

## The Micellar Shuttle: Thermoreversible, Intact Transfer of Block Copolymer Micelles between an Ionic Liquid and Water

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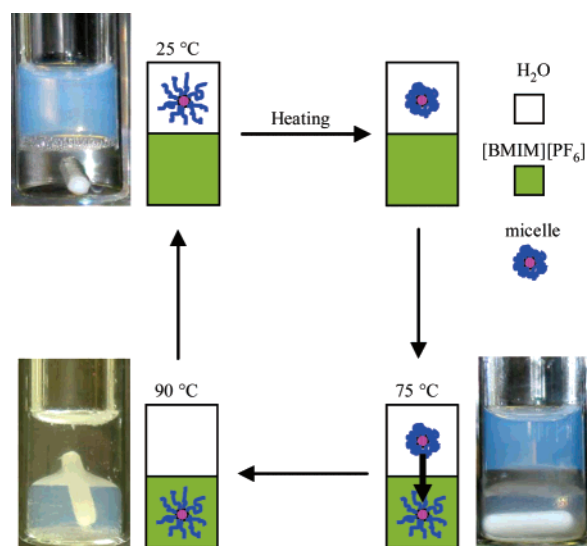
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Micelles have attracted much attention for their ability to package, transport, or manipulate small molecules in an inhospitable environment.<sup>1</sup> In recent years, micelles formed of block copolymers have been extensively investigated as potential delivery vehicles, especially as nanocarriers in the field of drug delivery<sup>2–5</sup> and phase transfer.<sup>6,7</sup> However, most systems only demonstrate one-way delivery capability. In some cases such as micellar reactions or micellar catalysis,<sup>8</sup> one might envision the necessity to transport an object from one phase to another and take it back after its mission is accomplished. Here we report a block copolymer micellar system which is able to make multiple round trips between two “green” solvents—an ionic liquid and water—without disrupting the micellar structure. The transfer of the micelles is simply controlled by temperature. Such a system could find application in transporting hydrophobic reactants/products to/from an ionic liquid reaction medium, with only the aqueous phase to handle in the ultimate recovery and purification steps.

Room-temperature ionic liquids are an interesting class of tunable solvents with many unique and attractive physicochemical properties, including negligible vapor pressure, fire resistance, favorable chemical and thermal stability, wide liquid temperature ranges, and wide electrochemical windows.<sup>9–11</sup> Their applications have rapidly expanded from alternative media for reactions and separations to multidisciplinary chemistry areas.<sup>12</sup> In some applications such as organic synthesis, chemical separation, or hazardous chemical storage and transportation, it is desirable that we can transfer insoluble chemicals into and out of ionic liquids easily without introducing complicated separation and purification procedures. Block copolymer micelles offer just this possibility.

In this study we demonstrate that the micelles formed by self-assembly of poly((1,2-butadiene)-*block*-ethylene oxide) (PB–PEO) diblock copolymers can move back and forth between an ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF<sub>6</sub>]) and water without perturbing the major micellar structure. Observations on a particular copolymer, designated as BO(9-10), are presented here. The numbers in the sample code refer to the number average molecular weights (kDa) of the PB and PEO blocks, respectively. However, equivalent results were also obtained on three other BO samples, as documented in Supporting Information. Molecular and micellar characterization information are also listed in Table S1 of Supporting Information. The micellization of PB–PEO diblock copolymers has been well investigated in both [BMIM][PF<sub>6</sub>]<sup>13</sup> and water.<sup>14,15</sup> Both [BMIM][PF<sub>6</sub>] and water are good solvents for the PEO blocks while the PB blocks segregate into the micellar cores. Depending on the PEO block length, the predominant micellar morphologies are spheres, cylinders, and vesicles, and these were unambiguously visualized by cryogenic transmission electron microscopy (cryo-TEM).

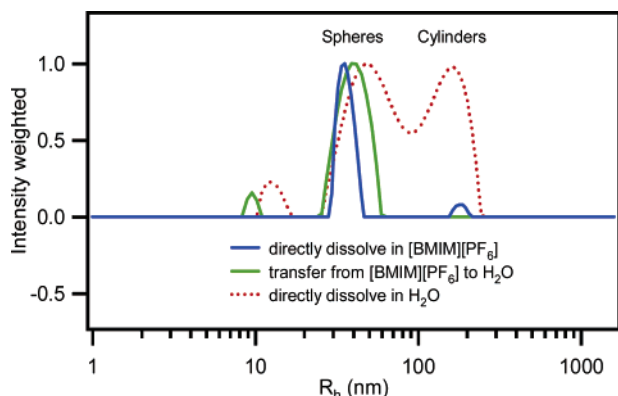
A schematic diagram of the round trip for spherical PB–PEO micelles between [BMIM][PF<sub>6</sub>] and water is illustrated in Figure



**Figure 1.** Schematic illustration of the round trip of PB–PEO micelles between [BMIM][PF<sub>6</sub>] (lower layer) and water (upper layer), accompanied by experimental images at each temperature.

1. First 1 wt % of PB–PEO block copolymer was directly dissolved in [BMIM][PF<sub>6</sub>], followed by addition of an equal amount of water. As [BMIM][PF<sub>6</sub>] and water are immiscible, the resulting solution phase separates, with the lower layer being the ionic liquid rich phase and the upper layer being the aqueous phase. After moderate agitation and equilibration at ambient temperature, the micelles reside in the aqueous phase, as confirmed by the opacity of the upper layer. Next the solution was slowly heated under gentle stirring. At a temperature around 75 °C the micelles start to leave the aqueous phase and enter the ionic liquid phase, and remain there at 90 °C. Finally the solution was cooled to ambient temperature, and the micelles returned to the aqueous phase. This cycling process was repeated successfully 10 times.

