Photoreversible Gelation of a Triblock Copolymer in an Ionic Liquid**

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Abstract: *The reversible micellization and sol–gel transition of block copolymer solutions in an ionic liquid (IL) triggered by a photostimulus is described. The ABA triblock copolymer employed, denoted P(AzoMA-r-NIPAm)-b-PEO-b-P(AzoMA-r-NIPAm)), has a B block composed of an IL-soluble poly(ethylene oxide) (PEO). The A block consists of a random copolymer including thermosensitive N-iso-propylacrylamide (NIPAm) units and a methacrylate with an azobenzene chromophore in the side chain (AzoMA). A phototriggered reversible unimer-to-micelle transition of a dilute ABA triblock copolymer (1 wt %) was observed in an IL, 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆), at an intermediate "bistable" temperature (50°C). The system underwent a reversible sol–gel transition cycle at the bistable temperature (53°C), with reversible association/fragmentation of the polymer network resulting from the phototriggered self-assembly of the ABA triblock copolymer (20 wt %) in [C₄mim]PF₆.*

Ion gels are composed of ionic liquids (ILs) immobilized within a three-dimensional molecular network. Such gels preserve the attractive physicochemical properties of ILs, such as nonvolatility, thermal stability, electrochemical stability, and high ionic conductivity,[1–4] while maintaining a soft solid consistency. Ion gels are a novel platform for many applications, and are currently being designed, for example, as electrolyte membranes,[5–7] actuators,[8,9] gas-separation membranes,[10–12] catalyst support membranes,[13] flexible electrochemiluminescent gels,[14] and as gate dielectrics in organic thin-film transistors.[15–17] Although the synthesis of ion-gel materials can be accomplished through several methods, including monomer chemical crosslinking,[5–7] low-molecular-weight gelation agents,[18,19] nanoparticle dispersions,[20] and liquid crystals,[21] the use of insoluble or thermosensitive block polymer domain formation to act as crosslinking points in ILs

is particularly attractive.[8,22–24] In developing ion gels for practical use, a liquid–solid transition aided by a straightforward physical trigger is highly desirable, with a view to patterning and membrane fabrication. Photorheology measures light-induced macroscopic viscoelastic property changes in soft materials and is a particularly appealing concept to employ in the fabrication of soft materials.[25] The applied stimulus can be easily controlled, that is, specific sample regions can be irradiated with selected wavelengths and intensities can be controlled in a contactless manner. Although sol–gel transitions with supramolecular-assembly structure changes induced by a photochromic reaction have been reported,[26–32] reversible sol–gel transitions based on changes in a self-assembled block copolymer structure induced by photostimuli have not been reported, either in aqueous or organic solvent media.

In this Communication, we describe the design, preparation, and characterization of photoreversible micellization and gelation processes of a photosensitive ABA triblock copolymer in an IL (Figure 1a). The ABA triblock copolymer contains an IL-soluble poly(ethylene oxide) (PEO) middle block. The end blocks of the copolymer are thermo- and photosensitive random copolymers of 4-phenylazophenyl methacrylate (AzoMA), containing a pendant azobenzene chromophore, and *N*-isopropylacrylamide (NIPAm). PNIPAm is an established thermosensitive polymer, showing LCST-type phase transitions in aqueous media (LCST = lower critical solution temperature), but exhibiting UCST-type phase transitions in certain hydrophobic ILs (UCST = upper critical solution temperature).[1,2,4,33–39] This ABA triblock copolymer shows reversible "upper critical" micellization and gelation in response to temperature in a typical hydrophobic IL, such as 1-butyl-3-methylimidazolium hexafluorophosphate ([C₄mim]PF₆). Moreover, high ionic conductivity of the gel resulting from the IL is demonstrated. As

