

# Dilute Solution Properties of Poly(benzyl methacrylate) in Ionic Liquids

Aakriti Kharel, Cecilia Hall, Peter Černoch, Petr Stepanek, and Timothy P. Lodge\*



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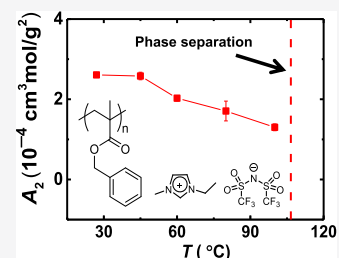


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**ABSTRACT:** The static and dynamic properties of a range of molecular weights ( $2 \times 10^4$  to  $1.6 \times 10^5$  g/mol) of poly(benzyl methacrylate) have been assessed in four different imidazolium- and pyrrolidinium-based ionic liquids over a wide temperature range (27–155 °C), primarily using light scattering techniques. All four systems exhibit lower critical solution temperature phase behavior. The relevant structural, dynamic, and thermodynamic parameters were examined as a function of concentration, temperature, and molecular weight. Some interesting observations were revealed. The phase boundaries suggest a shift of the critical composition toward the polymer-rich region, in contrast to the low critical concentrations for polymers commonly observed in polymer solutions. Surprisingly, the second virial coefficient ( $A_2$ ) remains positive, even at temperatures close to phase separation, where  $A_2 < 0$  is anticipated. Furthermore,  $A_2$  also shows stronger dependence on molecular weight than commonly observed for polymers in good solvents. On the dynamic side, the diffusion virial coefficients ( $k_d$ ) remained positive over the given temperature range, further corroborating the apparent good solvent behavior of  $A_2$ . The excluded volume exponents ( $\nu \approx 0.52$ – $0.55$ ) obtained from the dependence of hydrodynamic radii on molecular weight also indicate good solvent characteristics.



## INTRODUCTION

Ionic liquids (ILs) are emerging as promising solvents for polymers.<sup>1–5</sup> They exhibit excellent chemical and thermal stability, favorable ionic conductivity, and negligible vapor pressure, making them attractive alternatives to traditional solvents. Moreover, adding polymers to ILs can provide mechanical integrity to these materials while retaining their transport properties, enabling their use in various applications such as polymer electrolytes, gas separation membranes, and energy storage.<sup>6–12</sup> However, the use of these materials would benefit from a thorough understanding of polymer behavior in ILs.

Among various combinations of polymers and ILs that could be studied, poly(benzyl methacrylate) (PBzMA) in ILs is an appealing candidate for two reasons. First, PBzMA in ILs reveals interesting solution behavior, as demonstrated by Watanabe and co-workers in recent years.<sup>13–17</sup> Of particular interest is the lower critical solution temperature (LCST) phase behavior of PBzMA in ILs that originates primarily from the negative entropy of mixing ( $\Delta S_{\text{mix}} < 0$ ). It has been speculated that cation– $\pi$  interactions between the imidazolium cations and the aromatic rings in the PBzMA side chain result in a structurally ordered solvation shell, lowering the entropy of mixing. Watanabe and co-workers have reported the phase transition (cloud point) temperatures ( $T_{\text{cp}}$ ) of a fixed, low concentration of PBzMA in a number of ILs.<sup>13</sup> Interestingly, the values of  $T_{\text{cp}}$  were found to be significantly tunable with the IL cation and anion identity, an observation that is similar to polyethers and acrylates in ILs.<sup>2,3,18–22</sup>  $T_{\text{cp}}$  increased with the increasing cation chain length for imidazolium cations

( $C_n\text{mim}$ , where  $n = 1$ – $8$ ), spanning a temperature window of almost 200 °C. On the other hand, changing the cation structure from imidazolium to pyrrolidinium also increased  $T_{\text{cp}}$ , despite the absence of an aromatic ring in the latter. The miscibility was reported to be remarkably sensitive to the anions, as PBzMA only dissolved in bis-(trifluoromethylsulfonyl)imide (TFSI)-based and a few hexafluorophosphate ( $\text{PF}_6$ )-based ILs. This interesting LCST-type phase behavior motivates further study of the temperature-dependent static and dynamic properties of PBzMA in ILs. Second, the investigation of fundamental properties of PBzMA in ILs is also advantageous from the application standpoint. In the past decade, many advances have been made in utilizing PBzMA and IL composites in thermosensitive applications.<sup>23–27</sup> One such example is a thermoreversible ion gel that can be obtained by the self-assembly of an ABA triblock, with solvophobic block A and solvophilic block B.<sup>27</sup> PBzMA is generally used as the A block, resulting in an ion gel that forms on heating as the polymer becomes incompatible with the IL at higher temperature because of its LCST behavior.

Light scattering is a powerful tool to elucidate the structure, dynamics, and thermodynamics of polymer solutions. A few light scattering studies have been reported for polymers in ILs. Hoarfrost et al. reported a detailed investigation of polymer

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72 solution thermodynamics in ILs<sup>21</sup> using a combination of  
 73 techniques—turbidimetry, static light scattering (SLS), and  
 74 small-angle neutron scattering (SANS)—at various temper-  
 75 atures for poly(*n*-butyl methacrylate) (PnBMA) in mixtures of  
 76 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-  
 77 imide ([EMIM][TFSI]) and 1-butyl-3-methylimidazolium  
 78 bis(trifluoromethylsulfonyl)imide ([BMIM][TFSI]).<sup>21</sup> Wata-  
 79 nabe and co-workers used SANS to measure the second virial  
 80 coefficient ( $A_2$ ) and evaluate the effective interaction  
 81 parameter ( $\chi_{\text{eff}}$ ) as a function of temperature for poly(*N*-  
 82 isopropylacrylamide) (PNIPAm) and poly(2-phenylethyl  
 83 methacrylate) (PPhEtMA) in [EMIM][TFSI].<sup>17,28</sup> The theta  
 84 temperatures are found to be 45 and 28 °C for PNIPAm and  
 85 PPhEtMA, respectively, where  $A_2 = 0$  is obtained. For PBzMA  
 86 in IL, however, we are aware of only one work that has  
 87 reported an apparent  $R_g$  and hydrodynamic radius ( $R_h$ ) change  
 88 with temperature near phase separation, using SANS and  
 89 dynamic light scattering (DLS).<sup>14</sup> This study reveals that two  
 90 populations (free polymer chains and aggregates) appear near  
 91  $T_{\text{cp}}$ . The effective interaction parameter ( $\chi_{\text{eff}}$ ) was also assessed  
 92 for a fixed concentration of PBzMA using SANS model fits.  
 93 The authors report  $\chi_{\text{eff}} < 0.5$ , indicating that [EMIM][TFSI] is  
 94 a good solvent for PBzMA. However, the diffusion coefficients,  
 95 second virial coefficients, hydrodynamic radii, and their  
 96 dependence on concentration, polymer molecular weight,  
 97 and temperature are yet to be investigated.  
 98 This work describes the thermodynamic, dynamic, and  
 99 structural properties of a range of molecular weights of PBzMA  
 100 (20–160 kg/mol) in three different imidazolium-based ILs  
 101 and one pyrrolidinium-based IL, primarily using light  
 102 scattering techniques. The cloud point temperature is  
 103 evaluated by turbidimetry experiments to determine the  
 104 concentration dependence of  $T_{\text{cp}}$ . Furthermore,  $T_{\text{cp}}$  is  
 105 measured as a function of the cation chain length and cation  
 106 identity. SLS is employed to evaluate  $A_2$  for PBzMA, hence  
 107 establishing the molecular weight dependence of  $A_2$  for these  
 108 systems. For the longest PBzMA chain, the temperature  
 109 dependence of  $A_2$  is additionally examined over the range of  
 110 27–155 °C. DLS is used to measure the diffusivity as a  
 111 function of concentration and temperature (27–155 °C) to  
 112 evaluate the infinite dilution translation diffusion coefficient  
 113 ( $D_0$ ) and the infinite dilution hydrodynamic radii ( $R_{h,0}$ ). Flory  
 114 exponents ( $\nu$ ) are determined from the molecular weight  
 115 dependence of  $R_{h,0}$ . Additional relevant parameters such as the  
 116 diffusion virial coefficient ( $k_d$ ) and frictional coefficient ( $k_f$ ) are  
 117 determined from the concentration dependence of the mutual  
 118 diffusion coefficient,  $D_m$ , at several temperatures. Overall, the  
 119 key parameters of interest ( $T_{\text{cp}}$ ,  $A_2$ ,  $D_0$ ,  $R_{h,0}$ ,  $\nu$ ,  $k_d$ , and  $k_f$ ) that  
 120 describe the behavior of dilute solutions of PBzMA in four ILs  
 121 are summarized and discussed.

