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UCST Phase Transition of Azobenzene-Containing Random Copolymer in an Ionic Liquid

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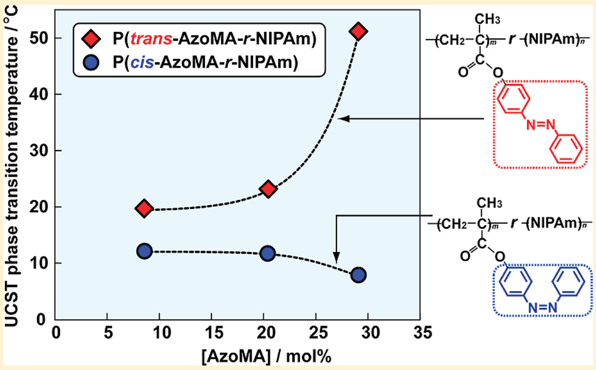
S *Supporting Information*



ABSTRACT: We present azobenzene-containing random copolymers exhibiting upper critical solution temperature (UCST) phase separation in an ionic liquid (IL). A series of well-defined random copolymers comprising *N*-isopropylacrylamide (NIPAm) and 4-phenylazophenyl methacrylate (AzoMA) were successfully prepared by reversible addition−fragmentation chain transfer (RAFT) polymerization, using *S*-1-dodecyl-*S*′-(α, α′-dimethyl-α″-acetic acid)trithiocarbonate as a RAFT agent. The UCST phase separation temperature depends on the photoisomerization state of azobenzene, as well as on the AzoMA composition in the random copolymers. Turbidity measurements of the random copolymers (P(AzoMA-*r*-NIPAm)s) in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)amide ([C_2mim]-[NTf_2]) confirmed that the phase separation temperature of *trans*-azobenzene (P(*trans*-AzoMA-*r*-NIPAm) significantly increased, whereas that of P(*cis*-AzoMA-*r*-NIPAm) slightly decreased, with an increase in the composition of AzoMA in the copolymer. This result implies that nonpolar *trans*-AzoMA behaves as a solvato-phobic comonomer for the majority NIPAm monomer, whereas polar *cis*-AzoMA is relatively solvato-philic. The phase separation temperature difference between *trans*- and P(*cis*-($AzoMA_{29.1}$-*r*-$NIPAm_{70.9}$) was as large as 43 °C. The triad sequence distribution of P(AzoMA-*r*-NIPAm) indicates that NIPAm copolymerization with AzoMA proceeds in a somewhat blocky manner. The trend of a significantly increasing phase separation temperature in P(*trans*-AzoMA-*r*-NIPAm) is qualitatively rationalized by the $\pi-\pi$ stacking interaction among neighboring azobenzene side chains. Finally, a reversible photoinduced phase transition in an IL is demonstrated by utilizing the large phase separation temperature differences between the trans and the cis polymers in the IL.

INTRODUCTION

Ionic liquids (ILs) are now recognized as a third class of solvent, following water and organic solvents, and have many useful properties for a variety of applications, such as nonvolatility, nonflammability, thermal stability, and (electro)chemical stability.[1−3] Composite materials consisting of a polymer and an IL can realize useful materials such as polymer electrolyte membranes with high ionic conductivity, gas separation membranes, and catalytic membranes.[4−7] We have also focused on stimuli-responsive polymers in ILs.[8−11] Poly(benzyl methacrylate) (PBnMA) was reported to exhibit LCST phase behavior at around 105 °C in a typically used hydrophobic IL 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone)amide ([C_2mim][NTf_2]). PBnMA ion gels show reversible and discontinuous volume phase transitions in the IL.[8] Phase changes of polymers in nonvolatile, thermally stable ILs can afford long-term stable smart materials without concern for solvent evaporation. The LCST behavior of a polymer has also been developed for thermosensitive self-assembly of block copolymers in ILs.[12,13] It was also reported that a PNIPAm exhibited upper critical solution temperature (UCST) phase behavior in an IL.[14] The phase-separation temperature (cloud point; T_c) depends on both the molecular weight and the concentration of PNIPAm. Although high-temperature homogenization as well as low-temperature phase separation is commonly observed, particularly in organic polymer solutions, these phenomena might still be interesting because the phase behavior of PNIPAm in an IL is the completely opposite phenomenon to that observed in aqueous solution. The UCST phase transition of PNIPAm in ILs has also been developed for a thermally reversible sol−gel transition of a triblock copolymer, which can be applied to a solvent-free, processable ion gel and a unique block copolymer self-assembly system.[15,16]

More recently, we have studied photosensitive polymers in an IL. A random copolymer of 4-phenyl azophenyl methacrylate and BnMA (P(AzoMA-*r*-BnMA)) shows not only LCST thermosensitivity but also photoresponsive ability in an IL.[17] The LCST