The above micelle transfer process was directly visualized as shown in Figure 1. [BMIM][PF<sub>6</sub>] is a colorless room-temperature ionic liquid with a density of 1.36 g/cm<sup>3</sup>, heavier than water. As documented elsewhere<sup>13–15</sup> the typical size of these PB–PEO micelles in [BMIM][PF<sub>6</sub>] and water is ~80 nm, and the micelle solutions appear bluish clear. Therefore it is straightforward to locate the micelles based on the solution appearance without introducing additional labeling. From Figure 1 it can be observed that the majority of the micelles reside in the aqueous phase (upper layer) at 25 °C and in the ionic liquid phase (lower layer) at 90 °C. At 75 °C, which is the transfer temperature, the micelles reside in both phases after very gentle stirring. It should be noted that at both 25 °C and 90 °C, we have performed dynamic light scattering (DLS) experiments on the clear phases; any residual micelles are below the detection limit.



**Figure 2.** Hydrodynamic radius of the PB–PEO micelles in three different solutions (1 wt %) by DLS at ambient temperature.

The temperature dependence of the micelle size and the micelle structure variation during the transfer processes were investigated by DLS. The micelle transfer mechanism can be inferred from this information. First we characterized the hydrodynamic radius ( $R_h$ ) of the BO(9–10) micelles in a 1 wt % aqueous solution. The average hydrodynamic radius  $\langle R_h \rangle$  decreases from 61 to 57 nm when the temperature was increased from 25 °C to 90 °C.<sup>16</sup> This observation is consistent with the known lower critical solution phase behavior of PEO in water and the break-up of ether–water hydrogen bonding at elevated temperatures.<sup>17,18</sup> Upon increasing temperature, water becomes a less good solvent for PEO, which causes some contraction of the PEO corona chains and results in the overall micelle size reduction. In contrast, we recently reported temperature independent  $\langle R_h \rangle$  between 25 °C and 100 °C for the PB–PEO micelles in 1 wt % [BMIM][PF<sub>6</sub>] solutions.<sup>13</sup> This finding suggests that the good solvent character of [BMIM][PF<sub>6</sub>] for PEO does not change significantly over this temperature range. As a result, the relative affinity of [BMIM][PF<sub>6</sub>] and water to the corona PEO chains reverses with increasing temperature, and 75 °C is the transition region as revealed in Figure 1. At temperatures below 75 °C PEO has stronger affinity to water than to [BMIM][PF<sub>6</sub>] and most micelles prefer to stay in the aqueous phase; at temperatures above 75 °C PEO is more favorable to [BMIM][PF<sub>6</sub>] than to water and most micelles prefer to stay in the ionic liquid phase; at 75 °C both [BMIM][PF<sub>6</sub>] and water are equally good for PEO and the micelles can be distributed in both phases.

A further experiment assessed the structural change of the PB–PEO micelles during the transfer process. When the micelles move from one phase to another, three scenarios could be envisioned: (1) each micelle crosses the [BMIM][PF<sub>6</sub>]/water interface individually as an intact entity; (2) there is micellar dissociation/reassembly at the interface, and new micelles are formed after crossing the interface; (3) direct transfer of single chains. In the latter two cases we would expect to detect some changes in the micelle structure, such as  $\langle R_h \rangle$  and/or micelle size distribution, as the micelles formed directly in the two solvents differ (Figure 2). In fact, the DLS results strongly support the first scenario. More detailed information is given in the Supporting Information (Figure S2, Table S2, and related description). Briefly, we measured  $\langle R_h \rangle$  and the size distribution of the PB–PEO micelles before and after they are transferred from [BMIM][PF<sub>6</sub>] to water. As shown in Figure 2, there is no essential difference in  $\langle R_h \rangle$  and size distribution for the PB–PEO micelles in the initial [BMIM][PF<sub>6</sub>] solution and after

they are transferred to water. In an additional experiment we directly dissolved the PB–PEO block copolymer in water. In this case both  $\langle R_h \rangle$  and size distribution of the resulting PB–PEO micelles (red line in Figure 2) are much different than those of the transferred micelles from [BMIM][PF<sub>6</sub>]. If either scenario 2 or 3 were the transfer mechanism, the newly formed micelles should be very close in structure to those obtained by direct water solvation, that is, we should observe some differences in the micelle size and/or micelle morphology after phase transfer. The preserved micelle size indicates that the first scenario is the right transfer mechanism. Furthermore, the micelle size was unchanged after five round trips between [BMIM][PF<sub>6</sub>] and water. Three other PB–PEO copolymers with different PEO block lengths were also studied and show similar features of micelle transfer; these include both cylindrical and vesicle aggregates, confirming that the phenomenon is independent of micellar morphology. These results are presented in the Supporting Information.

In conclusion, we have described an interesting and unusual round trip of block copolymer micelles between an ionic liquid and water. The reversible micelle transfer between the two media is based on the relative affinity of the two solvents to the corona chains and is triggered by temperature change. The micelle size and structure are preserved during the reversible transfer process. This phenomenon relies on finding a polymer (PEO in this case) that is nearly equally soluble in two otherwise immiscible solvents. Simple solubility parameter considerations indicate that this situation should be rather rare; generally if two solvents can dissolve a given polymer, their cohesive densities should not be very different.

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**Supporting Information Available:** Experimental details and results for other three block copolymers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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