Supporting Information:

Dissolution of Lithium Metal in Poly(ethylene oxide)

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I. Sample Preparation and Experimental Methods

Materials. All hydroxy terminated poly(ethylene oxide) (PEO) was purchased from Polymer Source. 2 kg mol^{-1} PEO terminated with dimethyl ether was purchased from Sigma Aldrich. Before use, polymers were dried under vacuum at 130°C for at least 24 hours. The polystyrene-*block*-poly(ethylene oxide) (SEO) block copolymers used in this study were synthesized, purified, and characterized using methods described by Teran et al.[1] and Hadjichristidis et al[2]. The block copolymer electrolyte used in Figure 4 of the main text (PS molecular weight of 1.7 and PEO molecular weight of 1.4 kg mol^{-1}) was prepared following the methods of Yuan et al.[3] to produce an SEO/LiTFSI mixture with a molality of 1.70 mol kg^{-1}. Lithium metal was purchased from MTI and scraped with a nylon brush prior to use to expose a fresh lithium surface.

Sample Preparation. All sample preparation was performed in an argon filled glove box (VAC) with oxygen and water concentrations maintained below 3 and 1 ppm respectively. Electrochemical and small angle X-ray scattering (SAXS) samples were assembled by placing polymer inside a silicone rubber spacer sandwiched by two lithium, stainless steel, or aluminum electrodes/windows and gently pressed on a hot plate at 90 °C. For electrochemical cells, nickel current collectors were attached. Electrochemical and small angle X-ray scattering (SAXS) samples were sealed in aluminum laminated pouch material purchased from MTI.

Nuclear Magnetic Resonance (NMR) Spectroscopy. NMR measurements were performed at 14.1 T using a 600 MHz Bruker Avance III spectrometer with a 5 mm PABBO direct detection broad-band probe (BB-1H/D Z-GRD) and a variable temperature unit. All measurements were performed at 90 °C. The temperature was calibrated prior to the experiment using the known temperature dependence of the 1H chemical shift of ethylene glycol[4]. Measurements were

performed on ^{7}Li at a resonance (Larmor) frequency of 233.23 MHz with a 90° pulse time of 12 µs at a power level of -1 dB, acquisition time of 0.1 s, and relaxation (recycle) delay of 1 s. Samples were placed in coaxial borosilicate NMR tubes (5.0 mm outer tube diameter and 3.3 mm inner tube diameter) purchased from Wilmad and sealed with custom built air-free caps. The PEO sample was placed in the inner tube and a standard solution of LiTFSI in tetraglyme was placed in the outer tube. The mass of both the PEO and standard were recorded (approximately 50 mg each). Because the volume of the sample was small (taking up less than 1 cm of the NMR tube), we assume that the entire sample contributed to the signal observed, and the signal can be normalized to the mass of the sample. Each individual spectrum was the result of 1600 scans to enhance signal to noise.

Electrochemical measurements. All electrochemical measurements were made using a Biologic VMP3 potentiostat. Cells were maintained at 120 °C using a custom-built heating stage. Ac impedance measurements were made in a frequency range from 1 MHz to 100 mHz with an amplitude of 80 mV.

Small angle X-ray Scattering (SAXS). Lithium symmetric cells were assembled shortly before the SAXS experiments and maintained at room temperature prior to the experiment. Sample temperature was maintained using a custom-built heating stage calibrated with a separate polyethylene standard. Silver behenate was used to determine the beam center and sample-to-detector distance. Two-dimensional scattering patterns were integrated azimuthally using the Nika program for IGOR Pro to produce one-dimensional scatter profiles[5]. The stage temperature was ramped at roughly 10 °C per minute. $t = 0$ for the SAXS experiments was set as the time that the heating stage reached 120 °C.

