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

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Supporting Information

ABSTRACT: Ionic liquids feature a combination of properties that make them very interesting solvents for polymers, but many questions remain regarding the thermodynamics of polymer/ionic liquid solutions. In this work, the lower-criticalsolution-temperature (LCST) phase behavior of poly(*n*-butyl methacrylate) (PnBMA) in mixtures of the ionic liquids 1butyl-3-methylimidazolium:bis(trifluoromethylsulfonyl)imide ([BMIm][TFSI]) and 1-ethyl-3-methylimidazolium:TFSI ([EMIm][TFSI]) is characterized by transmittance, light scattering, and small-angle neutron scattering measurements.



Several relevant thermodynamic parameters are easily tuned by varying the ionic liquid composition. In particular, the cloud point, spinodal, and Θ temperatures are all found to increase linearly with [BMIm] content. The interaction parameters, χ , are determined as a function of temperature and concentration using three different methods, and the results from each method are compared. The entropic and enthalpic components of the interaction parameter, χ , are also found to vary linearly with [BMIm] content in the ionic liquid, increasing and decreasing, respectively. The increase in the enthalpic driving force for mixing with increasing [BMIm] content dominates over the decrease in the entropic penalty for mixing, leading to improved solubility. This result is discussed in terms of molecular interactions and oriented solvation. This work characterizes the solution thermodynamics of one representative system in a very interesting class of polymer solutions, and provides insight into the molecular mechanisms underlying its LCST phase behavior.

■ INTRODUCTION

Ionic liquids feature a combination of properties that make them very interesting solvents for polymers. Their negligible volatility and wide range of thermal stability allow polymer solution thermodynamics to be studied over a much larger temperature range than with traditional aqueous or organic solvents. In addition, ionic liquids offer a wide range of solvation properties. They are often labeled as "designer solvents" due to the ability to select the appropriate anion and cation to achieve the desired properties.¹ For example, varying the alkyl chain length on a 1-alkyl-3-methylimidazolium cation, while keeping the anion constant, significantly affects the glass transition and melting temperatures, the density, viscosity, cohesive energy density, and the polarity of the ionic liquid, which in turn affect the solubility of polymers in the ionic liquid and the phase behavior of the mixtures.³ Even more simply, the solvation properties of ionic liquids can be tuned by mixing ionic liquids together. For example, the cloud point temperatures of polymers dissolved in binary ionic liquid mixtures have been shown to be linearly related to the composition of the ionic liquid, and can thus be controlled over a very large temperature range by choosing appropriate ionic liquid mixtures.⁴⁻⁷ Remarkably, mixing 1-ethyl-3-methylimidazolium:tetrafluoroborate ([EMIm][BF₄]) with 1-butyl-3-methylimidazolium:[BF₄] ([BMIm][BF₄]) results in a variation of the

cloud point temperature of poly(ethylene oxide) by over 150 $^{\circ}$ C.^{4,5} Furthermore, in contrast to traditional solvents, ionic liquids are generally composed of bulky molecules with asymmetric charge distribution, which can promote the formation of ordered structures and/or aggregates in the pure ionic liquid,^{8–10} thereby affecting the entropy of mixing the ionic liquid with solutes.^{10,11}

The phase behavior of polymers in ionic liquids exhibits several interesting features. Both lower-critical-solution-temperature $(LCST)^{4,6,12-17}$ and upper-critical-solution-temperature $(UCST)^{18-20}$ behavior have been observed for polymer/ionic liquid solutions. This is in contrast to the prevalence of LCST behavior among aqueous systems, and the prevalence of UCST behavior among polymers in molecular organic solvents (at readily obtainable temperatures and pressures²¹). Like water, some ionic liquids have the ability to form hydrogen bonds with polymer chains, which is one factor that can lead to LCST behavior in ionic liquid solutions.¹⁷ In addition to hydrogen bonding, it has been argued that ionic liquids form aggregates within polymer/ionic liquid solutions,^{6,11} or form ordered structures through a different type of specific interaction with

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the polymer, such as cation- π interactions between [EMIm]:bis(trifluoromethylsulfonyl)imide ([EMIm][TFSI]) and the benzyl groups on poly(benzyl methacrylate).^{16,22} Both of these features could also lead to a negative entropy of mixing and contribute to the LCST behavior observed in some systems. On the other hand, other ionic liquid/polymer systems exhibit UCST behavior, which generally reflects an overall positive entropy of mixing.¹⁸⁻²⁰ Another interesting feature of polymer/ionic liquid phase diagrams is that, in some instances, the critical concentration is shifted dramatically toward more polymer-rich compositions compared to most polymer solutions.^{4,11,17} One proposed contribution is the decreased entropy of mixing due to the self-organization of ionic liquid molecules within the mixtures; another is the higher cohesive energy densities, and lower free volumes, of ionic liquids compared to the polymers.¹¹

