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Light-Controlled Reversible Micellization of a Diblock Copolymer in an Ionic Liquid

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S Supporting Information

ABSTRACT: We report the reversible photoinduced self-assembly of a diblock copolymer in a typical hydrophobic ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]PF_6$). A series of random copolymers consisting of 4-phenylazophenyl methacrylate and N-isopropylacrylamide (P(AzoMA-r-NIPAm)) show both photoresponsive solubility changes and upper critical solution temperature (UCST) phase transitions in $[C_4mim]PF_6$. The UCST phase transition temperature of the random copolymer depends strongly on the composition of AzoMA as well as on the photo-isomerization state of the azobenzene moiety. The phase transition temperature of P($trans$-AzoMA-r-NIPAm) in the dark is lower than that of P(cis-AzoMA-r-NIPAm) under UV-light irradiation. Reversible solubility changes by changing the wavelength of incident light were demonstrated by using the difference between the phase transition temperatures. On the basis of the results, we apply the thermo- and photoresponsive property of the random copolymer to a block copolymer system. A well-defined diblock copolymer (PEO-b-P(AzoMA-r-NIPAm)) was successfully prepared by combining anionic ring-opening polymerization of ethylene oxide (EO) and reversible addition–fragmentation chain transfer (RAFT) polymerization of AzoMA and NIPAm. A PEO-b-P(AzoMA-r-NIPAm) diblock copolymer is found to exhibit low-temperature micelle and high-temperature unimer (upper critical micellization temperature (UCMT)) transition in $[C_4mim]PF_6$ from dynamic light scattering (DLS) measurements. The aggregation temperature of the diblock copolymer depends on the photoisomerization state of azobenzene, as expected. We demonstrated photoinduced self-assembly of the diblock copolymer in $[C_4mim]PF_6$ at a "bistable" temperature. Reversibility of the micelle formation and dissolution into single polymer chains was also demonstrated.
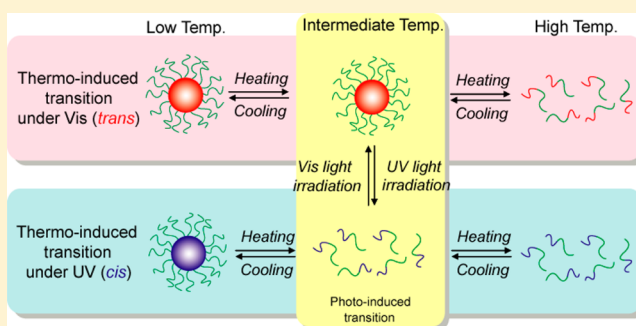
INTRODUCTION

Ionic liquids (ILs) have attracted much attention because of their unique properties such as thermal stability, nonvolatility, (electro)chemical stability, and high ionic conductivity. ILs are now becoming a third class of solvents, following aqueous and organic systems.[1−3] Polymer−IL composites have also received increasing attention from the materials science point of view.[4−6] We are interested in stimuli-sensitive polymers in ILs. For example, poly(N-isopropylacrylamide) (PNIPAm), which is the most familiar polymer exhibiting lower critical solution temperature (LCST) phase behavior in aqueous solution, shows the opposite upper critical solution temperature (UCST) phase transition in certain ILs.[6,7] On the other hand, certain polymethacrylates[8−10] or polyether derivatives[11,12] are found to show LCST phase behavior in ILs. Such phase transitions of polymers in thermally stable and nonvolatile ILs are interesting both in terms of fundamental science and for materials applications. In particular, the volume phase transition of polymer gels in ILs is important to develop smart gel materials while eliminating problems due to solvent evaporation.[8,13]

Most recently, we have extended thermosensitive polymers in ILs to photoresponsive polymers by using copolymerization of the azobenzene-containing monomer, 4-phenylazophenyl methacrylate (AzoMA), with either NIPAm[14] or benzyl methacrylate[13,15] as a main monomer.

Block copolymer chemistry is another promising area[16−20] in the field of polymer/IL composites. Block copolymer melt or dilute solution exhibit useful nanostructures owing to intra-molecular segregation. Lodge and co-workers reported self-assembly of systematically prepared diblock copolymer consisting of IL-insoluble polybutadiene block and soluble poly(ethylene oxide) block (P(B-b-EO)).[21] They found that the diblock copolymer self-assembles into micelles with PB-core surrounded by PEO-corona chains in a typical hydro-phobic IL: 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]PF_6$). The universal morphology sequence of

spherical, cylindrical, and bilayer-vesicle was observed as the volume fraction of PEO was reduced in the diblock copolymer, while keeping molecular weight of IL-incompatible PB block constant. They also achieved physical ion gels using ABA triblock copolymer having an IL-selective B block. Since polystyrene (PSt) is $[C_4mim]PF_6$ insoluble, when P(St-*b*-EO-*b*-St) triblock copolymer is loaded into $[C_4mim]PF_6$, PSt forms physical cross-links, resulting in an ion gel. The concentration of triblock copolymer required to form an ion gel is found to be as low as 4 wt %.[22] Physical ion gels based on self-assembly of block copolymers have been applied to for example organic transistors[23] and actuators.[24] Thermosensitive block copolymer systems also provide access to temperature-triggered micellization,[25] doubly thermosensitive micelles,[26] and thermoreversible ion gels.[27]

