Supporting Information for:

Lower Critical Solution Temperature Phase Behavior of Poly(n-butyl methacrylate) in Ionic Liquid Mixtures

Megan L. Hoarfrost,¹ Yanpu He,² and Timothy P. Lodge^{1,2}*

¹Department of Chemistry, and ²Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, MN 55455



Figure S1. Example Zimm plot for PnBMA-40 in 100% [BMIm][TFSI] at 25 °C, for seven concentrations spaced roughly evenly between 14–58 mg/mL. Data points from each concentration are alternately open and filled in to distinguish concentrations. Scattering is independent of angle.



Figure S2. Phase diagrams for PnBMA of various molecular weights in (a) 95% [BMIm][TFSI], (b) 85% [BMIm][TFSI], and (c) 75% [BMIm][TFSI]. The solid symbols represent cloud point temperatures, and the open symbols represent spinodal temperatures. The dashed lines are guides for the eye.



Figure S3. Phase diagrams for (a) PnBMA-25 and (b) PnBMA-115 in mixtures of [BMIm][TFSI] and [EMIm][TFSI]. The solid symbols represent cloud point temperatures, and the dashed lines are guides for the eye.



Figure S4. Cloud point temperatures as a function of ionic liquid composition for several concentrations of (a) PnBMA-25 and (b) PnBMA-115. The dotted lines are linear fits.



Figure S5. Values of χ determined using eq 3 as a function of PnBMA concentration. Solutions were all measured roughly at their theta temperatures (90 °C for solutions in 100% [BMIm][TFSI] and 40 °C for solutions in 85% [BMIm][TFSI]), so the value of χ in the limit of zero concentration is about 0.5 for all of the samples (black symbol). For concentrations *lower* than c^* , the values of χ are anomalously high, and increase monotonically as the PnBMA molecular weight decreases. The molecular weight dependence can be explained by c^* decreasing with molecular weight. Thus, it is underscored that eq 3 should only used to describe polymer solutions above their critical concentrations.