## 122 ■ EXPERIMENTAL SECTION

123 **Polymer Synthesis and Characterization.** All reagents were  
 124 purchased from Sigma-Aldrich and used as received. In a  
 125 representative ATRP protocol, benzyl methacrylate (10 g, 56.8  
 126 mmol), 1,1,4,7,10,10-hexamethyltriethylenetetramine (20 mg, 0.09  
 127 mmol), and ethyl-2-bromo-2-methylpropionate (7 mg, 0.09 mmol)  
 128 were combined with anisole (284 mL) in a Schlenk flask. The mixture  
 129 was degassed through three freeze–pump–thaw cycles and then  
 130 placed under positive pressure of argon. A needle was placed in the  
 131 septum to relieve pressure in the flask. The septum was removed from  
 132 the reaction flask under a constant flow of argon, and copper(I)  
 133 bromide (6 mg, 0.04 mmol) was added. After re-sealing the flask and  
 134 increasing the argon pressure to 5 atm, the reaction was allowed to

proceed at 75 °C for 3.5 h. The reaction mixture was quenched by  
 placing it in an ice water bath and purified by precipitation in hexanes  
 three times. The weight-average molecular weights ( $M_w$ ) and  
 dispersities ( $\bar{D}$ ) of the synthesized polymers (listed in Table 1)

**Table 1. Characteristics of PBzMA**

| $M_w$ (kg/mol) ( $\pm 10\%$ ) <sup>a</sup> | $\bar{D}$ <sup>a</sup> | $N^b$ | $c^*$ (g/mL) <sup>c</sup> |
|--------------------------------------------|------------------------|-------|---------------------------|
| 21                                         | 1.12                   | 106   | 0.13                      |
| 41                                         | 1.11                   | 208   | 0.08                      |
| 70                                         | 1.15                   | 335   | 0.05                      |
| 71 <sup>d</sup>                            | 1.06                   | 377   | 0.06                      |
| 156                                        | 1.16                   | 757   | 0.03                      |

<sup>a</sup>Obtained from SEC (refractive index and light scattering detector) using THF as a mobile phase/. <sup>b</sup>Calculated using  $M_n/M_o$ , where  $M_o$  is the mass of repeat unit taken as 178 g/mol. <sup>c</sup>Estimated using  $R_g = 0.011 M_w^{0.588}$  (nm) for PBzMA in methyl ethyl ketone. <sup>d</sup>Used for cloud point measurements.

were determined by size-exclusion chromatography (SEC) performed  
 in tetrahydrofuran (THF) at 25 °C on an Agilent 1260 Infinity  
 system. The eluents were monitored using a Wyatt Optilab T-rEX  
 refractive index detector (Figure S1), and the corresponding  
 molecular weights and distributions (summarized in Table 1) were  
 determined using Zimm plots obtained from a Wyatt Dawn Heleos II  
 multiangle laser light scattering detector, using a  $dn/dc$  of 0.144 mL/g  
 in THF.<sup>29</sup> The polymers are denoted as PBzMA-*x*, where *x* denotes  
 the  $M_w$  of PBzMA, represented as PBzMA-20, PBzMA-40, PBzMA-  
 70, and PBzMA-160 for 21, 41, 70, 156 kg/mol, respectively.

**Sample Preparation.** The ILs 1-ethyl-, 1-butyl-, and 1-hexyl-3-  
 methylimidazolium bis(trifluoromethyl-sulfonyl)imide ([EMIM]-  
 [TFSI], [BMIM][TFSI], [HMIM][TFSI], and 1-butyl-1-methyl-  
 pyrrolidinium TFSI [BMP][TFSI] were purchased from IoLiTec  
 and dried under dynamic vacuum ( $<100$  mTorr) for 48 h at 60 °C.  
 The overlap concentrations ( $c^*$ ) of PBzMA were estimated as  $c^* =$   
 $3M/(4\pi R_g^3 N_A)$ , where  $N_A$  is Avogadro's number and  $R_g$  is the radius  
 of gyration of PBzMA estimated using the relationship  $R_g = 0.011$   
 $M_w^{0.588}$  (nm) for PBzMA in methyl ethyl ketone (a good solvent).<sup>30</sup>  
 The values of  $c^*$  are listed in Table 1. In order to remain in the dilute  
 regime, all solutions were prepared with polymer concentrations  
 below  $c^*$ . The polymer/IL solutions were prepared using co-solvent  
 evaporation as described elsewhere.<sup>31</sup> PBzMA and the IL were added  
 by weight in the desired ratio followed by the addition of THF to  
 facilitate dissolution.<sup>13</sup> THF was then evaporated under stirring using  
 a nitrogen purge overnight, and the mixtures were further dried under  
 vacuum ( $<100$  mTorr) for 48 h at 60 °C. The solutions were carefully  
 filtered using a 0.45  $\mu\text{m}$  PTFE syringe filter into the sample cell for  
 scattering measurements. The concentrations in wt % were converted  
 into g/mL by using the appropriate density (assuming no change in  
 volume upon mixing) of the IL at each temperature.<sup>32–34</sup> The  
 temperature dependence of density ( $\rho$ ) is estimated as  $\rho = b - aT$ ,  
 where *a* and *b* are fitting parameters listed in Table S1 for all the ILs.