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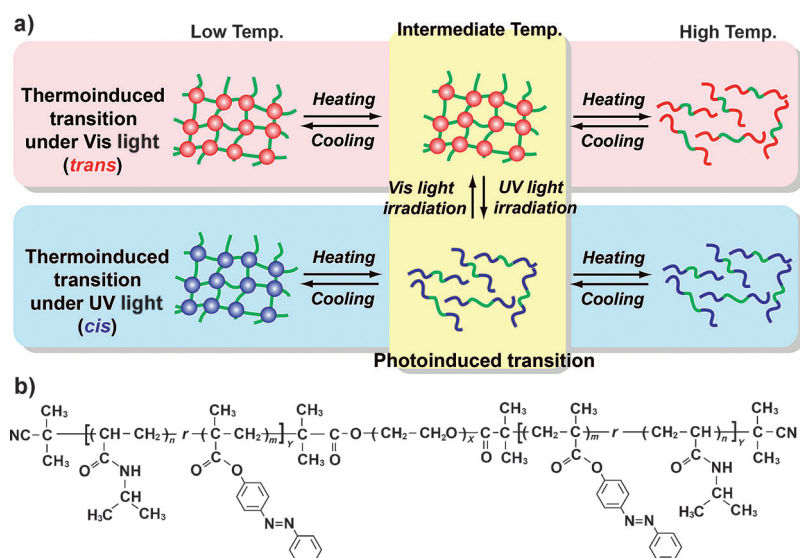[+] These authors contributed equally to this work.

Figure 1. a) Schematic representation of photoreversible ion gels, and b) chemical structure of the ABA triblock copolymer.

a contactless photostimulus is highly desirable for nano-patterning, the method revealed herein could be particularly useful for many applications that require functional ion gels.

The target ABA triblock copolymers (ABA-1 and ABA-2) were prepared by reversible addition–fragmentation chain-transfer (RAFT) random copolymerization of NIPAm and AzoMA from a PEO-based, telechelic macro-CTA (Figure 1 b; CTA = chain-transfer agent). Detailed preparation and characterization of the block copolymers are summarized in Figures S1–S3 in the Supporting Information. ABA-1 and ABA-2 were prepared to evaluate their reversible micellization and gelation properties, respectively. (ABA-1: 23.0–35.0–23.0 (kDa), $M_w/M_n = 1.41$, and [AzoMA]/[NIPAm] = 7.5/92.5. ABA-2: 15.0–35.0–15.0 (kDa), $M_w/M_n = 1.41$, and [AzoMA]/[NIPAm] = 10.4/89.6. M_n and M_w are number and weight average molecular weights, respectively. Molecular weights of each block are indicated by M_n). The temperature dependence of the mean hydrodynamic radius (R_h) of the ABA-1 (1 wt%) in [C$_4$mim]PF$_6$ was evaluated by means of dynamic light scattering (DLS; Figure S4 and S5). At higher temperatures than the aggregation temperature, that is, above the upper critical micelle temperature (UCMT), the R_h value was below 10 nm, consistent with individual ABA-1 polymer chains with a total molecular weight of 81 kDa.

Under dark conditions, the photochromic state of azobenzene is entirely the ground *trans* state, whereas under irradiation with UV light ($\lambda = 366$ nm, 8 mW cm^{-2}), the primary isomer was the *cis* state (85%). During a cooling process that started at 70 °C, the mean R_h value increases with decreasing sample temperature because of the UCST nature of the terminal P(AzoMA-*r*-NIPAm) segments,[38,39] suggesting that the triblock copolymers self-assemble predominantly into "flower-like" micelles.[40] Importantly, a wide interval, as large as 16 °C, was measured between the UCMTs of *trans*- and *cis*-ABA-1 triblock copolymers (*trans*: 60 °C; *cis*: 44 °C). The significantly higher polarity of the *cis* polymer results in more favorable solvation in the IL. A reversible unimer–

micelle transition induced by light stimuli was realized by utilizing this temperature difference. After holding the ABA-1 triblock copolymer at a bistable temperature (50 °C) under irradiation with UV light, the sample solution was subjected to visible (Vis) light irradiation ($\lambda = 437$ nm, 4 mW cm^{-2}) at time $t = 0$ s to form the *trans* polymer. As evidenced in Figure 2, it is clear that photoinduced self-assembly of the ABA-1 triblock copolymer at a constant (bistable) temperature was successfully realized. The average micellar size generated by the photoinduced transition was almost the same as the size formed under a temperature-induced transition of the ABA-1 triblock copolymer (≈ 120 nm; Figure S5 a). Following a 150 s induction time after initiating the irradiation under visible light, the scattering intensity monotonically increased until approximately 2000 s, whereas the average
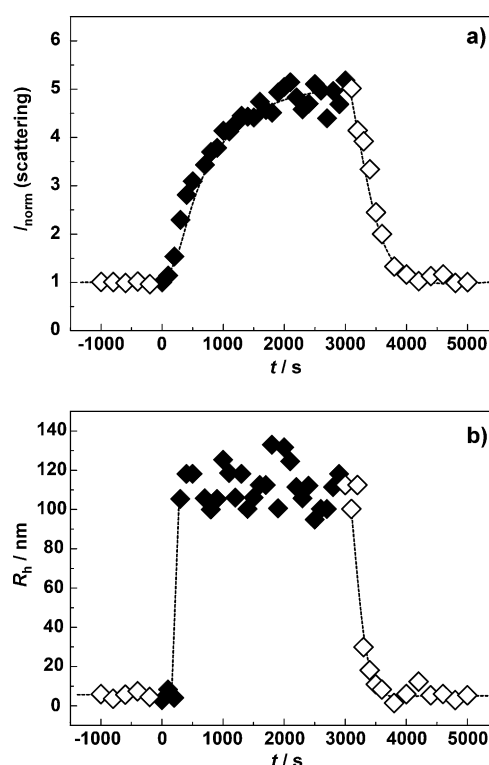

