

Supporting Information for
Effect of Added Salt on Disordered Poly(ethylene oxide)-Block-
Poly(methyl methacrylate) Copolymer Electrolytes

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NMR Spectra

The composition of the PEO-PMMA block copolymers was determined using ^1H NMR (CDCl_3 , Bruker AV400). The composition was calculated by integrating the ethylene proton peak at 3.64 ppm against the proton peak for the methyl group on the MMA repeat units at 1.02, 0.85 and 3.60 ppm.

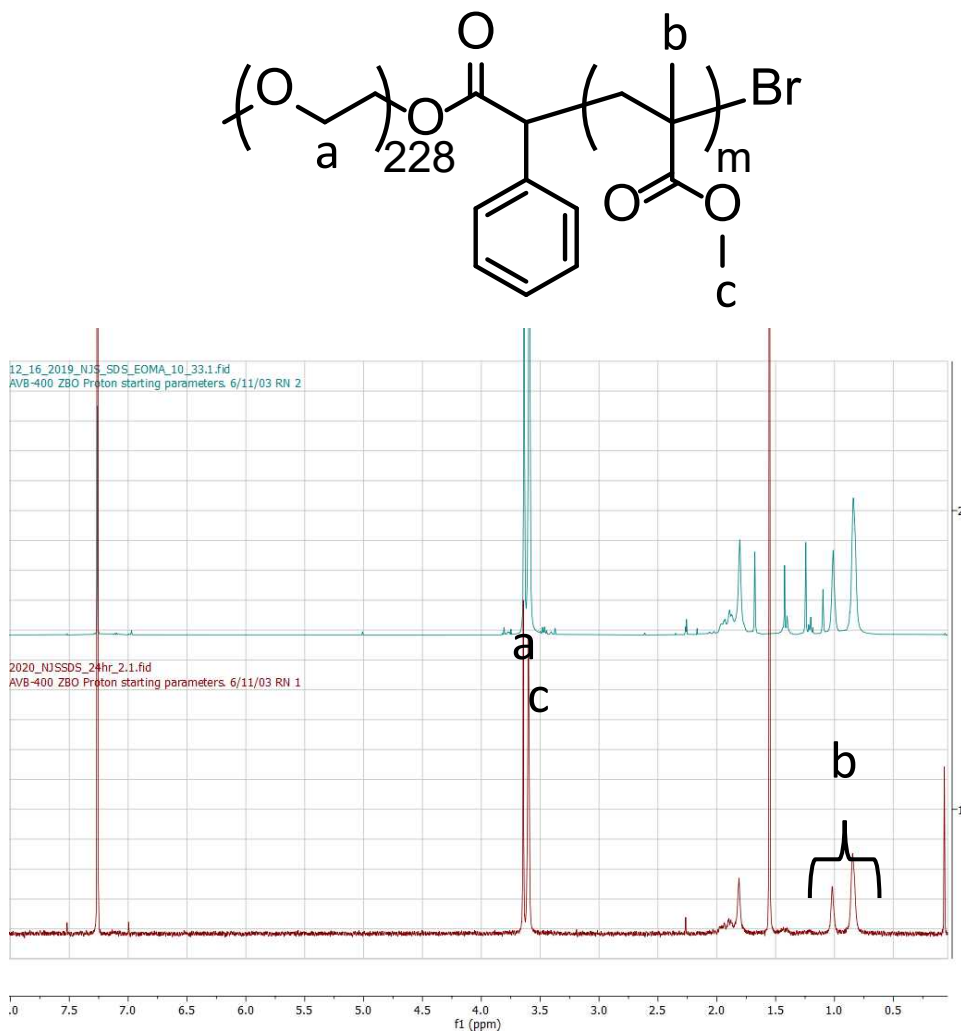


Figure S1: ^1H NMR of PEO-PMMA. The peak (a) at $\delta = 3.64$ ppm is the hydrogen peak for PEO. Peaks at 0.85 ppm and 1.02 ppm (b) represent the PMMA methyl hydrogens and the peak at 3.60 ppm (c) represents the PMMA carboxyl hydrogen.

