Dependence of Morphology, Shear Modulus, and Conductivity on the Composition of Lithiated and Magnesiated Single-Ion-Conducting Block Copolymer Electrolytes

Supporting Information

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Notes: The authors declare no competing financial interest.

Supporting Information

Nuclear Magnetic Resonance ^{1}H-NMR

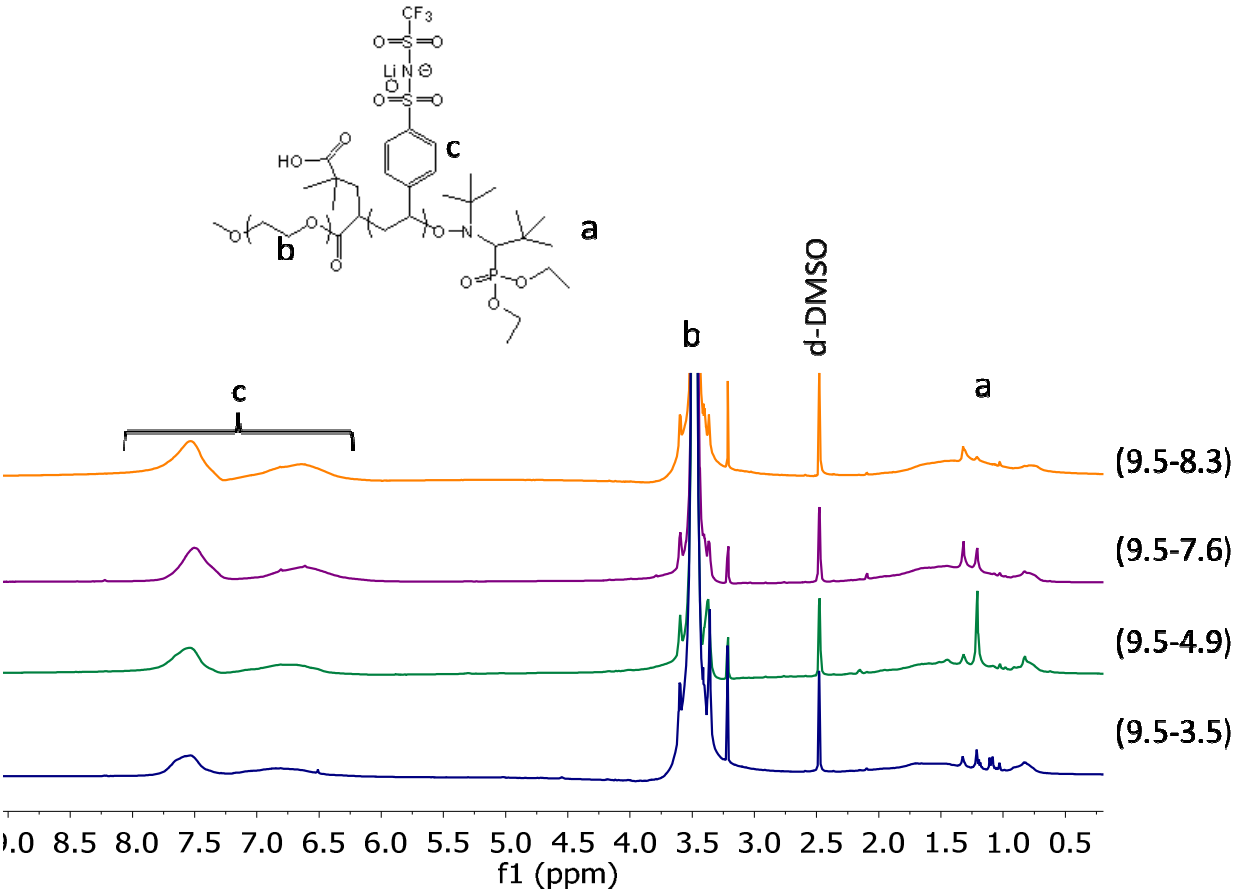

Figure S1. ^{1}H-NMR of the PEO-*b*-PSLiTFSI 9.5 kg·mol^{-1} series in d-DMSO at 25 °C. Blocbuilder® end-group (0.75-1.8 ppm), PEO ethyl ether groups (3.4-3.8 ppm), methyl end-group (3.36 ppm), PSLiTFSI aromatic ring (6.3-7.8 ppm).

