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Coil Dimensions of Poly(ethylene oxide) in an Ionic Liquid by Small-Angle Neutron Scattering

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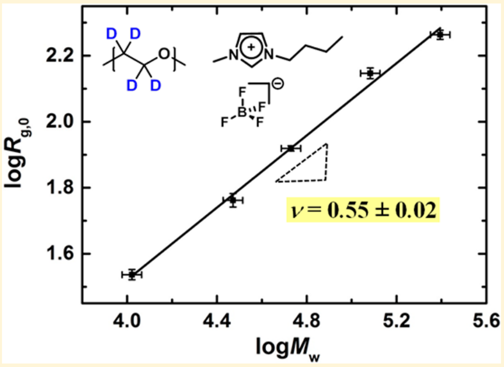
Supporting Information

ABSTRACT: The infinite dilution radii of gyration ($R_{g,0}$) for five different molecular weights (10−250 kg/mol) of perdeuterated poly(ethylene oxide) (*d*-PEO) have been determined at 80 °C in the ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) using small-angle neutron scattering (SANS). The results establish the dependence of $R_{g,0}$ on polymer molecular weight as $R_{g,0} \sim M_w^{0.55}$. An excluded volume exponent of $\nu \approx 0.55$ indicates that [BMIM][BF$_4$] is a moderately good solvent and that PEO remains a flexible random coil in this ionic liquid. These results clarify the uncertainty surrounding PEO coil dimensions in this ionic liquid, as computer simulations at various levels of complexity have led to conflicting results, and prior experimental results also do not present a completely consistent picture.



INTRODUCTION

Mixtures of polymers and ionic liquids (ILs) have gained attention in recent years as a versatile platform for designing novel materials.[1] Ionic liquids exhibit negligible vapor pressure, high thermal and chemical stability, and high ionic conductivity, which make them attractive for use in a variety of applications including fuel cells[2] and electrochemical devices.[3] One essential property that ionic liquids lack is mechanical integrity, which can instead be provided by the addition of suitable polymer architectures. However, optimization of these composite materials requires a thorough understanding of the behavior of polymers in ILs.

Among numerous combinations of polymers and ILs, the use of poly(ethylene oxide) (PEO) is particularly attractive from both fundamental and technological perspectives. For example, polymer gel electrolytes based on PEO and ILs are being investigated as replacements for current battery technologies that otherwise employ flammable and volatile organic solvents.[4] Moreover, ABA triblock block copolymers using PEO as the solvophilic block B in alkylimidazolium (C$_n$mim)-based ILs have been utilized in preparing temperature sensitive ion gels with high ion conductivity.[5] Despite the increasing significance of these mixtures, only a few experimental and theoretical studies have been conducted for PEO in these ILs; in particular, PEO in 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][BF$_4$]) is reported to have interesting structural and thermodynamic properties. Lee and Lodge[6,7] described the existence of unusual lower critical solution temperature (LCST) phase behavior of PEO in [BMIM][BF$_4$], where the critical composition (ϕ_c) is shifted to unusually high polymer volume fractions. Such behavior contrasts with typical polymer/IL and other polymer/solvent mixtures, where ϕ_c is generally low. On the computational side, Yethiraj and co-workers have reported conflicting conformational characteristics of PEO in [BMIM][BF$_4$], using various simulation methodologies. Fully atomistic simulations for modest degrees of polymerization, *N*, indicated that PEO is an extended chain at room temperature[8] (the excluded volume exponent $\nu \approx 0.9$) but adopts a random coil conformation ($\nu \approx 0.5$) when the temperature is increased closer to its LCST (400 K).[9] In contrast, when coarse-grained models were employed at similar temperatures, PEO chains were found to be collapsed ($\nu \approx 0.3$).[10] The inconsistency in the conformation of a neutral polymer chain (PEO) in an IL solvent by these models suggests a remarkable sensitivity of structural properties to the simulation parameters.