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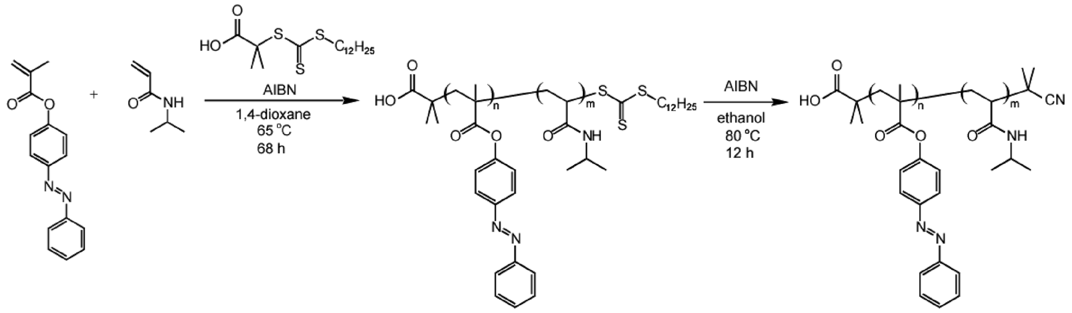
Scheme 1. Preparation of P(AzoMA-*r*-NIPAm) by RAFT Polymerization



phase separation temperature changes significantly with changes in the photoisomerization state of azobenzene.[17] The difference between the value of T_c of P(*trans*-AzoMA$_{4.1}$-*r*-BnMA) under dark conditions (*trans*-AzoMA = 100%) and that of T_c of P(*cis*-AzoMA$_{4.1}$-*r*-BnMA) under UV irradiation (*cis*-AzoMA = 80%) reached 22 °C, where the subscript number indicated after AzoMA denotes the molar composition of AzoMA in the random copolymer. We have also demonstrated the photoinduced phase transition of P(AzoMA-*r*-BnMA) in [C$_2$mim][NTf$_2$] at a bistable temperature between the T_c of trans and cis polymers. Phase changes in a polymer in an IL, induced by both thermal- and photostimuli, can be expected to yield many attractive smart materials, such as volume phase transition of ion gel, micellization, and the order−disorder transition of block copolymers induced by light stimuli.

Our previous report revealed that LCST phase changes in P(AzoMA-*r*-BnMA) occurred at relatively high temperatures. For instance, T_c of P(*cis*-AzoMA$_{4.1}$-*r*-BnMA) is as high as 102 °C. It is desirable to decrease the value of T_c in order to initiate the design of smart materials that can work around room temperature. Moreover, rapid thermal relaxation from excited *cis*-AzoMA to the ground state of *trans*-AzoMA under a high temperature is a problem for P(AzoMA-*r*-BnMA)/IL solution. For example, we estimate the half-life to be as short as 8 min at 102 °C from *cis*- to *trans*-polymer, from the first-order rate constant of P(*cis*-AzoMA$_{4.1}$-*r*-BnMA).[17] It is, thus, of interest to develop photoresponsiveness for phenomenologocally reverse UCST polymers with low T_c in ILs. Using this particular transition will be challenging to investigate the photoinduced phase transition of polymers in ILs, as well as to construct smart materials.

In this paper, we describe novel thermo- and photoresponsive linear random copolymers exhibiting UCST phase separation in [C$_2$mim][NTf$_2$] near room temperature. In order to realize UCST phase behavior in an IL, NIPAm and AzoMA were used as the main monomer and the comonomer, respectively, for polymerization of P(AzoMA-*r*-NIPAm). We attempted a well-established reversible addition−fragmentation chain transfer (RAFT) polymerization for preparation of the polymers.[18] As the phase transition temperature of PNIPAm-based polymers in an IL strongly depends on the molecular weight distribution and the concentration of PNIPm, it is better to use a relatively monodispersed polymer. Large differences in the values of T_c of P(AzoMA-*r*-NIPAm)s (43 °C at maximum) will be discussed from the perspective of the sequence distribution of polymers. In the final part of this manuscript, we further demonstrate the photoinduced phase transition in the ILs by utilizing the large difference in the values of T_c of various polymers.

EXPERIMENTAL SECTION

Materials. 1-Ethyl-3-methylimidazolium bis(trifluoromethane sulfone)amide ([C$_2$mim][NTf$_2$]),[19] *S*-1-dodecyl-*S*′-(α, α′-dimethyl-α″-acetic acid)trithiocarbonate[20] (CTA), and 4-phenylazophenyl methacrylate (AzoMA)[17,21] were synthesized and characterized according to previously reported procedures. 1-Dodecanthiol, acetone (dehydrated), and carbon disulfide were purchased from Kanto Chemical; 2,2-azobisisobutyronitrile (AIBN) and Aliquat 336 were from Sigma-Aldrich. *N*-isopropylacrylamide (NIPAm) was generously given by the Kojin Corporation and purified by recrystallization (two times) using a toluene/hexane (1:10 by weight) mixed solvent. AIBN was recrystallized from methanol prior to use. All other chemical reagents were used as received, unless otherwise noted.

