

## Morphology of Poly(ethylene oxide) Dissolved in a Room Temperature Ionic Liquid: A Small Angle Neutron Scattering Study

Alessandro Triolo,<sup>\*,†</sup> Olga Russina,<sup>‡</sup> Uwe Keiderling,<sup>‡</sup> and Joachim Kohlbrecher<sup>§</sup>

*Istituto per i Processi Chimico-Fisici, Consiglio Nazionale delle Ricerche, via La Farina,  
237 98123 Messina Italy, Hahn-Meitner Institut, Glienicker str. 100 D-14109 Berlin Germany,  
and Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

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Solutions of deuterated poly(ethylene oxide) (d-PEO) in 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]), a prototype room-temperature ionic liquid (RTIL), have been studied at room temperature over a range of polymer concentrations, using small angle neutron scattering (SANS), characterizing the conformation of PEO dissolved in RTILs. [bmim][BF<sub>4</sub>] behaves as a good solvent for d-PEO, which organizes in this solvent in non entangled random coils. These findings will help in optimizing the designing of microemulsions in these potentially environmentally friendly solvents.

### Introduction

Room-temperature ionic liquids<sup>1–4</sup> (RTILs) have a great potential as environmentally responsible and easily tunable replacements for volatile organic solvents. They are ionic substances, with a bulky asymmetric cation, which strongly hinders crystallization. They have negligible vapor pressure and are considered “designer solvents” for many applications.<sup>5–7</sup>

The partial solubility of many chemicals in RTILs presently limits their range of applications. The dispersion of otherwise insoluble chemicals in the core of RTIL-dissolved microemulsions may pave the way to many smart industrial applications. The possibility of efficiently dissolving surfactants in RTILs has been recently highlighted. Armstrong et al.<sup>8</sup> reported the existence of solvatophobic interactions between RTILs and the hydrocarbon portion of selected surfactants. Such an effect nicely resembles the driving force for the formation of micellar aggregates in more conventional solvents, such as water.<sup>9</sup> The polymorphism in concentrated solutions of PEO–PPO–PEO tri-block copolymers in RTILs<sup>10</sup> has similar features to the behavior in water. Moreover the self-assembly of polyoxyethylene-alkyl ether surfactants (C<sub>n</sub>E<sub>m</sub>) in a RTIL was reported, highlighting the formation of many lyotropic liquid crystalline phases.<sup>11</sup> A rationalization of these observations proposes a privileged interaction between RTIL and the ether portion of the block copolymer, which could be due to hydrogen bond interaction between the ether unit and the acid hydrogen on the imidazolium ring.

The characterization of RTIL-philic macromolecules will open the way to the preparation of bifunctional materials aiding the dispersion of otherwise insoluble components in RTILs. Poly(ethylene oxide) is soluble in many RTILs and can be used

as a biomimetic, solvo-philic moiety in block copolymers forming microemulsion in RTILs.

To fully exploit these potentialities, one needs a detailed characterization of the thermodynamic, structural, and dynamic properties of solutions of PEO-based products in RTILs.

In this letter we report a small angle neutron scattering (SANS) study on the morphology of a biocompatible homopolymer, poly(ethylene oxide), dissolved over a wide composition range, in a prototype RTIL, namely 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]), at ambient temperature. In particular we show that in the explored concentration range (up to ~0.2 molar ratio), [bmim][BF<sub>4</sub>] behaves as a good solvent for PEO, which organizes in the random coil configuration.

### Experimental Section

Fully deuterated PEO (d-PEO) (CD<sub>2</sub>–CD<sub>2</sub>–O–[CD<sub>2</sub>–CD<sub>2</sub>–O]<sub>n</sub>–D) was obtained from Polymer Source, Inc. with the following specifications: molecular weight MW = 27 300 and polydispersity 1.06. The deuterated homopolymer was preferred to hydrogenated (h-) PEO to enhance the contrast with the hydrogenated solvent. 1-Butyl-3-methyl imidazolium tetrafluoroborate (bmim)[BF<sub>4</sub>], density<sub>(25°C)</sub> = 1.17 g/cm<sup>3</sup>; see Figure 1) was purchased from Iolitec. Both materials were kept under vacuum at 55 °C for 24 h before preparing the solutions. The solutions were kept under vacuum at 60 °C overnight to facilitate dissolution and eliminate residual moisture.