These studies therefore emphasize the need for relevant experiments to elucidate the actual conformations of PEO chains in [BMIM][BF$_4$]. In particular, experiments that obtain conformations for a range of polymer molecular weights are desirable so that ν can be obtained. We are aware of only one such experimental work, using intrinsic viscosity measurements, which concluded that [BMIM][BF$_4$] is actually a moderately poor solvent ($\nu = 0.48$, M ranging from 10^5 to 10^7 g/mol).[11] This result is also surprising, as PEO is known to be miscible in [BMIM][BF$_4$] up to high temperatures (e.g., a 2 wt % solution of 20 kg/mol PEO in [BMIM][BF$_4$] has a lower critical temperature of 209 °C),[6] and thus underscores the need for direct measurements of chain conformations using, e.g., scattering techniques. The similarity in refractive indices of PEO and [BMIM][BF$_4$], however, makes it difficult to obtain

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the radius of gyration ($R_{g,0}$) or the hydrodynamic radius using established light scattering procedures. Such difficulties can be circumvented by small-angle neutron scattering (SANS), which permits the assessment of chain dimensions via contrast between deuterated polymer and hydrogenated solvent, or vice versa. Previously, SANS has been used to measure $R_{g,0}$ for one lower molecular weight PEO (ca. 30 kg/mol) in different ILs[12,13] including [BMIM][BF_4],[14] but to the best of our knowledge, there have been no reports that describe the scaling relationship between $R_{g,0}$ and polymer molecular weight (M) for PEO in ILs. Here, we report the chain dimensions from dilute solutions of five different molecular weights of perdeuterated PEO (*d*-PEO) in [BMIM][BF_4] by SANS. By extrapolating to zero concentration for each molecular weight, we obtained the weight-average molecular weight (M_w) dependence of $R_{g,0}$, which is found to follow $R_{g,0} \sim M_w^{0.55\pm0.02}$ at 80 °C. Thus, these results suggest that [BMIM][BF_4] is of moderately good quality and PEO chains behave as flexible coils in this ionic liquid.

EXPERIMENTAL SECTION

Synthesis and Characterization of *d*-PEO. Four deuterated PEO homopolymers were synthesized via living anionic polymerization (see Supporting Information, Figure S1) of deuterated ethylene oxide (98%, Sigma-Aldrich) using established air-free techniques described elsewhere.[15,16] A further *d*-PEO (54 kg/mol) was purchased from Polymer Source. Potassium *tert*-butoxide (1.0 M THF, Sigma-Aldrich) was used as the initiator, and the reaction was terminated with methanol. Cryptand (Kryptofix 222, Sigma-Aldrich) was added to the polymerization mixture to increase the propagation rate by sequestering the potassium ion.[17,18] The weight-average molecular weights (M_w) and dispersities (*Đ*) of the synthesized and commercial polymers (Table 1) were determined by size-exclusion chromatography (SEC) performed in THF at 25 °C on an Agilent 1260 Infinity system (see Figure S2). The eluents were monitored by a Wyatt Optilab T-rEX refractive index detector, and the corresponding molecular weights and distributions were determined by using Zimm plots obtained from a Wyatt Dawn Heleos II multiangle laser light scattering (MALS) detector. A refractive index increment (d*n*/d*c*) of 0.057 mL/g was used for the four highest molecular weights, which was measured on a Wyatt Optilab T-rEX refractometer. However, it has been reported that d*n*/d*c* depends on *M* at low *M* and approaches an asymptotic value typically when $M > 20$ kg/mol.[19] Therefore, an additional d*n*/d*c* measurement was conducted for the lowest molecular weight *d*-PEO, yielding a value of 0.053 mL/g. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry was also performed for the lowest molecular weight *d*-PEO; the measured M_w of 9.0 kg/mol was in close agreement to the value obtained from SEC (listed in Table 1). The MALDI recipe is provided elsewhere.[7] The chemical structures of the polymers were confirmed using ^1H and ^2H NMR spectroscopy (see Figures S5 and S6).