Preparation of P(AzoMA-*r*-NIPAm) Random Copolymers. Here, we describe a representative synthetic procedure for P(AzoMA$_{20.4}$-*r*-NIPAm) (Scheme 1). 0.0365 g of CTA (0.10 mmol), 1.45 g of AzoMA (5.45 mmol), and 5.55 g of NIPAm (49.1 mmol) ([AzoMA]/[NIPAm] = 10/90 by mol) were dissolved in 60 mL of 1,4-dioxane at 45 °C. The solution was deaerated by purging N_2 for 30 min at 45 °C. A total of 0.0102 g of AIBN (0.062 mmol) was separately dissolved in 10.2 mL of 1,4-dioxane in another round-bottom flask and dearated by purging N_2 for 30 min at room temperature. A total of 3.3 mL of AIBN solution (0.020 mmol) 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 diethyl ether as a poor solvent.

Following RAFT polymerization and purification, the dodecyl trithiocarbonate residue derived from CTA attached to the polymer (P(AzoMA$_{20.4}$-*r*-NIPAm)-CTA) terminus was removed according to the following procedure. A total of 3.4 g of P(AzoMA$_{20.4}$-*r*-NIPAm)-CTA (0.1 mmol) and 0.492 g of AIBN (3.0 mmol) were dissolved in 80 mL of ethanol. The solution was dearated by purging N_2 for 30 min at room temperature. The cleavage reaction was carried out at 80 °C for 12 h under N_2 atmosphere. The product was evaporated and purified by reprecipitation three times from acetone as a good solvent and diethyl ether as a poor solvent. All copolymers were characterized by ^{1}H NMR. Figure 1 shows a representaive ^{1}H NMR spectrum of P(AzoMA$_{20.4}$-*r*-NIPAm). The composition of AzoMA was calculated from the integrated intensity ratio between peaks (d) from AzoMA and (c) from NIPAm. The number average molecular weight (M_n) and the polydispersity index (M_w/M_n) of the copolymers were determined by gel permeation chromatography (GPC) using dimethylformamide (DMF) containing 0.01 mol L^{-1} LiBr as the carrier solvent. The columns (Tosoh) for the GPC were calibrated using polystyrene standards. Characterization results of all P(AzoMA-*r*-NIPAm) samples are summarized in Table 1. The polydispersity indices of all three random copolymers were relatively narrow (<1.2). The GPC profiles of random

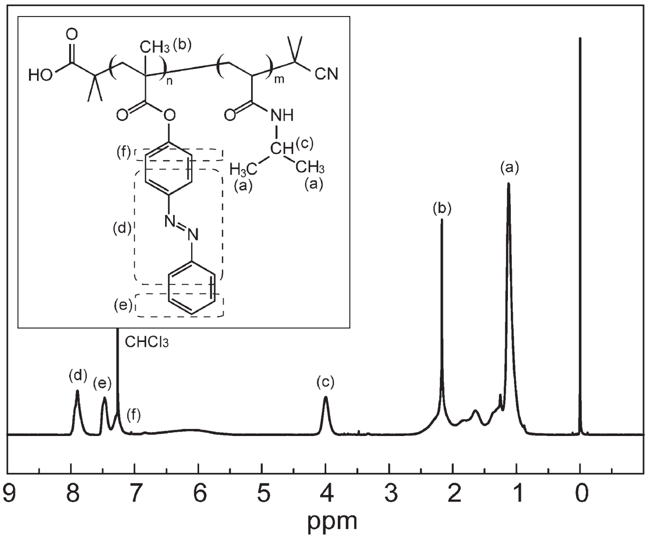


Figure 1. ^{1}H NMR spectrum of P(AzoMA$_{20.4}$-*r*-NIPAm). Inset shows the chemical structure of the polymer and attribution of each proton.

copolymers were also unimodal, without any high molecular weight species indicative of uncontrolled polymerization (see the Supporting Information, Figure S1). We previously reported that the UCST phase separation of PNIPAm in [C$_2$mim][NTf$_2$] depends on the molecular weight of the polymer;[14] however, the M_n values of the three PNIPAm-based random copolymers in this study are almost identical. The effect of molecular weight distribution on the phase behavior can be neglected, and a more accurate discussion can be presented than that of the previously reported LCST polymer prepared via free-radical polymerization.[17] The AzoMA composition incorporated into the random copolymers ranged from 8.6 to 29.1 mol %. The copolymer composition curve of NIPAm ([M$_1$]) with AzoMA ([M$_2$]) allows us to obtain the monomer reactivity ratio of r_1 = 0.65 and r_2 = 5.60 by the Kelen−Tüdos method.[22]

Preparation of P(AzoMA-*r*-NIPAm) in [C$_2$mim][NTf$_2$] Solution. For polymer solution preparation, P(AzoMA-*r*-NIPAm) was first dissolved in tetrahydrofuran (THF). Then, an appropriate amount of [C$_2$mim][NTf$_2$] was added to the homogeneous THF solution while stirring continuously for at least 3 h until a transparent solution was obtained. The volatile THF in the polymer solution was then evaporated by heating the solution at 60 °C under reduced pressure for 12 h.