Not only are the polymer solvation properties of ionic liquids interesting from a thermodynamic standpoint but also they have been exploited to design complex thermoresponsive materials.^{5,23-35} For example, "doubly thermoresponsive" micelles have been designed by using a block copolymer that contains one block that exhibits LCST behavior and one block that exhibits UCST behavior.²³ The two transition temperatures were tuned over a very large temperature range by mixing ionic liquids. Thermoresponsive block copolymer/ionic liquid systems such as these have a large number of potential applications, for instance as micelles and vesicles for molecular storage and delivery,^{27–29,31} thermoresponsive gels, sensors, and actuators.³⁵ Mixtures of polymers and ionic liquids are also of great interest as ion-conducting electrolytes in electrochemical applications such as batteries, fuel cells, and transistors, as well as for gas separation membranes.^{36–47} Thus, it is important to understand the phase behavior and mutual miscibility of polymers and ionic liquids to effectively design materials for these applications as well. Many questions remain regarding the thermodynamics of polymer/ionic liquid solutions. For example, only very recently have the Flory-Huggins interaction parameter, χ , and the Θ temperature been measured for a polymer/ionic liquid system.¹⁹ Much also remains to be explained regarding the origins of LCST versus UCST behavior in these systems.

In this work, we characterize the phase behavior of poly(nbutyl methacrylate) (PnBMA) in mixtures of the ionic liquids [BMIm][TFSI] and [EMIm][TFSI], a system which has previously been identified to demonstrate LCST phase behavior.⁶ The Θ temperatures for the solutions are determined using two different methods, extrapolation of the critical temperature to infinite molecular weight, and extrapolation of the second virial coefficient to zero, both of which yield consistent results. We demonstrate the tunability of the ionic liquid solvent properties by mixing ionic liquids, and show that the phase boundaries, as well as the enthalpic and entropic contributions to χ , all depend linearly on the ionic liquid composition. Finally, determinations of χ using three distinct methods are compared, and χ is found to increase with polymer concentration, in quantitative agreement with other polymer solutions in molecular solvents. The results presented herein shed light on the origin of LCST behavior for this polymer/ ionic liquid system, and contribute a detailed thermodynamic study of one system in this interesting class of polymer solutions.

EXPERIMENTAL SECTION

Synthesis of PnBMA Homopolymers. Five PnBMA homopolymers were synthesized via atom transfer radical polymerization (ATRP) using a procedure modified from the literature.^{6,48} Butyl methacrylate, ethyl 2-bromoisobutyrate (EBIB), N.N.N', N', N''-pentamethyldiethylenetriamine (PMDETA), and anhydrous anisole were used as received from Sigma-Aldrich. Copper(I) bromide (CuBr) was stored in a glovebox before use. An example polymerization procedure is described. Butyl methacrylate (30.0 g, 211 mmol), EBIB (0.099 g, 0.5 mmol), and PMDETA (0.051 g, 0.3 mmol) were combined with 120 mL of anhydrous anisole. CuBr (0.089 g, 0.6 mmol) was obtained from the glovebox, and added to the reaction mixture. Once the CuBr was added, the reaction vessel was quickly sealed and frozen with liquid nitrogen, and three freeze-pump-thaw cycles were performed. The reaction mixture was then heated to 70 °C, and the reaction was allowed to proceed for 6.5 h. The reaction was stopped by quenching in an ice bath, and exposing the mixture to air. The product was directly precipitated into cold methanol (0 °C), then redissolved in dichloromethane (DCM), and passed through a column of neutral alumina to remove CuBr. DCM was then removed under vacuum, and the product was dried for 24 h at 90 °C and ~100 mTorr to remove any remaining anisole or butyl methacrylate. Finally the PnBMA product was freeze-dried from benzene to produce a white powder. The number-average molecular weight, $M_{\rm N}$, and dispersity, D, of this example polymer were determined to be 46 kg/mol and 1.04, respectively. The values of $M_{\rm N}$ and D were determined by size exclusion chromatography (SEC) performed in THF at room temperature on an Agilent Technologies 1260 Infinity system equipped with a multiangle light scattering detector (Wyatt Technology Dawn Heleos-II). A value of 0.068 mL/g was used for the dn/dc of PnBMA in THF, which was measured using an Abbe Refractometer. The polymers, labeled PnBMA-xx, where xx is the $M_{\rm N}$ of the polymer in kg/mol, are PnBMA-25 (D = 1.16), PnBMA-37 (D= 1.09), PnBMA-40 (D = 1.06), PnBMA-46 (D = 1.04), and PnBMA-115 (D = 1.08)

Synthesis of Ionic Liquids. [EMIm][TFSI] and [BMIm][TFSI] were synthesized using a procedure modified from the literature.⁴⁹ For [BMIm][TFSI], 1-methylimidazole, and n-chlorobutane (Sigma-Aldrich, used as received) were combined in a 1.0:1.1 molar ratio in cyclohexane, and refluxed for 48 h. The cyclohexane phase was then removed, and the resulting [BMIm]:chloride ([BMIm][Cl]) phase was dried at 80 $^{\circ}\text{C}$ and ~100 mTorr for 24 h to remove unreacted 1methylimidazole. Lithium:bis(trifluoromethylsulfonyl)imide (LiTFSI, 3M Company, used as received) was added in a molar ratio of 1.0:1.1 [BMIm][Cl]:LiTFSI (assuming full conversion of 1-methylimidazole to [BMIm][Cl]), along with deionized water. The mixture was allowed to react at 70 °C for 48 h, after which the aqueous phase was removed and the [BMIm][TFSI] phase was washed with deionized water three times. The [BMIm][TFSI] product was diluted with DCM and passed through a column of neutral alumina. Then the DCM was removed under vacuum and the product was dried at 60 $^\circ C$ and ${\sim}100$ mTorr for 24 h. For [EMIm][TFSI], the starting materials were [EMIm]:bromide ([EMIm][Br], IoLiTec, used as received) and LiTFSI, and [EMIm][Br] was converted to [EMIm][TFSI] following the same procedure for converting [BMIm][Cl] to [BMIm][TFSI].