Table 1. Polymer Characteristics for *d*-PEO in [BMIM][BF_4] at 80 °C

M_w (kg/mol) (±10%)	*Đ*	c^* (wt %)	$R_{g,0}$ (Å) θ condition[a]	$R_{g,0}$ (Å) SANS
10	1.01	7.3	36	34 ± 1
30	1.01	4.3	60	58 ± 3
54	1.06	3.3	80	83 ± 2
120	1.04	2.2	120	140 ± 5
250	1.10	1.6	168	183 ± 6

[a] Estimated using eq 2.

Solution Preparation. The IL [BMIM][BF_4] was purchased from Sigma-Aldrich, diluted in dichloromethane (DCM), and washed with distilled water until no precipitate was observed using a silver nitrate test. The mixture was stirred with activated charcoal for 24 h and then run through a neutral alumina column to remove impurities. Finally, [BMIM][BF_4] was dried under vacuum (<100 mTorr) for 72 h at 70 °C. The dried product was characterized using ^1H, ^{19}F, and ^{13}C NMR spectroscopy (see Figures S3 and S4). The overlap concentrations (c^*) of *d*-PEO (listed in Table 1) were estimated using the equation

$$c^* = 3M/(\rho 4\pi R_{g,0}{}^3 N_A) \tag{1}$$

where N_A is Avogadro's number and ρ is the density of hydrogenated PEO (1.20 g/mL).[20] The value of $R_{g,0}$ under theta conditions was estimated using

$$R_{g,0}{}^2 = Nb^2/6 \tag{2}$$

where b is the statistical segment length, taken as 6 Å for PEO in the melt state.[21] In order to remain in the dilute limit, all solutions were prepared with polymer concentrations below $0.5c^*$. The polymer/IL solutions were prepared using cosolvent evaporation, where *d*-PEO and [BMIM][BF_4] were added by weight in the desired ratio followed by the addition of dichloromethane (DCM) to facilitate dissolution. DCM was then evaporated under stirring using a nitrogen purge overnight, and the mixtures were further dried under vacuum (<100 mTorr) for 48 h at 50 °C.

SANS Measurements. SANS experiments were performed on the NG-7 30 m and NG-B 30 m instruments at the National Institute of Standards and Technology (NIST) Center for Neutron Research.[22] Three sample-to-detector distances (SDD) of 13, 4, and 1 m and two mean neutron wavelengths (λ) of 6 and 8 Å, with wavelength spreads ($\Delta\lambda/\lambda$) of 0.125 and 0.115, respectively, were used to access a q range of approximately 0.003−0.430 Å^{-1}. The scattering wave vector is defined as $q = 4\pi\lambda^{-1} \sin(\theta/2)$, where θ is the scattering angle. The solutions were injected into 1 mm thick demountable cells and placed in a heating block equilibrated at 80 °C. The measured two-dimensional scattering patterns were azimuthally integrated to produce a one-dimensional $I(q)$ versus q plot, using Igor SANS reduction software provided by NIST.[23] The reduction protocol corrected for sample transmission, detector efficiency, scattering from the empty cell, and calibration to absolute intensity.

Mid-angle X-ray Scattering (MAXS) Measurements. MAXS data were collected at the DND-CAT 5-ID-D beamline at the Advanced Photon Source, Argonne National laboratory. A wavelength λ of 0.73 Å and SDD of 1 m were used to obtain a q range of approximately 0.14−0.82 Å^{-1}.The samples were contained in 1.5 mm diameter quartz capillaries, and the experiments were conducted at room temperature. The measured two-dimensional scattering patterns were converted to one-dimensional plots of $I(q)$ (in arbitrary units) vs q.