Photochromism of P(AzoMA-*r*-NIPAm). The photochromism of P(AzoMA-*r*-NIPAm) in [C$_2$mim][NTf$_2$] was investigated as follows. The absorption spectra of P(AzoMA-*r*-NIPAm) were measured using an Ocean Optics USB2000 optical fiber spectrometer under thermoregulated conditions. 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.

As a representative example, changes in the absorption spectrum of the trans and cis isomers of P(AzoMA$_{20.4}$-*r*-NIPAm) in [C$_2$mim][NTf$_2$] at 60 °C under UV light are shown in Figure S2(a) (Supporting Information). A decrease in the absorption maximum at 320 nm, which is attributed to the $\pi-\pi^*$ transition of the trans isomer of AzoMA, confirms the occurrence of trans-to-cis photoisomerization for 2500 s. We also confirmed the occurrence of photoisomerization from the absorption change observed at 430 nm, which can be attributed to the n-π^* transition of AzoMA. After keeping the solution under dark for 65 000 s, the absorption at 320 nm due to the $\pi-\pi^*$ transition of the trans isomer of AzoMA is clearly recovered (Figure S2(b)). The photoisomerization reaction of polymer in [C$_2$mim][NTf$_2$] was found to be completely reversible.

Table 1. Characterization Results of P(AzoMA-*r*-NIPAm) Copolymers

[AzoMA]/ [NIPAm] in feed	[AzoMA]/ [NIPAm] composition in polymers	M_n/kDa	M_w/kDa	M_w/M_n
5/95	8.6/91.4	47	55	1.18
10/90	20.4/79.6	34	40	1.16
15/85	29.1/70.9	40	44	1.12

To estimate the kinetics of thermal relaxation for excited P(*cis*-AzoMA-*r*-NIPAm) to the ground state of P(*trans*-AzoMA-*r*-NIPAm), 0.0324 g/L of P(AzoMA-*r*-NIPAm)/[C$_2$mim][NTf$_2$] was prepared. The solution was placed in a 1 cm quartz cell equipped with a cell holder (Ocean Optics CUV-ALL-UV), which enabled control of the sample temperature. During the thermal isomerization from P(*cis*-AzoMA-*r*-NIPAm) to P(*trans*-AzoMA-*r*-NIPAm), the solution was continuously stirred. After irradiation of UV light for sufficient time so that the sample reached the excited photosteady-state, the absorbance at 320 nm derived from the $\pi-\pi^*$ transition of *trans*-azobenzene was collected at 50, 60, and 70 °C. Absorption from the $\pi-\pi^*$ transition of *trans*-azobenzene in given time (A_t) under constant temperature is described by following relationship.

$$\ln(A_t - A_\infty/A_0 - A_\infty) = -kt \qquad (1)$$

where A_0 and A_∞ are absorption from $\pi-\pi^*$ of *trans*-azobenzene at time zero and infinite time, respectively. First order rate constant of cis−trans isomerization, k, is determined by fitting experimental data to eq 1. The first order kinetic plot and Arrhenius plot are shown in Figure S3 and S4, respectively.

Turbidity Measurements. The phase behavior of P(*trans*-AzoMA-*r*-NIPAm) and P(*cis*-AzoMA-*r*-NIPAm) in [C$_2$mim][NTf$_2$] was studied by performing transmittance measurements. A drop of the polymer/[C$_2$mim][NTf$_2$] solution (1−5 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$_2$mim][NTf$_2$] solution was monitored at 500 nm, where no absorption of azobenzene was seen (Figure S2), using an Ocean Optics USB-2000 fiber optic spectrometer at a cooling rate of 1 °C/min. T_c was determined 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 a 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 confirmed that the photostationary cis composition did not change under UV-irradiated conditions, even at temperatures as high as 93 °C.

RESULTS AND DISCUSSION

UCST Phase Behavior of P(AzoMA-*r*-NIPAm). Figure 2 shows the results of turbidity measurements for a series of P(AzoMA-*r*-NIPAm) solutions (3 wt %) in [C$_2$mim][NTf$_2$] with or without UV-light irradiation. As expected, the NIPAm-based random copolymer exhibited UCST phase behavior, with cloud point temperature (T_c) lower than that at which the

