

Direct observation of photo-induced reversible sol-gel transition in block copolymer self-assembly containing an azobenzene ionic liquid

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Abstract: Using atomic force microscopy, we directly observed the photo-induced reversible changes in a block copolymer self-assembly containing an azobenzene ionic liquid, which underwent sol-gel transition. This is the first report on the sol-gel transition of an ABA-type block copolymer consisting of upper critical solution temperature (UCST)-type A blocks in a photoresponsive ionic liquid mixture. The sol-gel transition was accompanied by an order-to-disorder structural change, which subsequently induced a change in the ionic conductivity. Surprisingly, the photo-induced ionic conductivity and rheological changes occurred rapidly (~30 s) despite the dense (~80 wt%) polymeric system. The rapid structural change was probably attributable to the fast diffusion of the ionic liquid.

Cross-linked PNIPAm aggregates at a temperature higher than the critical temperature (T_c), which results in shrinkage of the polymer.^[2] An ABA-type triblock copolymer having PNIPAm as the A block exhibits sol-gel transition by the self-assembly/disassembly of PNIPAm.^[3] The gel state is attained at a higher temperature—the PNIPAm segments aggregate to form cross-linked points at a high temperature, while the compatible B segments form a polymer network. It returns to the sol state when the temperature is lowered. These smart gels are mainly used in drug delivery systems and tissue culturing.^[4]

We focused our attention to room temperature ionic liquids (ILs) as neoteric solvents for polymers and found that certain polymers exhibited varying solubilities in ILs in the temperature range of interest, including completely compatible behaviour, upper critical solution temperature (UCST) behaviour, lower critical solution temperature (LCST) behaviour, and completely incompatible behaviour.^[5] For instance, PNIPAm exhibits UCST-phase behaviour in certain ILs,^[6] although it exhibits LCST-phase behaviour in aqueous media, and poly(ethylene oxide) (PEO) is compatible with many ILs. A unique feature of the UCST and LCST phase transitions is the drastic change in the phase transition temperature by a small change in the macromolecular and IL structures.^[7] This is due to the fact that the phase transitions in IL are governed by the extremely low magnitudes of the mixing enthalpy and entropy changes, compared with the changes in aqueous media, and by a subtle balance between them.

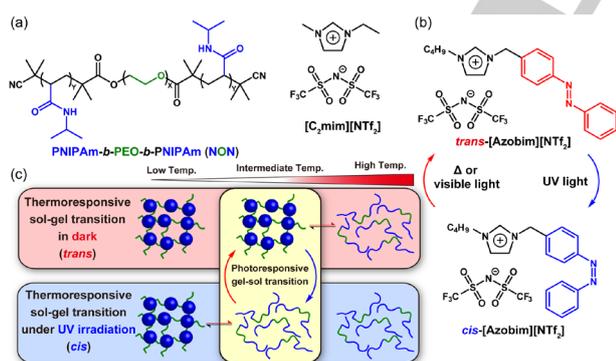


Figure 1. (a) Chemical structures of PNIPAm-*b*-PEO-*b*-PNIPAm (NON) and [C₂mim][NTf₂]. (b) *trans*-*cis* isomerisation of [Azobim][NTf₂]. (c) Schematic of the photoresponsive sol-gel transition of the ion gel.

Smart gel materials undergo drastic changes in their mechanical properties, shapes (swelling ratios), or sol/gel state under external stimuli and have attracted considerable attention from researchers.^[1] A thermoresponsive gel is a typical smart gel. Poly(*N*-isopropyl acrylamide) (PNIPAm), which is a typical thermoresponsive polymer, exhibits a lower critical solution temperature (LCST)-type phase behaviour (i.e., miscible at low temperatures and immiscible at high temperatures) in water.