Gel Permeation Chromatography (GPC)

The conditions for GPC were previously reported. [1] GPC traces of the PEO-macroinitiator (9.5 kg mol^{-1}) and the PEO-PSLiTFSI block copolymers confirm polymerization of the PSLiTFSI block (Figure S2). The small peaks in the vicinity of 17.8 and 18.7 mL correspond to precursor polymer: PEO methyl ether acrylate.

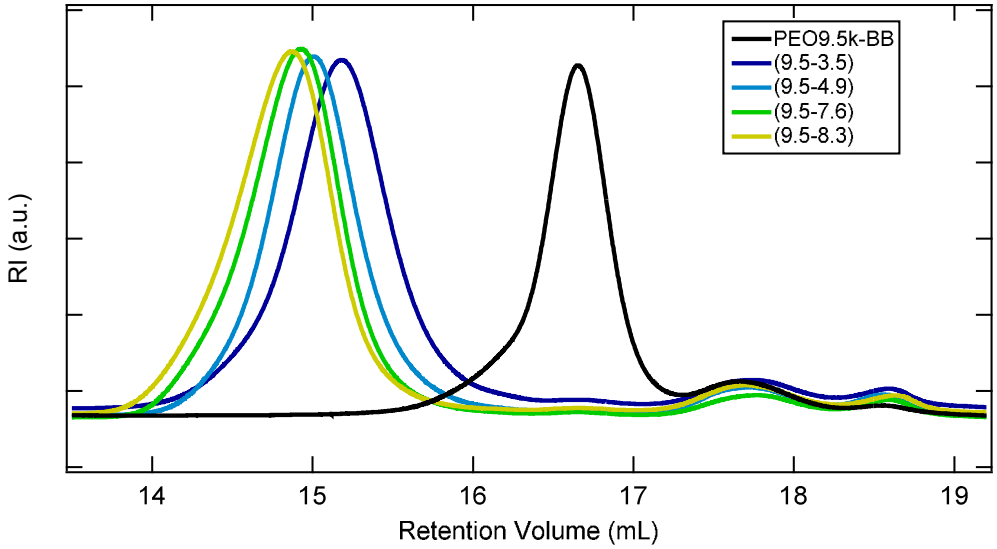

Figure S2. GPC traces of the polymers in the 9.5 kg·mol^{-1} series of PEO-*b*-PSLiTFSI

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES)

In this study, ICP-OES was used to determine the efficacy from the ion-exchange reactions. In Figure S3a, the ICP-OES results are shown for the 9.5 $kg \cdot mol^{-1}$ series of the lithiated copolymers. Three different wavelengths of light were used to detect the presence of Li^+ (274, 323, and 460 nm). It is evident that some K^+ remains in the block copolymers after dialysis. This quantity remaining is equivalent to 3 mol%; therefore, 97 mol% is Li^+. We take the small quantity of K^+ to be negligible. The ICP-OES results for the magnesiated block copolymers are shown in Figure S3b. Three different wavelengths of light were used to detect the presence of Mg^{2+} (280, 294, and 383 nm). While three wavelengths of light were used to detect the presence of K^+ (345, 404, and 770 nm), only one wavelength of light could detect the small quantities of K^+ remaining in the magnesiated block copolymers. The other two wavelengths of light reported values that were below the range of the calibration standards.