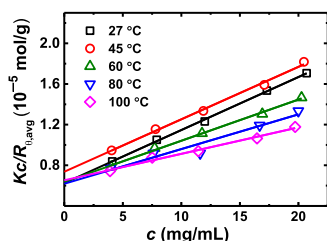
**Cloud Point Measurements.** PBzMA-71 solutions were flame-  
 sealed in glass ampoules under vacuum and placed in a heating stage  
 at a controlled temperature. The sample was heated at a rate of 1 °C/  
 min, and a HeNe laser beam of wavelength 633 nm was directed to  
 the sample, with a path length of approximately 7 mm. The  
 transmitted intensity was recorded as a function of temperature, and  
 the cloud point was defined as the temperature at which the  
 transmittance drops to  $<80\%$  of the original homogenous solution.  
 The cloud point temperature was recorded for an independent sample  
 (1 wt % PBzMA in [BMIM][TFSI]) upon heating and cooling at the  
 same rate. A relatively small hysteresis between demixing and  
 remixing was observed (see the Supporting Information, Figure S2)  
 with higher  $T_{\text{cp}}$  obtained upon cooling. Kobayashi et al. reported a  
 similar observation with PBzMA in solvate ILs.<sup>15</sup> They attributed the  
 hysteresis to the low mobility of polymer chains that dominated  
 remixing. For PBzMA in [BMIM][TFSI], the concentration range of  
 0.5–20 wt % was used to determine the concentration dependence of

$T_{cp}$ . Cloud point measurements were also performed for the highest concentration of each molecular weight (see the Supporting Information, Figure S3) and IL pair to decide the working temperature range for SLS and DLS studies. The values of  $T_{cp}$  for PBzMA-160 in [EMIM][TFSI], [BMIM][TFSI], [HMIM][TFSI], and [BMP][TFSI] are 106 °C, 157 °C, 226 °C, and 176 °C, respectively.

**Static Light Scattering.** Five different dilute concentrations for four molecular weights of PBzMA in four different ILs were prepared, resulting in a total of 80 samples. The corresponding solutions (~1 mL) were filtered into 12 mm glass ampoules and flame-sealed under Ar. SLS measurements were performed on an ALV/CGS-8F goniometer with a laser wavelength of 633 nm. The angular range was 40–120° in increments of 10°, corresponding to a scattering wave vector ( $q$ ) range of  $9.42 \times 10^{-3}$  to  $2.44 \times 10^{-3}$  nm<sup>-1</sup>. In the given angular range, no PBzMA exhibited any appreciable dependence on  $q$  (see the Supporting Information, Figure S4), indicating that the scattering falls in the Rayleigh regime ( $qR_g \ll 1$ ). Therefore, the values of second virial coefficients ( $A_2$ ) were determined using the following expression

$$\frac{Kc}{R_\theta} = \frac{1}{M_w} + 2A_2c + \dots \quad K = \frac{4\pi^2 n^2}{\lambda_o^4 N_A} \left( \frac{dn}{dc} \right)^2 \quad (1)$$

where  $R_\theta$  is the Rayleigh ratio,  $K$  is an optical constant including the solvent refractive index ( $n$ ), and the wavelength of light in vacuum ( $\lambda_o$ ).<sup>35</sup> The measured  $Kc/R$  values were averaged over all the angles, and plotted as a function of  $c$  to determine  $A_2$  from eq 1, as shown in Figure 1 and the Supporting Information, Figure S5.



**Figure 1.** Representative plot of  $Kc/R_{\theta,avg}$  as a function of  $c$  for PBzMA-160 in [EMIM][TFSI] at various temperatures.

For PBzMA-160, the measurements were performed at temperatures from 27 to 155 °C, maintained at  $\pm 0.5$  °C. The samples were placed in a preheated sealed oven at the desired temperature before placing in the thermostated instrument for 5–10 min prior to the measurement. For  $T$  up to 130 °C,  $R_\theta$  was calibrated using an ultrapure toluene standard. For  $T > 130$  °C (above the boiling temperature of toluene in a sealed ampoule),  $R_\theta$  was extrapolated from the linear dependence of  $R_\theta$  on  $T$  (see the Supporting Information, Figure S6). The values of the refractive index ( $n$ ) of the ILs at each temperature were obtained from the literature.<sup>36,37</sup>

For some systems at 27 °C, additional SLS measurements were performed on a Brookhaven BI-200SM research goniometer and laser light scattering system, with a laser wavelength of 637 nm. Scattering angles between 40 and 110° were used with 5° increments, corresponding to a  $q$  range of approximately  $9.62 \times 10^{-3}$  to  $2.30 \times 10^{-2}$  nm<sup>-1</sup>. The Rayleigh ratio of the sample was calibrated using an ultrapure toluene standard at 27 °C. PBzMA and ILs solutions (~1 mL) were filtered into 13 mm glass tubes using 0.45  $\mu$ m PTFE filters and covered with parafilm. The samples were equilibrated for 10 min at 27 °C prior to the measurement.

The refractive index increments were determined by Abbé refractometry. Five different solutions of PBzMA-40 were prepared in each IL, ranging in approximate concentration from 11 to 90 mg/mL. The temperature in the refractometer was controlled by circulating water at 27 °C and 70:30 ethylene glycol/water bath at 45 and 60 °C. The refractive index ( $n_D$ ) of neat IL and five solutions were measured using a red light source to mimic the wavelength of

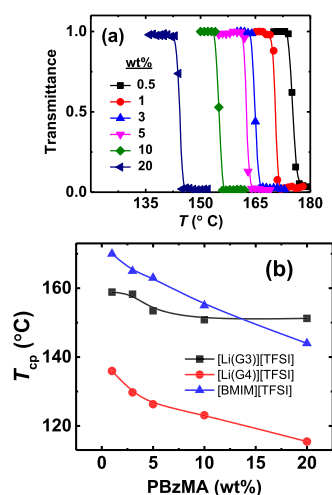
the laser in the light scattering instrument. Ideally, a wide temperature window would be used for accurate extrapolation of  $dn/dc$  versus  $T$ , but at higher temperatures, the measurement of  $n_D$  proved to be unstable. Furthermore,  $dn/dc$  is very sensitive to slight changes in  $n_D$ , which makes the error in measuring  $dn/dc$  larger than the dependence of  $dn/dc$  on  $T$ . Therefore, measurements were limited to 60 °C.

