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Photoisomerization-Induced Tunable LCST Phase Separation of Azobenzene-Containing Polymers in an Ionic Liquid

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4-Phenylazophenyl methacrylate (AzoMA) and benzyl methacrylate (BnMA) were copolymerized to produce multistimuli-responsive polymers (P(AzoMA-*r*-BnMA)s) in a hydrophobic ionic liquid (IL), 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide ([C₂mim][NTf₂]), as the solvent. P(AzoMA-*r*-BnMA)s with a maximum of ca. 4 mol % AzoMA were soluble in [C₂mim][NTf₂] at low temperatures, and they underwent lower critical solution temperature (LCST) phase separation with an increase in temperature. Under UV and visible light irradiation, P(AzoMA-*r*-BnMA)s underwent reversible photochromism of *trans*-to-*cis* and *cis*-to-*trans* isomerization, respectively. The LCST temperature differences between *trans*- and *cis*-form polymers in the IL were as large as 22 °C. Reversible photoinduced phase separation of the polymers was achieved at a certain temperature; at this temperature, the *cis*-form polymers were soluble in the IL, but the *trans*-form polymers were not.

Ionic liquids (ILs), as solvents of bio- and synthetic polymers, have attractive properties such as tunable solvation properties, negligible volatility, nonflammability, high ionic conductivity, and wide electrochemical window.^{1,2} It has recently been discovered that like water, ILs exhibit structure-forming solvation properties. We reported for the first time that poly(benzyl methacrylate) (PBnMA) undergoes lower critical solution temperature (LCST) phase separations in certain ILs.^{3b–c} This is a similar phenomenon observed for poly(*N*-isopropylacrylamide) (PNIPAm) in aqueous solutions. As hydrophobic solvation induces the LCST behavior of PNIPAm in water, structure-forming solvation of ILs for PBnMA is suggested to be a principal reason for the LCST behavior.^{3b–d} Polymers and their gels that undergo phase changes in ILs may be used to prepare smart materials with a wide usable temperature range; these materials can function even in vacuum as well as in an open atmosphere, because of the nonvolatility of ILs.³ Phase changes of polymers in ILs cause thermoreversible gelation of ILs, which results in the production of highly ion-conductive gels.^{3,4} These gels are applied, for example, to organic transistors.^{4d}

Many important studies on photoresponsive polymers in molecular solvents have been conducted.^{5–7} Reversible photoisomerization of azobenzene has been considered to be a suitable trigger for the development of on–off light switches using photoresponsive polymers, which are likely to alter the phase changes of polymers in an IL. In this study, we present the tunable LCST phase separation of azobenzene-containing PBnMA copolymers (Scheme 1) in an IL by photoirradiation. The LCST temperature differences between *trans*- and *cis*-form polymers in the IL were as large as 22 °C. Reversible photoinduced phase separation of the polymers was achieved at a certain temperature; at this temperature, the *cis*-form polymers were soluble in the IL, but the *trans*-form polymers were not.

4-Phenylazophenyl methacrylate (AzoMA) and BnMA were copolymerized to produce multistimuli-responsive polymers (P(AzoMA-*r*-BnMA)) in an IL (Scheme 1). We selected a common hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide ([C₂mim][NTf₂]), as the solvent. UV–vis spectra measurements of P(AzoMA-*r*-BnMA) in [C₂mim][NTf₂] performed under UV (366 nm, 8.0 mW/cm²) and visible light (437 nm, 4.0 mW/cm²) irradiation confirmed that P(AzoMA-*r*-BnMA) underwent reversible photochromism, without any decomposition of the polymer or the solvent. Under our experimental conditions, photoisomerization reactions (*trans*-to-*cis* and *cis*-to-*trans*) of the polymers attained photostationary states within 240 s of photoirradiation. The photostationary *cis* contents of the polymers under UV and visible light irradiation were 80% and 15%, respectively, and they were insensitive to the experimental temperatures. Complete *cis*-to-*trans* isomerization could be carried out in the dark. The thermal *cis*-to-*trans* isomerization of P(AzoMA(4.1 mol %)-*r*-BnMA) in [C₂mim][NTf₂] was