Gel Permeation Chromatography

PEO-PMMA was characterized on an Agilent 1260 Infinity Series gel permeation chromatography (GPC) system with Waters Styragel HR3 and HR4 columns with a *N*-methyl-2-pyrrolidone (NMP) mobile phase. GPC was used to determine molecular weight distribution and was used to verify NMR determined molecular weights.

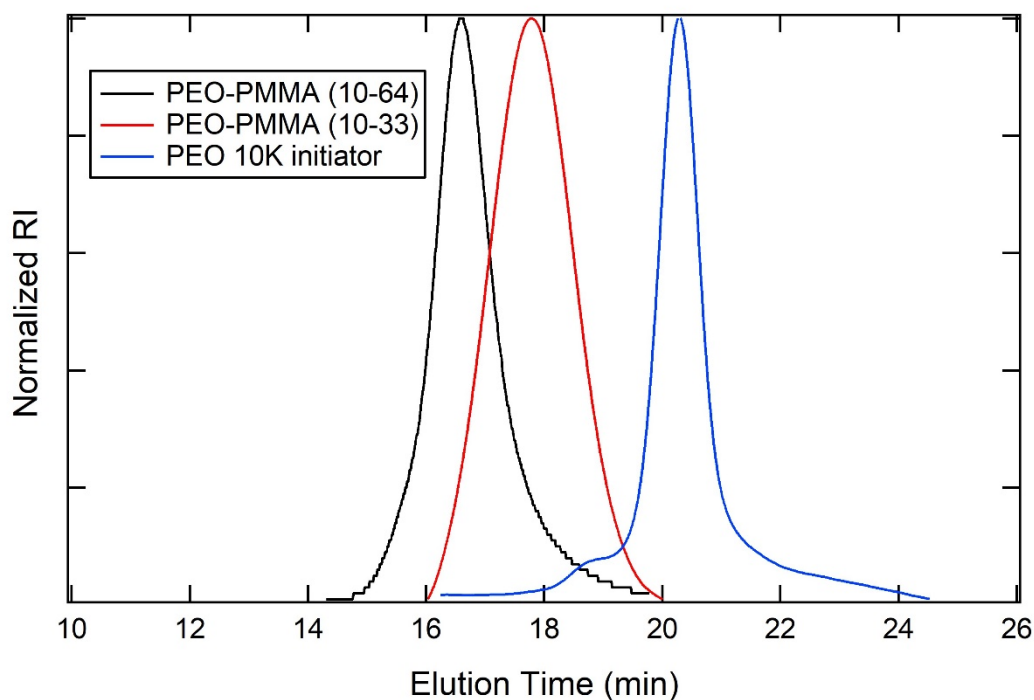


Figure S2: Gel permeation chromatography data on PEO-PMMA copolymers and PEO macroinitiator used in this study.

PEO-PMMA Synthesis

PEO-PMMA(10-33)

PEO-PMMA block copolymer was synthesized via atom transfer radical polymerization (ATRP) using a macroinitiator comprising of a 10 kg mol⁻¹ PEO chain with a α -bromophenylacetate terminus. The PEO- α -bromophenylacetate macroinitiator (5 g, 0.5 mmol, 1 equiv.) was dissolved in degassed anisole (20 mL) at room temperature in a sealed 50 mL round bottom flask. A copper wire (treated in a solution of HCl in methanol), CuBr₂ (2.1 mg, 9.4 μ mol, 0.02 equiv. dissolved in DMSO), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 18 μ L, 0.18 equiv.) and methyl methacrylate monomer (20 mL, 188 mmol, 400 equiv.) were added to the reaction mixture. The reaction proceeded for 18 hours at room temperature. The reaction was stopped by dilution with tetrahydrofuran (THF) and subsequent passage through a basic alumina filter to remove the copper ions. The polymer was twice reprecipitated in water.