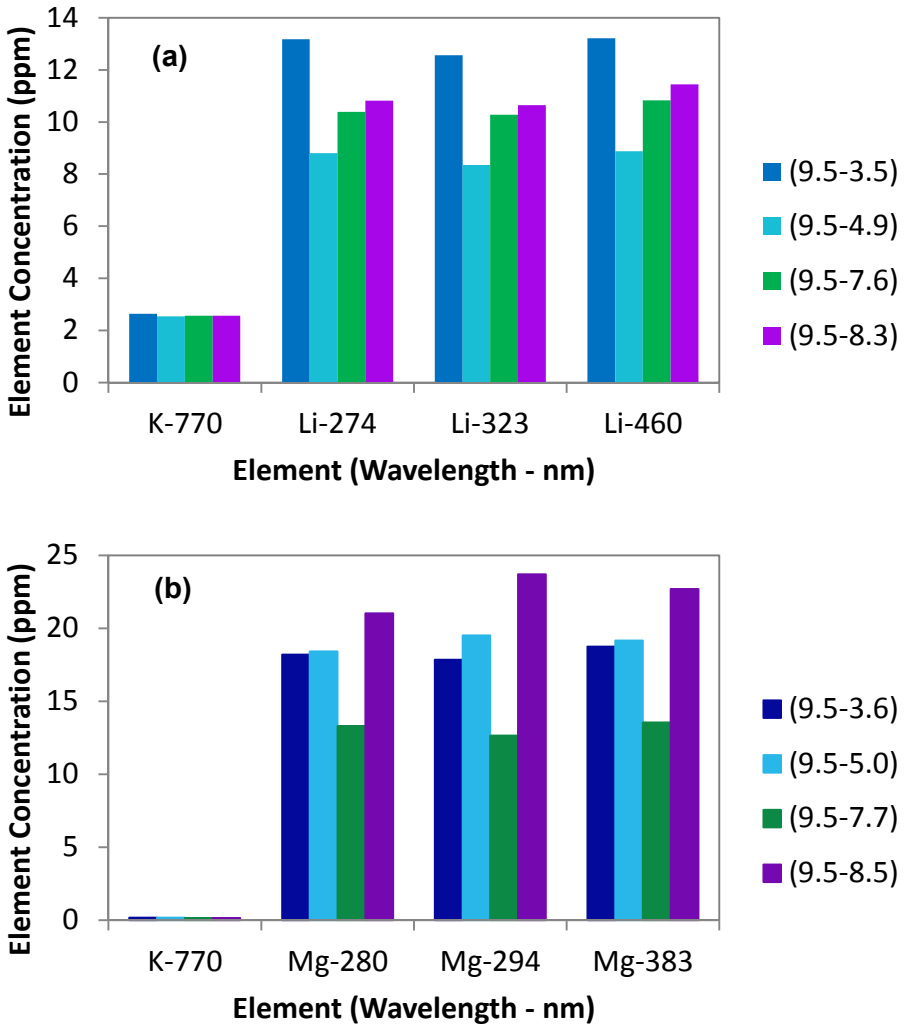

Figure S3. ICP-OES results for the (a) lithiated and (b) magnesiated block copolymers.

Teubner-Strey Fitting Parameters for PEO-P[(STFSI)$_2$Mg]

Teubner-Strey Fitting Parameters for PEO-P[(STFSI)$_2$Mg](9.5-3.6)							
T (°C)	ξ (nm)	d (nm)	a	b	c	e	g
60	17.3	18.2	5.01	-77.3	333	17.9	0.767
70	16.1	19.2	1.91	-32.0	154	3.64	10.64
80	16.7	19.0	1.91	-31.9	151	9.02	4.34
90	18.3	18.8	2.26	-37.4	172	13.1	0.723

Teubner-Strey Fitting Parameters for PEO-P[(STFSI)$_2$Mg](9.5-5.0)							
T (°C)	ξ (nm)	d (nm)	a	b	c	e	g
70	11.6	29.1	0.468	-12.6	160	9.30×10^{7}	4.21×10^{8}
80	14.3	27.7	0.542	-16.0	172	54.6	-0.301
90	16.9	26.5	0.606	-17.9	170	22.0	1.63