Gel permeation chromatography (GPC). Measurements were made on an Agilent 1260 Infinity series GPC with Waters Styragel HR 3 and 4 columns. The eluent was n-methyl-2-pyrrolidone (NMP) with 0.05 M LiBr at 70 °C. The GPC was calibrated using a set of PEO standards (Fluka).

Fourier transform infrared (FTIR) spectroscopy. Measurements were taken on a Thermo Fisher FTIR spectrometer using an air-free attenuated total reflectance attachment at room temperature.

II. Supporting discussion

Fitting of NMR data. All processing of NMR spectra was performed using TopSpin software package from Bruker. The NMR spectra in Figures 1a-c were fitted to two peaks in order to deconvolute the peak integrations with a linear the offset. The function used to fit the data is given by:

$$I(\delta) = I_0 + G(\delta) + L(\delta), \tag{S1}$$

where $I(\delta)$ is the intensity at ^{7}Li chemical shift δ in ppm, I_0 is a constant offset, $G(\delta)$ is a Gaussian function given by S2 and $L(\delta)$ is a Lorentzian function given by S3.

$$G(\delta) = a \exp\left[\frac{-(\delta - b)^2}{2c^2}\right] \tag{S2}$$

$$L(\delta) = \frac{d}{(\delta - e)^2 + f} \tag{S3}$$

In Eqn. S2 and S3 a, b, c, d, e and f are fitting parameters.

The resulting fits allowed integration of $G(\delta)$ and $L(\delta)$ to obtain the peak integration for the broad peak, A_{PEO}, at 1.5 ppm (corresponding to lithium dissolved in the PEO sample) and the sharp peak, A_{std} at -0.2 ppm (corresponding to LiTFSI in tetraglyme), respectively:

$$A_{PEO} = \int_{-\infty}^{\infty} G(\delta)\, d\delta \tag{S4}$$

$$A_{std} = \int_{-\infty}^{\infty} L(\delta)\, d\delta. \tag{S5}$$

We assume that each lithium atom contributes equal intensity. We can then calculate the mass fraction of lithium in the PEO sample, x_{Li}, by:

$$x_{Li} = x_{Li,std} \frac{m_{std}}{m_{PEO}} \frac{A_{PEO}}{A_{std}}, \tag{S6}$$

where m_{std} and m_{PEO} are the total mass of the LiTFSI in tetraglyme standard solution and PEO sample, respectively, and $x_{Li,std}$ is the mass fraction of lithium atoms in the standard (note: this value differs from the mass fraction of LiTFSI in the standard solution by a factor equal to the ratio of the molar mass of lithium to the molecular weight of LiTFSI). For all three experiments, $x_{Li,std}$ = 0.000102. Because there is a small amount of lithium (μgs of lithium compared to mgs of PEO), we can assume that the mass of the sample is approximately equal to the mass of the PEO. We can then convert x_{Li} to molality by:

$$m = \frac{x_{Li}}{M_{Li}} \tag{S7}$$

where M_{Li} is the molar mass of lithium in (6.941×10^{-3} kg mol^{-1}).

Conductivity measurements. Ac impedance spectroscopy was used to measure the conductivity of the, initially neat, 35 kg mol^{-1} PEO samples annealed against lithium electrodes at 120 °C. The resistance of the cell was obtained by fitting the Nyquist plot to an equivalent circuit consisting of a resistor and constant phase element in series. The choice of equivalent circuit is justified by the single semi-circle observed in the Nyquist plot. From the fit, the cell resistance, R, was obtained. Conductivity, κ, was calculated using Equation S8.