RESULTS AND DISCUSSION

Crystallization of PEO in [BMIM][BF_4] was observed at room temperature, and consequently experiments were conducted above the melting temperature (65 °C) of PEO.[20] Such crystallization behavior was also recently reported in the literature.[11] The scattering curve of neat [BMIM][BF_4] shows an upturn above $q \approx 0.1$ Å^{-1}, indicating the existence of relatively long-ranged local structure within the solvent (Figure 1a).[24] MAXS was subsequently utilized to probe this structure at higher q (Figure 1b). The MAXS profile of [BMIM][BF_4] suggests the presence of spatial correlations on the nanometer length scale, and these correlations become more prominent when the alkyl chain length in the imidazolium cation is increased to six carbons (hexyl). The existence of such spatial correlations in imidazolium-based ILs, and the strong dependence of ordering on alkyl chain length, were previously identified by Triolo and co-workers via X-ray diffraction.[25]

To minimize uncertainty in the background subtraction for the polymer/IL solutions, the solvent SANS data were fit to a

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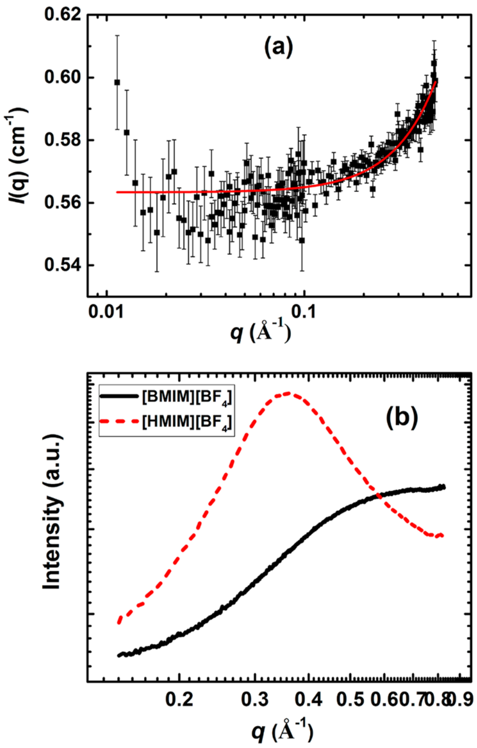

Figure 1. Solvent scattering profiles of as-prepared ILs at room temperature. (a) SANS scattering profile (symbols) of [BMIM][BF$_4$] fit to a quadratic equation (represented by solid curve). A sharp upturn at $q \geq 0.1$ Å^{-1} can be observed. (b) MAXS patterns of [BMIM][BF$_4$] and 1-hexyl-3-methylimidazolium ([HMIM])[BF$_4$] at room temperature, emphasizing the existence of spatial correlations within the ionic liquid.

quadratic form $I_{\text{solvent}} = C + Dq^2$, where C and D are fitting constants. The incoherent background weighted by the solvent volume fraction was then subtracted from the polymer/IL scattering data.

The background-subtracted SANS profiles of several dilute solutions of *d*-PEO (10 kg/mol) measured at 80 °C are shown in Figure 2 (and as log–log plots in Figure S8). As expected, the absolute scattering intensity increases with increasing polymer concentration. Guinier analysis is typically preferred for R_g determination, as prior assumptions about the chain conformation are not necessary. In this case, however, due to low signal-to-noise ratio, significant incoherent scattering, and insufficient usable data points in the Guinier regime ($qR_g < 1$), this fitting approach was not used. Instead, the background-subtracted profiles were fit to the Debye function[26]

$$I(q) = 2A(e^{-x} - 1 + x)/x^2 + B; \quad x = q^2 R_g^{\ 2} \tag{3}$$

where A, B, and R_g are used as fitting parameters. The use of a Debye fit for polymer coils that may deviate from Gaussian statistics has been previously justified in the literature by both experiment and theory.[27,28] Although the concentrations used in this study are in the dilute regime, there are still interchain polymer contributions, and thus the Debye function fit for each concentration yields an apparent R_g. For all molecular weights, the residual incoherent scattering (B) values obtained from the fits were roughly 1 to 10% of the corresponding $I(0)$ (see Table S1). The Debye function fits are depicted in Figure 2 and are in good agreement with the observed scattering profiles.