Partially deuterated ionic liquids were synthesized for small-angle neutron scattering (SANS) experiments. Hydrogenated [BMIm]-[TFSI] and [EMIm][TFSI] were stirred in D_2O in the presence of K_2CO_3 at 120 °C for 24 h. The aqueous layer was removed, and the ionic liquid phase was washed twice with D_2O , and then diluted in DCM and passed through a column of neutral alumina. The DCM was removed by vacuum, and the product was dried at 60 °C and ~100 mTorr for 24 h. This procedure resulted in 86–92% deuteration of the three aromatic proton sites, as determined by ¹H NMR spectroscopy.

Preparation of PnBMA Solutions in Ionic Liquid Mixtures. Ionic liquid mixtures were made by combining [EMIm][TFSI] and [BMIm][TFSI] in a predetermined ratio, and codissolving the mixture in DCM. The DCM was removed slowly (over 24 h) using a nitrogen gas purge, and then the mixtures were dried under vacuum (~100

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mTorr) for 24 h. In this manuscript, the ionic liquids are generally referred to by the wt % of [BMIm][TFSI] in the mixture. Solutions of PnBMA in ionic liquid mixtures were made by combining PnBMA and the ionic liquid mixture in a predetermined ratio, and codissolving the mixture in either DCM or THF. (THF was used for higher polymer concentrations, in general \geq 5 wt %.) The cosolvent was removed slowly (over 24 h) using a nitrogen gas purge, and then the solutions were dried under vacuum (~100 mTorr) for 24 h. For static light scattering (SLS) experiments, a stock solution was made of the highest polymer concentration solution, and this stock solution was diluted with further ionic liquid according to the cosolvent procedure described above to make lower concentration solutions.

Cloud Point Measurements. PnBMA solutions in ionic liquid mixtures were flame-sealed in glass ampules under vacuum (<100 mTorr) for cloud point measurements. The cloud points of the solutions were determined by optical transmittance measurements, using a 633 nm HeNe laser, and heating at a rate of 1 °C/min. The cloud point was defined as the temperature at which the optical transmittance dropped to \leq 80% of the transmittance of the fully dissolved solution.

Static Light Scattering (SLS). PnBMA solutions in ionic liquid mixtures were filtered through 0.45 μ m PTFE filters into glass tubes 0.5 in. in diameter, which had been rinsed with filtered DCM and dried at 90 °C overnight. The concentrations of the solutions ranged between 6-58 mg/mL. The tubes were then flame-sealed under vacuum (<80 mTorr), and SLS measurements were performed on a Brookhaven BI-200SM research goniometer and laser light scattering system, version 2.0, with a laser wavelength of 637 nm. Measurements were taken at temperatures between 5-80 °C. Scattering angles between 40-105 degrees were utilized, with 5 degree increments. For this range of angles, and for the $M_{\rm N}$ range of the polymers used (37– 40 kg/mol), the estimated values for qR_g vary between 0.05-0.11 (where R_{σ} is estimated as $(Nb^2/6)^{1/2}$, with b equal to 0.49 nm based on ref 50). These qR_g values are $\ll 1$, so scattering from the polymer solutions is dominated by Rayleigh scattering, as supported by the measured excess scattering being invariant to angle (Supporting Information, Figure S1). Therefore, the following expression was used to determine the second virial coefficients, A_2 :

$$\frac{Kc}{R_{\theta}} = \frac{1}{M_{\rm w}} + 2A_2c \tag{1}$$

where *K* contains optical constants, including the refractive index of the solvent and the refractive index increment, dn/dc, for the solutions, *c* is the concentration of polymer in the solution, and R_{θ} is the reduced scattered intensity, which takes into account subtraction of the scattering from the pure solvent, as well as the sample-to-detector distance. The refractive indices of the ionic liquid mixtures and the dn/dcvalues for the polymer/ionic liquid solutions were measured using an Abbe Refractometer. The dn/dc values were found to be 0.044 mL/ g between 60–80 °C and 0.043 mL/g between 5–45 °C for solutions of PnBMA in 100 wt % [BMIm][TFSI] and mixtures of [BMIm]-[TFSI] containing up to 15 wt % [EMIm][TFSI]. The refractive indices of the ionic liquid compositions that were not explicitly measured were extrapolated based on the observed linear dependence of the refractive index on these variables.

The measured Kc/R_{θ} values were averaged over all of the measured angles, and plotted as a function of *c* to determine A_2 from eq 1. An example is shown in Figure 2. The data were fit linearly, and the slopes were taken to be $2A_2$.