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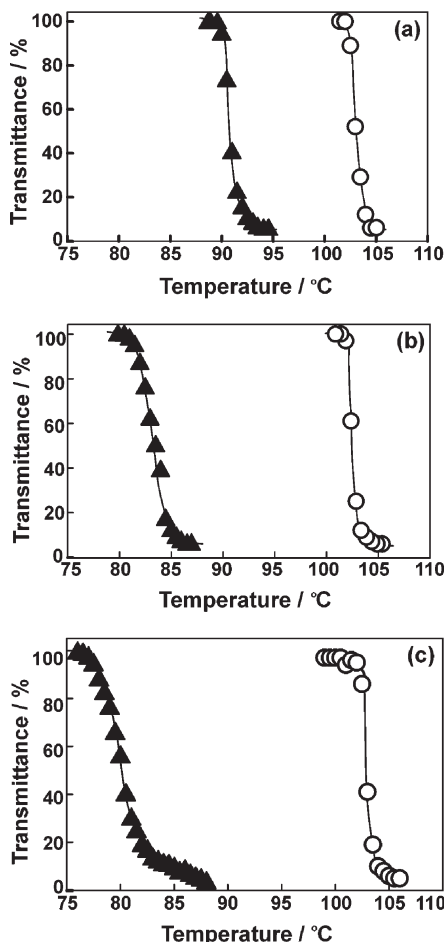
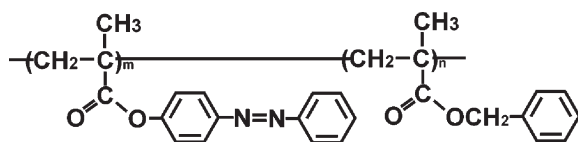
Scheme 1. Chemical Structure of P(AzoMA-*r*-BnMA)

Figure 1. Turbidity measurements for 3 wt % P(AzoMA-*r*-BnMA) in [C₂mim][NTf₂] either in the dark or under UV-light (366 nm) irradiation: triangles denote P(*trans*-AzoMA-*r*-BnMA) in the dark; circles denote P(*cis*-AzoMA-*r*-BnMA) under UV-light irradiation. (a) [AzoMA] = 1.9 mol %; (b) [AzoMA] = 3.0 mol %; (c) [AzoMA] = 4.1 mol %.

also investigated at different temperatures, in order to study the effect of temperature on the rate of the isomerization. The thermal isomerization rate corresponding to the *trans* π - π^* transition was determined from the first-order plots of the absorbance at 325 nm.⁸ The first-order rate constants at different temperatures are listed in Table S2 in the Supporting Information (SI). These rate constants are comparable to or slightly lower than the reported rate constants of a novel azobenzene-bridged aza-crown ether in common organic solvents⁹ and a monomeric azobenzene in imidazolium-based ILs.¹⁰ The activation energy (E_a) and frequency factor (A) of the thermal isomerization of the azo

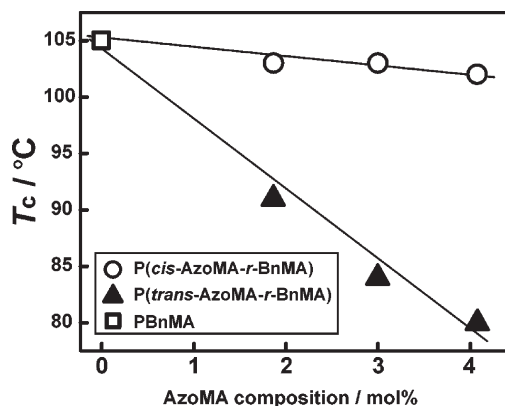


Figure 2. Relationship between phase separation temperature (T_c) and AzoMA composition in P(AzoMA-*r*-BnMA). The circles and triangles denote the T_c of P(*cis*-AzoMA-*r*-BnMA) and P(*trans*-AzoMA-*r*-BnMA), respectively.

polymer in [C₂mim][NTf₂] were also evaluated from the Arrhenius plots of the rate constants (Figure S6 in SI). The estimated value of E_a (70 kJ/mol) is also comparable to those reported (84–100 kJ/mol) for monomeric azobenzene derivatives in common organic solvents and in ILs.¹⁰ The value of A ($2.0 \times 10^8 \text{ s}^{-1}$) for the azopolymer in an IL is similar to that reported for monomeric azobenzene in ILs.¹⁰ All the above results confirm that the IL medium has a negligible effect on the *cis*-to-*trans* thermal isomerization process of P(AzoMA-*r*-BnMA).