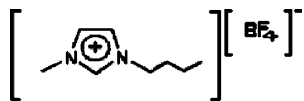
SANS measurements were run on the SANS I<sup>12</sup> instrument (at the Paul Scherrer Institut), using 1 mm thick quartz cells. Selected measurements were also collected on the SANS instrument<sup>13</sup> at the Hahn-Meitner Institut. The samples were kept at constant temperature (25 °C) using a water bath. Data correction was done using the BerSANS software<sup>14</sup> that is available at both facilities. The software corrects the raw data for transmission, empty cell background scattering, and the overall background and electronic noise of the detector. The

\* Corresponding author. E-mail: triolo@me.cnr.it.

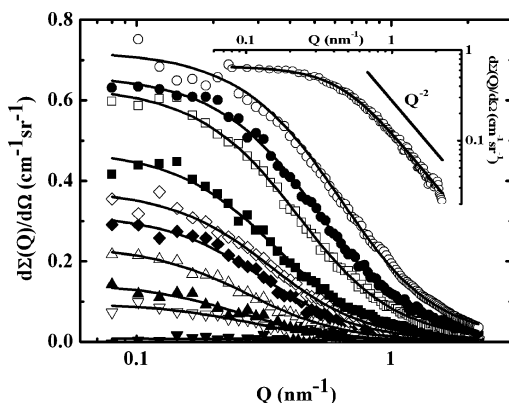
<sup>†</sup> Istituto per i Processi Chimico-Fisici.

<sup>‡</sup> Hahn-Meitner Institut.

<sup>§</sup> Paul Scherrer Institut.



**Figure 1.** Schematic representation of 1-butyl-3-methyl imidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]).



**Figure 2.** Background subtracted small angle neutron scattering data,  $d\Sigma(Q)/d\Omega$ , from solutions of d-PEO in [bmim][BF<sub>4</sub>] at 25 °C ( $10^2 c$  (g/cm<sup>3</sup>) = 0.021 (▼); 0.131 (▽); 0.222 (▲); 0.371 (△); 0.653 (◆); 0.831 (◇); 1.14 (■); 2.44 (□); 3.55 (●); 7.05 (○)). The continuous lines correspond to a fit in terms of the random coil model. Experimental error bars are smaller than the symbols' sizes. In the inset a log–log representation of data for  $c = 3.55 \times 10^{-2}$  g/cm<sup>3</sup> is reported together with the fit, highlighting the  $Q^{-2}$  power law dependence at high  $Q$ .

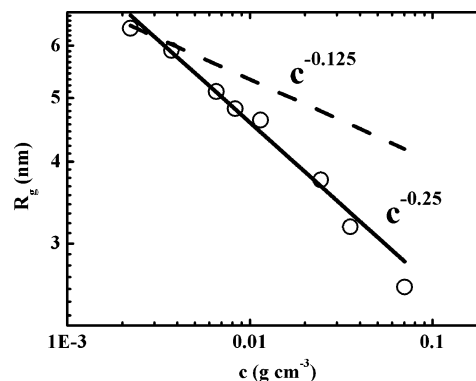
same software was used to calibrate the data in absolute units (cm<sup>−1</sup> sr<sup>−1</sup>) using a corrected SANS measurement of water scattering. After corrections, the data collected at the two instruments were in overall agreement. Data have been collected over a large concentration range ( $2.1 \times 10^{-4} < c$  (g/cm<sup>3</sup>)  $< 7.5 \times 10^{-2}$ ), extending slightly above the overlap concentration ( $c^* \sim 2.3 \times 10^{-2}$  g/cm<sup>3</sup>).