Here, we utilize an azobenzene-containing diblock copolymer (PEO-*b*-P(AzoMA-*r*-NIPAm)) in $[C_4mim]PF_6$. This builds on our recent report on the phase behavior of random copolymers of AzoMA and NIPAm (P(AzoMA-*r*-NIPAm)).[14] P(AzoMA-*r*-NIPAm) showed UCST phase behavior due to the thermosensitivity of NIPAm in a common hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)amide ($[C_2mim][NTf_2]$). The UCST phase transition temperature is quite sensitive to changes in the composition of azobenzene as well as to the photoisomerization state of azobenzene in the P(AzoMA-*r*-NIPAm). The phase transition temperature difference between ground *trans*-form polymer and excited *cis*-form polymer was much larger than the previously reported difference of typical azobenzene-containing random copolymer in aqueous solution.[28−34] The largest aggregation temperature difference between *trans* and *cis* random copolymers reached 42 °C,[14] when the AzoMA composition loaded in the P(AzoMA-*r*-NIPAm) was 29 mol %. We further realized optically regulated solubility changes of P(AzoMA-*r*-NIPAm) in $[C_2mim][NTf_2]$[14] by using the large phase transition temperature difference.[14] In the work described here, we prepared a well-defined PEO-*b*-P(AzoMA-*r*-NIPAm) diblock copolymer by combining anionic ring-opening polymerization of EO and reversible addition−fragmentation chain transfer (RAFT) polymerization. Since it is covalently connected, the well-solvated PEO block suppresses the critical micelle temperature below 5 °C, the lower limit of the current apparatus. Therefore, $[C_4mim]PF_6$ is used as solvent instead of the previously used $[C_2mim][NTf_2]$, in order to increase the UCST phase transition temperature of the second block.[6] We first show the thermosensitive self-assembly of diblock copolymer in $[C_4mim]PF_6$ and then describe the reversible photoinduced unimer/micelle transition by illuminating the system with light of the appropriate wavelength, at a suitably selected temperature. To the best of our knowledge, this is the first report of the unimer/micelle transition in an IL induced by light, although many systems related to photoresponsive block copolymers in water and/or organic solvents are available.[35−47]

■ EXPERIMENTAL SECTION

Materials. $[C_4mim]PF_6$,[48,49] S-1-dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (CTA),[50] AzoMA,[51] and P(AzoMA-*r*-NIPAm)[14] were synthesized and characterized according to procedures reported earlier. Ethylene oxide (EO) was purchased from Mitsubishi Chemical; phenothiazine (PT), dichloromethane (dehydrated), 1,4-dioxane, and oxalyl chloride were from Wako Chemical. 1-Dodecanethiol, acetone (dehydrated), and carbon disulfide were from Kanto Chemical. 2,2-Azobis(isobutyronitrile) (AIBN) and Aliquat 336 were from Sigma-Aldrich. NIPAm was

generously provided by the Kojin Corporation and purified by recrystallization (two times) using a toluene/hexane (1:10 by weight) mixed solvent. PT was recrystallized from ethanol. EO was distilled prior to use. AIBN was recrystallized from methanol prior to use. All other chemical reagents were used as received, unless otherwise noted. Water content in the $[C_4mim]PF_6$ was determined by Karl Fischer titration to be below 10 ppm. Chloride content in the aqueous phases in contact with the $[C_4mim]PF_6$ could not be detected by the addition of an $AgNO_3$ aqueous solution. This suggests the chloride content of the $[C_4mim]PF_6$ remained at least below the solubility limit of AgCl in water (1.4 mg L^{-1}).

Preparation of PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) Diblock Copolymer. The PEO first block was prepared by anionic ring-opening polymerization of EO from PT according to the procedure reported previously.[11] The PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) diblock copolymer was synthesized following the procedure shown in Scheme 1. The first

Scheme 1. Synthetic Procedure for the PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) Diblock Copolymer

