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A Thermoreversible Micellization−Transfer−Demicellization Shuttle between Water and an Ionic Liquid

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There is great interest in micellar systems for applications in delivery, separations, extraction, and catalysis,[1] arising from their distinct amphiphilic core−shell structure, which provides solubilization of small molecules in an otherwise inhospitable environment. Stimuli-sensitive polymeric micelles are particularly promising because one can control micellization/demicellization and hence loading/release via external triggers, such as temperature or pH.[2] Here we report a fully reversible micellization−transfer−demicellization shuttle between water and a hydrophobic ionic liquid. The block copolymer micelles are designed to be thermosensitive and show reversible micellization in both water and the ionic liquid. Moreover, in contrast to common "single shot" delivery strategies, this system exhibits an unusual round-trip delivery between the two solvents,[3] which could enable recycling of valuable payloads, such as catalysts. All three sequential processes—micellization, transfer, and demicellization—are simply controlled by a single stimulus—temperature. Specifically, at room temperature the copolymers reside preferentially in water, before forming micelles on heating. At a higher temperature the micelles transfer spontaneously to the ionic liquid, as the solubilizing capability of water for the corona block diminishes. Finally, further heating induces the micelles to break up into free chains, but now in the ionic liquid. The entire process is reversible on cooling.

Ionic liquids are molten salts with low melting points. Because of their attractive features, such as negligible volatility, widely tunable solvation properties, and chemical and thermal stability, they are extensively explored as media for reactions,[4] catalysis,[5] and separations.[6] Nanostructures provided by self-assembly of amphiphiles[7] may expand or enhance the applications of ionic liquids. Recently, we reported the micellization[8] and gelation[9] of block copolymers in ionic liquids and their application as gate dielectrics for plastic electronics.[10] Moreover, we discovered an interesting and unusual phenomenon, which we termed the micelle shuttle:[11] poly((1,2-butadiene)-*block*-ethylene oxide) (PB−PEO) block copolymer micelles transfer from water at room temperature to a hydrophobic ionic liquid at high temperature. The transfer is fully reversible, with preservation of micelle structure between the two solvents. The kinetically trapped micelle structures, originating from the high amphiphilicity between the blocks and the extremely low solvent compatibility of the PB core block in both water and ionic liquid,[11] indicate stable nanocarriers. An analogous shuttle system with poly(oxazoline) copolymers was recently reported.[12] However, it is highly desirable to control the stability of these vehicles to trigger immediate loading or release of cargo.

To this end we prepared a poly(*N*-isopropylacrylamide-*block*-ethylene oxide) (PNIPAm−PEO) block copolymer for the micelle shuttle system. The PNIPAm core block is doubly and inversely thermosensitive, in that it shows a lower critical solution temperature (LCST) in water around 32 °C[2] but an upper critical solution temperature (UCST) in an ionic liquid.[13] An interesting, related duality has been reported in some diblock copolymer systems in which the two blocks show different thermoresponses in a single solvent, water; i.e., one block shows an LCST and the other a UCST. This leads to a thermally triggered micelle inversion.[14] Our system is fundamentally different in that the PNIPAm block is consistently the core-forming block, although it shows different thermoresponses in water and ionic liquids. This remarkable duality provides an opportunity to control micellization and demicellization in both media. On the other hand, the LCST phase behavior of the PEO corona block in water provides the driving force for the micelle transfer, as the relative affinity of the micelles for water and ionic liquid changes with temperature.[11b] The PNIPAm−PEO block copolymer was synthesized via reversible addition−fragmentation chain transfer polymerization (RAFT) from a PEO macroinitiator. It has a 12 kDa PNIPAm block, a 19 kDa PEO block, and a polydispersity of 1.16 (see Supporting Information for details).

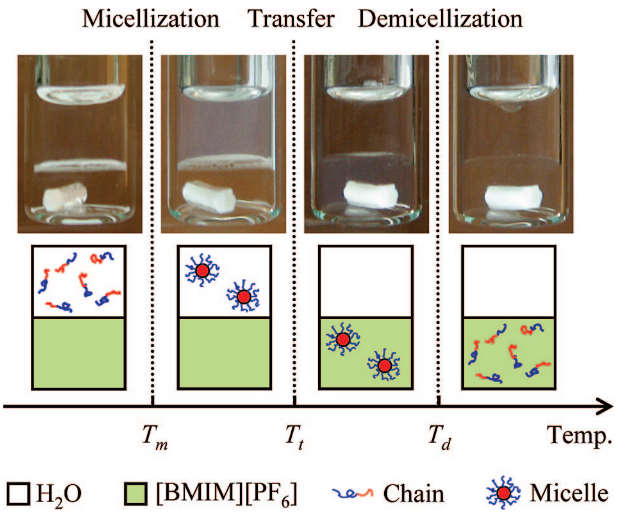

Figure 1. Thermoreversible PNIPAm−PEO block copolymer micelle shuttle between water (upper phase) and [BMIM][PF$_6$] (lower phase).