Teubner-Strey Fitting Parameters for PEO-P[(STFSI)$_2$Mg](9.5-7.7)							
T (°C)	ξ (nm)	d (nm)	a	b	c	e	g
60	24.5	26.5	1.98	-64.7	594	0.486	2.69
70	23.5	26.8	2.69	-88.4	829	14.3	1.27
80	13.0	28.5	1.02	-29.2	341	-1623	288.27
90	9.28	35.1	0.363	-7.79	190	2.95×10^{7}	1.21×10^{8}
110	12.3	36.4	0.281	-9.85	212	35.9	12.94
130	16.0	31.4	0.365	-13.7	189	-4.04	6.71

Frequency Dependent Moduli for the PEO-PSTFSILi Copolymers

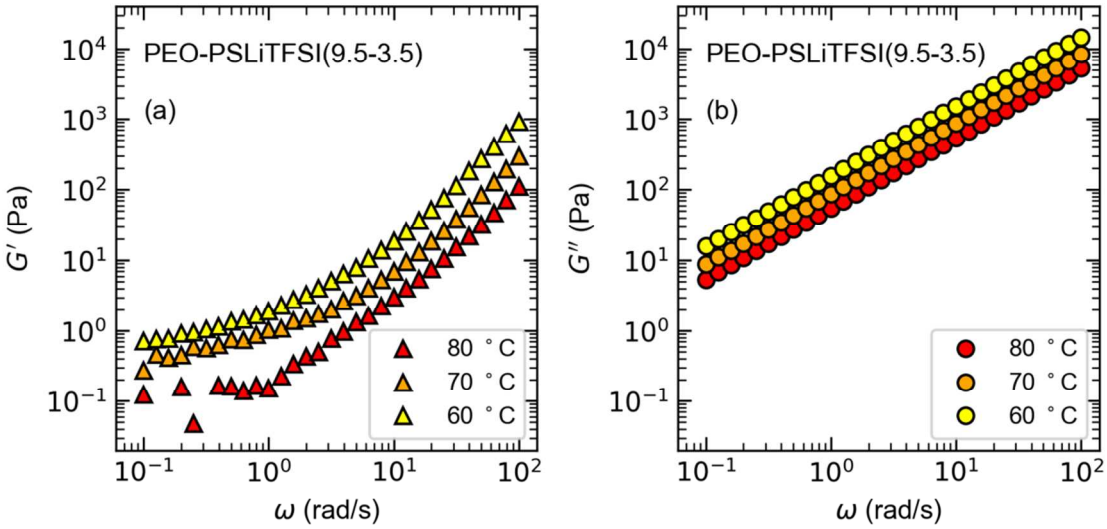

Figure S4. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-PSLiTFSI(9.5-3.5)