Figure 2. Reversible photoinduced self-assembly and dissociation of ABA-1 triblock copolymer micelles at 50 °C under irradiation with UV light (open diamonds) or visible light (closed diamonds). a) Normalized scattering intensity and b) mean R_h values plotted as functions of time.

R_h value exhibited a more abrupt increase. Early in the aggregation process, there are many unimers and a few relatively large aggregates (micelles). The scattering intensity depends strongly on the size of the particle; once the aggregation of small particles starts, the DLS signal is heavily weighted by the larger component.[41] Thus, the scattering

intensity increasing from 0 to 150 s is roughly proportional to the increase in the number of micelles. The aggregation process appeared to be complete after approximately 2000 s.

We further confirmed the reversibility of this photo-induced unimer–micelle transition. After formation of micelles triggered by visible-light illumination at a constant temperature, UV light was used at $t = 3000$ s to generate the *cis* polymer. As expected, both the scattering intensity and the R_h value decreased, indicating the breakup of micelles into individual single polymer chains, owing to the fact that the aggregation temperature of the *cis*-ABA-1 triblock copolymer was lower than the measurement temperature. Not surprisingly, the de-micellization process is more rapid than micellization, as less polymer diffusion is required. It is also interesting that the photochromic state of azobenzene in the ABA-1 triblock copolymer strongly influenced the micelle size; the self-assembled structure formed using the *trans*-ABA-1 triblock copolymer exhibited a mean R_h value of over 100 nm with a wide distribution, whereas that derived from *cis* micelles was approximately 40 nm with a narrower distribution. Inverse Laplace transformation of the correlation functions using CONTIN (continuous distribution) analyses[42,43] for the distribution function for each photochromic state, and direct observation using cryo-TEM, suggests that *trans* polymers aggregate to form a mixture of a number of small spherical micelles with a small quantity of larger aggregates of spherical micelles. This presumably comes from bridging of copolymer chains between micelles, whereas more narrowly distributed spherical micelles can be formed from the *cis* polymer (Figure S6 and S7). We could not carry out cryo-TEM measurements of the *cis* polymer because of the experimental limitation that the sample should be continuously irradiated under UV light during the sample preparation procedure as well as during imaging. In the case of *cis* polymer micelles, the sphere-to-micelle-cluster structural transition did not occur under irradiation with UV light at 30 °C for at least 3600 s. The fact that this transition did not occur is perhaps because of slow structural transition kinetics of the micelles compared to the kinetics of the micelle-formation process (Figure S8). Grubbs et al. and Zhuo and co-workers previously investigated the thermosensitive structural transition of micelles in aqueous solution using a combination of direct observation and light-scattering techniques.[44,45] Very sluggish sphere-to-vesicle transitions that continue to evolve over several days were reported. Thus, for kinetic reasons, the structural transition could not be detected under the present experimental conditions.