## Results and Discussion

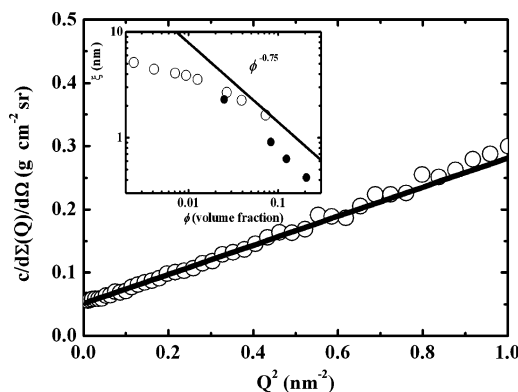
In Figure 2, SANS data from d-PEO dissolved in [bmim][BF<sub>4</sub>] at different concentrations and 25 °C are reported, after subtraction of the flat background that mainly originates from the hydrogenated solvent and was measured on the pure solvent to be equal to  $\sim 0.66$  cm<sup>−1</sup> sr<sup>−1</sup>. These data can be analyzed to extract information on the polymer configuration.

In the absence of excluded volume effects, Debye<sup>15</sup> showed that the chain-like architecture of a flexible polymer leads to the scattering law:  $d\Sigma(Q)/d\Omega \sim 2/(QR_g)^4 (\exp(-(QR_g)^2) - 1 + (QR_g)^2)$ , where  $R_g$  is the radius of gyration of the polymer random coil dispersed in an homogeneous matrix. The fits to the data in terms of this model are plotted in Figure 2 and allow extracting the concentration dependence of  $R_g$  (Figure 3):  $R_g$  decreases at increasing polymer content.<sup>16,17</sup> Such a (non linear) concentration dependence may indicate changes either in the three-dimensional configuration of PEO<sup>18</sup> or in the intermolecular interactions. The data deviate from the predicted scaling law ( $R_g \sim c^{-0.125}$  or  $R_g^2 \sim c^{-0.25}$ ) proposed for Gaussian chains.<sup>19</sup> We rather observe a  $R_g \sim c^{-0.25}$  dependence. At present we have no explanations for such a behavior.

In the inset of Figure 2 we also show the (background-subtracted) SANS data for  $c = 3.55 \times 10^{-2}$  g/cm<sup>3</sup> and the corresponding fit in a log–log scale, highlighting the good agreement with the Debye model. In particular, we note that in the high  $Q$  limit the data follow the power law dependence:  $d\Sigma(Q)/d\Omega \sim Q^{-\nu}$ , with  $\nu = 2$ . This behavior differs from the observations done on h-PEO dissolved in other more conven-



**Figure 3.** Concentration dependence of the radius of gyration,  $R_g$ , extracted from the fitting of the SANS data from d-PEO solutions in [bmim][BF<sub>4</sub>] at 25 °C, in terms of the random coil model. Two power law limits are plotted for comparison.



**Figure 4.** Zimm plot ( $c/d\Sigma(Q)/d\Omega$  vs  $Q^2$ ) of the SANS data collected on a solution of d-PEO in [bmim][BF<sub>4</sub>] at 25 °C ( $c = 3.55 \times 10^{-2}$  g/cm<sup>3</sup>) and the corresponding fit with the Zimm model. In the inset the volume fraction dependence of the screening length,  $\xi$ , is plotted (○) together with the power law trend expected for an entangled polymer mesh ( $\xi \sim \phi^{-3/4}$ ). For the sake of comparison, the corresponding data reported by Abbott et al.<sup>18</sup> for the case of h-PEO (MW = 21 000) dissolved in D<sub>2</sub>O are also reported (●).

tional solvents, such as D<sub>2</sub>O ( $\nu = 1.44$ ,<sup>20</sup> 1.54,<sup>21</sup> 1.62<sup>22</sup>), CD<sub>3</sub>CN ( $\nu = 1.55$ ,<sup>20</sup> 1.66<sup>21</sup>), CD<sub>3</sub>OD ( $\nu = 1.55$ ).<sup>20,23</sup> In general,  $\nu$  accounts for effects arising from excluded volume:  $\nu = 1$  corresponds to completely stretched chains (e.g., rigid rods), while  $\nu = 2$  corresponds to random Gaussian coils, in the absence of excluded volume effects.<sup>24</sup> To further validate this model, we obtained a Kratky plot ( $Q^2 d\Sigma(Q)/d\Omega$  vs  $Q$ ) for the data of Figure 2, and at all the concentrations the data reach a plateau at high  $Q$  (data not shown), thus further confirming the Gaussian nature of d-PEO coils dissolved in [bmim][BF<sub>4</sub>].