Small-Angle Neutron Scattering (SANS). For spinodal temperature and χ determinations using SANS, solutions were injected into 2 mm thick (for 10 and 20 wt % solutions) or 4 mm thick (for 2 and 5 wt % solutions) standard solution sample cells with quartz windows. These SANS experiments were performed on the NG-7 30 m instrument at the National Institute for Standards and Technology (NIST) Center for Neutron Research. A sample-to-detector distance of 4 m, a monochromated neutron wavelength of $\lambda = 8.09$ Å, and a wavelength spread of $\Delta\lambda/\lambda = 0.115$ were used to achieve a scattering Article



Figure 1. Refractive indices of mixtures of [BMIm][TFSI] and [EMIm][TFSI] as a function of temperature and composition.



Figure 2. Kc/R_{θ} plotted as a function of *c* for PnBMA-40 in 100% [BMIm][TFSI] at 25 °C. The slope of the linear fit gives $2A_2$.

wavevector range of q = 0.0064-0.0875 Å⁻¹. Using established procedures,⁵¹ the two-dimensional scattering patterns were reduced by azimuthal integration to yield one-dimensional I(q) versus q scattering profiles. The reduction included correction for background detector efficiency, empty cell scattering, and sample transmission, and then conversion to absolute intensity using direct beam flux measurements. The incoherent scattering from the samples was estimated as the scattering from the pure (partially deuterated) ionic liquids, and was subtracted from the reduced data.

For A2 determinations using SANS, solutions containing PnBMA-46 were injected into 1 mm thick quartz banjo cells. These SANS experiments were performed at the CG-2 General Purpose SANS instrument at the High Flux Isotope Reactor (HFIR) facility at Oak Ridge National Laboratory (ORNL). A sample-to-detector distance of 9.5 m and a neutron wavelength of $\lambda = 4.72$ Å were used to achieve a scattering wavevector range of q = 0.0053 - 0.1630 Å⁻¹. The twodimensional scattering patterns were reduced by azimuthal integration using the Igor package provided by ORNL, which included correction for background detector efficiency, empty cell scattering, and sample transmission. The one-dimensional I(q) versus q scattering profiles were converted to absolute intensity using an amorphous carbon standard, and incoherent scattering was estimated as the scattering from the pure (partially deuterated) ionic liquids and subtracted from the reduced data. Zimm plots were constructed using data with a scattering wavevector range of q = 0.0066-0.0163 Å⁻¹ for solution concentrations between 14 and 71 mg/mL. An example Zimm plot is shown in Figure 3. Data for each concentration were extrapolated to q= 0, and the extrapolated data were fit linearly to yield A_2 .

RESULTS AND DISCUSSION

LCST Phase Diagrams. Phase diagrams for PnBMA in mixtures of [BMIm][TFSI] and [EMIm][TFSI] were constructed using cloud point measurements and spinodal temperature measurements by SANS. Measuring the cloud point is a simple technique for detecting liquid–liquid phase separation in a polymer solution. The cloud point is not a



Figure 3. Sample SANS Zimm plot for PnBMA-46 in 95% [BMIm][TFSI] at 20 °C. The red symbols indicate the data extrapolated to q = 0 for each concentration. The slope of the linear fit to the extrapolated data yields A_2 .

thermodynamic property; it generally falls between the binodal and spinodal, but for polymer solutions, the cloud point usually lies much closer the binodal (coexistence) curve. For the PnBMA/ionic liquid systems, the reversibility of the cloud point temperature upon heating and cooling confirms that the cloud point is a good estimate of the binodal. The cloud point temperatures were observed upon heating, as demonstrated in Figure 4, consistent with LCST phase behavior. The cloud point decreases with increasing PnBMA concentration below the critical concentration (i.e., between 0.5 and 20 wt % for PnBMA-46). The phase transition also becomes noticeably sharper with increasing PnBMA concentration.



Figure 4. Example transmittance versus temperature data for PnBMA-46 in 95% [BMIm][TFSI]. The cloud point temperature decreases with increasing PnBMA concentration below the critical concentration (0.5–20 wt % for PnBMA-46).

SANS was used to determine the spinodals for the solutions. As shown in Figure 5a, the scattered intensity increases with increasing temperature as the temperature approaches the spinodal due to increased composition fluctuations in the sample. The low-q data were plotted in Ornstein–Zernike format as 1/I(q) versus q^2 (for example, Figure 5b), and fit linearly to obtain the 1/I(0) intercepts. Then, the fitted values for 1/I(0) were plotted as a function of 1/T (for example, Figure 5c). These data were fit linearly to yield the spinodal temperature from the 1/I(0) = 0 intercept.