The  $dn/dc$  was evaluated from the slope of  $n_D$  versus  $c$  (see the Supporting Information, Figure S7). The values of  $dn/dc$  for PBzMA in ILs at three different temperatures are shown in Supporting Information Figure S8, and listed in Table S2. The reported error is obtained from linear fits of refractive index versus  $c$ . All systems show a negligible temperature dependence for  $dn/dc$  within the uncertainty, except for PBzMA in [BMIM][TFSI], which has a slight dependence on  $T$ ,  $d(dn/dc)/dT = -1.1 \times 10^{-4}$  (mL/g °C). It is quite common to observe a very weak dependence of  $dn/dc$  on  $T$  (typically on the order of  $10^{-4}$  mL/g °C) as reported in the literature.<sup>21,38,39</sup> For SLS measurements above 60 °C, an average  $dn/dc$  value (measured at 3 temperatures) was used. On the other hand, for PBzMA in [BMIM][TFSI],  $dn/dc$  at higher temperatures was calculated by linear extrapolation.

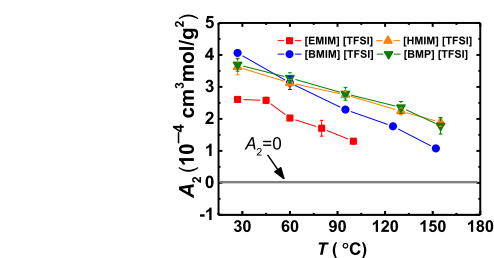
**Dynamic Light Scattering.** DLS measurements were performed on two different instruments. Measurements were conducted at 27 °C on a Brookhaven BI-200SM research goniometer, laser light scattering system, with a laser wavelength of 637 nm, and BI-9000AT autocorrelator. Scattering angles of 30, 50, 70, 90, and 110° were used corresponding to a  $q$ -range of  $5.33 \times 10^{-3}$  to  $5.34 \times 10^{-2}$  nm<sup>-1</sup> and a typical acquisition time of 10 min per angle. The value of the mean decay rate  $\Gamma$  was obtained from cumulant fitting of the intensity autocorrelation function  $|g^{(1)}|^2$  (see the Supporting Information, Figure S9), and the size distribution was obtained via Laplace inversion using REPES and the Stokes–Einstein equation (see the Supporting Information, Figure S10). For the majority of the samples, DLS measurements were performed on an ALV/CGS-8F goniometer with a laser wavelength of 633 nm and an ALV 6010 correlator. The angle was varied from 30 to 110° in increments of 20°, corresponding to a  $q$  range of  $5.34 \times 10^{-3}$  to  $5.35 \times 10^{-2}$  nm<sup>-1</sup>. For each angle, the measurement was performed three times, averaged over 60 s each. The value of  $\Gamma$  was also obtained from a third cumulant fit (see the Supporting Information, Figure S9) determined by the inbuilt ALV software, and the size distribution was obtained via Laplace inversion using REPES and the Stokes–Einstein equation (see the Supporting Information, Figure S10). Measurements at 27 °C for PBzMA-160 were made on both instruments for independent sets of samples with equivalent concentrations. The values of  $D_0$  obtained were generally within 5% from the two independent measurements, emphasizing that the collection time of 10 min versus 1 min does not significantly affect the experimental values.

## RESULTS AND DISCUSSION

**Phase Behavior.** As can be seen in Figure 2a, cloud point temperatures are obtained upon heating, consistent with the known LCST phase behavior of PBzMA in ILs.<sup>13</sup> According to the Flory–Huggins theory, particularly for UCST systems, the critical concentration ( $\phi_c$ ) is generally shifted to low concentrations of polymer and decreases with increasing molecular weight ( $\phi_c \approx 1/N$ , where  $N$  is the degree of polymerization in units of solvent molar volume).<sup>40</sup> Using the former relationship,  $\phi_c$  is estimated to be 4 wt % for PBzMA-71 ( $N = 393$ ). However, as seen in Figure 2b, the observed cloud point temperature decreases consistently up to at least 20 wt %, suggesting that the actual  $\phi_c$  may be far above the estimated  $\phi_c$  for PBzMA in [BMIM][TFSI]. Watanabe and co-workers also conducted cloud point measurements for a similar molecular weight of PBzMA in glyme-based ILs (equimolar mixtures of triglyme (G3) or tetraglyme (G4) and LiTFSI, resulting in Li(G3)TFSI and Li(G4)TFSI, respectively) and observed a trend consistent with the results in Figure 2b.<sup>16</sup>



**Figure 2.** Cloud point measurements for PBzMA in ILs. (a) Transmittance vs temperature data for PBzMA (71 kg/mol) in [BMIM][TFSI] at a heating rate of 1 °C/min. (b) Cloud point temperature decreases continuously with increasing polymer concentration for PBzMA (71 kg/mol) in [BMIM][TFSI]. Watanabe and co-workers<sup>15</sup> measured cloud points for equivalent molecular weight PBzMA ( $M_w = 70$  kg/mol,  $D = 1.19$ ) in glyme-based ILs (shown in red and black) and observed a similar trend. In all cases, the critical composition possibly lies far from the expected  $\phi_c$  of 4 wt %.



**Figure 3.**  $A_2$  obtained from Zimm plots shown as a function of  $T$ .  $A_2$  decreases with increasing  $T$  as anticipated for LCST systems. However,  $A_2$  shows a weak dependence on  $T$  as the values of  $A_2$  remain significantly positive even at  $T$  close to  $T_{cp}$ . Solid lines are intended as guide to the eye.

**Table 2.** Entropic and Enthalpic Contributions to  $\chi_{eff}$

| solvent      | A           | B (K <sup>-1</sup> ) |
|--------------|-------------|----------------------|
| [EMIM][TFSI] | 0.64 ± 0.04 | −73 ± 12             |
| [BMIM][TFSI] | 0.72 ± 0.01 | −115 ± 5             |
| [HMIM][TFSI] | 0.55 ± 0.01 | −65 ± 4              |
| [BMP][TFSI]  | 0.58 ± 0.03 | −72 ± 10             |

four ILs. This is particularly surprising for PBzMA in [EMIM][TFSI] and [BMIM][TFSI], as the highest temperatures used are approximately  $T_{cp} - 5$  °C, where  $A_2 < 0$  is anticipated. The consistently positive values of  $A_2$  throughout the temperature range imply that all these ILs are reasonably good solvents in dilute solution. According to the Flory–Huggins theory, the second virial coefficient can be related to the interaction parameter,  $\chi$

$$A_2 = \left( \frac{1}{2} - \chi \right) \frac{\bar{V}_2^2}{\bar{V}_1} \frac{1}{M^2} \quad (2)$$

where  $\bar{V}_2$  is the partial molar volume of the polymer and  $\bar{V}_1$  is the partial molar volume of the solvent. Because  $\chi$  typically has an inverse dependence on  $T$ ,  $A_2$  is proportional to  $T^{-1}$ . Therefore,  $A_2$  is also plotted as a function of inverse  $T$  (see the Supporting Information, Figure S11), which shows that the experimentally obtained  $A_2$  values are far from the  $A_2 = 0$  line. The major implication of this observation is that  $T_\Theta$  is well above  $T_{cp}$ , an unusual characteristic, but one that is also observed for hydroxypropylmethylcellulose in water.<sup>44</sup> For that system, it was speculated that the solutions include some form of aggregates that restrict the simple interpretation of  $A_2$ . However, for the PBzMA/IL system, DLS measurements at various concentrations ( $\sim 4$ –21 mg/mL) and temperatures (27–100 °C) show no evidence of aggregation (see the Supporting Information, Figure S10), particularly for PBzMA-160 in [EMIM][TFSI] and [BMIM][TFSI], where the highest measurement temperature is close to  $T_{cp}$ .