$$\kappa = \frac{L}{AR} \tag{S8}$$

L is the distance between electrodes and A is the interfacial contact area between the electrode and PEO.
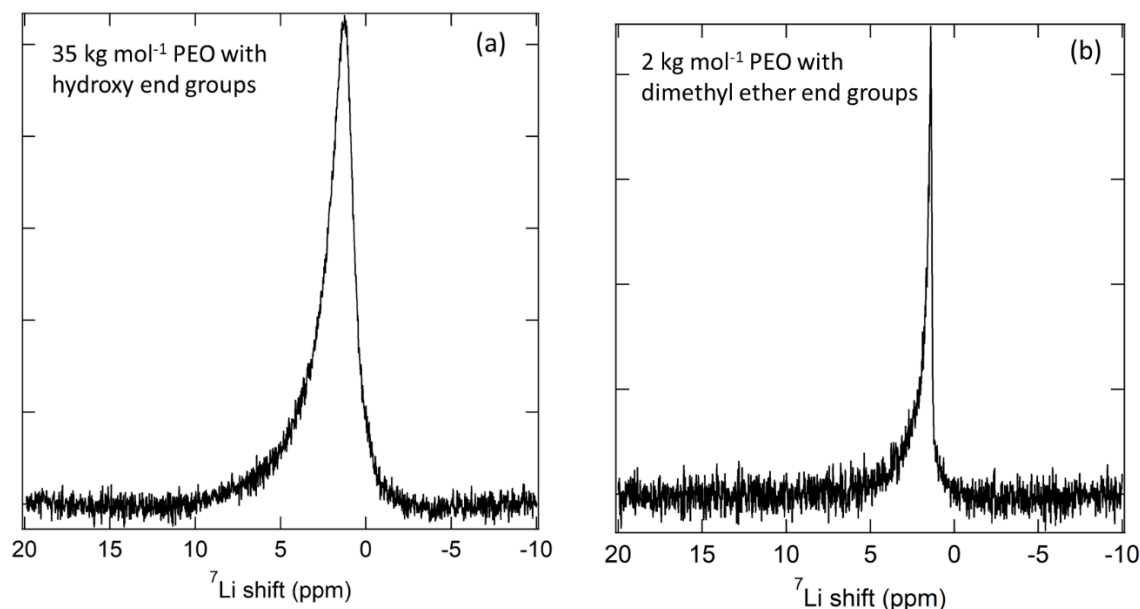
III. Supporting Figures

Figure S1. (a) ^{7}Li NMR spectrum taken at 90 °C of 35 kg mol^{-1} PEO annealed against lithium in a Li/PEO/Li cell configuration at 90 °C for 12 days. The lithium foils were removed inside the glove box prior to placing the sample in a 5 mm borosilicate NMR tube for characterization. Qualitatively similar spectra were obtained for PEO annealed against lithium at a range of temperatures between 90 and 140 °C and a variety of annealing times from 6 to 20 days. (b) ^{7}Li NMR taken at 90 °C of a 2 kg mol^{-1} PEO sample terminated with dimethyl ether end groups (Sigma Aldrich) annealed against lithium metal for 6 days at 90 °C. Because this sample has a low viscosity at this temperature which makes it difficult to contain in a symmetric cell configuration, the PEO was placed in a glass vial with small pieces of lithium foil placed on top. The sample was then stirred at 90 °C for 6 days before approximately 50 mg of the PEO was removed with a pipette and placed in a 5 mm borosilicate NMR tube for analysis. The peak location for this sample with DME end groups is identical to that shown in (a) for 35 kg mol^{-1} PEO with hydroxy end groups. We attribute the width of the peak in (b) being narrower than in (a) to faster diffusion in 2 kg mol^{-1} PEO. These results indicate that the lithium dissolution

process is not limited to PEO molecules terminated with hydroxy end groups, and the nature of