The cloud points and spinodal temperatures for different PnBMA molecular weights, concentrations, and ionic liquid compositions were compiled to construct phase diagrams for the PnBMA/ionic liquid solutions (Figures 6a-c). The cloud points and spinodals shift to lower temperature as the molecular weight of PnBMA is increased, as shown in Figure

6, parts a and b, for solutions in 100% [BMIm] [TFSI]. (Similar phase diagrams are shown in Supporting Information Figure S2 for the other ionic liquid mixtures.) This is expected for LCST systems based on the decrease in the entropy of mixing for longer polymer chains predicted by a simple lattice mixing theory (i.e., Flory-Huggins theory). The critical concentration shifts to lower polymer concentrations as the PnBMA molecular weight is increased, which is also expected based on the increasing asymmetry of the entropy of mixing expression. Interestingly, the critical concentrations are located at higher polymer concentrations than typically observed for polymer/solvent systems. Flory-Huggins theory predicts critical concentrations of 7 wt % (10 vol %) for PnBMA-25 solutions, 6 wt % (8 vol %) for solutions containing PnBMA-40 or PnBMA-46, and 4 wt % (5 vol %) for PnBMA-115 solutions. The observed critical concentrations are significantly higher, \geq 20 wt % for solutions containing the three lowest molecular weight polymers, and ~10 wt % for PnBMA-115 solutions. Unusually symmetric phase diagrams have also been observed previously for other LCST polymer/ionic liquid systems.^{4,17} Computational studies have suggested two sources for this behavior.¹¹ The first is the significantly stronger cohesive energy density, and lowered free volume, of the ionic liquid relative to the polymer, which is the opposite scenario than in most polymer/solvent systems. The second is a putative reduction in the entropy of mixing that results from some type of aggregation of the ionic liquid within the mixture. Such aggregation would also contribute to the system demonstrating LCST behavior, as we will discuss in more detail subsequently.

The phase behavior is tunable by mixing ionic liquids. The cloud points and spinodals monotonically decrease with decreasing [BMIm] content in the ionic liquid, as shown in Figure 6c for PnBMA-46. Figure 6d shows that the cloud point temperatures and spinodal temperatures seem to follow the same roughly linear correlation with ionic liquid composition. Similar phase diagrams and linear correlations are shown for PnBMA-25 and PnBMA-115 in the Supporting Information, Figures S3 and S4, respectively. A linear change in phase transition temperatures by mixing ionic liquids has also been observed for several other polymer/ionic liquid systems.⁴⁻ This characteristic of ionic liquid solvents leads to a robust way to tune the solvent quality. Furthermore, it suggests that mixing the ionic liquids is close to an ideal mixing process; i.e., since the chemical structures of the cations are quite similar, the molecular interactions are not altered very much by mixing. This renders polymer solutions in ionic liquid mixtures amenable to further thermodynamic analysis using traditional methods for pure solvent systems.

Θ Temperatures. The Θ temperatures for the mixtures were determined using two different methods, which yielded consistent results. The first method involved extrapolating the critical temperatures from the phase diagrams, $T_{\rm C}$, to infinite molecular weight. For PnBMA-115, $T_{\rm C}$ was estimated as the cloud point/spinodal temperatures of the 10 wt % solutions. As is evident from Figure 6, the phase boundaries are relatively flat, and thus the value of $T_{\rm C}$ is reliable even if the critical composition is not precisely located. For PnBMA-25, PnBMA-40, and PnBMA-46, $T_{\rm C}$ was taken as the cloud point temperature of the 20 wt % solutions. Within error, the spinodal and cloud point temperatures of the 20 wt % PnBMA-40 and PnBMA-46 solutions were equal, indicating that 20 wt % is a good estimate of the critical concentration. On the other hand, the spinodal temperature measured for 20 wt % PnBMA-



Figure 5. (a) Sample I(q) SANS profiles for 20 wt % PnBMA-46 in 100% [BMIm][TFSI] at various temperatures. The solid lines are fits using eq 3. (b) Sample Ornstein–Zernike plots for the SANS data shown in part a. (c) Sample plot of 1/I(0) versus 1/T for the data shown in parts a and b. The intercept of the linear fit yields the spinodal temperature.



Figure 6. (a) Phase diagrams for PnBMA of various molecular weights in [BMIm][TFSI]. The solid symbols represent cloud point temperatures, and the open symbols represent spinodal temperatures. The dashed lines are guides for the eye. (b) Zoomed-in view of the phase diagrams in part a. (c) Phase diagrams for PnBMA-46 in mixtures of [BMIm][TFSI] and [EMIm][TFSI]. (d) Cloud point temperatures (solid symbols) and spinodal temperatures (open symbols) as a function of ionic liquid composition for several PnBMA-46 concentrations. The dotted lines are linear fits.

25 in [BMIm][TFSI] (129 ± 2 °C) was still slightly higher than the cloud point temperature (125 °C). However, on average, the cloud point temperatures of the PnBMA-25 solutions decreased by only 1 °C between the 10 and 20 wt % samples, so the cloud point temperatures of the 20 wt % samples are good estimates of $T_{\rm C}$ (within 1 °C).