PNIPAm-*b*-poly(ethylene oxide)-*b*-PNIPAm (NON, **Figure 1(a)**, left) is an ABA-type block copolymer of PNIPAm (UCST block) and PEO (compatible block) and undergoes sol-gel transition in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C₂mim][NTf₂], **Figure 1(a)**, right) with decreasing temperature. This transformation is induced by the UCST-type solubility transition of the A block.^[8] The gel materials comprising IL, viz. ion gels, have intrinsic unique characteristics to ILs like negligible volatility, low flammability, good thermal and chemical stabilities, and high ionic

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conductivity.^[5, 9] Thus, they can be used as thermoplastic, flexible and ion-conducting materials for electrochemical devices.^[10]

We previously bestowed photoresponsiveness to NON by introducing an azobenzene moiety to the A block by random copolymerisation.^[11] Azobenzene undergoes *trans*-to-*cis* photoisomerisation upon UV irradiation, and the better compatibility of *cis* azobenzene decreases the UCST of the A block. The decreased UCST of the A block upon UV irradiation results in the photoresponsive sol-gel transition at a certain temperature. The ion gel exhibits photo-healing ability by the virtue of the spatiotemporal sol-gel transition upon UV irradiation.^[11] Using small-angle X-ray scattering (SAXS), Lodge et al.^[12] demonstrated that the sol-gel transition of photoresponsive ABA-type block copolymer was correlated to the order-disorder transition.

Recently, we showed that the introduction of an azobenzene moiety to the imidazolium cation of an IL ([Azobim][NTf₂]; **Figure 1(b)**) instead of the polymer could also bestow photoresponsiveness to the ABA-type thermoresponsive triblock copolymer.^[13] The photoresponsiveness was triggered by the isomerisation of [Azobim][NTf₂], and the solubility of the LCST-type poly(benzyl methacrylate) polymer, which was employed as the A block, drastically changed.

In this study, we combined NON, [Azobim][NTf₂], and [C₂mim][NTf₂] (**Figure 1(a, b)**) to form a photoresponsive ion gel. This is the first report on the sol-gel transition of an ABA-type block copolymer consisting of UCST-type A blocks in the photoresponsive IL gel (**Figure 1(c)**). To date, only the macroscopic changes in mechanical properties owing to structural transitions during the block copolymer self-assembly have been observed;^[12] however, there are no studies on the direct observation of the real time microscopic structural changes. In this study, we visualized the microphase-separated structural changes induced by external stimuli using atomic force microscopy (AFM) and SAXS. Interestingly, rapid changes in the rheological properties and ionic conductivity were observed upon the UV-induced sol-gel transition. To elucidate the mechanism at a molecular level, we investigated how the change in the microphase-separated structure and its dynamics afforded the changes in the polymer properties.

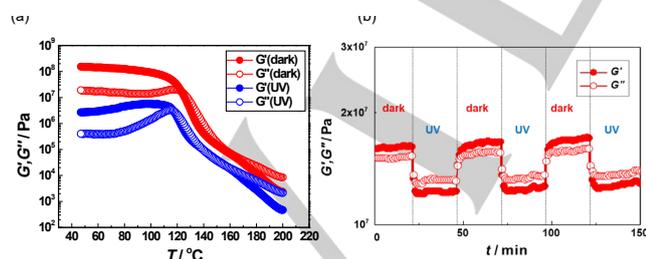


Figure 2. (a) Temperature sweep measurements of storage and loss moduli (G' and G'' , respectively) under dark conditions and upon UV irradiation. (b) Time sweep measurements of G' and G'' at 116 °C. Material: 80 wt% NON/4 wt% [Azobim][NTf₂]/16 wt% [C₂mim][NTf₂].

The IL, [C₂mim][NTf₂], was synthesized and dried prior to use.^[14] ABA-type triblock copolymer, NON, was synthesized by reversible addition-fragmentation chain transfer (RAFT)

polymerisation. The experimental methods, including details on the syntheses of [Azobim][NTf₂] and NON, are described in the Supporting Information. We first conducted rheological measurements to investigate the effect of UV irradiation on the mechanical properties.

Figure 2(a) shows the temperature-dependent change in the elastic modulus during the cooling of a mixture containing 80 wt% NON, 4 wt% [Azobim][NTf₂], and 16 wt% [C₂mim][NTf₂]. The red and blue circles indicate the moduli under dark conditions and upon UV irradiation, respectively. In both the systems, a rapid increase in G' and the cross-over of G'' and G' were observed with decreasing temperature; specifically, the crossover was observed at 117 °C upon UV irradiation and 123 °C under dark conditions (**Figure 2(a)**). It is worth noting that only 4 wt% [Azobim][NTf₂] could induce such a remarkable change in the rheological properties. The crossover suggested that the material was in the sol state at high temperatures ($G'' > G'$) and in the gel state at low temperatures ($G' > G''$). This sol-gel transition could be ascribed to the UCST-type phase separation of PNIPAm. A previous report suggests that T_c of PNIPAm in [C₂mim][NTf₂] at low polymer concentrations (< 10 wt%) is ~40 °C.^[6] The polymer concentration in this system (80 wt%) is far higher than this. Since T_c depends on the polymer concentration, the remarkable increase in T_c can be ascribed to the high polymer concentration.