PEO-PMMA(10-64)

PEO-PMMA block copolymer was synthesized via atom transfer radical polymerization (ATRP) using a macroinitiator comprising of a 10 kg mol⁻¹ PEO chain with a α -bromophenylacetate terminus. The PEO- α -bromophenylacetate macroinitiator (0.5 g, 0.05 mmol, 1 equiv.) was dissolved in degassed anisole (2 mL) at room temperature in a sealed 10 mL round bottom flask. A copper wire (treated in a solution of HCl in methanol), CuBr₂ (0.21 mg, 0.94 μ mol, 0.02 equiv. dissolved in DMSO), *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 1.8 μ L, 0.18 equiv.) and methyl methacrylate monomer (6 mL, 56 mmol, 1130 equiv.) were added to the reaction mixture. The reaction proceeded for 24 hours at room temperature. The reaction was stopped by dilution with tetrahydrofuran (THF) and subsequent passage through a basic alumina filter to remove the copper ions. The polymers were twice reprecipitated in water.

RPA Fits- α values

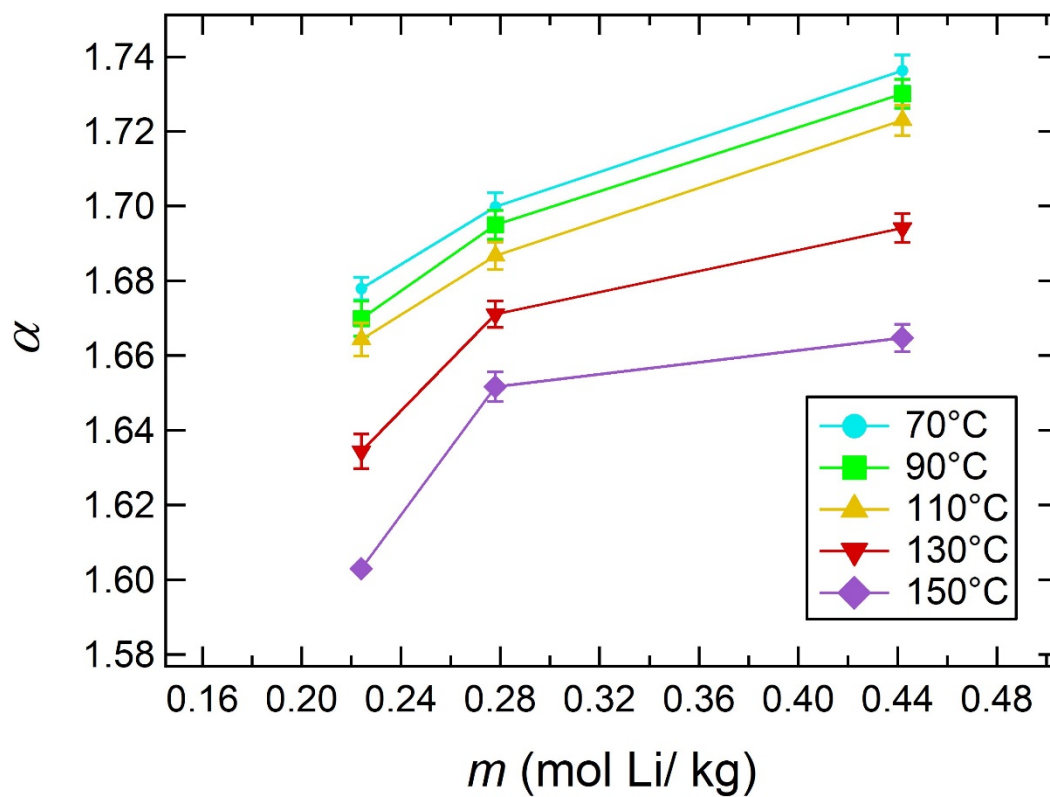


Figure S3: Chain stretching (α) of PEO-PMMA copolymers used in this study.