PAzoMA homopolymers were insoluble in [C₂mim][NTf₂], irrespective of the temperature. However, P(AzoMA-*r*-BnMA) copolymers with a maximum of ca. 4 mol % AzoMA were soluble in [C₂mim][NTf₂] at low temperatures, and, as expected, they underwent LCST phase separation with an increase in temperature. Results of the transmittance measurements of P(AzoMA-*r*-BnMA) in [C₂mim][NTf₂] are shown in Figure 1; the measurements were performed either in the dark (*trans* contents: 100%) or under UV irradiation after the photoisomerization reaction attained a photostationary state (*cis* contents: 80%). In the dark, the LCST phase separation temperature (T_c ; defined as the temperature at which transmittance at 500 nm is 50%) of P(*trans*-AzoMA-*r*-BnMA) in [C₂mim][NTf₂] is lower than that of the thermosensitive PBnMA homopolymer, and it decreases with an increase in the composition of AzoMA, due to the solvatophobic nature of AzoMA. It should be noted that the difference in T_c between *trans*- and *cis*-rich P(AzoMA(4.1 mol %)-*r*-BnMA) is as large as 22 °C. In an aqueous medium, the difference in T_c of azo polymers between their two photostationary states is generally much smaller than that observed in the present case,^{7a-f} though exceptionally large differences of up to 20 °C have been reported for azobenzene-containing *N,N*-dimethylacrylamide copolymers.^{7g}

It is interesting to note that the T_c of P(*trans*-AzoMA-*r*-BnMA) decreases significantly with an increase in the concentration of AzoMA, while that of the *cis*-rich azo polymer changes slightly with the concentration of AzoMA (Figure 2). The polarity of ILs, including [C₂mim][NTf₂], is relatively high and is comparable to that of common polar organic solvents such as dimethylsulfoxide, 2-propanol, and acetone.^{1,11} The phase separation temperature of P(*cis*-AzoMA-*r*-BnMA) is high as compared to that of *trans*-azo polymer because of the strong interaction of the *cis*-rich polymer with a polar IL. In addition, it is known that the structure-forming

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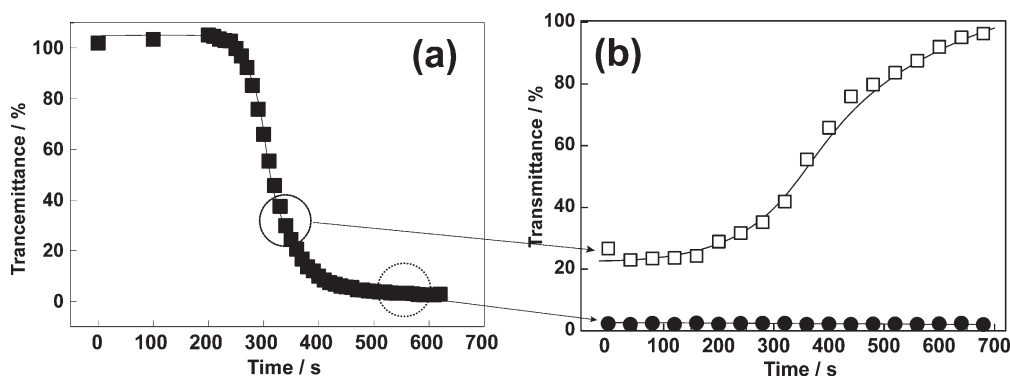


Figure 3. (a) Isothermal phase separation observed in 3 wt % P(*cis*-AzoMA(4.1 mol %)-*r*-BnMA) in [C₂mim][NTf₂] at 93 °C under visible light (437 nm) irradiation. Before performing the measurement, the polymer solution was irradiated with UV light (366 nm) for a sufficient amount of time so that it attained a photostationary state. (b) Redissolution of the phase-separated P(*trans*-AzoMA(4.1 mol %)-*r*-BnMA) under UV light (366 nm) irradiation. A polymer solution that is completely phase-separated (circles) remains turbid within the time scale, whereas a polymer solution with 25% transmittance (squares) transforms into a completely transparent solution under UV light irradiation.

solvation that results in a negative entropy change for mixing is responsible for the LCST phase separation. The entropy loss of IL/aromatic compound mixtures that exhibit LCST phase separation is due to the formation of liquid clathrate by cation- π interaction.^{3b-e,12,13} In the case of PBnMA in [C₂mim][NTf₂], structure-forming solvation appears to occur around the aromatic group. In the case of P(AzoMA-*r*-BnMA), the azo moiety is likely to have a stronger cation- π interaction in the *trans*-form polymers than in the *cis*-form polymers, because of higher planarity of *trans*-azobenzene compared with *cis*-azobenzene. Consequently, [C₂mim][NTf₂] favors structure-forming solvation around the *trans*-form azo moiety, which results in a large entropy loss due to mixing and a decrease in the LCST phase separation temperatures.