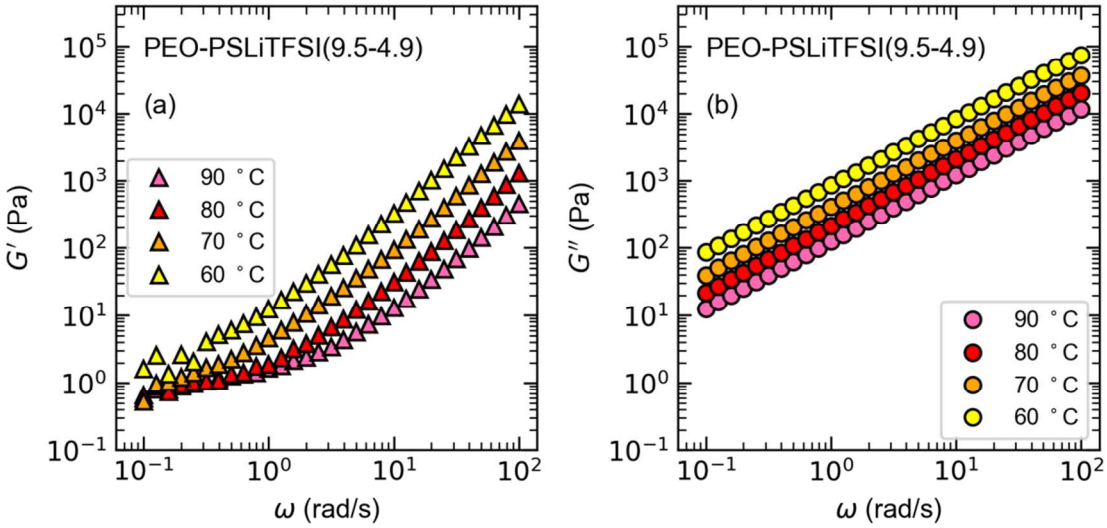

Figure S5. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-PSLiTFSI(9.5-4.9)

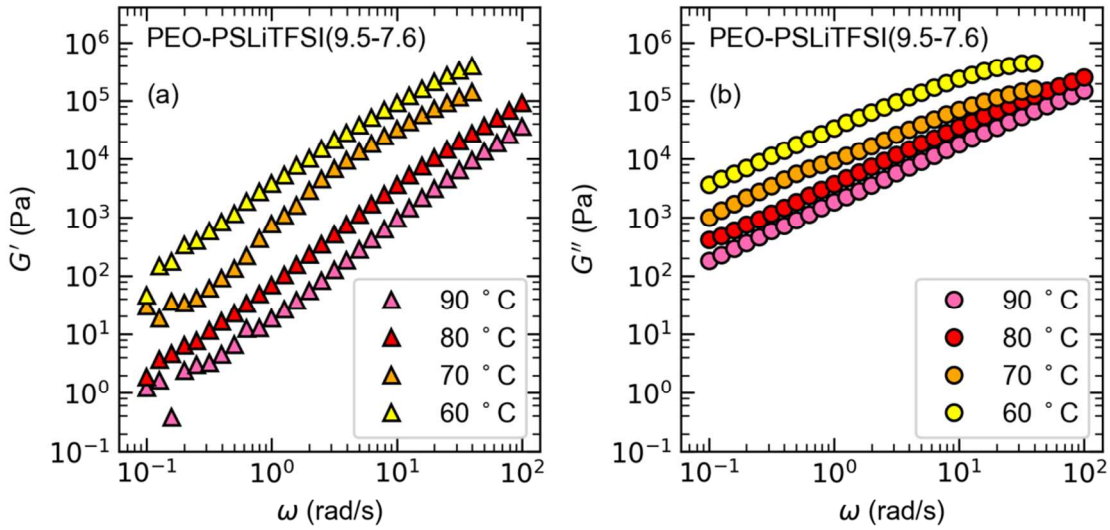

Figure S6. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-PSLiTFSI(9.5-7.6)