PDI Model Figures

All of the analysis of the SAXS profiles in the main text is based on RPA for monodisperse block copolymers. In this section we quantify the effect of polydispersity on that analysis. The expressions for scattering from a diblock copolymer with finite polydispersity index (PDI) are given below.^{1,2} The procedures used to match experiment and theory were identical to those described in the main text and the results are displayed in Figures 4 to 9. The value of PDI used in the calculation was 1.21. None of the conclusions in the main text are affected by finite polydispersity.

$$S_{ii}^{\circ} = Ng(f_i) \ (i = A, B) \quad (S1)$$

$$S_{AB}^{\circ} = S_{BA}^{\circ} = \left(\frac{N}{2}\right) (g(1) - g(f_A) - g(f_B)) \quad (S2)$$

$$k = \frac{1}{PDI-1} \quad (S3)$$

$$g(f_i) = \left(\frac{2}{x^2}\right) \left[f_i x + \left[\frac{k}{(k+f_i x)} \right]^k - 1 \right] \ (i = A, B) \quad (S4)$$

$$x = q^2 R_g^2 \quad (S5)$$

$$R_g^2 = \left(\frac{(N_a b_a^2 + N_b b_b^2)}{6} \right) \quad (S6)$$

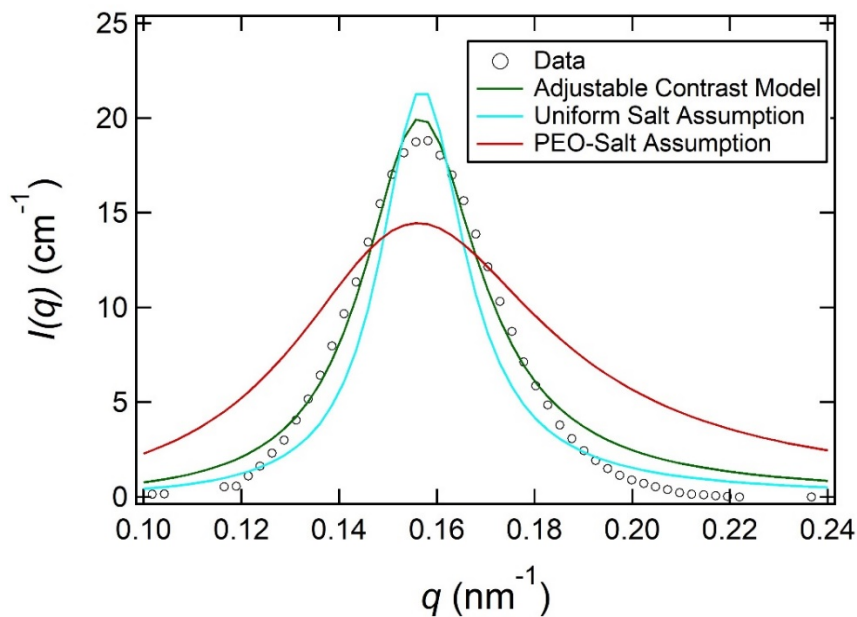


Figure S4: The circles represent data of PEO-PMMA(10-64)/LiTFSI with $m = 0.44$ mol Li/ kg polymer at 90 °C. The curves represent best fits using the three different models described in the main text but using equations (S1-S6) with PDI equal to 1.21 and χ_{eff} as the main adjustable parameter.