step is to prepare the PEO-CTA macro-chain-transfer agent. 0.21 mL of oxalyl chloride (2.5 mmol) and 0.608 g of CTA were mixed in dry dichloromethane (10 mL) under a N_2 atmosphere and stirred at room temperature until gas evolution stopped (~2 h). Excess reagents were then removed under vacuum, and the residue was redissolved in dry dichloromethane (12 mL), followed by the addition of 5.0 g of PEO (0.33 mmol). The reaction was allowed to proceed for 24 h at room temperature, after which the contents were reprecipitated 3 times from tetrahydrofuran (THF) as a good solvent and cold diethyl ether as a poor solvent and dried in a vacuum at 50 °C. Then 1.10 g of PEO-CTA (0.073 mmol), 0.101 g of AzoMA (0.38 mmol), 2.10 g of NIPAm (18.6 mmol) ([AzoMA]/[NIPAm] = 2/98 by mol), and 1,4-dioxane (30 mL) were placed in a round-bottom flask and deaerated by purging N_2 for 30 min at 45 °C to avoid crystallization of NIPAm monomer during bubbling. 0.0114 g of AIBN (0.069 mmol) was separately dissolved in 5.7 mL of 1,4-dioxane in another round-bottom flask and deaerated by purging N_2 for 30 min at room temperature. 1.6 mL of AIBN (0.019 mmol) solution was then added to the monomer solution. RAFT polymerization was carried out at 65 °C for 68 h. The products were evaporated and purified by reprecipitation three times from acetone as a good solvent and cold diethyl ether as a poor solvent.

Following RAFT polymerization and purification, the dodecyl trithiocarbonate residue derived from CTA attached to the polymer (PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm)-CTA) terminus was removed accord-

ing to the following procedure. 1.53 g of PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm)-CTA (0.0434 mmol) and 0.163 g of AIBN (0.99 mmol) were dissolved in 25 mL of ethanol. The solution was deaerated by purging N$_2$ for 30 min at room temperature. The cleavage reaction was carried out at 80 °C for 12 h under a N$_2$ atmosphere. The product was evaporated and purified by reprecipitation three times from acetone as a good solvent and cold diethyl ether as a poor solvent and dried in a vacuum at 50 °C overnight. The structure and average molecular weight of the polymers were characterized by a combination of ^{1}H NMR and gel permeation chromatography (GPC) using dimethylformamide (DMF) containing 0.01 mol L^{-1} LiBr as the carrier solvent (Table 1 and Supporting Information). The number-average molecular

Table 1. Characterization Results of PEO and PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm)

polymer	M_n/kDa	M_w/M_n	[AzoMA]/[NIPAm]
PEO	15	1.08	
PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm)	35	1.17	2.0/98.0

weight (M_n) of PEO was calculated from the ratio of integrated signal intensities between PT protons (δ = 6.8 ppm) and PEO main chain (δ = 3.6 ppm). The total M_n of block copolymer was calculated from the ratio of integrated signal intensities between PEO main chain and second block (δ = 4.1 ppm from NIPAm and δ = 7.8 ppm from AzoMA). AzoMA composition was calculated from the ratio of integrated signal intensities between NIPAm and AzoMA (see Supporting Information). The columns (Tosoh) for the GPC were calibrated using PSt standards.

Preparation of Solutions. Polymers (P(AzoMA-*r*-NIPAm) or PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm)) were first dissolved in THF. Then, an appropriate amount of [C$_4$mim]PF$_6$ was added to the homogeneous THF solution while stirring continuously for at least 3 h until a transparent solution was obtained. The volatile THF was then evaporated by heating the solution at 80 °C under reduced pressure for 24 h.

Turbidity Measurements. The phase behavior of P(*trans*-AzoMA-*r*-NIPAm) and P(*cis*-AzoMA-*r*-NIPAm) in [C$_4$mim]PF$_6$ was studied by performing transmittance measurements. A drop of the polymer/[C$_4$mim]PF$_6$ solution (3 wt %) was placed on a glass plate with a shallow concave depression and covered by a cover glass. The optical path length for the turbidity measurements was 200 μm. The glass plate was placed on a hot stage (Imoto), which enabled temperature control. The transmittance of the P(AzoMA-*r*-NIPAm)/[C$_4$mim]PF$_6$ solution was monitored at 500 nm, where no absorption of azobenzene was seen, using an Ocean Optics USB-2000 fiber-optic spectrometer at a cooling rate of 1 °C/min. Photoirradiation was carried out using a 500 W high-pressure mercury lamp (Ushio Optical Modulex BA-H500). The wavelength and intensity of the irradiated light (UV light: 366 nm, 8 mW cm^{-2}; visible light: 437 nm, 4 mW cm^{-2}) were adjusted using color filters. A heat-absorbing filter was equipped to dissipate the heat generated by the mercury lamp. The cloud point (T_c) was taken as the temperature of 50% transmittance.

While performing turbidity measurements on P(*trans*-AzoMA-*r*-NIPAm), the polymer solution was kept in the dark for a sufficient period of time so that the polymer attained the photostationary ground state (*trans*-AzoMA = 100%); the subsequent measurement was carried out in the dark. For P(*cis*-AzoMA-*r*-NIPAm) measurements, UV light (366 nm) was continuously irradiated on the polymer solution in order to avoid thermal *cis*-to-*trans* relaxation. We have previously established that the photostationary *cis*-composition (*cis*-AzoMA ≈ 80%) does not change under UV-irradiated conditions, even at temperatures as high as 93 °C.[15]

Dynamic Light Scattering (DLS) Measurements. Sample solutions for DLS measurements were passed through 0.20 μm filters to eliminate dust prior to use. DLS measurements were performed on an Otsuka Electronics DLS-6500 equipped with an ALV correlator and a He−Ne laser (633 nm). Experiments were performed at different temperatures (60−80 °C) within an accuracy of ±0.1 °C, and the intensity autocorrelation functions $g_2(q,t)$ were recorded at a scattering angle of 90° at each temperature for 30 s. Samples were equilibrated at constant temperature for 30 min before data collection.