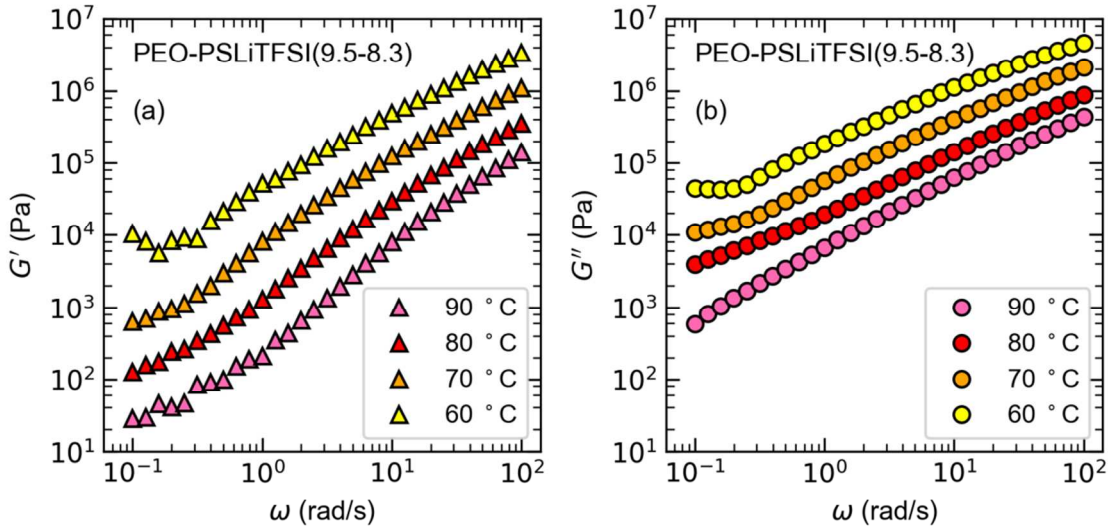

Figure S7. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-PSLiTFSI(9.5-8.3)

Frequency Dependent Moduli for the PEO-P[(STFSI)$_2$Mg] Copolymers

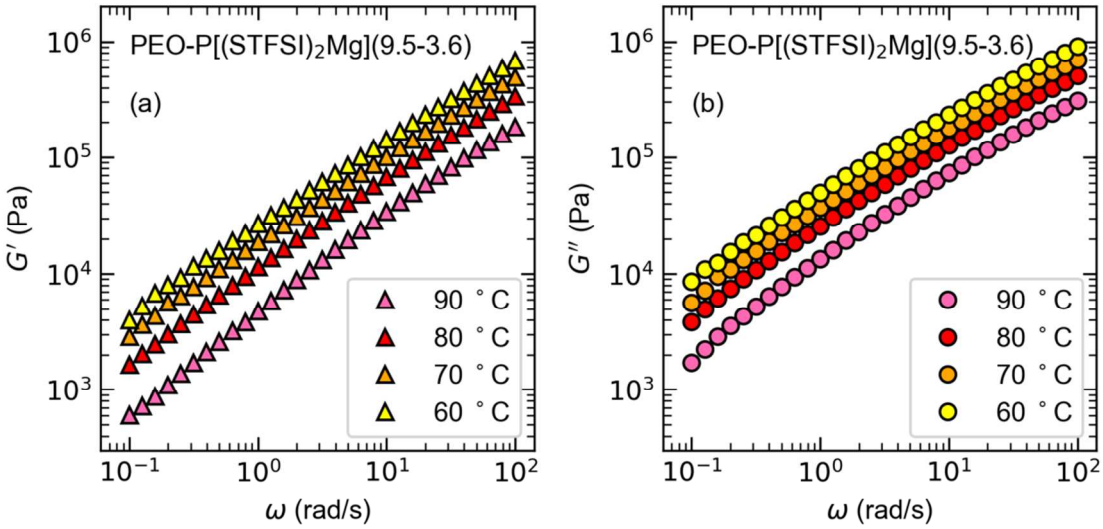

Figure S8. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-3.6)