According to Flory–Huggins theory, the critical value of χ , $\chi_{\rm C}$, depends on the degree of polymerization, $N = \hat{V}_{\rm P} / \hat{V}_{\rm IL}$, where $\hat{V}_{\rm P}$ and $\hat{V}_{\rm IL}$ are the molar volumes of the polymer and ionic liquid, respectively, as

$$\chi_{\rm C} = A + \frac{B}{T_{\rm C}} = \frac{1}{2N} + \frac{1}{\sqrt{N}} + \frac{1}{2}$$
(2)

By definition, the Θ temperature is equal to $T_{\rm C}$ for infinite N (or, equivalently, the temperature at which χ is equal to 1/2). Thus, the inverse of $T_{\rm C}$ is plotted as a function of $1/2N + 1/\sqrt{N}$ in Figure 7a, and extrapolated to determine the Θ temperatures for solutions of PnBMA in each ionic liquid mixture. As with the cloud point and spinodal temperatures, the Θ temperature is found to depend linearly on the ionic liquid



Figure 7. (a) Determination of the Θ temperatures for PnBMA/ionic liquid solutions by extrapolating $T_{\rm C}$ to infinite molecular weight. (b) Θ temperature as a function of ionic liquid composition. The solid diamond symbols are from extrapolation of the data in part a. The open circle and asterisk symbols are from the second viral coefficients determined by SLS and SANS, respectively. The solid line is a linear fit to all of the data.

composition, as shown in Figure 7b, increasing with [BMIm] content.

There is one major shortcoming associated with eq 2, which is that it is derived assuming χ is independent of concentration. As will emerge, χ strongly depends on concentration, so this is not a good assumption. However, the definition of the Θ temperature as the $T_{\rm C}$ for infinite N is still valid, so the extrapolation treatment demonstrated in Figure 7a provides a good estimate of the Θ temperature.

The second virial coefficients, A_2 , determined using SLS and SANS were also used to verify the Θ temperatures of the PnBMA/IL solutions. The values of A_2 are plotted in Figure 8 as a function of temperature. As expected based on the phase diagrams, the values of A_2 are higher for the ionic liquid mixtures with the larger [BMIm] contents. The data for each solution were fit linearly, and extrapolated to $A_2 = 0$ to determine the Θ temperatures. There is some difference between the values of A_2 determined by SLS versus SANS, but the Θ temperatures determined using each method are consistent. The Θ temperatures determined using this method are in excellent agreement with the Θ temperatures determined by extrapolating the critical temperatures to infinite molecular weight, as shown in Figure 7b.

Interaction Parameters. The effective interaction parameters, χ , were determined for the PnBMA/ionic liquid solutions using three different methods. First, it is shown that χ depends on concentration by determining χ for high concentration solutions using SANS. Scattering profiles were fit using the de Gennes equation (random phase approximation):



Figure 8. A_2 as a function of temperature for PnBMA of various molecular weights in four different ionic liquid mixtures of [BMIm][TFSI] with [EMIM][TFSI]. The circle symbols indicate data collected using SLS, while the diamond symbols indicate data collected using SANS. The solid lines are linear fits to the data, which were extrapolated to $A_2 = 0$ to determine the Θ temperatures.

$$\frac{(\Delta \rho)^2}{I(q) + k_{\rm Inc}} = \frac{1}{\phi_{\rm P} N \hat{V}_{\rm P} P(q)} + \frac{1}{\phi_{\rm IL} \hat{V}_{\rm IL}} - \frac{2\chi}{\hat{V}_{\rm IL}}$$
(3)

Here $\phi_{\rm P}$ and $\phi_{\rm IL}$ are the volume fractions of the polymer and ionic liquid, respectively, $\hat{V}_{\rm P}$ and $\hat{V}_{\rm IL}$ are the molar volumes of the polymer and ionic liquid, respectively, and $\Delta \rho$ is the difference between the scattering length densities of the polymer and ionic liquid. A constant, $k_{\rm Inc.}$, was added to the equation to account for possible incorrect subtraction of incoherent scattering. The fitted values for $k_{\rm Inc.}$ are small for all experiments reported here, generally an order of magnitude smaller than the scattered intensity, on the order of 10^{-1} cm⁻¹, and in fact they do not strongly influence the fitted value of χ . The Debye equation was used for the form factor of the polymer chains, P(q)

$$P(q) = \frac{2}{q^4 R_g^4} \left[\exp(-q^2 R_g^2) - 1 + q^2 R_g^2 \right]$$
(4)

where $R_{\rm g}$ is the radius of gyration of the polymer. Example fits with χ , $k_{\rm Inc}$, and $R_{\rm g}$ as fitting parameters are shown with the data in Figure 5a.

The random phase approximation (RPA) assumes spatial uniformity and local randomness, so it is most appropriate for concentrated mixtures, i.e., above the critical overlap concentration.⁵² The critical concentrations, c^* , were estimated for Θ conditions by

$$c^* = \frac{3M_{\rm N}}{4\pi R_{\rm g}^3 N_{\rm A}} \tag{5}$$

where the value of $R_{\rm g}$ for PnBMA-46 was determined from SANS Zimm plots (i.e., Figure 3) at Θ conditions, and the values of $R_{\rm g}$ for PnBMA-25 and PnBMA-115 were estimated based on the relationship $R_{\rm g} \sim N^{1/2}$. The estimated values for c^* are 2, 7, and 17 wt % or 3, 10, and 22 vol % for PnBMA-115, PnBMA-46, and PnBMA-25, respectively. In Figure 9, the values for χ obtained using eq 3 are plotted for solutions with concentrations greater than or equal to these values.