In the intermediate temperature range (6 °C) between the sol-gel transition temperatures under UV and dark conditions, UV irradiation could induce sol-gel transition. The decrease in the moduli was attributed to the *trans*-to-*cis* isomerisation of azobenzene upon UV irradiation, which resulted in a stronger interaction with the polymer. Generally, PNIPAm aggregates via strong hydrogen bonding between N–H and C=O. However, the UV-isomerised azobenzene (*cis*) is highly polar and interacts strongly with the polar part of PNIPAm. Thus, the hydrogen bonds are weakened, and the forces driving the PNIPAm aggregation become small, thereby leading to a decrease in G' . After cooling, the G' value under UV radiation is more than one order of magnitude smaller than that under dark conditions. This indicates that the structural change, i.e., persistent interaction of *cis*-[Azobim][NTf₂] with PNIPAm, was retained after cooling, resulting in reduced G' upon UV irradiation.

We also investigated the effect of [Azobim][NTf₂] concentration (**Figure S3**). At 2 and 10 wt% [Azobim][NTf₂], there was little or almost no change in the moduli. It was concluded that a concentration of 2 wt% was too low to cause any noticeable change. On the other hand, we can estimate penetration length from UV spectra of [Azobim][NTf₂] in [C₂mim][NTf₂] solution (**Figure S9**). The penetration length, where UV intensity drops to 1% of the incident beam, at 10 wt% is only 3.8 μm. Thus, a concentration of 10 wt% was too high to allow the passage of UV light through the material. Note that it is possible that a high degree of stacking and aggregation of nonpolar azobenzene moieties also contributed to the result. Thus, 4 wt% was determined to be the optimal concentration for photoresponsiveness. The [Azobim][NTf₂] sample (4 wt%) was subjected to UV irradiation for ~25 min, following which the UV irradiation was paused (dark) for the next ~25 min. This process was repeated at 116 °C up to 150 min. The change in the dynamic moduli during this procedure is shown in **Figure 2(b)**. The figure demonstrates the reversible changes in G' and G'' when the material is subjected to alternating dark and UV conditions. The

changes in the moduli originate from the gel-to-sol-to-gel transition. The response to UV light was rapid, and G' remained constant until the UV irradiation was paused. In contrast, G' under dark conditions increases gradually, indicating that aggregation (gel formation) is slower than dissolution (sol formation) in this system. Here, it is noteworthy that the thermal relaxation rate from *cis*- to *trans*-state could be high at 117 °C, which can reduce the concentration of *cis*-[Azobim][NTf₂]. We estimated the ratio of *cis*-[Azobim][NTf₂] at 117 °C from UV spectra to be 0.12 (See the Supporting Information), which is significantly smaller than the reported value at room temperature (0.65).^[15] It is reported that azobenzene moiety shows rapid isomerization between *cis*- and *trans*-forms.^[16] Therefore, we speculate that the macroscopic property of the system is affected not only by the effective *cis*-[Azobim][NTf₂] concentration but also by the dynamic isomerization of azobenzene moiety.

Figure S4(a) shows the results of the rheological measurements at different temperatures. No change in the dynamic moduli upon UV irradiation (broken line) was observed at 20 °C. **Figure S4(b)** shows a slight change at 60 °C, but it is not large enough to induce sol-gel transition. This is because the hydrogen bonding in PNIPAm is strong at low temperatures and is not affected by the azobenzene isomerisation upon UV irradiation. This indicates that it is essential to conduct the measurement at around the sol-gel transition temperature to observe any change in the modulus.

