

Supplementary Information

Unlocking of Interlocked Heteropolymer Gel by Light: Photoinduced Volume Phase Transition in an Ionic Liquid from a Metastable State to an Equilibrium Phase

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Synthesis and characterization of P(AzoMA-*r*-BnMA) gel

All chemical reagents were purified prior to use. 4-phenylazophenyl methacrylate (AzoMA), the ionic liquids (ILs: [C₂mim][NTf₂], and 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C₆mim][NTf₂])) were synthesized and characterized as previously reported.^{S1} There have been many studies to prepare ion gel particles.^{S2} In the present study, the P(AzoMA-*r*-BnMA) gel was obtained by dispersion polymerization using a hydrophobic IL as the dispersion medium. The continuous phase was deionized water with dissolved 4.76 wt% poly(vinyl alcohol) acting as a polymeric stabilizer. The aqueous mixture was introduced into a two-necked round-bottom glass flask, and the atmosphere in the flask was replaced with N₂ by repeated evacuation and N₂ gas purge. The hydrophobic [C₆mim][NTf₂] phase, containing BnMA (679 mM), AzoMA (21 mM), EGDMA (28 mM) as a cross-linker, and 2,2'-azobisisobutyronitrile (7 mM) as an initiator, was deaerated by N₂ purge for 20 min and dispersed into the aqueous continuous phase by vigorous stirring. Radical polymerization was carried out at 60 °C for 12 h. Overhead mechanical agitation at around ~300 rpm gave us ion gel particles with a proper size for the microscopic observation. An average gel diameter calculated from 50 randomly selected gel particles was 10.1 μm with a standard deviation of 3.5. The [C₆mim][NTf₂] solvent that was included in the spherical ion gel was washed with methanol and tetrahydrofuran (THF) and then replaced by [C₂mim][NTf₂] under reduced pressure. The copolymer composition of AzoMA was determined to be 2.2 mol% by elemental analysis. Although the preparation of P(AzoMA-*r*-BnMA) ion-gel particles using [C₂mim][NTf₂] is easier, this procedure did not work in the

present case, because of lower LCST of P(AzoMA-*r*-BnMA) in [C₂mim][NTf₂] than that of PBnMA. When [C₂mim][NTf₂] was used as a dispersion medium for the random copolymerization of AzoMA and BnMA, prepared ion-gel particles always became opaque due to micro-phase separation resulted from decreasing solubility of the propagating polymer by local heat of the reaction due to the LCST nature. Thus, we needed to change dispersion solvent from [C₂mim][NTf₂] to [C₆mim][NTf₂] to keep good solubility of the polymer in the reaction medium. In the cases using [C₆mim][NTf₂], we always successfully prepared transparent, homogeneous ion gel particles.

Volume swelling ratio measurements for micro-spherical gel

A drop of the dispersion, placed on a concave glass plate and covered by a cover glass, was temperature-controlled by using a hot stage. The diameter of the micro-spherical gel, D , was measured under controlled temperatures by using a digital microscope (KEYENCE VH-8000). The temperature was increased in steps of 1 °C, and the measurements were carried out after waiting for at least 15 min. The relative swelling ratio (D/D_0) was determined, where D_0 is the gel particle diameter at 25 °C. Swelling ratio measurements for P(*trans*-AzoMA-*r*-BnMA) were performed in the dark to ensure the 100% *trans*-azobenzene state. Photo-irradiation 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, 8.0 mW cm⁻²; visible light: 437 nm, 4 mW cm⁻²) were adjusted using colour filters and by variegation. A heat-absorbing filter was used to dissipate the heat generated by the mercury lamp.

Thermal reversibility of swelling ratios of P(*trans*-AzoMA-*r*-BnMA) gel

We investigated the ability of P(*trans*-AzoMA-*r*-BnMA) gel to return to the original equilibrium swollen state under three different heating-cooling cycles by paying attention to the plateau ($D/D_0 = 0.55$) observed around 77 °C–80 °C (**Fig. S1**). In the first cycle, P(*trans*-AzoMA-*r*-BnMA) gel was heated to 68 °C, a point just below the plateau. P(*trans*-AzoMA-*r*-BnMA) gel exhibits a reversible return to the original state (Fig. S1(a)). However, once the gel goes through the plateau, the gel falls in the metastable shrunken structure and cannot return to the original swollen state (**Fig. S1(c)**). In the intermediate situation, when the temperature of the ion gel was increased to 77 °C, which is the starting point of the plateau, the gel can return to the original swollen phase with a small hysteresis (**Fig. S1(b)**). These results strongly suggest that the plateau, which appears in the swelling ratio measurements, is indicative of P(*trans*-AzoMA-*r*-BnMA) gel falling into a local free energy minimum.