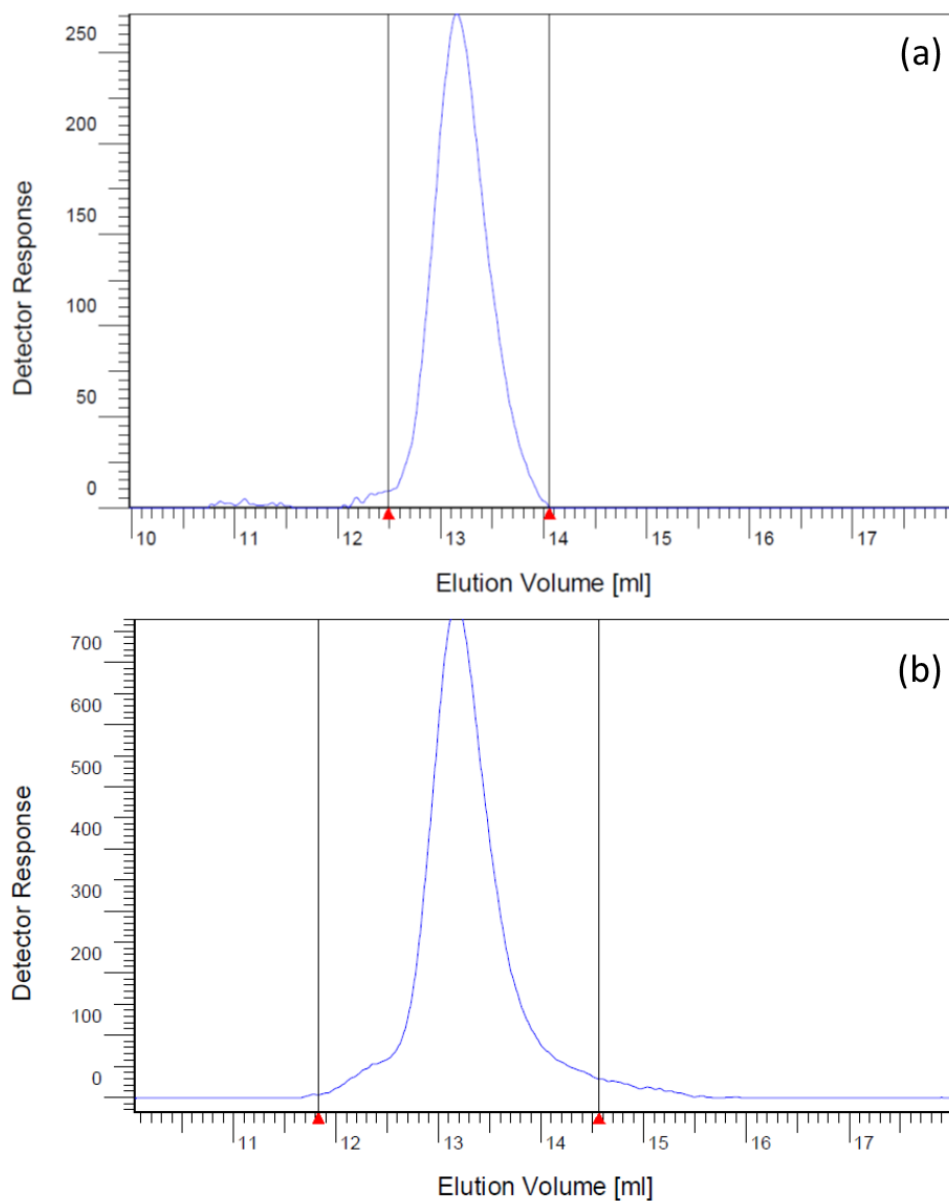the dissolved lithium species is independent of the end group.

Figure S2. Gel permeation chromatography (GPC) results for 35 kg mol^{-1} PEO (a) annealed

against lithium metal at 120 °C for 6 days and (b) annealed under the same conditions with no

lithium metal present. There are no significant differences in the GPC traces between (a) and