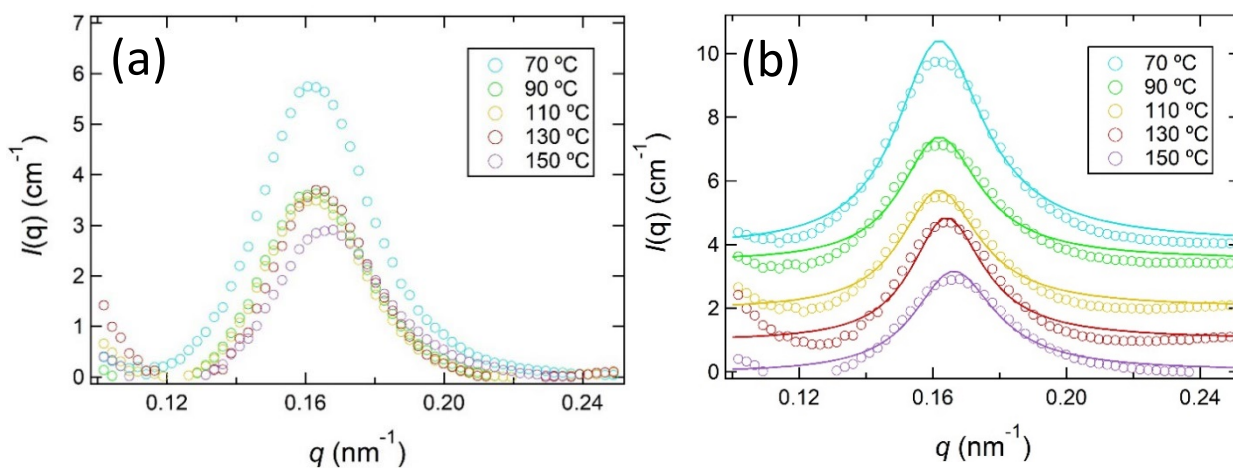


Figure S5: In (a) background subtracted scattering profiles of the PEO-PMMA(10-64) $m = 0.22$ mol Li/kg polymer electrolyte are plotted as a function of the scattering vector, q from 70 to

150°C. In (b) the RPA fits for each scattering profile of the PEO-PMMA(10-64) $m = 0.22$ mol Li/kg polymer electrolyte are plotted against the background subtracted data as a function of the scattering vector, q from 70 to 150°C. The curves represent best fits at each temperature using equations (S1-S6) with PDI equal to 1.21. The absolute $I(q)$ for $T = 150^\circ\text{C}$ is presented. Data from 130, 110, 90 and 70°C are shifted vertically by 1, 2, 3.5, and 4 cm^{-1} respectively for clarity.

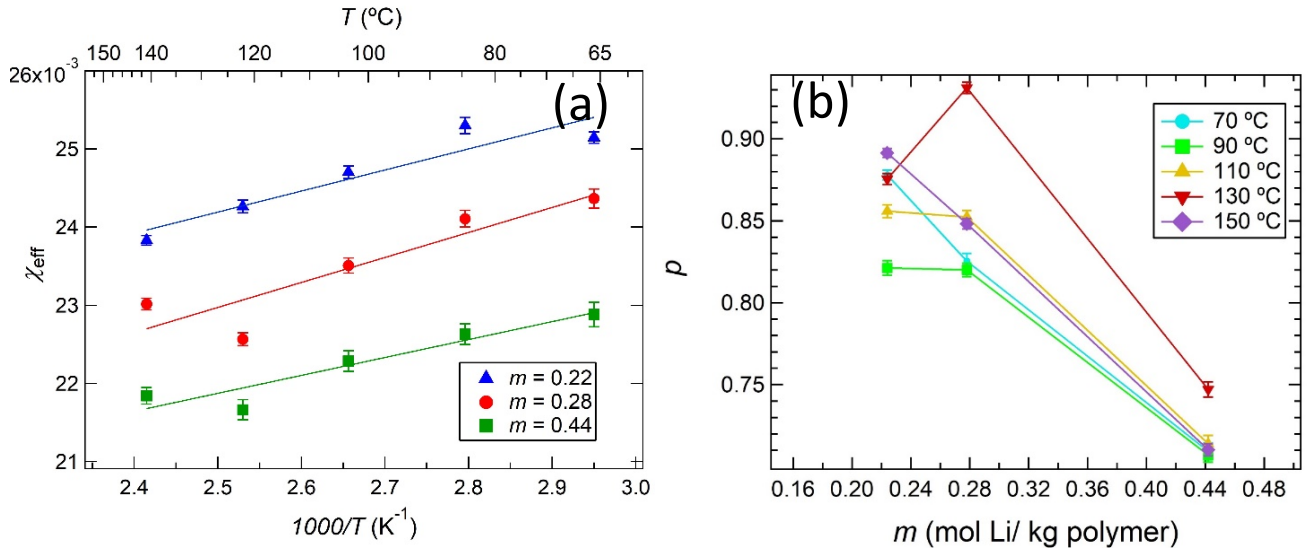


Figure S6: In (a) χ_{eff} is plotted against inverse temperature to calculate χ_{eff} as a function of temperature at each salt concentration with a disordered peak. Fit parameters can be seen in Table 2. In (b) fraction of lithium salt in PEO fluctuation (p) as derived from RPA fits is plotted as a function of salt concentration. Each trace represents a temperature from SAXS measurements. Both p and χ_{eff} are extracted from RPA fits accounting for a PDI of 1.21.