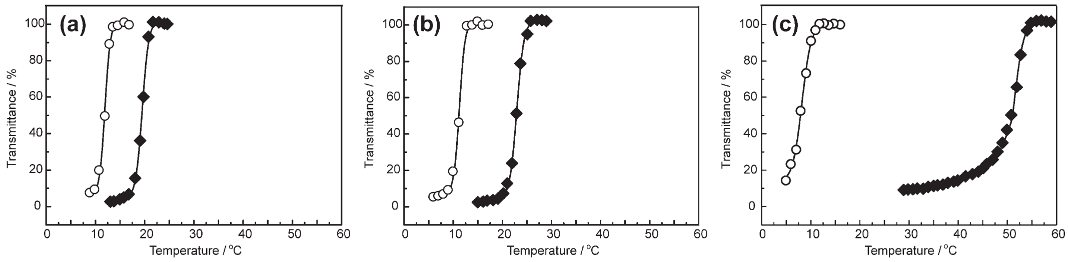


Figure 2. Turbidity measurements for (a) P(AzoMA$_{8.6}$-*r*-NIPAm), (b) P(AzoMA$_{20.4}$-*r*-NIPAm), and (c) P(AzoMA$_{29.1}$-*r*-NIPAm) in [C$_2$mim][NTf$_2$] solution with UV-light (366 nm) irradiation (open circles) or under dark (closed diamonds).

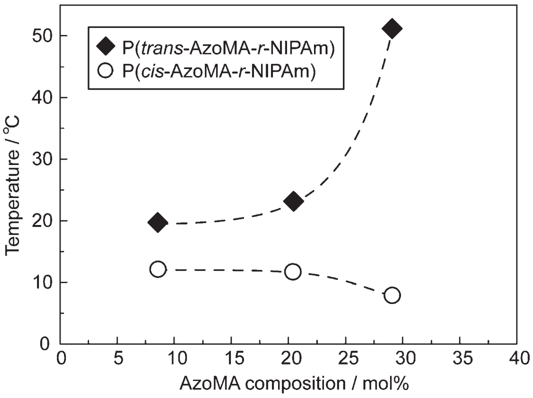


Figure 3. Relationship between UCST phase separation temperature (T_c) of P(AzoMA-*r*-NIPAm) and AzoMA composition in the random copolymers. T_c of P(*trans*-AzoMA-*r*-NIPAm) drastically increases (closed diamonds) but that of P(*cis*-AzoMA-*r*-NIPAm) slightly decreases with increases in the composition of AzoMA (opened circles). T_c was determined as the temperature of 50% transmittance.

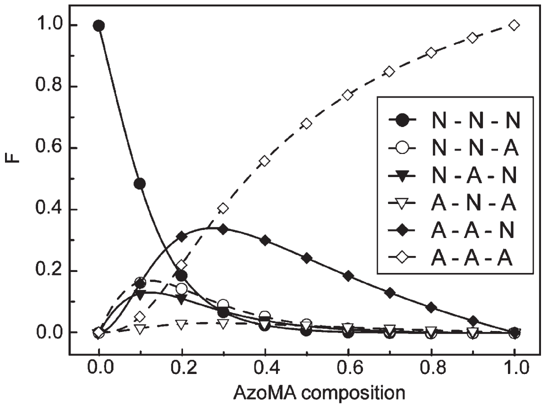


Figure 4. Triad sequence distribution for P(AzoMA-*r*-NIPAm) as a function of mole fraction of AzoMA in the copolymer calculated from the monomer reactivity ratio of NIPAm ([M$_1$]) and AzoMA ([M$_2$]).

previously reported PBnMA-based polymers exhibited LCST phase transitions. UCST T_c's observed ranged from 7.9 °C [P(*cis*-AzoMA$_{29.1}$-*r*-NIPAm)] to 50.9 °C [P(*trans*-AzoMA$_{29.1}$-*r*-NIPAm)], thus including room temperature. It is apparent that the T_c of P(AzoMA-*r*-NIPAm) depends strongly on the AzoMA composition in the polymers, as well as on the photochromic state of AzoMA. Sharpness of the phase transition appears to become sluggish with increasing the AzoMA compositions in the polymers. This may come from the composition distribution of AzoMA in the random copolymers not only in individual chains but also along one chain. We have already reported similar phenomena elsewhere.[13] We have also checked how concentration of the polymers affects the phase transition in terms of its sharpness (Figure S5, Supporting Information), however, almost no change was observed in this concentration range. On the contrary, the phase transition temperatures were found to increase with increasing concentration of the polymers, irrespective of the photochromic state of AzoMA, which is a typical characteristic of UCST phase transition. The dependence of the T_c of P(AzoMA-*r*-NIPAm) on the composition of AzoMA is shown in Figure 3. Interestingly, the value of T_c of P(*trans*-AzoMA-*r*-NIPAm) increases strongly, whereas that T_c of P(*cis*-AzoMA-*r*-NIPAm) does not change or slightly decreases with an increase in the composition of AzoMA in the random copolymer. In other words, *trans*-AzoMA behaved as a solvato-phobic comonomer and *cis*-AzoMA behaved as a solvato-philic monomer, relative to the majority NIPAm monomers. Such different effects of the photoisomerization state of azobenzene on T_c provides a larger T_c difference, reaching a maximum of 43 °C for the P(AzoMA$_{29.1}$-*r*-NIPAm) solution. It is well-known that the polarity of azobenzene varies with changes in the photoisomerization state of azobenzene. Planar *trans*-azobenzene has a dipole moment of 0.5 D; however, *cis*-azobenzene has a higher polarity of 3.1 D.[23] 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 [C$_2$mim][NTf$_2$], which has relatively higher polarity.