For solutions containing monodisperse particles, the electric field correlation function $g_1(q,t)$ displays a single-exponential decay

$$g_1(q, t) = \exp(-\Gamma t) = \exp(-D_0 q^2 t) \tag{1}$$

where t is the time, q is the scattering vector ($q = (4\pi n/\lambda) \sin(\theta/2)$, where n is the refractive index of the solvent, λ is the wavelength of the light in vacuum, and θ is the scattering angle), Γ is the decay rate, and D_0 is the mutual diffusion coefficient. The recorded intensity correlation function $g_2(q,t)$ was converted to $g_1(q,t)$ through the Siegert relation.[52] The hydrodynamic radius, R_h, can be estimated with knowledge of the solvent viscosity, η, by using the Stokes−Einstein equation

$$R_h = (k_B T)/6\pi\eta D_0 \tag{2}$$

where k_B and T are the Boltzmann constant and absolute temperature, respectively. For solutions that contain a monomodal distribution of polydisperse particles, $g_1(q,t)$ can be analyzed using the method of cumulants:[53]

$$g_1(q, t) = A \exp(-\Gamma t)(1 + (1/2!)\mu_2 t^2 - (1/3!)\mu_3 t^3) \tag{3}$$

where Γ is the mean decay rate and μ_2/Γ^2 characterizes the width of the distribution. In this work, the apparent hydrodynamic radius, R_h, was calculated using eq 2 by substituting the $D = \Gamma/q^2$ of 0.1 wt % solutions for D_0. The distribution of R_h was also examined by applying the inverse Laplace transformation to $g_1(q,t)$ with the well-established CONTIN program[54] and by fitting to a sum of two exponentials. To estimate R_h, the temperature dependence of the viscosity of [C$_4$mim]PF$_6$ (η, mPa s) was calculated from the appropriate Vogel−Tammann−Fulcher (VTF) equation[48]

$$\eta = 0.36 \exp[639/(T - 201)] \tag{4}$$

where T (K) is the absolute temperature. The refractive index of [C$_4$mim]PF$_6$ (n = 1.41) was obtained from previous reports.[55] The
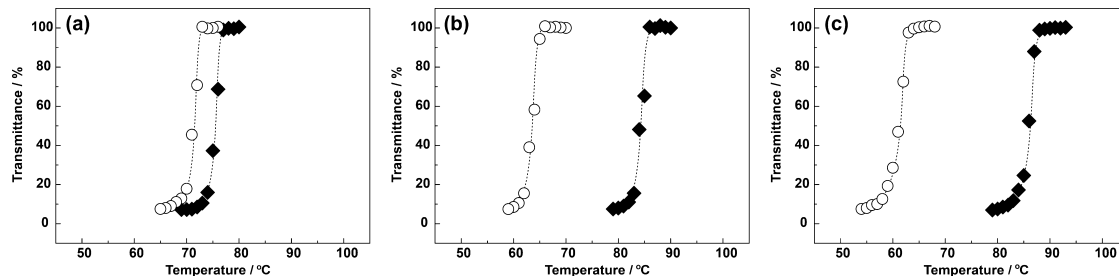
Figure 1. Turbidity measurements for (a) P(AzoMA$_{1.9}$-*r*-NIPAm), (b) P(AzoMA$_{5.4}$-*r*-NIPAm), and (c) P(AzoMA$_{8.6}$-*r*-NIPAm) in [C$_4$mim]PF$_6$ solution with UV light (366 nm) irradiation (open circles) or in the dark (closed diamonds). The numbers denoted after AzoMA indicate composition (mol %) of AzoMA in the random copolymers.

experimental setup for light irradiation to the sample is same as that for the case of turbidity measurements. UV or visible light was irradiated from the upper side of DLS sample tube having 1 cm diameter. A transparent heat absorbing filter covers the top of the sample tube to avoid dust contamination.

■ RESULTS AND DISCUSSION

Thermo- and Photosensitivity of P(AzoMA-*r*-NIPAm) in [C₄mim]PF₆. We first conducted turbidity measurements to determine the aggregation temperature of P(AzoMA-*r*-NIPAm) in [C$_4$mim]PF$_6$, which was used as the multistimuli responsive segment in the target diblock copolymer. The three different random copolymers having different AzoMA compositions were independently synthesized from the PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) diblock copolymer. Preparation and characterization of a series of random copolymers are described in the Supporting Information.