For each molecular weight, measurements were performed for four concentrations in the estimated dilute regime (see Figures S7 and S8). The apparent R_g determined for various concentrations are plotted in Figure 3, where the error bars represent the uncertainty in the nonlinear fits. The *y*-intercepts of $R_g(c)$ vs c plots provide the infinite dilution radii of gyration, $R_{g,0}$, which are listed in Table 1 along with the errors represented by the estimated uncertainty from the linear fits.

The infinite dilution radii are plotted versus molecular weight in Figure 4 in double-logarithmic form to evaluate the excluded

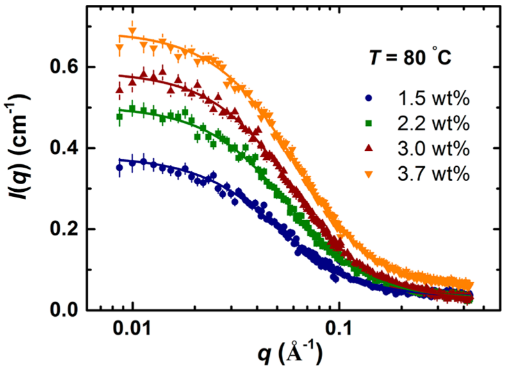

Figure 2. Background subtracted SANS $I(q)$ profiles for dilute solutions of *d*-PEO (10 kg/mol) in [BMIM][BF$_4$] at 80 °C. Symbols represent the solution scattering, and smooth curves represent the corresponding Debye function fits (eq 3).

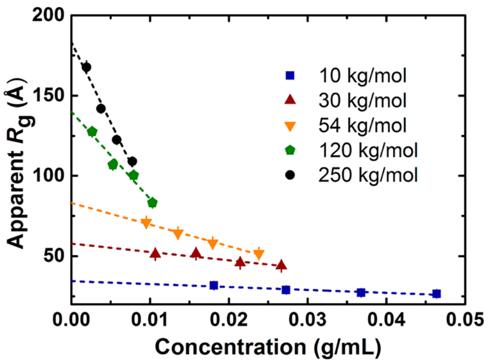

Figure 3. Apparent R_g as a function of concentration extrapolated to infinite dilution for various molecular weights of *d*-PEO in [BMIM]-[BF$_4$] at 80 °C.

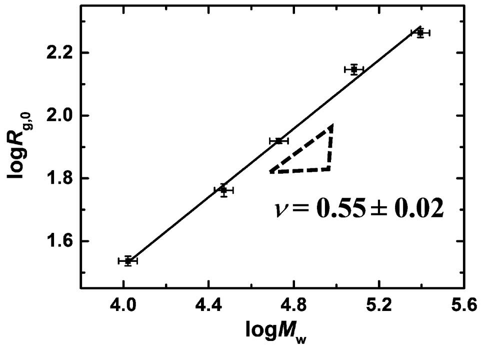

Figure 4. Double-logarithmic plot of $R_{g,0}$ vs M_w for *d*-PEO in [BMIM][BF$_4$] at 80 °C. The slope gives $\nu = 0.55$, indicating that [BMIM][BF$_4$] lies in the intermediate regime between a theta and a very good solvent.

volume exponent from the slope of a linear fit. The errors in M_w are approximated by the accuracy in determination of molecular weights by SEC, which is roughly ±10%. The dependence of $R_{g,0}$ on M_w was found to be

$$R_{g,0} = (0.22 \pm 0.05)M_w^{0.55\pm0.02}\ (\text{Å}) \tag{4}$$

where the uncertainty in the exponent and the prefactor are obtained from the errors in the slope and intercept of the linear fit, respectively.