Changes in redissolution dynamics of linear polymers by the incorporation of azobenzene moiety

P(AzoMA-*r*-BnMA) linear polymer ([AzoMA] = 2.82 mol%) was prepared and

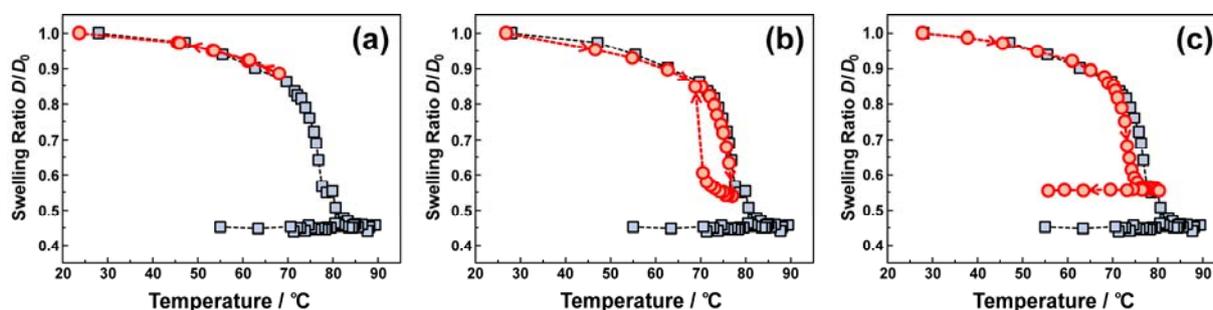


Fig. S1 Reversibility of swelling ratios of P(*trans*-AzoMA-*r*-BnMA) gel in [C₂mim][NTf₂] under three different heating-cooling cycles is shown by red circle plots. The highest temperatures of the heating are (a) 68 °C (before plateau), (b) 77 °C (beginning of the plateau), and (c) 80 °C (higher than the plateau). The swelling ratio measurements up to 90 °C are indicated by grey square plots.

characterized by using previously reported methods.^{S3} The number average molecular weight and polydispersity index of the polymer were determined to be 50 kDa and 2.68, respectively, by gel permeation chromatography using THF as the carrier solvent. PBnMA^{S4} and P(AzoMA-*r*-BnMA) sample solutions (3 wt%) in [C₂mim][NTf₂] were prepared by the co-solvent evaporation method using THF. Phase separation temperatures (T_{cs}) of the PBnMA, P(*trans*-AzoMA-*r*-BnMA), and P(*cis*-AzoMA-*r*-BnMA) solutions were determined to be 105 °C, 83 °C, and 99 °C, respectively. To evaluate the rate of redissolution, transmittance spectra of the samples were periodically recorded while decreasing the temperature from ($T_c + 10$) °C to ($T_c - 10$) °C. The samples were heated to ($T_c + 10$) °C and allowed to stand for 5 min at that temperature to undergo phase separation (precipitation); then, the phase-separated solutions were allowed to cool to ($T_c - 10$) °C.