Figure 1 shows the results of turbidity measurements for a series of P(AzoMA-*r*-NIPAm)s (3 wt %) in [C$_4$mim]PF$_6$ with or without UV light irradiation. The photoisomerization state of azobenzene is the ground *trans*-form (P(*trans*-AzoMA-*r*-NIPAm)) in the dark. When UV light (366 nm) is incident on the sample, the photoisomerization reaction of azobenzene occurred to form the *cis*-state (P(*cis*-AzoMA-*r*-NIPAm)), which has higher polarity. The random copolymers exhibited UCST phase behavior, with T_c higher than the previously reported P(AzoMA-*r*-NIPAm) in [C$_2$mim][NTf$_2$] solution, as expected. It is apparent that the T_c of P(AzoMA-*r*-NIPAm) depends on the AzoMA composition in the polymers as well as on the photochromic state of AzoMA. Figure 2 summarizes the
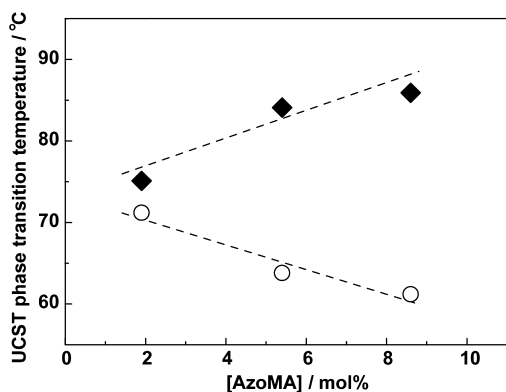
Figure 2. Relationship between UCST phase separation temperature (T_c) of P(AzoMA-*r*-NIPAm) and AzoMA composition in the random copolymers. T_c of P(*trans*-AzoMA-*r*-NIPAm) increases (closed diamonds) but that of P(*cis*-AzoMA-*r*-NIPAm) decreases (opened circles) with increases in the composition of AzoMA. T_c was determined as the temperature of 50% transmittance.

relationship between T_c of P(AzoMA-*r*-NIPAm) and AzoMA composition in the random copolymer, either in the dark or with UV light irradiation. The T_c value of P(*trans*-AzoMA-*r*-NIPAm) is always higher than that of P(*cis*-AzoMA-*r*-NIPAm). Also, the value increases, whereas that T_c of *cis*-form polymer decreases with an increase in the composition of AzoMA. In other words, *trans*-AzoMA behaved as a solvatophobic comonomer and *cis*-AzoMA behaved as a solvatophilic comonomer, relative to the majority monomer. This trend is consistent with a previous report.[14] It is well-known that the polarity of azobenzene varies with changes in photoisomerization state; for example, planar *trans*-azobenzene has a dipole

moment of 0.5 D, while *cis*-azobenzene has a higher polarity of 3.1 D.[56] Thus, the UCSTs of (more insoluble) P(*trans*-AzoMA-*r*-NIPAm) are higher than those of (more soluble) P(*cis*-AzoMA-*r*-NIPAm).

The higher polarity of the *cis*-polymer results in a more stabilized solvation in an IL. Dipole moment and dielectric constant of [C$_4$mim]PF$_6$ are reported to be μ = 5.3 D and ε = 11.4, respectively, indicating moderate polarity.[57,58] This is also collaborative evidence that the *cis* polymer becomes more stabilized in the IL. The T_c difference between *trans*- and *cis*-form polymers was as large as 25 °C by using P(AzoMA$_{8.6}$-*r*-NIPAm), where the subscript after AzoMA indicates the composition (mol %) of AzoMA in the random copolymer.

We next demonstrate the photoinduced phase transition of P(AzoMA-*r*-NIPAm) in [C$_4$mim]PF$_6$ by utilizing the large difference in the values of T_c depending on the photoisomerization state of azobenzene. P(AzoMA$_{8.6}$-*r*-NIPAm) was used for the experiment (T_c(*trans*) = 85.9 °C and T_c(*cis*) = 61.2 °C). Under UV-light irradiation, the temperature of a 3 wt % P(AzoMA$_{8.6}$-*r*-NIPAm) solution was set to 72.5 °C, at which it is bistable. Before the measurements, the sample was subjected to UV light irradiation for 2 h and was confirmed to be transparent (i.e., phase separation did not occur) owing to the fact that the T_c of P(*cis*-AzoMA$_{8.6}$-*r*-NIPAm) was lower than the measurement temperature. The polymer solution becomes turbid under the illumination of visible light (437 nm) to form P(*trans*-AzoMA$_{8.6}$-*r*-NIPAm) (Figure 3) because the UCST T_c
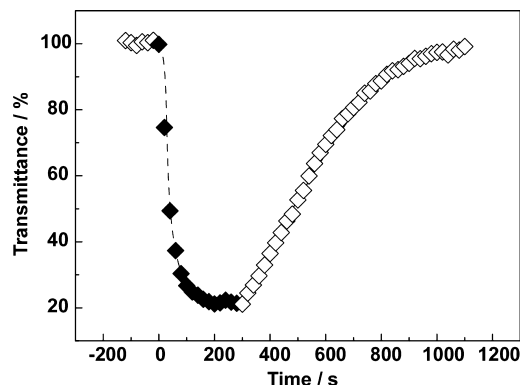