Using eq 2 and the experimental values of  $A_2$ , an effective interaction parameter,  $\chi_{eff}$ , can be evaluated at each temperature.  $\chi_{eff}$  can be expressed as a function of temperature as  $\chi_{eff} = A + B/T$ , where  $A$  represents the entropic contribution and  $B$  includes the enthalpic contribution. In terms of the Flory–Huggins theory, the excess entropy of mixing is equal to  $-kA\phi_p(1 - \phi_p)$ , and enthalpy of mixing is equal to  $kB\phi_p(1 - \phi_p)$ . The partial molar volume of the IL was used as the reference volume, calculated using the density of the ILs at each temperature.<sup>32–34</sup> The density of PBzMA was assumed to vary insignificantly with temperature and, hence, a constant value of 1.18 g/mL was used to estimate the partial molar

Although few full phase diagrams have been established for polymers in ILs, some detailed work has been done for polyethers in imidazolium-based ILs that also exhibit LCST behavior. Unlike the PBzMA system,  $\phi_c$  lies at low polymer concentration ( $\phi_c \approx 4$  wt % for 22 kg/mol) for poly(ethyl glycidyl ether) (PEGE) in [EMIM][TFSI].<sup>41</sup> Furthermore, this characteristic persists irrespective of the molecular weight of PEGE. In contrast, poly(ethylene oxide) in [EMIM][BF<sub>4</sub>] and [BMIM][BF<sub>4</sub>] exhibits unusually high  $\phi_c$  (50–80 wt %), similar to our observation for PBzMA in [BMIM][TFSI].<sup>19,20</sup> The origin of the higher critical composition is not fully resolved in the PEO system but has been speculated to result from the formation of dense polymer phases, as described by de Gennes.<sup>42</sup> Recent theoretical work by Lipson and White has provided two major explanations for occurrence of polymer-rich critical compositions in the PEO/[EMIM][BF<sub>4</sub>] system.<sup>43</sup> First, the self-organization of IL molecules decreases their contribution to the ideal entropy of mixing, as opposed to the case if the solvent molecules were evenly distributed. Second, the IL component has a significantly stronger cohesive energy density compared to the polymer, which shifts the excess entropy of mixing to higher polymer composition. These arguments could partially explain the shift to higher polymer concentrations in our system as well. However, these explanations do not hold for the PEGE system, where the IL also has stronger cohesive energy density and the potential for self-organization. Therefore, the occurrence of higher critical compositions in these systems remains to be fully understood.

**Thermodynamic Properties.** For PBzMA-160, the temperature dependence of the second virial coefficient,  $A_2$ , is shown in Figure 3 in all the ILs, and the values are summarized in Table 3.  $A_2$  decreases with increasing  $T$ , as anticipated for an LCST system. However,  $A_2$  remains significantly positive even at temperatures close to the phase separation temperature,  $T_{cp}$ . The temperature at which  $A_2 = 0$  (i.e., the theta temperature,  $T_\Theta$ ) is never reached in any of the

Table 3. Structural, Dynamic, and Thermodynamic Parameters of PBzMA-160 in ILs

| $T$ (°C)                  | $R_{h,0}$ (nm) | $D_0$ ( $10^{-12}$ m <sup>2</sup> /s) | $k_d$ (mL/g) | $A_2$ ( $10^{-4}$ cm <sup>3</sup> mol/g <sup>2</sup> ) | $k_{f, \text{expt}}$ (mL/g) | $k_{f, \text{theory}}$ (mL/g) | $k_{f, \text{expt}}/k_{f, \text{theory}}$ |
|---------------------------|----------------|---------------------------------------|--------------|--------------------------------------------------------|-----------------------------|-------------------------------|-------------------------------------------|
| PBzMA-160 in [EMIM][TFSI] |                |                                       |              |                                                        |                             |                               |                                           |
| 27                        | 8.3            | 0.90                                  | 8.7          | 2.61                                                   | 73                          | 58                            | 1.3                                       |
| 45                        | 8.0            | 1.73                                  | 5.2          | 2.58                                                   | 75                          | 57                            | 1.3                                       |
| 60                        | 7.9            | 2.68                                  | 5.4          | 2.03                                                   | 58                          | 46                            | 1.3                                       |
| 80                        | 7.1            | 4.40                                  | 4.2          | 1.71                                                   | 49                          | 38                            | 1.3                                       |
| 100                       | 5.9            | 6.55                                  | 1.0          | 1.30                                                   | 39                          | 28                            | 1.4                                       |
| PBzMA-160 in [BMIM][TFSI] |                |                                       |              |                                                        |                             |                               |                                           |
| 27                        | 8.3            | 0.58                                  | 10           | 4.06                                                   | 116                         | 85                            | 1.4                                       |
| 60                        | 8.1            | 2.06                                  | 8.8          | 3.13                                                   | 89                          | 67                            | 1.3                                       |
| 95                        | 7.9            | 4.95                                  | 9.2          | 2.29                                                   | 62                          | 51                            | 1.2                                       |
| 125                       | 7.4            | 9.00                                  | 5.4          | 1.77                                                   | 50                          | 40                            | 1.3                                       |
| 152                       | 6.5            | 14.9                                  | 0            | 1.08                                                   | 34                          | 25                            | 1.4                                       |
| PBzMA-160 in [HMIM][TFSI] |                |                                       |              |                                                        |                             |                               |                                           |
| 27                        | 8.4            | 0.42                                  | 12           | 3.62                                                   | 101                         | 77                            | 1.3                                       |
| 60                        | 8.7            | 1.56                                  | 13           | 3.12                                                   | 84                          | 69                            | 1.2                                       |
| 95                        | 8.1            | 4.32                                  | 10           | 2.75                                                   | 76                          | 60                            | 1.3                                       |
| 130                       | 7.5            | 9.12                                  | 6.1          | 2.24                                                   | 64                          | 49                            | 1.3                                       |
| 155                       | 7.1            | 14.2                                  | 3.1          | 1.89                                                   | 56                          | 41                            | 1.4                                       |
| PBzMA-160 in [BMP][TFSI]  |                |                                       |              |                                                        |                             |                               |                                           |
| 27                        | 8.5            | 0.38                                  | 12           | 3.70                                                   | 103                         | 79                            | 1.3                                       |
| 60                        | 8.4            | 1.40                                  | 13           | 3.28                                                   | 89                          | 71                            | 1.3                                       |
| 95                        | 7.7            | 3.73                                  | 11           | 2.79                                                   | 76                          | 59                            | 1.3                                       |
| 130                       | 6.4            | 7.74                                  | 7.0          | 2.36                                                   | 66                          | 48                            | 1.4                                       |
| 155                       | 6.3            | 12.3                                  | 2.8          | 1.79                                                   | 53                          | 37                            | 1.4                                       |

volume of the polymer.<sup>45</sup> The resulting dependence of  $\chi_{\text{eff}}$  on temperature is shown in Figure 4, where  $\chi_{\text{eff}} < 0.5$  for all cases.