In Figure 9a, the values of χ determined by SANS and eq 3 are shown for a variety of solutions, containing three different



Figure 9. (a) Values of χ determined using eq 3 as a function of PnBMA concentration. Solutions were all measured roughly at the Θ temperatures (90 °C for solutions in 100% [BMIm][TFSI] and 40 °C for solutions in 85% [BMIm][TFSI]). (b) χ as a function of concentration for PnBMA-46 in 100% [BMIm][TFSI] at various temperatures. The open symbols are the values of χ from SLS.

polymer molecular weights and two different ionic liquid compositions. The measurements were all performed roughly at the Θ temperatures, so the value of χ in the limit of zero concentration is about 0.5 for all of the samples. Clearly, χ strongly depends on PnBMA concentration, increasing from 0.5 at $\phi_{\rm P}$ = 0 to about 0.68 at $\phi_{\rm P}$ = 0.26. In Figure 9b, χ for PnBMA-46 in 100% [BMIm][TFSI] is shown at several different temperatures, spanning from ~25 degrees above to ~30 degrees below the Θ temperature (~89 °C). χ depends on concentration at each temperature, but the concentration dependence is weakest at the lowest temperatures. These results are consistent with previous observations of χ increasing with concentration for many different polymer solutions, where the concentration dependence is stronger at Θ conditions than in a good solvent.⁵² The dependence for the PnBMA/ionic liquid systems is quantitatively quite similar to that observed for other systems. For example, χ depends similarly on concentration for solutions of polystyrene/cyclohexane, polyisobutylene/benzene, polydimethylsiloxane/methyl ethyl ketone, polydimethylsiloxane/benzene, and polydimethylsiloxane/2-butanone at their Θ temperatures, where the values of χ determined from scattering experiments increase from 0.5 at $\phi_{\rm P} = 0$ to about 0.65 at $\phi_{\rm P} = 0.26$.^{52,53}

A few additional observations regarding Figure 9a can be made. First, χ does not depend strongly on molecular weight. Second, the similar values obtained for χ for solutions in 100% and 85% [BMIm][TFSI] provide further validation of the Θ temperatures determined by extrapolating $T_{\rm C}$ and A_2 . Finally, for concentrations *lower* than c^* , the values obtained for χ were anomalously high, and increased monotonically at a given concentration as the PnBMA molecular weight decreased (Figure S5 in Supporting Information). The molecular weight dependence can be explained by c^* decreasing with molecular weight. Thus, it is underscored that eq 3 should only be used to describe polymer solutions above their overlap concentrations.

In general, χ can be expressed as a function of temperature as $\chi = A + B/T$, where A encompasses the entropic contributions to the free energy of mixing that are not included in the lattice model ideal mixing and B encompasses the temperaturedependent enthalpic contributions to the free energy of mixing. Specifically, when interpreted in terms of Flory-Huggins theory, the excess entropy of mixing is equal to $-kA\phi_{\rm P}(1-\phi_{\rm P})$ and the enthalpy of mixing is equal to $kB\phi_{\rm p}(1-\phi_{\rm p})$. To investigate the entropic and enthalpic components of χ , Flory– Huggins analysis of the phase diagrams was performed, using the slopes and intercepts of the linear fits in Figure 7a along with eq 2. A and B determined using this analysis are plotted as a function of ionic liquid composition in Figure 10. As discussed previously, eq 2 is not strictly valid for this system due to the concentration dependence of χ_i and it is emphasized that the particular values obtained for A and B using this method are not quantitatively reliable. However, the trends for how A and B vary with ionic liquid composition do provide information about the entropic and enthalpic driving forces for phase separation.



Figure 10. (a) Temperature-independent and (b) temperaturedependent components of χ , A, and B, respectively, determined from the data in Figure 7a, as a function of ionic liquid composition. The solid lines are linear fits.

In Figure 10a, A is shown to increase roughly linearly with the amount of [BMIm] in the ionic liquid. In other words, the entropic penalty for mixing increases with increasing [BMIm] content in the ionic liquid (the entropy of mixing decreases). Lee et al. proposed two mechanisms for a negative entropy of mixing that is generally associated with LCST behavior in the PnBMA/[BMIm][TFSI] + [EMIm][TFSI] system.⁶ First, they proposed that the presence of solvatophobic n-butyl groups from the polymer leads to oriented solvation of the ionic liquid molecules around the *n*-butyl groups in the mixture (analogous to the hydrophobic effect in aqueous solutions). Second, they proposed that oriented solvation results from van der Waals interactions between the ionic liquid and the polymer. With these proposed mechanisms in mind, the decrease in mixing entropy with increasing [BMIm] content could be explained by the longer alkyl side chains on the cation leading to more oriented solvation, either via stronger inter-alkyl interactions in

the ionic liquid and/or stronger interactions between the alkyl side chains and the *n*-butyl groups on the polymer.

Despite the decrease in mixing entropy, the one-phase region *expands* with increasing [BMIm] content. The reason for the increase in the cloud point/spinodal phase boundary is a decrease in the *enthalpy* of mixing. As shown in Figure 10b, *B* decreases roughly linearly with [BMIm] content in the ionic liquid. This result also supports the arguments made above for stronger inter-alkyl interactions in the ionic liquid and/or stronger interactions between the alkyl side chains and the *n*-butyl groups on the polymer as the fraction of butyl side chains is increased. The greater enthalpic benefit overcomes the greater entropic penalty in the high-[BMIm] content ionic liquids, ultimately resulting in higher-temperature phase boundaries.