Figure 3. Photoinduced phase transition of P(AzoMA$_{8.6}$-*r*-NIPAm) at 72.5 °C under irradiation of UV light (open diamonds) or visible light (closed diamonds).

of the *trans* polymer is higher than 72.5 °C. After completing the photoinduced phase separation, the transparency of the P(*trans*-AzoMA$_{8.6}$-*r*-NIPAm) solution can be recovered by switching to UV light irradiation to form P(*cis*-AzoMA$_{8.6}$-*r*-NIPAm), where the UCST T_c is below 72.5 °C. Here the reversibility of the photoinduced redissolution of the polymer in the IL is kinetically a little slower than the phase-separation process. Slow kinetics in the redissolution process arises from a light scattering problem. When the polymer (solid) and IL (liquid) phases are segregated, the UV light that induces redissolution is greatly scattered.[13,14] This causes a decrease in the absorption of incident light, resulting in low efficiency of the photoisomerization reaction. However, the photoinduced phase transition process of P(AzoMA$_{8.6}$-*r*-NIPAm) in [C$_4$mim]PF$_6$ is faster than the previous P(AzoMA$_{20.1}$-*r*-NIPAm) in the [C$_2$mim][NTf$_2$] system. Complete phase separation in P(AzoMA$_{8.6}$-*r*-NIPAm)/[C$_4$mim]PF$_6$ only re-

quires 200 s, whereas the previous P(AzoMA$_{20.1}$-r-NIPAm)/ [C$_2$mim][NTf$_2$] took longer than 3000 s.[14] Phase separation kinetics depend on the viscosity of the IL. The viscosity of [C$_4$mim]PF$_6$ is estimated to be 29.8 mPa s (72.5 °C),[48] whereas the viscosity of previously reported photoinduced phase transition in [C$_2$mim][NTf$_2$] is 42.8 mPa s (15.8 °C).[48] The successful demonstration of photoreversible solubility changes of P(AzoMA-r-NIPAm) encouraged us to investigate thermo- and photosensitive self-assembly of diblock copolymer in [C$_4$mim]PF$_6$.

Thermosensitivity of PEO-b-P(AzoMA-r-NIPAm) in [C$_4$mim]PF$_6$. Figure 4 compares the normalized scattering
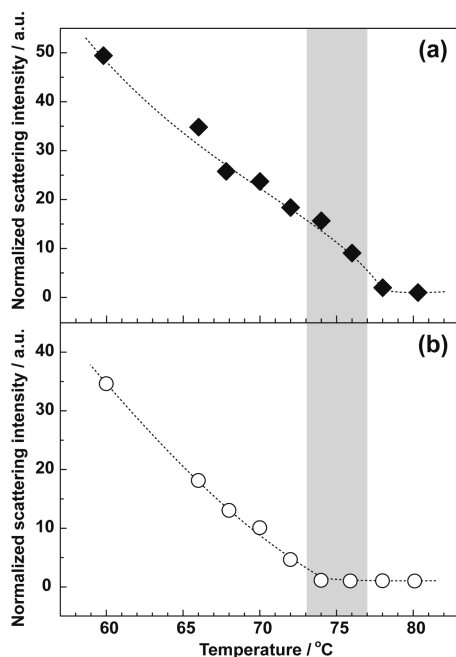
Figure 4. Temperature dependence of the normalized scattering intensity for 1 wt % PEO-b-P(AzoMA$_{2.0}$-r-NIPAm) in [C$_4$mim]PF$_6$ (a) under dark or (b) with UV light irradiation at a scattering angle of 90°. The normalized scattering intensity is defined as the intensity at each temperature divided by that measured at 80 °C.