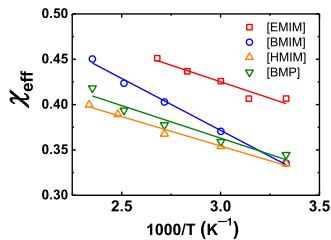
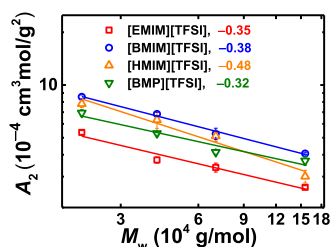


Figure 4. Temperature dependence of effective interaction parameter,  $\chi_{\text{eff}}$  for PBzMA-160 in ILs. Solid lines are fit to  $\chi_{\text{eff}} = A + B/T$ , where  $A$  and  $B$  are fitting constants.

The values of  $A$  and  $B$  can be evaluated from the intercepts and the slopes of the linear fits, respectively (listed in Table 2 and plotted in the Supporting Information, Figure S12, with the errors obtained from the linear fits). It should be emphasized that the values of  $\chi_{\text{eff}}$ ,  $A$ , and  $B$  should all be viewed with caution. For example, eq 2 does not incorporate any composition dependence of  $\chi_{\text{eff}}$ <sup>46</sup> therefore, the values of  $A$  and  $B$  are not necessarily applicable at all compositions. However, some prior reports have compared the values of  $A$  and  $B$  to resolve the entropic and enthalpic components.<sup>17,21</sup> For example, Hoarfrost et al. showed that for PnBMA in [EMIM][TFSI]/[BMIM][TFSI],<sup>21</sup>  $A$  increased with the incorporation of the BMIM cation (75–100 wt %) and concluded that the entropy of mixing decreases with higher BMIM content. On the other hand,  $B$  decreased with increasing BMIM content, which lowers the enthalpy of mixing. From Table 2, it can be seen that the values of  $B$  is negative in all cases, implying some kind of specific attractive interaction between the polymer and solvent. This result, combined with

the positive values of  $A$ , is indicative of LCST phase behavior. Prior work by Watanabe and co-workers has proposed that the benzyl groups in the polymer interact with the IL cation via cation– $\pi$  interactions, forming localized cage structures.<sup>14,17,47</sup> This interaction could be the primary driving force for the negative enthalpy of mixing and decrease in entropy of mixing. A recent study proposed that PBzMA solvation in IL is further influenced by intrapolymer interactions between benzyl side groups.<sup>16</sup> It can also be observed that the value of  $A$  increases from EMIM to BMIM, indicating that the entropy of mixing decreases. This observation is in agreement with prior reports, where the incorporation of longer alkyl tails in the cations decreased the mixing entropy because of oriented solvation.<sup>21</sup> However, this trend does not hold for the case when the HMIM cation is used. In fact, the value of  $A$  decreases. On the enthalpic side, the magnitude of  $B$  also exhibits a similar trend, where  $|B|$  increases from EMIM to BMIM but decreases for HMIM. Interestingly, the magnitude of  $A$  and  $B$  are very similar for the EMIM and BMP cations. Therefore, no specific trend can be concluded from these parameters. Hirose et al. used SANS model fits to determine the parameters  $A$  and  $B$  for a 40 kg/mol PBzMA in [EMIM][TFSI]. They report values of  $A = 0.73$  and  $B = -84 \text{ K}^{-1}$ , which are close to the experimental values obtained here.<sup>17</sup> The Flory–Huggins theory predicts that  $A_2$  is independent of  $M$  (eq 2). In fact,  $A_2$  is typically found to vary as  $A_2 \approx M_w^a$ , where  $a$  is  $\approx -0.2$  for polymers in good solvents, as predicted by the scaling theory<sup>48–50</sup> and reported in experiments.<sup>51–54</sup> The  $A_2$  values were also determined for the lower molecular weight PBzMA samples at 27 °C (see the Supporting Information, Figure S13), and the resulting values are shown in Figure 5 for all systems and molecular weights. In all cases,  $A_2$  exhibits a stronger dependence on  $M_w$  than anticipated, with  $a$  values of  $-0.35$ ,  $-0.38$ ,  $-0.48$ , and  $-0.32$  for PBzMA in



**Figure 5.**  $A_2$  plotted as a function of  $M_w$  for PBzMA in ILs.  $A_2$  decreases with increasing  $M_w$  as anticipated.  $A_2 \approx M_w^a$ , where  $a$  is  $-0.35$ ,  $-0.38$ ,  $-0.48$ , and  $-0.32$  for PBzMA in [EMIM][TFSI], [BMIM][TFSI], [HMIM][TFSI], and [BMP][TFSI], respectively. However, the dependence of  $A_2$  on  $M_w$  is surprisingly stronger than observed for polymers in good solvent systems, where  $a \approx -0.2$ .

[EMIM][TFSI], [BMIM][TFSI], [HMIM][TFSI], and [BMP][TFSI], respectively.

**Dynamic Properties.** The mutual diffusion coefficient ( $D_m$ ) was determined from the slope of the mean decay rate  $\Gamma$  plotted versus  $q^2$  (see the Supporting Information, Figure S14) for PBzMA-160 in all four ILs at 27 °C and  $T_{cp} - 5$  °C. The plots were linear for all cases. For all other temperatures (between 27 °C and  $T_{cp} - 5$  °C), DLS measurements were performed only at a 90° scattering angle, where  $D_m$  was evaluated as  $D_m = \Gamma/q^2$ . The concentration dependence of the mutual diffusion coefficient in dilute solutions can be represented by

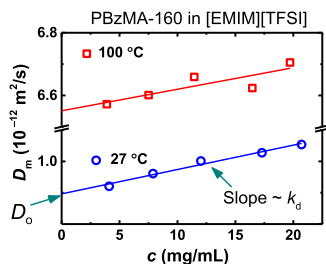
$$D_m = D_0(1 + k_d c + \dots) \quad (3)$$

where  $D_0$  is the infinite dilution translational diffusion coefficient,  $c$  is the concentration, and the constant  $k_d$  is known as the diffusion virial coefficient.<sup>54</sup>  $k_d$  is given by

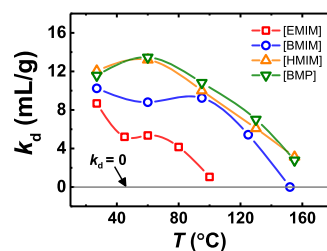
$$k_d = 2A_2M - k_f - V_p \quad (4)$$

where  $k_f$  is the linear term in the concentration expansion for the friction coefficient and  $V_p$  is the partial specific volume of the polymer.<sup>55,56</sup> The relations in eqs 3 and 4 contain both thermodynamic and dynamic information. The coefficient  $k_d$  is determined by the thermodynamic driving force ( $2A_2M$ ) and an opposing frictional resistance,  $k_f$  (the contribution of  $V_p$  is usually negligible). Positive values of  $k_d$  indicate good solvent behavior, while in theta solvents,  $k_d \leq 0$ .