The exponent of 0.55 ± 0.02 suggests that [BMIM][BF_4] is a moderately good solvent for PEO. Since the effect of excluded volume is dependent on both the chain length (range of M) and the experimental temperature, it is common to obtain scaling exponents between 0.5 and 0.6.[29] Table 1 contains the estimated (melt) unperturbed dimensions for each molecular weight of PEO used here. By comparing the obtained $R_{g,0}$ values for PEO in [BMIM][BF_4] and in the melt, it is apparent that the lowest three molecular weights exhibit dimensions close to the theta condition. On the other hand, excluded volume influences the dimensions of the two highest molecular weights as the coil expands more than the unperturbed state. Such behavior is consistent with the fact that excluded volume effects do not strongly influence the chain dimensions until relatively large values of M are reached.[30] The measured $R_{g,0}$ for the highest molecular weight PEO used (250 kg/mol) increases by roughly 10% of its R_{g0} estimated at theta conditions. In comparison, a PEO chain of the same length expands by almost a factor of 2 in water and methanol at room temperature, both of which are reported to be good solvents on the basis of light scattering[31,32] and intrinsic viscosity.[33,34] This relatively modest expansion of PEO chains in [BMIM][BF_4] relative to their substantial expansion in good solvents suggests that the IL is of intermediate quality at 80 °C. We note that the presence of deuterons rather than protons on the backbone of the PEO may also have some modest influence on the values of R_g and the exponent obtained. Indeed, it has been reported that the deuteration of [BMIM][BF_4] lowered the miscibility of PEO slightly (i.e., decreased the lower critical solution transition by a few degrees).[7] It is possible that the coil dimensions would be slightly larger if hydrogenated PEO were used instead.

Nonetheless, these results provide strong evidence that PEO adopts a flexible random coil-like conformation in [BMIM][BF_4], which deviates substantially from the conclusions drawn from some of the simulations mentioned previously.[8,10] However, more recent atomistic simulations[9] employed a polarizable force field approach that predicted theta-like behavior for PEO in [BMIM][BF_4] at 127 °C, which is closer to our experimental results. On the basis of this agreement, it appears that polarizable force fields better depict the polymer/IL interactions, but the use of very short chains (N = 9−40) and a different temperature compromises exact comparison of theory and experiment. However, it is clear that the results of simulations studies are very sensitive to the parametrization of the interaction between polymers and ILs, and thus this experimental study can help to benchmark better simulation models to accurately predict polymer conformations in ILs.

Triolo et al. previously conducted a room temperature SANS study of d-PEO (27 kg/mol) in [BMIM][BF_4] and reported $R_{g,0} \approx 65$ Å, which is not far from our interpolated $R_{g,0}$ of 57 Å for the same chain length.[14] The discrepancy can be attributed to a combination of the differences in temperature, concentration range, polymer end groups, and uncertainty in molecular weight. However, it seems that the radii at infinite dilution (M_w = 38 kg/mol) are considerably smaller in [BMIM][BF_4] (69 Å) than in ethylammonium nitrate (EAN)[12] (81 Å) and lithium tetraglyme bis(trifluoromethanesulfonyl)imide ([Li(G4)][TFSI])[13] (86 Å). The reported radii in these two ILs are almost 15 Å larger than in [BMIM][BF_4], suggesting that they are better solvents, but it would be helpful to confirm this hypothesis by determining ν for these ILs for larger values of N.