Alternate Table 2: χ_{eff} fit parameters

| m (mol Li/kg polymer) | $A \times 10^3$ (K) | B | R^2 |
|-------------------------|---------------------|--------------------|-------|
| 0.22 | 2.7 ± 0.68 | 0.017 ± 0.0012 | 0.87 |
| 0.28 | 3.2 ± 0.85 | 0.015 ± 0.0023 | 0.82 |
| 0.44 | 2.3 ± 0.46 | 0.016 ± 0.0012 | 0.89 |

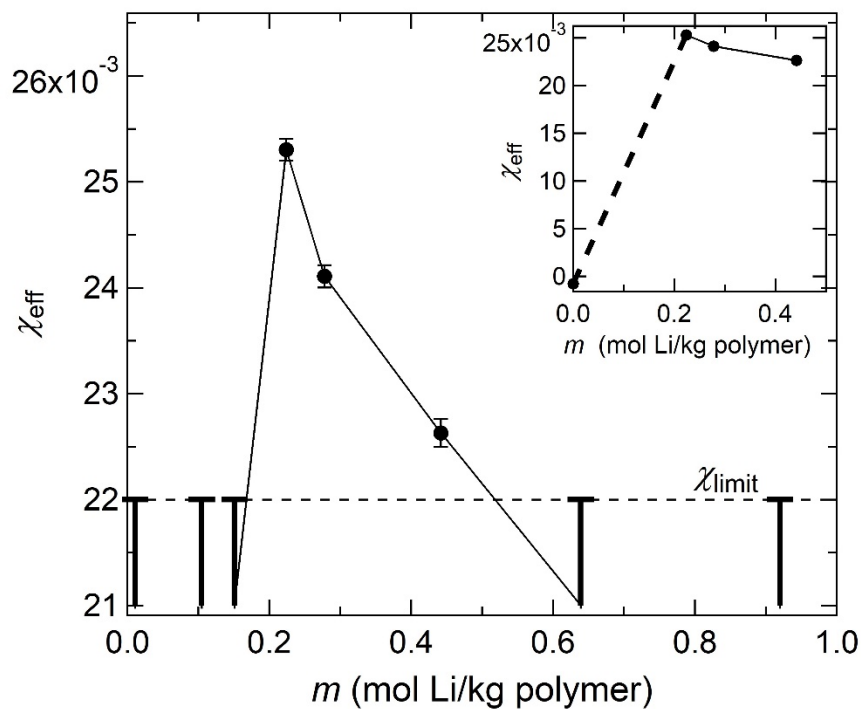


Figure S7: χ_{eff} is plotted as a function of salt concentration at 90 °C. χ_{eff} was calculated from RPA fits using equations (S1-S6) with a PDI equal to 1.21. The error bars represent the minimum χ value required for a disordered peak. The inset plots the three calculated χ_{eff} with the negative χ parameter from Russell and coworkers for a neat PEO-PMMA system.³⁴ The dotted line represents χ_{limit} , or the minimum χ parameter required to observe a disordered peak.