(b), indicating that the molecular weight distribution of the PEO chains does not change due to annealing against lithium metal.   For reasons that are unclear, the GPC peak is narrower after exposure to lithium metal.
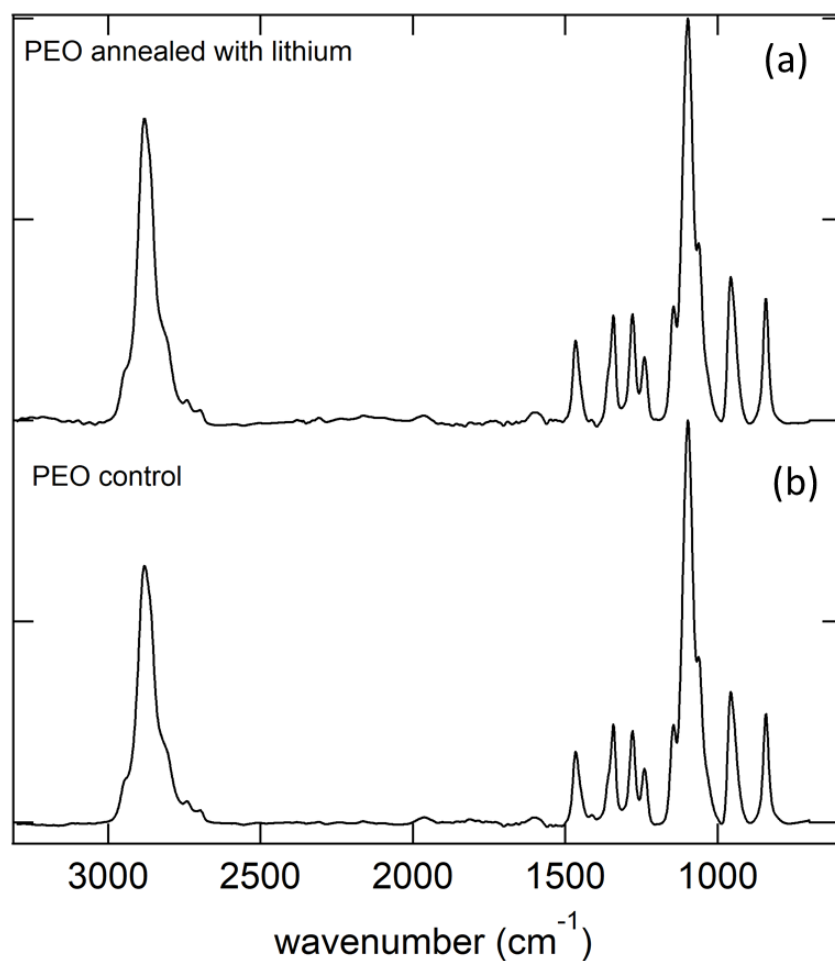