Figure 3 shows the storage (G') and loss (G'') moduli of a 20 wt% ABA-2 triblock copolymer solution in [C$_4$mim]PF$_6$ under irradiation with visible or UV light. In both azobenzene photochromic states, the value of G' exceeded that of G'' at lower temperatures (below the aggregation temperature), indicating that the polymer was in a quasi-solid gel phase. In contrast, the G'' value was greater than G' in the high temperature region, indicative of the liquid state. The aggregation temperature for 20 wt% polymer in [C$_4$mim]PF$_6$ was confirmed to be lower than that for dilute (1 wt%) solution. This tendency is related to the molecular weight of the A segments. The molecular-weight dependence
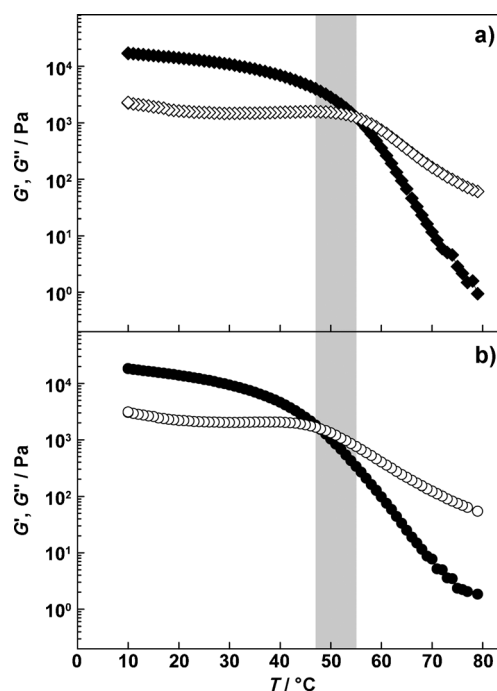

Figure 3. Variation of dynamic storage (G', solid symbols) and loss (G'', open symbols) moduli of the ABA-2 solution (20 wt%) in [C$_4$mim]PF$_6$ as a function of temperature at frequency $\omega = 6.28$ rad s^{-1} and strain amplitude $\gamma = 1$% under irradiation with a) visible and b) UV light.

of the cloud points for PNIPAm/IL composites was also in agreement with this result.[36] A detailed thermodynamic study on the UCST phase transition of PNIPAm in ILs by means of highly sensitive differential scanning calorimetry (DSC) measurements, recently established for the measurement of LCST polymers in ILs,[46] will be reported elsewhere. The results confirmed the formation of a three-dimensional polymer network through physical crosslinking points that consist of the thermosensitive A segments at lower temperatures. This network reversibly melts inside the polymer/IL composite upon increasing the temperature, resulting in a viscous liquid at higher temperatures.

Strain-dependent measurements of the ABA-2 triblock copolymer solution showed that G' and G'' values were not strain dependent in the range $\gamma = 0.01$–10% in the gel (at 10 °C; Figure S9). Frequency-sweep measurements at 10 °C revealed that G' values of the 20 wt% *trans* form ABA-2 solution was consistently higher than G'' and independent of frequency. At higher temperatures (80 °C), G' was smaller than G'', with $G' \approx \omega^2$ and $G'' \approx \omega$, indicating the rheological characteristics of a viscous liquid. Under dark conditions at 58 °C, the rheology of *trans*-ABA-2 triblock copolymer solutions at lower frequency ($\omega \approx 1$ rad s^{-1}) tended to resemble that of the liquid state. In contrast, at higher frequencies (> 1 rad s^{-1}), the solution showed an intermediate state between sol and gel, where G' and G'' had almost the same values with a similar dependence ($G' \approx G'' \approx \omega^{0.5}$). The data measured at 58 °C corresponded to a liquid–solid phase transition, generally defined as the gelation point (T_{gel}; Figure S10).[47,48] Importantly, a difference of 8 °C between

the T_{gel} values of the *trans* form ($T_{gel} = 56\,°C$) and the *cis* form ($T_{gel} = 48\,°C$) polymers was measured.

We thus demonstrated a photoinduced sol–gel transition cycle at a bistable temperature by irradiating the ion gel repeatedly with UV and visible light. Figure 4 shows the reversible sol–gel transition cycle of an ABA-2 triblock
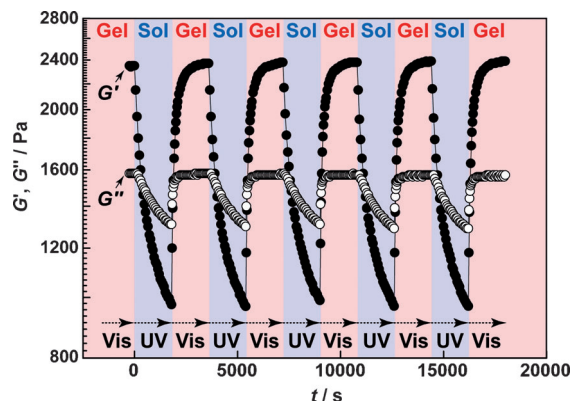

Figure 4. Reversible sol–gel transition cycle of the ABA-2 triblock copolymer (20 wt%) in [C$_4$mim]PF$_6$ by alternately switching between UV and visible-light irradiation at 53°C. Period of UV and visible-light irradiation indicated by arrows.