To access information on interchain correlations, we modeled the low  $Q$  portion of the data in terms of a Lorentzian model:  $d\Sigma(Q)/d\Omega \sim 1/(Q^2 + \xi^{-2})$ ;  $\xi$  being the screening length.<sup>18,19</sup> In the inset of Figure 4, the concentration dependence of  $\xi$  is plotted. It can be appreciated that  $\xi$  deviates from a power law dependence from  $\phi$ , the solution volume fraction, though it seems that at higher concentrations (not accessed in this work)  $\xi$  would converge to the theoretical dependence expected for an entangled polymer mesh within which the identities of the individual polymer coils are lost.<sup>18,19,25</sup> In the dilute concentration range that we are presently probing,  $\xi$  departs from the scaling behavior, indicating that individual, fully identifiable polymer coils are probed.<sup>18</sup> Similar to the findings of ref 18,  $\xi$  tends to the low concentration limit value ( $R_g/3^{1/2}$ ).

At the limit of low concentration and low  $Q$ ,  $d\Sigma(Q)/d\Omega$  can be described in terms of the Zimm formula (see Figure 4 for

the case  $c = 3.55 \cdot 10^{-2} \text{ g/cm}^3$ ):  $Kc/(\Delta\Sigma(Q)/d\Omega) = MW^{-1}(1+Q^2R_g^2/3) + 2A_2c$ , where  $K = [\Delta(SLD)]^2/\rho_{\text{PEO}}^2 N_A$  (for the present case,  $K \sim 0.004 \text{ mol cm}^2 \text{ g}^{-2}$ ) is the contrast factor (with  $\Delta(SLD)$  the contrast in coherent scattering length density,  $\rho_{\text{PEO}}$  the polymer density, and  $N_A$  the Avogadro number),  $MW$  is the polymer molecular weight and  $A_2$  is the second virial coefficient accounting for mutual interaction between polymer chains.<sup>26</sup> Application of this model in the limit of zero concentration confirms the stated molecular weight of d-PEO ( $\sim 23,800$ ) and leads to  $A_2 = 2.0 \cdot 10^{-3} \text{ cm}^3 \text{ mol g}^{-2}$ , indicating that [bmim][BF<sub>4</sub>] behaves as a good solvent for d-PEO.<sup>27</sup> The estimated values for  $R_g$  are in good agreement with the corresponding quantities derived from the Debye model, showing the same power law dependence from concentration. The chain dimensions versus the polymer MW ratio:  $(R_g^2/MW)^{0.5} = 0.43 \text{ \AA g}^{-0.5} \text{ mol}^{0.5}$ , a value that is similar to the one shown by poly(ethylene),<sup>26,29</sup> in agreement with the similar architecture of the two polymers.

In summary, by using small angle neutron scattering, we showed that d-PEO when dissolved in [bmim][BF<sub>4</sub>] organizes in random coil configurations. No phase separation was detected up to a molar fraction  $[\text{d-PEO}]/[\text{[bmim][BF}_4\text{]}] = 0.23$ , and the Debye random coil model successfully described the SANS data, confirming the Gaussian nature of the coils. Moreover the description of the experimental data in terms of the Zimm analysis led to the observation that [bmim][BF<sub>4</sub>] is a good solvent for the individual, distinguishable coils of d-PEO.

Work is now in progress to achieve further information on the nature of the interaction between poly(ether)s and [bmim][BF<sub>4</sub>]. It can be expected that the ionic nature of [bmim][BF<sub>4</sub>] might play a crucial role in determining the appealing solvating performance toward d-PEO. Though further investigations are required to probe the effect of other RTILs on PEO morphology, we believe that the present results open the way to an understanding of polymer solutions in RTILs and represent a first step toward a detailed characterization of aggregation processes in these potentially environmentally friendly solvents.

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