Figure S3. Results of Fourier transform infrared (FTIR) spectroscopy on 35 kg mol^{-1} PEO (a) annealed against lithium metal at 120 °C for 6 days and (b) annealed under the same conditions with no lithium metal present. The spectra for the lithium annealed sample and control are identical, indicating that the chemical bonds in the PEO chains are not impacted by the dissolved lithium metal.
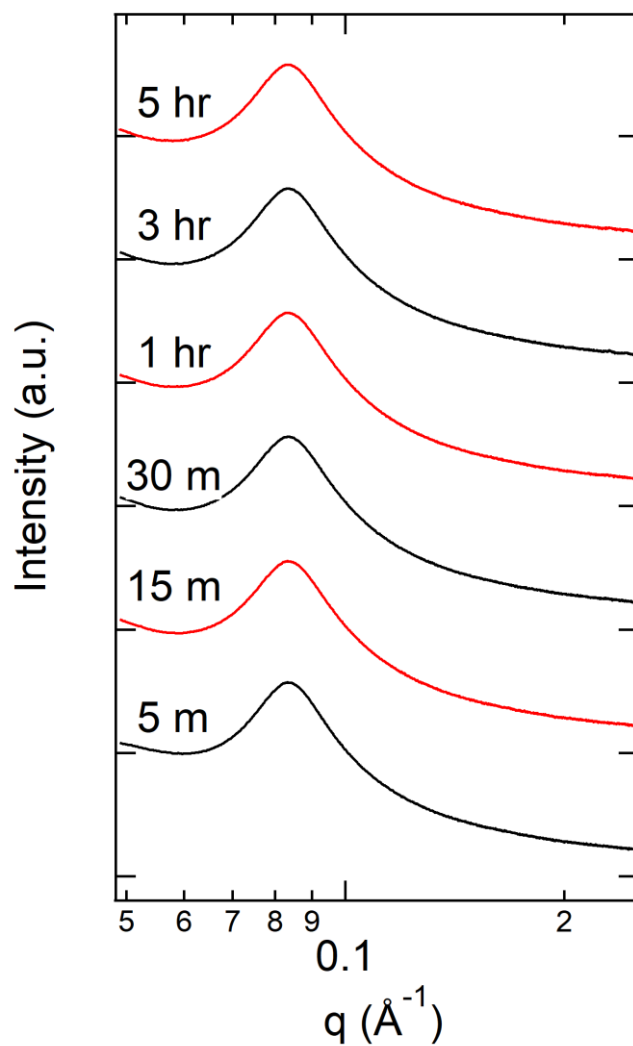
Figure S4. (a) Time dependent SAXS profiles of a 0.5 mm thick SEO/LiTFSI mixture (with 1.7 and 1.4 kg mol^{-1} PS and PEO molecular weight) against aluminum windows at 120 °C.
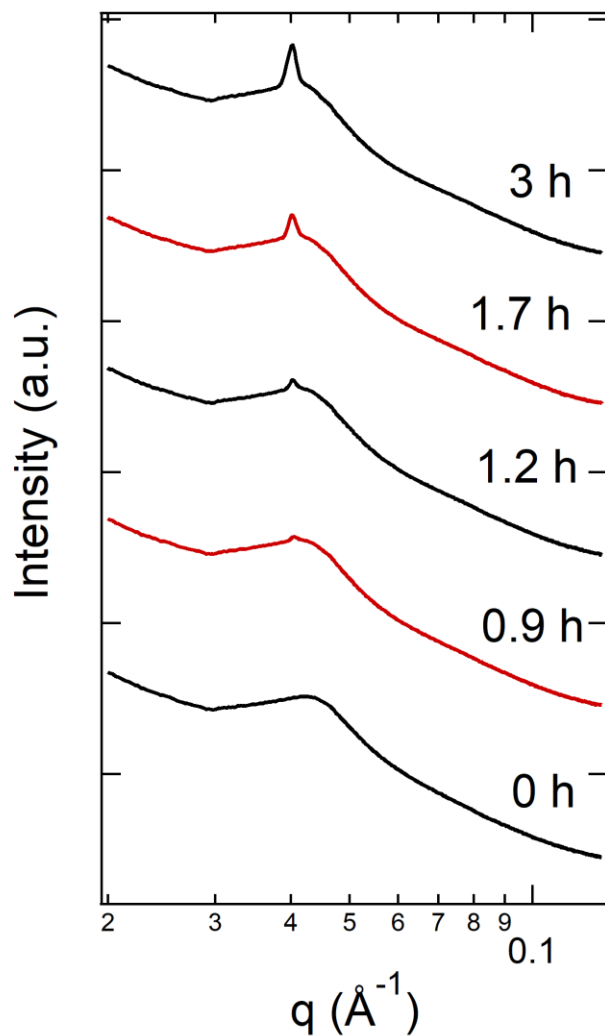
Figure S5. Time dependent SAXS profiles of a neat SEO block copolymer ($L = 0.5$ mm) against lithium windows at 120 °C. Lithium dissolution stabilizes an ordered phase without the presence of salt. For this polymer, the PS and PEO molecular weights were 6.4 and 7.3 kg mol^{-1} respectively and it exhibits an order-to-disorder transition at 78 °C[6].

IV References.

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