intensity of PEO-b-P(AzoMA$_{2.0}$-r-NIPAm) (1 wt %) in [C$_4$mim]PF$_6$ solution with or without UV-light irradiation. In the cooling process from 80 °C, the scattered intensity goes up with a decrease in the sample temperature, due to the UCST nature of the P(AzoMA-r-NIPAm) segment. This implies that the diblock copolymer self-assembles into micelles sufficiently large size to scatter incident light. The mean hydrodynamic radius (R_h) was also determined in terms of *trans*- and *cis*-form polymer (Figure 5). At high temperature above the upper critical micellization temperature (UCMT), R_h of diffusion component in the [C$_4$mim]PF$_6$ is below 10 nm, consistent with the size of PEO-b-P(AzoMA$_{2.0}$-r-NIPAm) single polymer chains having 35 kDa molecular weight. Although CONTIN analysis for the diblock copolymer above the UCMT shows a bimodal distribution function, the weight fraction of unimer is estimated to be over 0.999 (see Supporting Information). It seems that almost all of particles in the [C$_4$mim]PF$_6$ above UCMT were single polymer chains together with very small amount of aggregates, which might result from solubility differences due to chain-to-chain variations in comonomer distribution and composition in the random copolymer block.
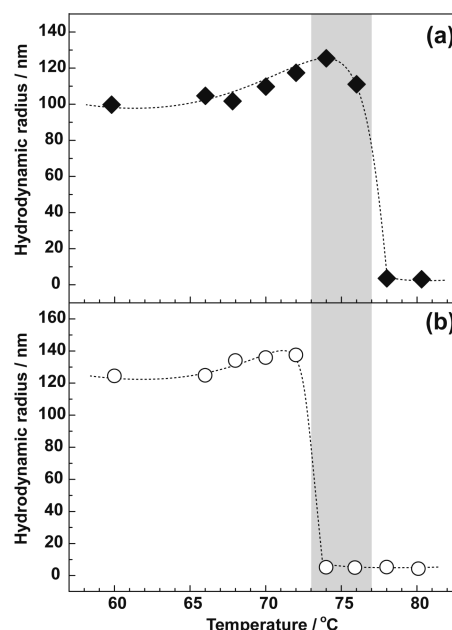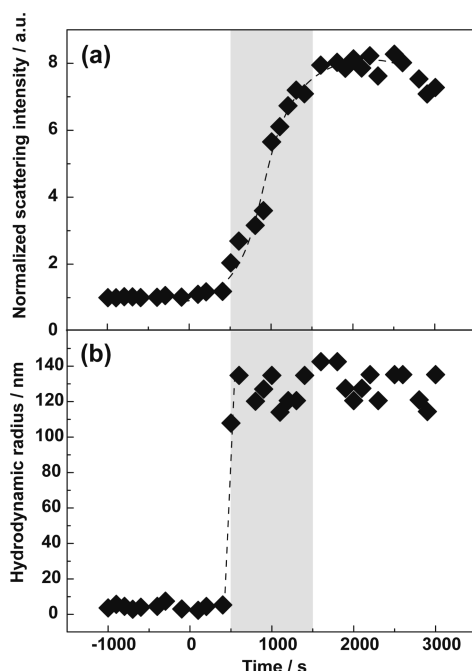

Figure 5. Temperature dependence of the hydrodynamic radius (R_h) of PEO-b-P(AzoMA$_{2.0}$-r-NIPAm) in [C$_4$mim]PF$_6$ (a) under dark and (b) with UV light irradiation.

When the temperature was reduced below the UCMT, the R_h peak of the smaller particle completely disappeared, and only an intense peak around large R_h remained (see Supporting Information). The reversibility of the unimer−micelle transition with respect to temperature was also checked. The mean size of the micelle was estimated to be over 100 nm, possibly suggesting a vesicular morphology. A previous report on micelle morphology of PB-b-PEO in [C$_4$mim]PF$_6$ by using cryo-TEM direct observation confirmed that the bilayer vesicle having almost 100 nm R_h was observed when the length of PEO corona block was significantly shorter than solvatophobic PB block.[21] Since the molecular weight of P(AzoMA$_{2.0}$-r-NIPAm) (20 kDa) is larger than that of PEO (15 kDa), the present diblock copolymer might form bilayer vesicles at lower temperatures, although there are reports on block copolymers that do not exhibit the full morphological sequence even with widely changing volume fraction of insoluble blocks.[59−61] The scattering intensity monotonically increases (Figure 4), whereas R_h of the diblock copolymer almost keeps constant with decreases in temperature (Figure 5), after passing through the aggregation temperature. Since scattering intensity is generally proportional to the sixth power of the size of the micelle and is linear in the number of particles, this result may imply that the number of particles gradually increases keeping the size of micelle constant during the cooling process.[62]

Importantly, there is about a 4 °C difference in the UCMTs between PEO-b-P(*trans*-AzoMA$_{2.0}$-r-NIPAm) (gray regions of upper panels in Figures 4 and 5) and *cis*-form polymers (lower panels). The UCMT difference comes from the polarity difference of the photoisomerization states of AzoMA, as in the case of the random copolymers. The UCST temperature difference between *cis*- and *trans*-P(AzoMA$_{1.9}$-r-NIPAm) having a similar AzoMA composition of the diblock copolymer was found to be 4.0 °C (compare Figures 1a and 2), which is consistent with the UCMT difference of the diblock copolymer. In the *trans*-form, the diblock copolymer starts to aggregate below 77 °C, while the *cis*-polymer aggregates below 73 °C. By

using this transition temperature difference, we next demonstrate a photoinduced unimer/micelle transition.