The enhanced sensitivity of the UCST phase separation of the series of P(*trans*-AzoMA-*r*-NIPAm) random copolymers can be explained by the sequence distribution. The monomer reactivity ratios of NIPAm ([M$_1$]) and AzoMA ([M$_2$]) were determined to be $r_1 = 0.65$ and $r_2 = 5.60$, respectively, from the relationship between the AzoMA composition in the random copolymers and AzoMA in the feed. The distribution of P(AzoMA-*r*-NIPAm)s is statistically determined by the monomer reactivity ratio of M$_1$ to M$_2$. Figure 4 shows the triad sequence distribution curve for P(AzoMA-*r*-NIPAm) calculated by Wall's method,[24] and Table 2 summarizes the triad sequence distribution for a series of P(AzoMA-*r*-NIPAm)s ([AzoMA] = 8.6, 20.4, and 29.1 mol %). These results confirm that the monomer arrangement in the P(AzoMA-*r*-NIPAm) polymer chain is rather blocky. In the case of P(AzoMA$_{8.6}$-*r*-NIPAm), 70% of the triads are NIPAm—NIPAm—NIPAm (N-N-N) or NIPAm—NIPAm-AzoMA (N-N-A). This suggests that the microscopic environment of P(AzoMA$_{8.6}$-*r*-NIPAm) is similar to that of a PNIPAm homopolymer itself. Therefore, T_c does not change so much. In contrast, in the case of

Table 2. Triad Sequence Distribution of P(AzoMA-*r*-NIPAm) ([M_1], NIPAm; [M_2], AzoMA)

[AzoMA]/mol %	F_{111} (N-N-N)	F_{112} (N-N-A)	F_{121} (N-A-N)	F_{212} (A-N-A)	F_{221} (A-A-N)	F_{222} (A-A-A)
8.6	0.552	0.152	0.112	0.010	0.134	0.040
20.4	0.175	0.132	0.097	0.025	0.315	0.256
29.1	0.071	0.085	0.063	0.026	0.328	0.427

the triad sequence distribution of P($AzoMA_{29.1}$-*r*-NIPAm), the sum of the sequence distribution ratios of AzoMA—AzoMA—AzoMA (A-A-A) and AzoMA-AzoMA-NIPAm (A-A-N) is 75.5%, indicating that the azobenzene side chains coalesce at a high density along the random copolymer chain. Such a blocky distribution could lead to the generation of an intramolecular attractive force based on a $\pi-\pi$ stacking interaction among the azobenzene side chains, together resulting in a much higher UCST phase separation in the IL for P(*trans*-$AzoMA_{29.1}$-*r*-NIPAm). In the intermediate case of P($AzoMA_{20.4}$-*r*-NIPAm), the distribution bias of the monomer arrangement still remains. The frequency of NIPAm-adjacent triads (NIPAm-NIPAm-NIPAm (N-N-N) and NIPAm-NIPAm-AzoMA (N-N-A)) and the AzoMA-adjacent triads (AzoMA-AzoMA-AzoMA (A-A-A) and AzoMA-AzoMA-NIPAm (A-A-N)) are estimated to be 30.7% and 57.1%, respectively. The cooperative effect arising from the monomer distribution bias in the random copolymer is one of the reasons for the strong increases in the UCST T_c of P(*trans*-AzoMA-*r*-NIPAm) with increasing the AzoMA composition. In order to obtain more randomly arranged copolymers comprising NIPAm and an azobenzene-containing monomer, we attempted to prepare P(AzoAm-*r*-NIPAm) (AzoAm: 4-phenylazophenyl acrylamide); however, the amide proton of AzoAm has a strong chain transfer ability in the polymerization process, which leads to difficulty in obtaining a uniform molecular weight of the random copolymer.