The values of  $D_0$  and  $k_d$  are summarized in Table 3 at all temperatures and plotted in Figure 6 for PBzMA-160 in [EMIM][TFSI] and in the Supporting Information, Figure S15, for all other systems.  $k_d$  is also plotted as a function of temperature for PBzMA-160 in all ILs in Figure 7. For PBzMA-160 in [EMIM][TFSI],  $k_d > 0$  at  $T_{cp} - 5$  °C,



**Figure 6.** Representative plot of  $D_m$  vs  $c$  for PBzMA-160 in [EMIM][TFSI].  $D_m$  varies linearly with  $c$ , and the slope and intercept of the linear fits give  $k_d$  and  $D_0$ , respectively.



**Figure 7.** Temperature dependence of the diffusion virial coefficient for PBzMA-160 in ILs. The solid lines are the guide to the eye.

consistent with the good solvent behavior of the second virial coefficient ( $A_2 > 0$ ) obtained from the Zimm plots. For PBzMA in [BMIM][TFSI],  $k_d$  is essentially zero at  $T_{cp} - 5$  °C, also indicating that  $A_2$  is positive at  $T_{cp} - 5$  °C from eq 4. For [HMIM][TFSI] and [BMP][TFSI],  $T = 155$  °C is far from the observed  $T_{cp}$ , and thus, the positive values of  $k_d$  are not surprising. Overall, data from DLS further corroborate the good solvent behavior of PBzMA in most of the ILs.

The frictional virial coefficient,  $k_f$ , is estimated using the measured experimental values of  $A_2$  and  $k_d$  in eq 4 (assuming  $V_p$  is negligible). Yamakawa<sup>48</sup> has established  $k_f$  as

$$k_f \approx 1.2A_2M + N_A \frac{V_m}{M} \quad (5)$$

where  $V_m$  is the hydrodynamic volume of the polymer chain and  $N_A$  is Avogadro's number. Accordingly,  $k_f$  was also calculated using Yamakawa's approach.<sup>48</sup> Here, the hydrodynamic volume is obtained by the relation,  $V_m = (4/3)\pi R_h^3$ , where  $R_h$  is obtained from the DLS measurements. From Table 3, it can be seen that the magnitude of calculated  $k_f$  is in reasonable agreement with that estimated from the theory.

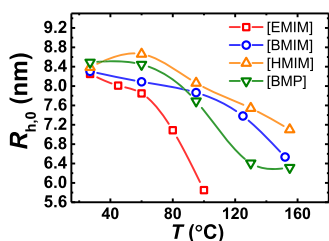
Based on the cloud point measurements and prior reports, the miscibility of PBzMA-160 decreases with the cation type in the following order: HMIM > BMP > BMIM > EMIM. In the case of imidazolium-based cations, a similar conclusion may be inferred from the  $A_2$  and  $k_d$  values over the temperature range of 27–100 °C (listed in Table 3 and shown in Figures 3 and 7). In particular, the values of  $A_2$  are considerably lower for PBzMA-160 in [EMIM][TFSI] compared to other ILs. This observation is further supported by the  $k_d$  values shown in Figure 7. Overall, the combined results from the cloud point, SLS, and DLS measurements support a consistent picture of better solvation of PBzMA with increasing alkyl chain length of the imidazolium cation. For PBzMA-160 in [BMP][TFSI], the  $A_2$  and  $k_d$  values are larger than those obtained in [EMIM][TFSI] and [BMIM][TFSI], which is consistent with the cloud point measurement. However, between BMP and HMIM, no significant variation in  $A_2$  and  $k_d$  was observed. This suggests that the solvation properties of [BMP][TFSI] are very similar to [HMIM][TFSI], a result that is particularly surprising as the cloud point temperature is about 40 °C higher in [HMIM][TFSI].

The concentration dependence of  $D_m$  was also measured for the three lower molecular weights of PBzMA in all ILs at 27 °C (see the Supporting Information, Figure S16). The values of  $k_d$  and  $D_0$  evaluated from the slopes and intercepts of the linear fits of  $D_m$  versus  $c$  plots, respectively, are listed in the Supporting Information, Table S3 and plotted in the Supporting Information, Figure S17. As seen in Table S3,  $k_d$  remains positive for PBzMA-40 and PBzMA-70 but is negative for all the cases of PBzMA-20. The negative values of  $k_d$  for

PBzMA-20 are not surprising as the  $A_2M$  term contribution is smaller for lower molecular weight polymers in eq 4. The infinite dilution hydrodynamic radii ( $R_{h,0}$ ) were calculated from the Stokes–Einstein relation

$$D_0 = \frac{kT}{6\pi\eta_s R_{h,0}} \quad (6)$$

where the solvent viscosity ( $\eta_s$ ) was calculated using the Vogel–Fulcher–Tamman (VFT) equation<sup>32,34</sup> given as  $\eta_s = \eta_0 \exp(B/T - T_0)$  and  $\eta_0$ ,  $B$ ,  $T_0$  are fitting constants listed in Table S4.<sup>32,34</sup> Figure 8 shows the temperature dependence of



**Figure 8.** Temperature dependence of infinite dilution hydrodynamic radii for PBzMA-160 in ILs. The solid lines are the guide to the eye.

$R_{h,0}$  for PBzMA-160 in all ILs, and the absolute values are summarized in Table 4. For PBzMA-160 in [EMIM][TFSI],

**Table 4. Hydrodynamic Radii and Scaling Exponents in Various ILs at 27 °C**

| solvent      | $R_{h,0}$ (nm) |     |     |      | $R_{h,0} = b M_w^\nu$ |          |
|--------------|----------------|-----|-----|------|-----------------------|----------|
|              | 20k            | 40k | 70k | 160k | $\nu$                 | $b$ (nm) |
| [EMIM][TFSI] | 2.8            | 4.2 | 5.7 | 8.3  | 0.54                  | 0.014    |
| [BMIM][TFSI] | 2.9            | 4.3 | 5.9 | 8.3  | 0.53                  | 0.014    |
| [HMIM][TFSI] | 2.9            | 4.5 | 5.9 | 8.4  | 0.53                  | 0.016    |
| [BMP][TFSI]  | 3.0            | 4.5 | 5.9 | 8.5  | 0.53                  | 0.016    |

[BMIM][TFSI], [HMIM][TFSI], and [BMP][TFSI],  $R_{h,0}$  decreases by approximately 30, 21, 15, 26% over the temperature range investigated, respectively. This behavior is in agreement with other LCST systems, where solvent quality worsens with increasing temperature, reducing the size of the polymer chain.