Unimer−Micelle Phase Transition of PEO-*b*-P-(AzoMA$_{2.0}$-*r*-NIPAm) in [C$_4$mim]PF$_6$ Induced by Photostimuli. After keeping the PEO-*b*-P(*cis*-AzoMA$_{2.0}$-*r*-NIPAm) diblock copolymer at a bistable temperature (75 °C) under UV-light irradiation, the sample solution was then subjected to visible light at time 0 s to form the *trans*-polymer. It is clear that photoinduced self-assembly of PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) at a constant (bistable) temperature is successfully realized (Figure 6). The size of the micelles made by the photoinduced

copolymer is evident. In the present system, there appears to be two elementary steps to form micelles. The first step is the photoisomerization reaction of azobenzene side chain from *cis* to *trans*, while the second, slower step is diffusion of the PEO-*b*-P(*trans*-AzoMA$_{2.0}$-*r*-NIPAm) to form micelles after the photoisomerization. As the photoisomerization reaction of *cis*- to *trans*-form in azobenzene containing random copolymer in IL is complete in only 240 s under UV-light illumination,[14,15] the rate-determining step for photoinduced micellization is likely polymer diffusion. Here we can estimate the average distance between unimers (Δ) to be 10 nm from the concentration and R_h of polymer. Thus, we can roughly estimate the diffusion time (t) as 17 s that one polymer chain encounters other polymer chain based on Δ and the diffusion coefficient of the unimer by $t = \Delta^2/\pi D$. In fact, a much longer time is required to see photoinduced micellization, as aggregation requires multiple polymers collisions.

After a 500 s induction time after starting UV-light irradiation, the scattering intensity monotonically increases until about 1500 s, while the average R_h becomes larger more abruptly. Early in the aggregation process there appears to be a number of unimers with very small amount of large aggregates (micelles). Scattering intensity strongly depends on the size of scatter rather than the number of scatter, as mentioned previously. Once aggregation of small particles starts, the DLS signal is heavily weighted by the larger component. Thus, the scattering intensity increasing from 500 to 1500 s is roughly proportional to the increasing the number of micelles. The aggregation process appears to be complete after about 1700 s.

We further confirmed the reversibility of the photoinduced unimer/micelle transition of the diblock copolymer. Figure 7 shows the scattering intensity and corresponding R_h of the diblock copolymer as a function of time. After formation of micelles triggered by visible light illumination at constant temperature, visible light was switched back to the UV-light again at time 3000 s to form *cis*-form polymer. As expected, both scattering intensity and R_h decrease, indicating the breakup of micelles into individual single polymer chains, owing to the fact that the aggregation temperature of PEO-*b*-P(*cis*-AzoMA-*r*-NIPAm) is lower than the measurement temperature. The demicellization process appears to be more rapid than micellization, as there is no polymer diffusion step required.

Figure 6. Photoinduced self-assembly of PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) at 75 °C by illumination of visible light after reaching a photostationary state by UV light irradiation. Upper panel (a) shows time dependence of the normalized scattering intensity. Lower panel (b) shows R_h against the time.

transition is almost the same as the size of micelles formed under temperature-induced transition of PEO-*b*-P(*trans*-AzoMA$_{2.0}$-*r*-NIPAm) shown in Figure 5a (~120 nm). An induction time (~500 s) before self-assembly of the diblock

Figure 7. Reversible photoinduced self-assembly and dissociation of PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm) micelle at 75 °C with irradiation of UV light (open diamonds) or visible light (closed diamonds). Panel a shows normalized scattering intensity, and panel b does R_h as a function of time.

CONCLUSION

The UCST phase behavior of systematically prepared P-(AzoMA-*r*-NIPAm) was studied in terms of photoisomerization state and composition of azobenzene in the random copolymer. The UCST phase separation temperature depends strongly on the photoisomerization state as well as the composition of AzoMA. The UCST T_c of P(*trans*-AzoMA-*r*-NIPAm) increases whereas that of *cis*-form polymer decreases with increasing composition of AzoMA. This result can be explained by the polarity change accompanying changes in the photoisomerization state of azobenzene. We next demonstrated the reversible photoinduced phase transition of P(AzoMA$_{8.6}$-*r*-NIPAm) at a bistable temperature, i.e., a temperature between the cloud points of the two photostates of the azopolymer.

We then prepared a diblock copolymer having PEO as the solvatophilic first block and P(AzoMA$_{2.0}$-*r*-NIPAm) as a multistimuli-responsive second block and investigated its phase behavior in $[C_4\text{mim}]PF_6$. Temperature dependence of the scattering intensity and R_h from DLS measurements confirmed that UCMT aggregation of *cis*-form block copolymer occurred about 4 °C below that of the *trans*-polymer. Finally, we achieved a photoreversible unimer/micelle transition of diblock copolymer by utilizing the UCMT difference between *trans*- and *cis*-form polymer in an IL. To the best of our knowledge, this is the first report on the reversible unimer/micelle transition of block copolymer in an IL induced by light illumination. Study on the development of photoreversible sol−gel transition utilizing the self-assembly of triblock copolymers is now in progress.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Characterization results of P(AzoMA-*r*-NIPAm) random copolymer, a GPC trace of PEO-*b*-P(AzoMA$_{2.0}$-*r*-NIPAm), distribution functions of the diblock copolymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENTS

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