Highly sensitive differential calorimetry measurements reveal that the changes in both enthalpy and entropy of the demixing of PBnMA from [C₂mim][NTf₂] are positive,¹⁴ which is in good agreement with the demixing behavior of PNIPAm from water. In water, the changes in enthalpy (ΔH) and entropy (ΔS) are 62.8 J g⁻¹ of polymer and 0.2 J K⁻¹ g⁻¹ of polymer, respectively,¹⁵ whereas these changes in [C₂mim][NTf₂] are found to be much smaller ($\Delta H = 4.3$ J g⁻¹ of polymer, $\Delta S = 0.011$ J K⁻¹ g⁻¹ of polymer). This implies that the T_c of P(AzoMA-*r*-BnMA) is determined by a subtle balance between ΔH and ΔS , and that can be altered by a slight change in the chemical structures of the polymers, which can be a reason for the large change in T_c induced by the photoisomerization of a small amount of azobenzene in P(AzoMA-*r*-BnMA).

Finally, we demonstrate the isothermal photoinduced phase transition of P(AzoMA(4.1 mol %)-*r*-BnMA) in [C₂mim][NTf₂] by analyzing the significant changes in solubility associated with the reversible photoisomerization of the azo moiety. Figure 3a shows the transmittance of a polymer solution at a bistable temperature in terms of *cis*- and *trans*-form solubility (93 °C) as a function of the visible light irradiation time. Before performing

the measurement, the polymer solution was irradiated with UV light for a sufficient amount of time so that it achieved a photostationary state (*cis* contents = 80%). The transparent polymer solution became opaque after visible light irradiation for 200 s (*cis* contents = 20%), and transmittance of the solution became 0% at 550 s. After observing the phase separation induced by visible light, the opaque polymer solution was irradiated with UV light in order to redissolve the phase-separated polymer by *trans*-to-*cis* isomerization. A polymer solution with 25% transmittance can be transformed into a transparent solution by irradiating it with UV light, as this triggers a T_c change caused by *trans*-to-*cis* isomerization, as shown in Figure 3b. On the other hand, when a polymer solution with 0% transmittance is irradiated by UV light, there is a slight change in the transmittance of the solution within the above-mentioned period, and it takes 1 h for complete redissolution to be achieved. The further a system goes on phase separation, the larger the length-scale of the two phases, and thus the slower the redissolution kinetics. The redissolution kinetics in ILs is also determined by polymer dynamics.¹⁶ The glass transition temperature (T_g) of the phase-separated polymer is one of the dominant factors that have an effect on the dynamics of the phase-separated polymer, and therefore, the polymer redissolution process.¹⁶ The polymer phase that is completely separated from the IL (circles in Figure 3b) should have a significantly higher T_g than the polymer-rich phase that is moderately separated from the IL (squares in Figure 3b), since the T_g of the polymer is 70 °C, while that of [C₂mim][NTf₂] is -87 °C. The kinetic difference in the redissolution process may also arise from a possible light scattering problem. When the polymer (solid) and IL (liquid) phases are completely segregated, as indicated by the circles in Figure 3b, the UV light that induces redissolution is greatly scattered.

In this study, the photo- and temperature-induced phase transitions of a polymer in an IL were demonstrated for the first time by using P(AzoMA-*r*-BnMA)/[C₂mim][NTf₂] systems. It should also be noted that a combination of polymer/IL sometimes shows unexpected dynamics, including nonergodicity effect on the micellar morphology,¹⁷ which were hardly observed in commonly used molecular solvents. In this study, it was observed that the recovery process of the phase-separated P(AzoMA-

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r-BnMA)/[C₂mim][NTf₂] solution is significantly affected by the degree of phase separation that occurred previously. It will be interesting to discover the unique dynamics of phase transition of polymers in the combination of polymer/IL, which is not observed yet in molecular solvents. This will be the basis of our future study.

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Supporting Information Available: Detailed experimental procedures and Figures S1–S6. This material is available free of charge via the Internet at <http://pubs.acs.org>.