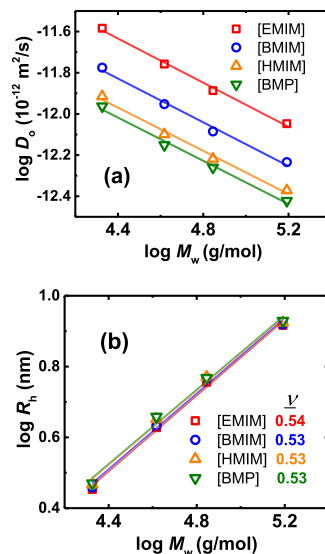
The molecular weight dependence of both  $D_0$  and  $R_{h,0}$  are shown in Table 4 and correspond to

$$R_{h,0} = bM_w^\nu$$

$$D_0 \sim M_w^{-\nu} \quad (7)$$

where  $\nu$  is the Flory exponent and  $b$  is the prefactor. The hydrodynamic radius is proportional to the radius of gyration, where the proportionality factor is approximately 1.5 for flexible polymer coils.<sup>57</sup> Because of this proportionality,  $R_{g,0}$  and  $R_{h,0}$  follow the same dependence on  $M_w$  ( $R_g \approx R_h \approx M^\nu$ ).<sup>58</sup> The experimental values of  $\nu$  along with the individual hydrodynamic radii at 27 °C are listed in Table 4. The exponents lie between 0.52 and 0.54, indicating that all ILs are moderately good solvents for PBzMA at 27 °C. Consistent with the Flory–Krigbaum theory, it is common to observe values of  $\nu$  between 0.5 and 0.6 because of the broad crossover between Gaussian and swollen chain behavior.<sup>59,60</sup> It is also possible that the values of  $\nu$  would be higher if the dependence of  $R_g$  on  $M_w$  were determined instead. The equilibrium

property,  $R_g$ , reflects solvent quality more directly than the dynamic property,  $R_h$ . As pointed out by des Cloizeaux<sup>61</sup> and further verified by Han and Akcasu,<sup>62</sup> in practice,  $R_h \approx M^{\nu'}$  and  $R_g \approx M^\nu$ ,  $\nu' < \nu$ , despite the expectation that  $\nu' \approx \nu$  (Figure 9).



**Figure 9.** Infinite dilution dynamic properties of PBzMA in ILs at 27 °C. (a)  $\log D_0$  varies linearly with  $\log M_w$ , where the slope yields  $-\nu$ . (b)  $R_{h,0}$  vs  $M_w$  also gives  $\nu$ , where  $\nu$  is between 0.52 and 0.54 for all solvents. Thus, the ILs are moderately good solvents for PBzMA at 27 °C.

## SUMMARY

The static and dynamic properties of a range of molecular weights ( $2 \times 10^4$  to  $1.6 \times 10^5$  g/mol) of PBzMA were assessed in four different ILs using light scattering. The relevant structural, dynamic, and thermodynamic parameters have been examined as a function of concentration, temperature, and molecular weight. The primary conclusions are as follows

1. Turbidimetry measurements reveal that the critical concentration is shifted toward more polymer-rich composition, as opposed to lower concentrations of polymer anticipated by the original Flory–Huggins theory. The phase separation temperatures increase with increasing imidazolium-cation chain length and changing the cation from imidazolium to pyrrolidinium, consistent with prior reports.
2. Using SLS, second virial coefficients were obtained for PBzMA-160 in the temperature range from 27 to 155 °C.  $A_2$  is found to be consistently positive for all the cases. This observation is particularly surprising for PBzMA-160 in [EMIM][TFSI] and [BMIM][TFSI], as the measurements were performed close to their phase separation temperatures, where  $A_2 < 0$  is anticipated. The major implication of this result is that the theta temperature ( $A_2 = 0$ ) lies above  $T_{cp}$ , an unusual behavior.
3.  $A_2$  was also evaluated for other molecular weights of PBzMA in all four ILs. It is found that  $A_2$  exhibits a stronger dependence on  $M_w$  ( $A_2 \approx M_w^{-0.3-0.5}$ ) in all cases, compared to commonly observed dependence of  $A_2 \approx M_w^{-0.2}$  for polymers in good solvents.

4. The mutual diffusion coefficients of PBzMA-160 in ILs were measured as a function of concentration at several temperatures (27–155 °C) using DLS. The  $k_d$  values obtained from the slopes of  $D_m$  vs  $c$  remain positive for almost all the cases, consistent with the positive values of  $A_2$  obtained from the SLS measurements.
5. The frictional coefficients ( $k_f$ ) calculated from the experimental  $A_2$  and  $k_d$  values are in reasonable agreement with theoretical predictions.
6.  $R_{h,0}$  decreases approximately 15–30% with increasing  $T$  for PBzMA-160 as anticipated for an LCST system, where the solvent quality worsens with increasing  $T$ .
7. Flory exponents obtained from the  $M_w$  dependence of both  $D_0$  and  $R_{h,0}$  lie between 0.52 and 0.54, indicating the ILs are moderately good solvents for PBzMA at 27 °C.

Overall, PBzMA in ILs, a representative LCST system, reveals some interesting solvation characteristics. The most remarkable observation is that the thermodynamic and diffusion virial coefficients remain positive even in the proximity of phase separation. The presence of such unusual behavior in other polymer and ILs systems is an open question. We also present one of the first detailed sets of thermodynamic and dynamic parameters for a polymer and IL system using light scattering, which lays the groundwork for future studies to investigate more relevant polymers and ILs mixtures that are viable in light scattering.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.9b02618>.

SEC traces, light scattering data, refractive index data, DLS correlation functions, fitting, and diffusion characteristics (PDF)

## AUTHOR INFORMATION

### Corresponding Author

Timothy P. Lodge – University of Minnesota,  
Minneapolis, Minnesota; [orcid.org/0000-0001-5916-8834](https://orcid.org/0000-0001-5916-8834); Email: [lodge@umn.edu](mailto:lodge@umn.edu)

### Other Authors

Aakriti Kharel – University of Minnesota, Minneapolis, Minnesota

Cecilia Hall – University of Minnesota, Minneapolis, Minnesota; [orcid.org/0000-0003-2773-1279](https://orcid.org/0000-0003-2773-1279)

Peter Černoch – Czech Academy of Sciences, Prague, Czech Republic

Petr Štepanek – Czech Academy of Sciences, Prague, Czech Republic; [orcid.org/0000-0003-1433-678X](https://orcid.org/0000-0003-1433-678X)

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.macromol.9b02618>

### Notes

The authors declare no competing financial interest.

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