A cartoon of the overall scheme, and the corresponding experimental images of the PNIPAm−PEO micelle shuttle between water and the hydrophobic ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM][PF$_6$]), are shown in Figure 1. Since the presence of the large micelles (mean hydrodynamic radius, R_h, ≈ 30 nm) leads to a clear but bluish solution, the micelle formation, transfer, and dissociation processes can be directly visualized without introducing additional labeling;[11] the transitions were consistent with dynamic light scattering (DLS) data (see Supporting Information). At room temperature, 2 wt % PNIPAm−PEO block copolymers exist primarily as free chains in the aqueous phase, but as reported by other groups,[15] there is a noticeable presence of larger aggregates; the total scattered intensity is low, however (Figure 2). Upon heating

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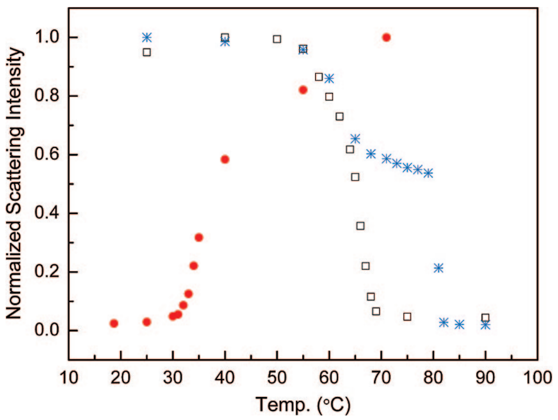

Figure 2. Temperature dependence of normalized scattering intensity at $\theta = 90°$ in three PNIPAm−PEO solutions (2 wt %) (circles: in water; squares: in dry [BMIM][PF_6]; stars: in water-saturated [BMIM][PF_6]).

Table 1. Transition Temperatures T_m, T_t, and T_d in Two Biphasic Transfer Systems[a]

transfer system (2 wt % copolymer)	T_m (°C)	T_t (°C)	T_d (°C)
[BMIM][PF_6]/H_2O	34	68	81
[BMIM][PF_6]/0.35 M NaCl H_2O	27	57	83

[a] The T_m and T_d are taken as the temperatures in which the normalized scattering intensity in Figure 2 reaches 20%, which is also consistent with the change in solution appearance from colorless to bluish.

above the micellization temperature ($T_m \approx 34$ °C), micelles are formed with a large increase in scattered intensity, as indicated by the bluish aqueous phase. Above the transfer temperature ($T_t \approx 68$ °C), the micelles transfer to the ionic liquid phase, as indicated by the disappearance of the bluish color in the aqueous phase and its reappearance in the ionic liquid phase. Finally, above the demicellization temperature ($T_d \approx 81$ °C), they disintegrate to form free chains with no evidence of larger aggregates, as indicated by two clear phases and further DLS results (not shown). This process is fully reversible (see Supporting Information for details) and was repeated at least 10 times.[16]

The micellization and demicellization processes are further characterized by light scattering. Figure 2 shows the temperature dependence of the scattering intensity of various PNIPAm−PEO solutions. In aqueous solution, a sharp increase in scattering intensity just above 30 °C indicates micelle formation. The intensity trace and T_m (Table 1) are consistent with previously reported results.[17] Similarly, in the ionic liquid solution, a significant decrease in scattering intensity beginning near 60 °C indicates micelle dissociation. Because the ionic liquid is in contact with water in the micelle shuttle system, water-saturated [BMIM][PF_6][18] was also characterized as a solvent. Both the scattering results and the change in solution appearance show that the T_d is ca. 14 °C higher in water-saturated [BMIM][PF_6] than in dry [BMIM][PF_6]. This is not surprising since water is a poor solvent for PNIPAm at high temperature. This scattering trace actually reveals an apparent two-step decrease in scattering intensity. As the first step coincides with the onset of demicellization in the dry ionic liquid, we speculate that it might reflect penetration of [BMIM][PF_6] into the micelle cores. The micelle size increases (Supporting Information), consistent with solvent penetration. The origins of the intensity decrease at $\theta = 90°$ are not completely apparent, but the changing form factor is a significant contributor. The size and size distribution of the micelles formed in water and water-saturated [BMIM][PF_6] are also characterized by DLS (Supporting Information), which further corroborate the process of the micelle shuttle.

The three critical temperatures are the key parameters of the system, and their tuning is of specific interest. To be effective, the three temperatures must be ordered as $T_m < T_t < T_d$, and they should be spaced by intervals at least 10 deg. We have shown that the relatively high T_t can be effectively depressed by adding ionic or nonionic additives to the aqueous phase in the PB−PEO micelle shuttle due to the corresponding decrease in the LCST of the PEO corona block in water.[11b] In the current system, a similar depression in T_t is observed by adding sodium chloride to the aqueous phase (Table 1). The addition of salt also leads to a decrease in the LCST of the PNIPAm core block in water[19] and hence a depression in T_m. Little change in T_d with the addition of the salt suggests that unfavorable ion exchange between the salt and [BMIM][PF_6] and partitioning of NaCl into the ionic liquid phase are not significant, which is consistent with previous results.[11b] The value of T_d is dictated by the UCST of PNIPAm in the ionic liquid, and in the specific case of [BMIM][PF_6] it is sufficiently high to lie well above T_t. It has been reported that the solubility of polymers in ionic liquids depends on the structures and Lewis acidity/basicity of cations and anions of ionic liquids.[13,20] Accordingly, we find that the UCST can be effectively tuned by using blends of [BMIM][PF_6] and hydrophobic 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]),[21] which is also available for the micelle shuttle,[11b] thereby indicating a way to adjust T_d over a wide range if desired.

In summary, we have demonstrated a fully thermoreversible micellization−transfer−demicellization block copolymer micelle shuttle between water and an ionic liquid. This interesting phenomenon requires an appropriate ordering of the three critical temperatures triggering the micellization, transfer, and demicellization processes ($T_m < T_t < T_d$). These temperatures are systematically tunable by changing the solvent quality of the two solvents for the block copolymer. Such a simple, flexible, and scalable round-trip delivery system has potential applications in phase transfer, separations, and catalysis.

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Supporting Information Available: Experimental details, polymer synthesis, and DLS results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Preliminary results. PNIPAm has a UCST several tens of degrees higher in [BMIM][PF_6] than in [EMIM][TFSI].

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