copolymer solution (20 wt%) under irradiation with UV light at a bistable temperature of 53°C. The sample was kept at 53°C under irradiation with visible light prior to the measurements to form the *trans* gel, followed by irradiating the sample with UV light at $t = 0$. The G' value dropped dramatically upon exposure to UV light, and dropped below the G'' value within 200 s. The UV light was then switched back to the visible light again at $t = 1800$ s and the G' value suddenly recovered to a value greater than the G'' value indicating reversible gelation. Photoinduced sol–gel transition cycles are clearly observed with good reversibility. The terminal A segments of the ABA-2 triblock copolymer change their solubility in [C$_4$mim]PF$_6$ under light illumination by the photoisomerization reaction of azobenzene in the triblock copolymer, resulting in the formation/breakup of a self-assembled structure corresponding to irradiation with light. The results indicate that the polymer network composed of photosensitive physical crosslinking points formed inside the composites can melt and rebuild rapidly under light irradiation, inducing a sol–gel transition. Moreover, this material maintains a stable sol–gel transition behavior without solvent evaporation even after light exposure at 53°C for at least 18 000 s (5 h). The G' value after 5 cycles of sol–gel transition is also found to be constant. Percolation theory predicts that the network modulus is proportional to kT per network strand,[49] that is, $G' \approx nkT$, where n is the number density of network strands inside the correlation volume and k and T are the Boltzmann constant and the absolute temperature, respectively. From this relation, the value of n before and after the sol–gel transition cycle are estimated to be $5.2 \times 10^{23}\ m^{-3}$, and $5.3 \times 10^{23}\ m^{-3}$, respectively. Keeping the value of n constant, the G' value confirms an efficient reversibility

of the formation/breakup of the network strands during photoswitching cycles.

Figure 5 demonstrates that the resulting photoreversible ion gels display high ion conductivity, comparable to neat [C$_4$mim]PF$_6$. Although several classes of soft material have been proposed to induce microscopic structural changes by

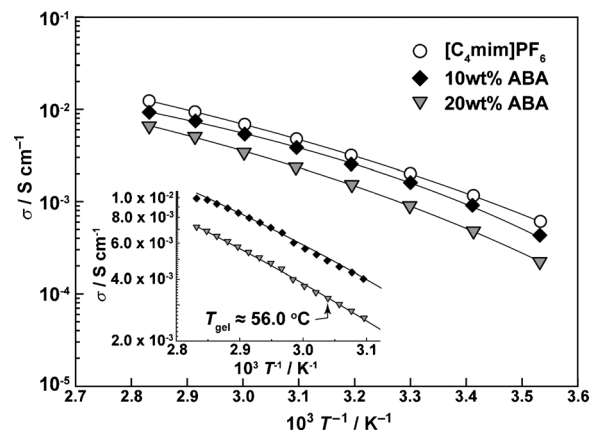**Figure 5.** Temperature dependence of the ionic conductivity (σ) for neat [C$_4$mim]PF$_6$ and two ion-gels with 10 and 20 wt% ABA-2 triblock copolymer. Inset shows magnified view of the relationship between ionic conductivity of ion gels around sol-gel transition temperature.

photorheology, the resulting solution or gels were not designed to exhibit specific function. In contrast, this photoprocessible polymer network swollen with a functional IL is promising from the perspective of designable soft materials, such as gate dielectrics, actuators, and electrochromic gels. A large change in the ionic conductivity upon the sol–gel transition is not detected (Figure 5, inset). The absence of a change suggests that the ion transport in an ion gel is not significantly affected by the macroscopic states (either sol or gel) and is almost independent of translational motion of the polymers. This observation is consistent with the earlier report that the ionic conductivity of the ion gels is predictable from an obstruction model,[50] where the existence of the polymer network only blocks the pathway of solute transport without changing the mobility.[6,23]

In this Communication, we present the reversible manipulation of a macroscopic physical change in the state of a block copolymer solution by a phototriggered change in the microscopic self-assembled structure. Furthermore, the IL medium is advantageous in terms of its nonvolatility, nonflammability, electrochemical stability, and high ionic conductivity. The photostimulus can be directly applied to the object in a contactless manner, easily controlled (on–off switching), and localized. These results are therefore of interest not only for the fundamental science of photosensitive self-assemblies of block copolymers, but also for processing IL materials to develop solid thin-film and nanopatterning applications.

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