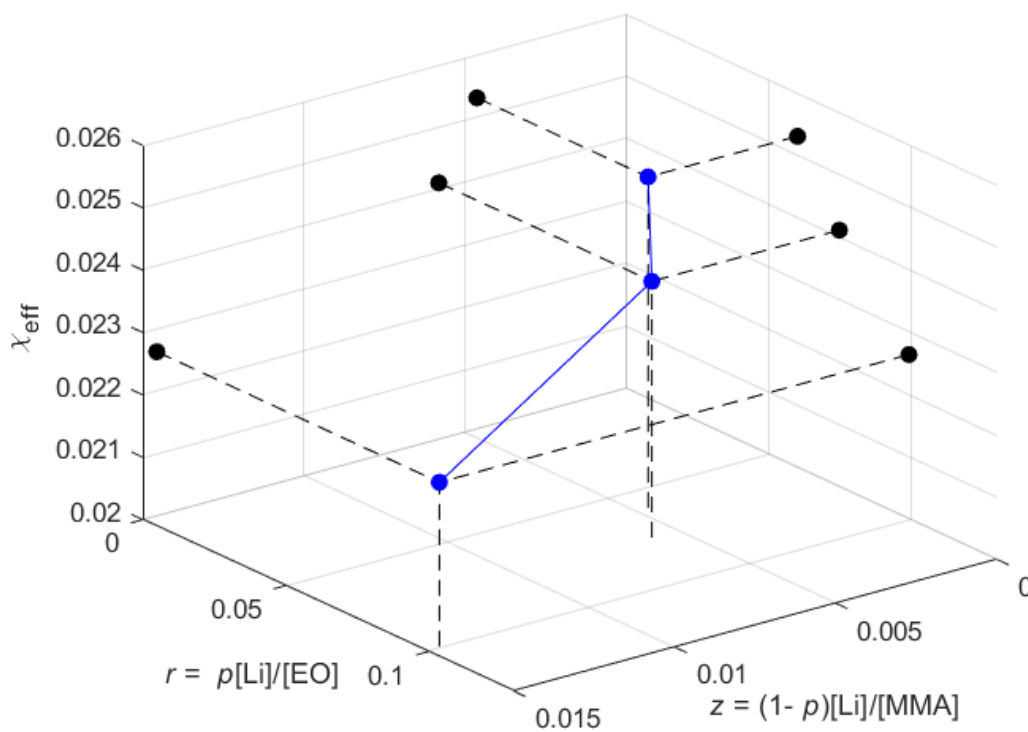


Figure 8: χ_{eff} plotted as a function of salt concentrations $r = p[\text{Li}]/[\text{EO}]$ and $z = (1-p)[\text{Li}]/[\text{MMA}]$. χ_{eff} was calculated from RPA fits using equations (S1-S6) with a PDI equal to 1.21. The blue trace is measured χ_{eff} as a function of both salt concentrations.

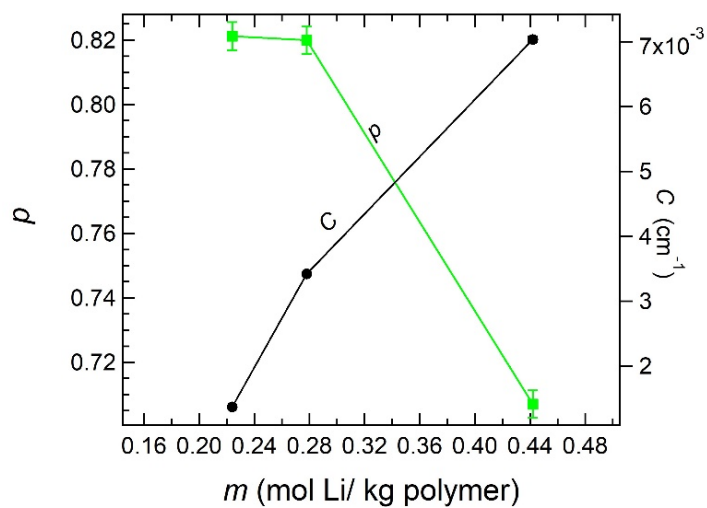


Figure 9b: p and contrast are plotted as a function of salt concentration (m) at 90°C. p was calculated from RPA fits using equations (S1-S6) with a PDI equal to 1.21.

References

- (1) Mori, K.; Tanaka, H.; Hasegawa, H.; Hashimoto, T. Small-Angle X-Ray Scattering from Block Copolymers in Disordered State: 2. Effect of Molecular Weight Distribution. *Polymer (Guildf)*. **1989**, *30* (8), 1389–1398. [https://doi.org/10.1016/0032-3861\(89\)90206-1](https://doi.org/10.1016/0032-3861(89)90206-1).
- (2) Teran, A. A.; Balsara, N. P. Thermodynamics of Block Copolymers with and without Salt. *J. Phys. Chem. B* **2014**, *118* (1), 4–17. <https://doi.org/10.1021/jp408079z>.