Thermal Relaxation from P(*cis*-AzoMA-*r*-NIPAm) to P(*trans*-AzoMA-*r*-NIPAm). In order to evaluate the kinetics of the cis-to-trans isomerization of the P(AzoMA-*r*-NIPAm) in [C_2mim][NTf_2], we studied the thermal relaxation process from P(*cis*-AzoMA-*r*-NIPAm) to P(*trans*-AzoMA-*r*-NIPAm). Figure S4 in the Supporting Information shows an Arrhenius plot for the first order k from the absorbance of 320 nm derived from the $\pi-\pi^*$ transition of *trans*-azobenzene in the dark as a function of time for the P($AzoMA_{20.4}$-*r*-NIPAm), at constant temperatures of 50, 60, and 70 °C. All of the sample solutions used in this experiment were confirmed to be transparent. Before the measurements, samples were exposed to 320-nm UV-light irradiation for a sufficient period of time to achieve a photosteady excited state. The first-order k at different temperatures is summarized in Table S1 (Supporting Information). These rate constants are comparable to the reported rate constants of an azobenzene-bridged aza-crown ether in common organic solvents,[25] a monomeric azobenzene in imidazolium-based ILs,[26] and P(AzoMA-*r*-BnMA).[17] The activation energy (E_a = 75 kJ mol^{-1}) and frequency factor ($A = 3.4 \times 10^7\ s^{-1}$) of the thermal isomerization of P(AzoMA-*r*-NIPAm) in [C_2mim][NTf_2] were obtained from the Arrhenius plots of the k's. Moreover, the E_a and A values of P(AzoMA-*r*-NIPAm) are comparable to those reported for monomeric azobenzene derivatives in common organic solvents and ILs. All of the above results confirm that an IL medium has a negligible effect on the cis-to-trans thermal isomerization process of P(AzoMA-*r*-NIPAm). In addition, a large retardation of thermal relaxation from P(*cis*-AzoMA-*r*-NIPAm) to P(*trans*-AzoMA-*r*-NIPAm) owing to phase separation temperature suppression can be confirmed. From the first-order k of P(AzoMA-*r*-NIPAm) obtained from the kinetic analysis of the photochromism of the polymer, it is found that the half-lives of the previously reported P(AzoMA-*r*-BnMA) (T_{cLCST} = 102 °C) and the presently studied P(AzoMA-*r*-NIPAm) (T_{cUCST} = 12.1 °C, [AzoMA] = 8.6 mol %) are 8 min at 102 °C and 13 days at 12.1 °C, respectively. Therefore, these azobenzene-containing polymers that respond at low temperatures may be suitable for smart material applications.

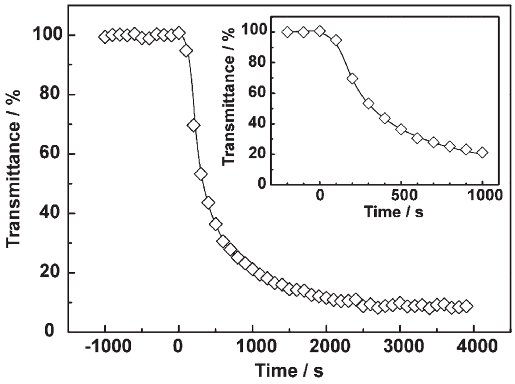


Figure 5. Photoinduced phase separation of P(*trans*-$AzoMA_{20.4}$-*r*-NIPAm) at 15.0 °C under illumination of visible light (437 nm). Inset shows enlarged illustration during the initial period.

Photoinduced Phase Transition of Polymer in IL. We further demonstrate the photoinduced phase transition of P(AzoMA-*r*-NIPAm) in [C_2mim][NTf_2] by utilizing the large difference in the values of T_c between the trans and the cis polymers. P($AzoMA_{20.4}$-*r*-NIPAm) was used for the experiment ($T_c$trans = 22.9 °C and $T_c$cis = 11.2 °C). Under UV-light irradiation, the temperature of a 3 wt % P($AzoMA_{20.4}$-*r*-NIPAm) solution was set to 15.0 °C, at which it is bistable. Before the measurements, the sample was subjected to UV irradiation for 2 h and was confirmed to be transparent (phase separation did not occur) owing to the fact that the T_c of P(*cis*-$AzoMA_{20.4}$-*r*-NIPAm) was lower than the measurement temperature. The polymer solution became turbid under the illumination of visible light (437 nm) to form P(*trans*-$AzoMA_{20.4}$-*r*-NIPAm) (Figure 5), because the UCST T_c of the trans polymer is higher than 15.0 °C. In the phase separation process of P(*trans*-AzoMA-*r*-NIPAm) under visible light illumination, phase separation occurred immediately, without an induction period (Figure 5, inset). This contrasts with the observation of an induction time before phase separation in the previously reported LCST system of P(AzoMA-*r*-BnMA).[17]

Another aspect of the photoinduced phase transition of P(AzoMA-*r*-NIPAm) that differs from P(AzoMA-*r*-BnMA) is the sluggish decrease in transmittance under irradiation of visible light. Complete phase separation in P(AzoMA-*r*-NIPAm)/[C_2mim][NTf_2] solution required more than 3000 s. Nevertheless, the previously reported LCST-type polymer

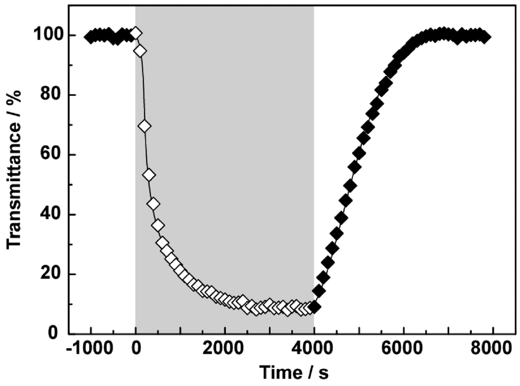


Figure 6. Transmittance recovery process from turbid to transparent solution of P(AzoMA$_{20.1}$-*r*-NIPAm) at 15.0 °C by irradiation of UV light, shown along with photoinduced phase transition before recovery process.

