT from minority conducting cylinder phase to a gyroid phase. Based on the framework presented in this paper, an increase by a factor of 3 would be expected for this transition.

In conclusion, in situ measurements of SAXS and ionic conductivity of a block copolymer electrolyte as it transitioned from an ordered lamellar structure to a disordered phase revealed a discontinuous increase in conductivity at the phase transition by a factor of about 1.8. A simple framework for understanding this result is presented.

EXPERIMENTAL METHODS

The SEO copolymer was synthesized using methods described in refs 18 and 19 and purified using methods described in ref 20. In situ conductivity samples were prepared by pressing material into insulating spacers with 17 μm thick electrochemical grade aluminum foil electrodes. The samples were vacuum sealed inside airtight pouches after aluminum tabs were attached to the electrodes. The pouches were loaded into a custom heating stage for simultaneous electrochemical and X-ray scattering experiments. A Biologic-VMP3 Potentiostat measured the complex impedance of the samples over a 0.1–10⁶ Hz frequency range with an applied potential amplitude of 50 mV. The electrolyte resistance, R , was determined from the low-frequency minimum on a Nyquist impedance plot. The conductivity reported was measured during the second heating run, and the sample was allowed to equilibrate for 10 min at each temperature. In situ

small-angle X-ray scattering experiments were performed at beamline 7.3.3 at the Advanced Light Source. The azimuthally averaged scattering intensity, I , is reported as a function of the magnitude of the scattering vector q . The domain spacing, d , is defined as $d = 2\pi/q^*$, where q^* is the value of q at the primary scattering peak.

ASSOCIATED CONTENT

Supporting Information

Additional experimental detail and small-angle X-ray scattering profile. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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