Figure 11. Values of χ determined using RPA treatment of SANS data for PnBMA-46 solutions as a function of 1/T. The solid and dashed lines are linear fits to $\chi = A + B/T$, where the fitted values for A and B are given. In general, A increases and B decreases with increasing [BMIm][TFSI] content in the ionic liquid.

The values of A and B determined by Flory-Huggins analysis are compared to those determined by temperaturedependent χ measurements using RPA treatment of SANS data (eq 3). Figure 11 shows χ obtained using eq 3 as a function of 1/T for 10 and 20 wt % solutions of PnBMA-46 in two different ionic liquid mixtures (85% and 100% [BMIm]-[TFSI]). The data are described well by linear fits, which are shown with the data in Figure 11, along with the resulting values for A and B. All of the values for A and B determined by RPA analysis are compiled in Table 1. In general, A is higher and B is lower for the solutions in 100% [BMIm][TFSI] compared to the solutions in 85% [BMIm][TFSI], which is qualitatively consistent with the results of the Flory-Huggins analysis shown in Figure 10. The magnitudes of A and B determined by RPA treatment, on the other hand, are smaller than those determined by Flory-Huggins analysis. This further

Table 1. Values for A and B Determined Using RPATreatment of SANS Data

	100% [BMIm][TFSI]		85% [BMIm][TFSI]	
	A	В	A	В
20 wt % PnBMA-25	1.16	-173	_	_
10 wt % PnBMA-46	0.88	-101	0.82	-70
20 wt % PnBMA-46	1.00	-119	0.97	-96
5 wt % PnBMA-115	0.79	-83	-	-
10 wt % PnBMA-115	0.83	-87	-	-
20 wt % PnBMA-115	1.07	-149	-	-

reflects the limitations of Flory–Huggins analysis for quantitatively describing this system. Values of *A* and *B* determined by converting the second virial coefficients (shown in Figure 8) to χ range from 0.64 to 0.77 and from -49 to -87, respectively. Like the values from RPA treatment, these are significantly smaller in magnitude than those determined by Flory–Huggins analysis of the phase diagrams, and are more quantitatively reliable.

From the values of A and B in Table 1, it appears that the magnitudes of A and B both increase with polymer concentration. Since oriented solvation of the ionic liquid around the polymer chains is expected to contribute significantly to the excess entropy and enthalpy of mixing, it makes sense that these contributions increase with polymer concentration, as more of the ionic liquid molecules would be affected by the local presence of the polymer. However, since χ for other polymer solutions exhibit similar concentration dependences to the PnBMA/ionic liquid systems, it is also possible that other factors, such as cohesive energy or free volume differences, influence how A and B vary with concentration.

To summarize this section, χ was determined in the dilute regime from second virial coefficient measurements and in the concentrated regime by RPA treatment of SANS data, and it was shown that χ increases with polymer concentration similarly to other polymer solutions in molecular solvents. Comparison of $\chi(T)$ for different ionic liquid mixtures suggests that stronger intra-ionic liquid and/or polymer-ionic liquid interactions are present when the alkyl chain length on the ionic liquid is lengthened, leading to an increased entropic penalty for mixing, and an increased enthalpic driving force for mixing. The change in enthalpy of mixing is the dominant contribution, leading to higher phase transition temperatures for the solutions with high [BMIm][TFSI] contents.

SUMMARY

Understanding the thermodynamic driving forces for mixing and phase separation in polymer/ionic liquid solutions is of great interest. Here, we have characterized the LCST phase behavior of PnBMA in mixtures of the ionic liquids [BMIm][TFSI] and [EMIm][TFSI]. To the best of our knowledge, this work presents the first set of Θ temperatures and interaction parameters for an LCST polymer/ionic liquid system. The analysis presented herein also provides insight into the molecular driving forces for the LCST phase behavior.

Relevant thermodynamic parameters were easily tuned by varying the relative ratios of [BMIm][TFSI] and [EMIm]-[TFSI] in the ionic liquid. In particular, the cloud point, spinodal, and Θ temperatures were all found to increase linearly and rapidly with [BMIm] content. The entropic and enthalpic components of χ were also found to vary linearly with [BMIm] content, increasing and decreasing, respectively. This suggests that the increase in the average alkyl chain length on the ionic liquid cation leads to stronger intra-ionic liquid and/or polymer-ionic liquid interactions, which simultaneously increase the entropic penalty and enthalpic driving force for mixing. The change in the enthalpy of mixing is the dominant contribution, as evidenced by the increase in the phase transition temperatures. The values of χ for solutions in the various ionic liquid mixtures were determined from second virial coefficients measured in the dilute regime and by RPA treatment of SANS data in the concentrated regime, and were found to increase with polymer concentration, in quantitative

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similarity with other polymer solutions in traditional molecular solvents.

ASSOCIATED CONTENT

S Supporting Information

Representative Zimm plot, additional PnBMA/ionic liquid phase diagrams, cloud point temperatures as a function of ionic liquid composition, and χ values determined by RPA treatment of SANS for concentrations less than c^* . 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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