Intrinsic viscosity ([η]) measurements made by Liu et al. for PEO in [BMIM][BF_4] at 80 °C suggest different solvent characteristics than our SANS study.[11] A Mark−Houwink exponent (a) of 0.44 (ν = 0.48, where $a = 3\nu - 1$) was obtained, suggesting poor solvent behavior. Although the source of this discrepancy is not immediately clear, there are a few factors to consider. First, these scaling exponents (a and ν) are sensitive to the range of molecular weights used. Our SANS experiment probes a different range of molecular weights ($10^3 < M_w < 10^5$ g/mol) than the intrinsic viscosity study ($10^5 < M_w < 10^7$ g/mol). Second, the polymers used in intrinsic viscosity are broadly distributed ($1.2 < Đ < 1.6$), with $Đ$ varying significantly with M_w, compared to those used in SANS ($1.01 < Đ < 1.10$). Since both $R_{g,0}$ and [η] are measures of the average properties of all the polymer chains in the sample, nearly monodisperse polymer samples are preferred. Although the Mark−Houwink expression is assumed to be independent of dispersity, using polymers that are heterogeneous, with dispersities varying with M, can affect the values of the exponent.[35] Some reports have emphasized the importance of using narrowly distributed polymers in order to accurately establish the [η]−M_w relationships.[36,37] Third, the equilibrium property, R_g, more directly reflects solvent quality than the dynamic properties [η] and hydrodynamic radius (R_h). This has been attributed to the weaker dependence of R_h on M as compared to that of R_g, which also reduces the dependence of [η] on M due to the proportionality $[\eta] \sim R_h R_g^2/M$.[38,39] Therefore, it is conceivable that intrinsic viscosity would yield a smaller exponent than scattering studies, but it is still surprising that the exponent would be as low as 0.48. Another major consideration is that based on phase separation studies, PEO is well-soluble in [BMIM][BF_4] at temperatures below 200 °C. Cloud point measurements showed that 2 wt % PEO (20 kg/mol) in [BMIM][BF_4] phase separates at approximately 209 °C and that the critical temperature (T_c) is not a strong function of PEO molecular weight. Therefore, assuming the T_c does not change significantly across the molecular weight range used, all PEO coils of different chain lengths should be well miscible in [BMIM][BF_4] at 80 °C (below the LCST), which is not consistent with the intrinsic viscosity results.

Several studies[7,40,41] have reported that hydrogen bonding between oxygen atoms in PEO and hydrogen atoms in the imidazolium cations (particularly those attached to C_2 position) dictates the solvation of PEO in [BMIM][BF_4]. The anion also plays a significant role in polymer dissolution because it competes with the ether oxygen atoms to form hydrogen bonds with the cation. A strongly basic anion such as BF_4 will reduce PEO miscibility by tightly interacting with the cation via hydrogen bonding and disrupting the polymer−solvent interactions.[41] The use of a less basic anion such as TFSI may help elucidate the role of anion identity and basicity on coil dimensions. Overall, the favorable interactions via hydrogen bonding and the competition between the ether oxygen and the anion are likely to govern the extent of expansion of PEO coils in [BMIM][BF_4].

SUMMARY

The dependence of R_g on polymer molecular weight for model polymer/IL systems has not been experimentally determined to date. The study of polymer conformations in ionic liquids is therefore of great interest from a fundamental standpoint. Here, we report the dimensions of *d*-PEO chains of accessible molecular weights (10−250 kg/mol) in [BMIM][BF_4] using small-angle neutron scattering. We find an excluded volume exponent of 0.55 at 80 °C, which strongly suggests that PEO adopts a slightly swollen, flexible coil conformation in [BMIM][BF_4]. The infinite dilution radii for lower molecular weights are similar to the unperturbed radii in the melt state, indicating theta-like behavior. On the other hand, the coils expand relatively more for larger molecular weights *d*-PEO, revealing the onset of excluded volume effects. However, compared to good solvents for PEO such as water and methanol, the expansion of PEO of the same chain length in [BMIM][BF_4] is more modest. Therefore, this study reveals that [BMIM][BF_4] is a moderately good solvent for PEO at 80 °C. Moreover, these results clarify the discrepancies among simulation studies of PEO chain dimensions in [BMIM][BF_4], hence emphasizing the need for models that account for the complexity of intermolecular interactions in ionic liquids that affect the solvation of polymer chains.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.7b02014.

Synthesis scheme, ^1H and ^2H NMR spectra and SEC traces of all the perdeuterated PEOs, ^1H, ^{13}C, and ^{19}F NMR spectra of [BMIM][BF_4], background subtracted SANS scattering profiles, and list of fitting parameters (Figures S1−S8 and Table S1) (PDF)

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Notes

The authors declare no competing financial interest.

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