solution of P(AzoMA-*r*-BnMA)/[C$_2$mim][NTf$_2$] requires only 600 s to reach a complete phase separation.[17] phase separation kinetics will depend on the viscosity of the IL. Our previously reported photoinduced phase transition of LCST system, P(AzoMA-*r*-BnMA) in [C$_2$mim][NTf$_2$], was measured at 102 °C (6.2 mPa s), whereas the viscosity of [C$_2$mim][NTf$_2$] at 15.0 °C (Figure 5) is 48.4 mPa s,[19] consistent with the difference in kinetics.

After completing the UV-illumination phase transition, the transmittance of the turbid P(*trans*-AzoMA-*r*-NIPAm) solution can be recovered by switching to UV light irradiation to form P(*cis*-AzoMA-*r*-NIPAm), where the UCST T_c is below 15.0 °C (Figure 6). Here, the reversibility of the photoinduced phase transition of the polymer in the IL is confirmed. The recovery process of the dissolution is kinetically a little slower than that observed in the phase-separation process.

■ CONCLUSION

In this manuscript, we have reported the design, synthesis, and phase behavior of a novel azobenzene-containing polymer exhibiting UCST-type phase behavior in an ionic liquid. Well-defined random copolymers comprising AzoMA and NIPAm [P(AzoMA-*r*-NIPAm)] have been successfully prepared by RAFT polymerization. Photochromic analysis of P(AzoMA-*r*-NIPAm) showed that the photoisomerization reaction of azobenzene in the polymers occurs reversibly, as observed in common organic solvents or for low molecular weight azobenzenes in an IL. The E_a and A values for thermal relaxation of *cis*- to *trans*-azobenzne are comparable or slightly lower than those previously reported for an LCST polymer in an IL. As expected, the UCST phase transition of the NIPAm-based polymers in an IL occurred over a wide range of temperatures (7.9 to ~50.9 °C), including room temperature. Interestingly, the UCST T_c of the trans polymer strongly increased, whereas that of the cis polymer slightly decreased with increases in the AzoMA composition in the random copolymer. *trans*-Azobenzene, having a lower polarity than NIPAm, does not stabilize the copolymer in a higher polarity IL, resulting in an increase in T_c. In contrast, P(*cis*-AzoMA-*r*-NIPAm) increases the total polarity of polymers and therefore decreases T_c. To the best of our knowledge, such different effects on T_c depending on the photoisomerization state of azobenzene have not been reported. Statistical analysis using the monomer reactivity ratios determined from the copolymer composition curve confirmed that the arrangement of monomers in a series of random copolymers is somewhat blocky. Strong increases in the T_c of P(*trans*-AzoMA-*r*-NIPAm) can be explained by the cooperative effect of aggregation with the aid of the $\pi-\pi$ stacking attractive interaction among adjacent AzoMAs. Furthermore, reversible photoinduced phase transition of polymers in an IL has been demonstrated.

In our previous report, the LCST phase separation of P(AzoMA-*r*-BnMA) occurs at around 100 °C.[17] This makes the experimental conditions much more difficult to achieve, because the thermal relaxation from *cis*- to *trans*-azobenzene rapidly occurs even under the condition of continuous irradiation of UV light. However, in the case of P(AzoMA-*r*-NIPAm), the retardation of thermal relaxation from *cis*- to *trans*-photoisomer could be realized. From the first-order k of P(AzoMA-*r*-NIPAm) obtained from the kinetic analysis, it was found that the half-lives of the previously reported P(*cis*-AzoMA$_{4.6}$-*r*-BnMA) (T_{cLCST} = 102 °C)[17] and the presently studied P(*cis*-AzoMA$_{8.6}$-*r*-NIPAm) (T_{cUCST} = 12.1 °C) are 8 min at 102 °C and 13 days at 12.1 °C, respectively. The thermal reconversion kinetics of *cis*-azobenzene is found to depend on the local mobility of the medium.[27] The viscosity of the IL at both temperatures were 6.2 and 52.2 mPa s, respectively. Photoinduced "contactless" reversible stimuli-responsive phase transition of polymers in nonvolatile, thermally stable IL is expected to be a unique way to realize novel smart materials. We are now investigating a block copolymer system having P(AzoMA-*r*-NIPAm) segment in an IL.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. GPC traces of P(AzoMA-*r*-NIPAm)s, photochromism, Arrhenius analysis of P(AzoMA$_{20.4}$-*r*-NIPAm), and concentration dependency of UCST phase transition temperature for P(AzoMA$_{20.4}$-*r*-NIPAm). This material is available free of charge via the Internet at http://pubs.acs.org.

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