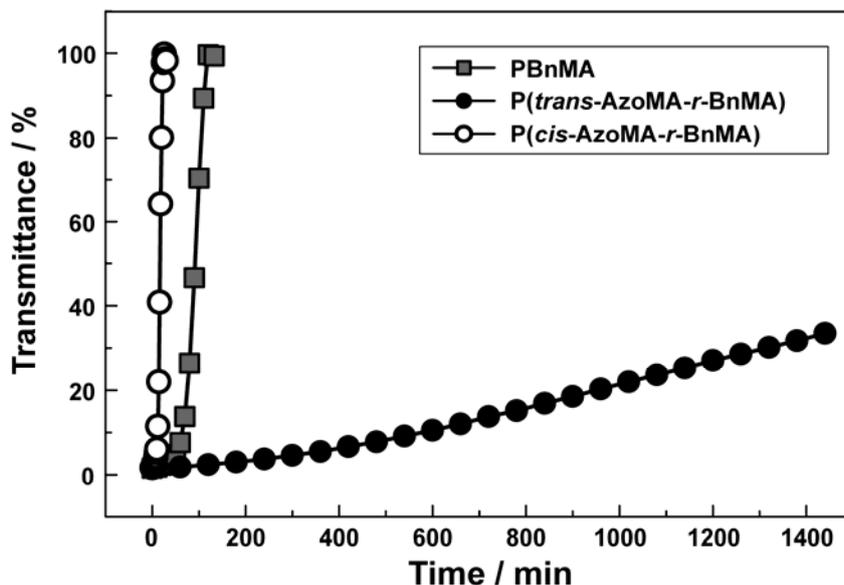


Fig. S2 Time dependence of the transmittance at 500 nm for 3 wt% [C₂mim][NTf₂] solutions of P(*trans*-AzoMA-*r*-BnMA), P(*cis*-AzoMA-*r*-BnMA), and PBnMA after a temperature jump from (T_c+10) °C to (T_c-10) °C.

As shown in **Fig. S2**, the kinetic recovery order of the transmittance of the phase-separated solutions is P(*cis*-AzoMA-*r*-BnMA) > PBnMA > P(*trans*-AzoMA-*r*-BnMA). The recovery from turbid to transparent of the linear polymer solutions roughly corresponds to the swelling process from the shrunken gels although the swelling-shrinking process of the gels is generally much slower because cross-linking makes collective diffusion of the polymer chain much slower. The redissolution process of P(*trans*-AzoMA-*r*-BnMA) is too slow to reach complete dissolution on a time scale of 1400 min. Solution viscosity does not affect the recovery kinetics because it does not change very much in this temperature range (7.2 mPa·s (83 °C) ~ 5.3 mPa·s (105 °C))^{S1}. Note that the kinetics of the redissolution process of P(*cis*-AzoMA-*r*-BnMA) is much faster than that of PBnMA. This result indicates that the *cis*-

azobenzene structure significantly enhances the rate of redissolution. The exact reason for the observed *speed-up effect* is still unclear; however, it might be related to fast photoisomerization reactions between *cis*- and *trans*-azobenzenes under steady UV light irradiation conditions at a high temperature (99 °C) which continuously perturb the solution. The first-order rate constant of the thermal isomerization reaction from P(*cis*-AzoMA-*r*-BnMA) to P(*trans*-AzoMA-*r*-BnMA) is estimated to be as high as $1.36 \times 10^{-3} \text{ (s}^{-1}\text{)}$ at this temperature according to the previously reported activation energy and frequency factor for P(AzoMA-*r*-BnMA) in [C₂mim][NTf₂].^{S3}

Estimation of average distance between azobenzene moieties

The average distance between AzoMAs in P(*trans*-AzoMA-*r*-BnMA) gel can be estimated from the volume swelling ratios of microgel. With respect to the volume swelling ratio (Fig. 1 in the main text), the radii of the swollen P(*trans*-AzoMA-*r*-BnMA) gel ($D/D_0 = 1.0$, 25 °C) and shrunken P(*trans*-AzoMA-*r*-BnMA) gel ($D/D_0 = 0.45$, 90 °C) were observed as 15 μm and 6.45 μm, respectively. The volumes of both gels are $V_{\text{swollen micro-gel}} = 1.41 \times 10^{-8} \text{ cm}^3$, $V_{\text{shrunken micro-gel}} = 1.12 \times 10^{-9} \text{ cm}^3$. The number of AzoMA per unit volume can be estimated as:

The number of AzoMA in swollen microgel: $3.85 \times 10^{19} \text{ cm}^{-3}$

The number of AzoMA in shrunken microgel: $4.83 \times 10^{20} \text{ cm}^{-3}$

These values correspond to one AzoMA occupying an average spherical volume with a 3.94 nm radius (swollen state) and a 1.70 nm radius (shrunken state), respectively. Given that the distance of both ends of the *trans*-azobenzene molecule is 0.9 nm, these radii appear to be too

long for azobenzenes to stack together, even in the specific shrunken state. Therefore, we speculate that the inter-locking structure involves cation/ π interactions between the imidazolium cation and the *trans*-azobenzene side chains.

References

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