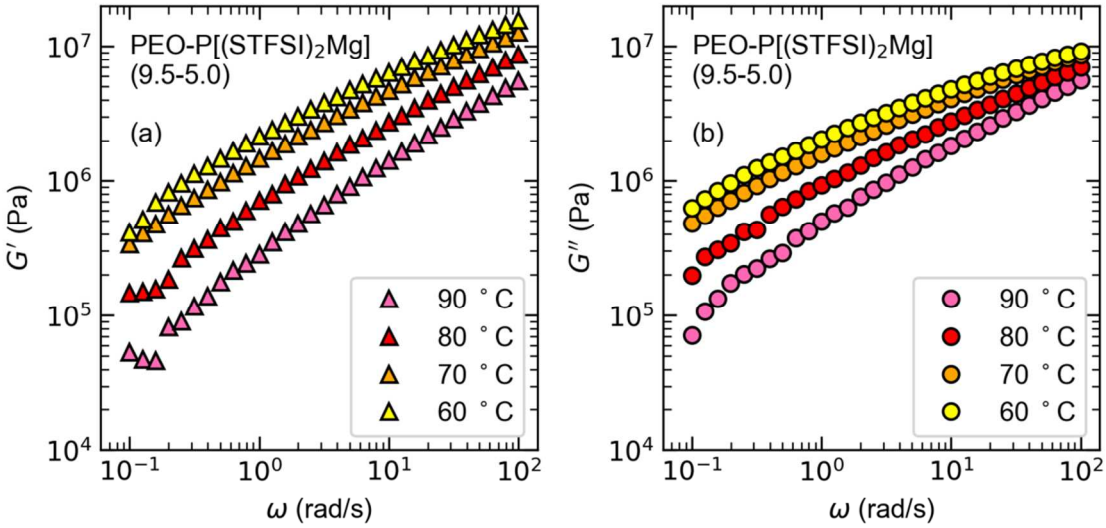

Figure S9. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-5.0)

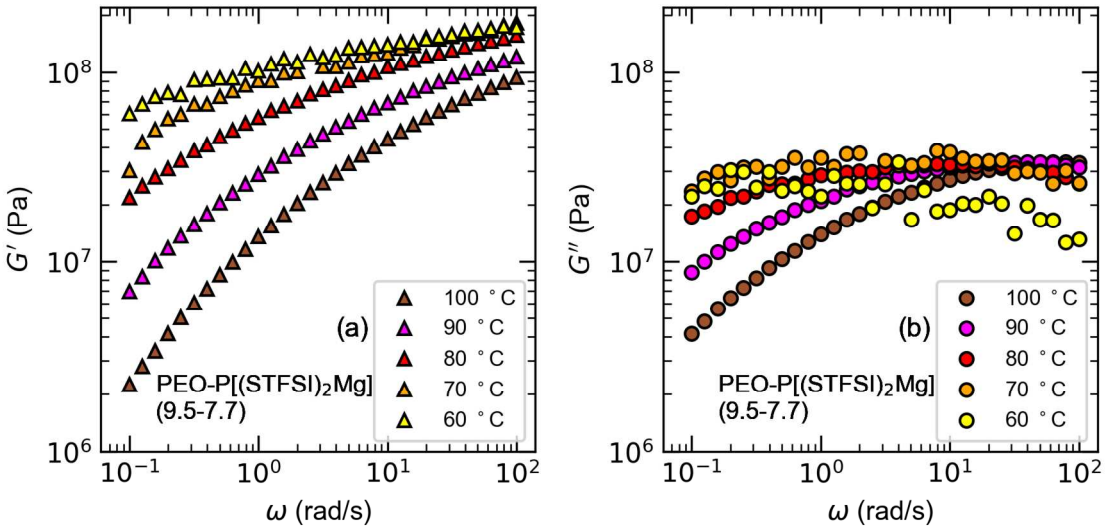

Figure S10. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-7.7)

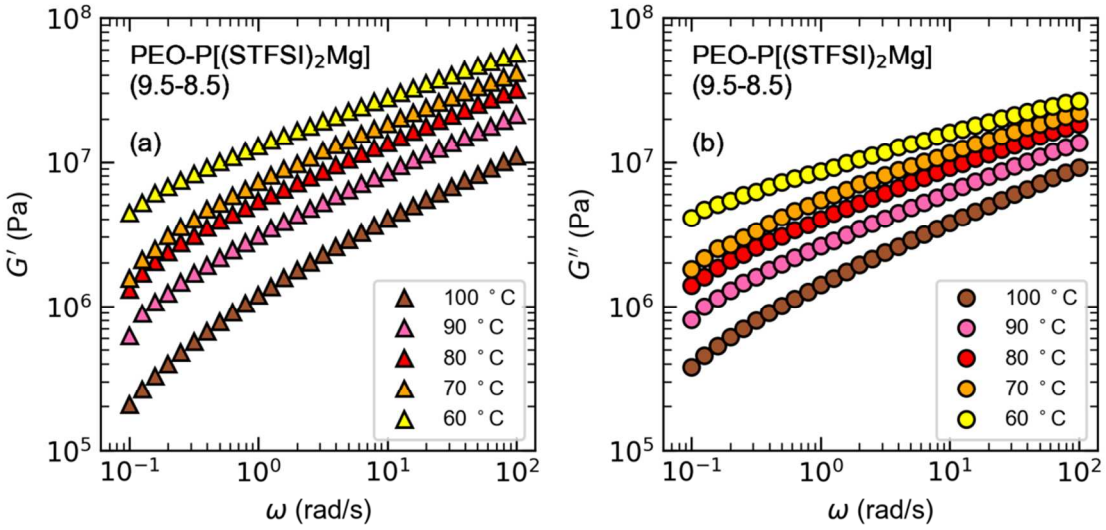

Figure S11. Frequency dependent (a) G' and (b) G'' at several temperatures for PEO-P[(STFSI)$_2$Mg] (9.5-8.5)

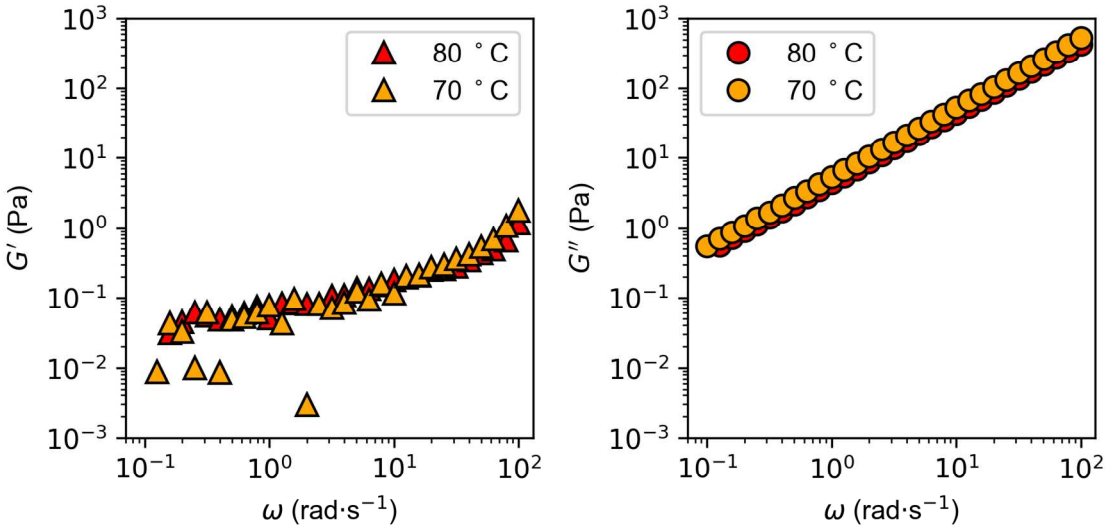

Figure S12. Frequency dependent (a) G' and (b) G'' at 80 and 90 °C for PEO 9.5 kg·mol^{-1} homopolymer.

Reference

[1] Rojas, A.A.R.; Inceoglu, S.; Mackay, N.G.; Thelen, J.L.; Devaux, D.; Stone, G.M.; Balsara, N.P. Effect of Lithium-Ion Concentration on Morphology and Ion Transport in Single-Ion-Conducting Block Copolymer Electrolytes. *Macromolecules* **2015**, 48, 6589-6595.