Next, we performed AFM to clarify the relationship between the changes in moduli and microphase-separated structures (**Figure 3**). In the AFM phase images, the bright regions correspond to soft parts and the dark regions correspond to hard parts. For the ion gel, the bright regions correspond to the ionic conduction phases consisting of PEO and the IL mixture, while the dark regions correspond to the aggregation phase consisting of PNIPAm. Two kinds of samples were prepared in this study—one was irradiated with UV for one day and the other was not irradiated at all. The samples were kept at 117 °C and their structures were frozen in liquid nitrogen. The measurement was performed at room temperature. A significant structural change was observed upon UV irradiation. Before UV irradiation (left), the microstructures were clearly phase-separated, and spherical soft domains were formed. However, after UV irradiation, the phase-

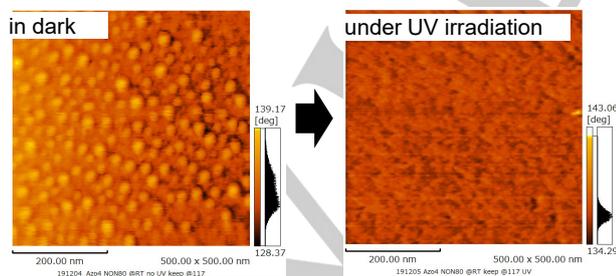


Figure 3. AFM phase images of the NON/[Azobim][NTf₂]/[C₂mim][NTf₂] mixture (weight ratio: 80:4:16) before and after UV irradiation for one day at 117 °C.

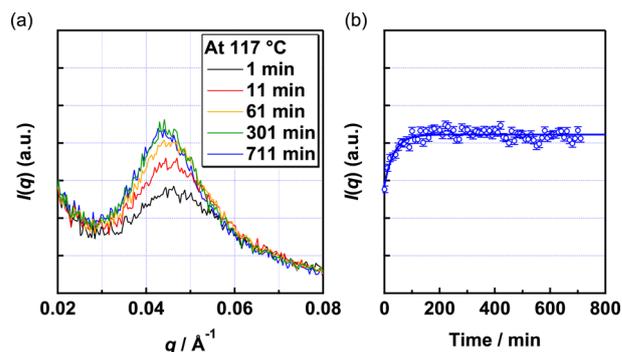


Figure 4. (a) Time evolution of the SAXS profiles of NON/[Azobim][NTf₂]/[C₂mim][NTf₂] (weight ratio: 80:4:16) at 117 °C immediately after changing the UV conditions to dark conditions. (b) Plot of the scattering intensity at 0.045 Å⁻¹ as a function of time. The data were fitted to a simple single exponential function ($I(q) = A \exp(-t/\tau)$).

separated structures disappeared, indicating the mixing of the two phases due to the swelling of the PNIPAm block at 117 °C upon UV irradiation. Under dark conditions, the soft conduction phase was isolated, whereas upon UV irradiation, the paths were connected. This influenced the ionic conductivity of the gel, as discussed later.

We also observed the structural change using SAXS. **Figure S5** shows the temperature-dependent SAXS profile under dark conditions. The broad peak at 0.045 Å⁻¹ indicated the phase separation of 14-nm size in the ion gel. There was no periodic peak due to the large size distribution of the sphere, as shown in **Figure 3**. It is also plausible that the PNIPAm segment is not completely isolated from the IL, resulting in the broad peak. The decrease in peak intensity with increasing temperature indicated the partial swelling of the PNIPAm block due to the UCST behaviour. For the SAXS experiments, we irradiated UV light on the ion gel (thickness: 0.1 mm) at 117 °C for 90 min and then switched it off. The time evolution of the SAXS profiles during the thermal relaxation of the structure due to the transformation of [Azobim][NTf₂] from the *cis*-form to *trans*-form in the dark was observed (**Figure 4(a)**). Although no remarkable structural transition, such as the disappearance of a peak, was observed upon UV irradiation in the SAXS measurement, the peak intensity increased with the progress of thermal relaxation, and the peak maximum shifted to lower q values. This indicated that the phase separation was not distinct under UV irradiation, and the characteristics separation length increased during the dark recovery, which is consistent with the AFM images. The time constant of the structural change, τ , was estimated from the equation $I(q) = A \exp(-t/\tau)$, where A is constant, t is the time, and τ is the characteristics time of transition. The τ value was estimated to be 32 min, which is in the same order as that obtained by the rheological measurements during the sol-gel transition. Thus, we concluded that the change in the mechanical properties is correlated to the change in the microstructure.

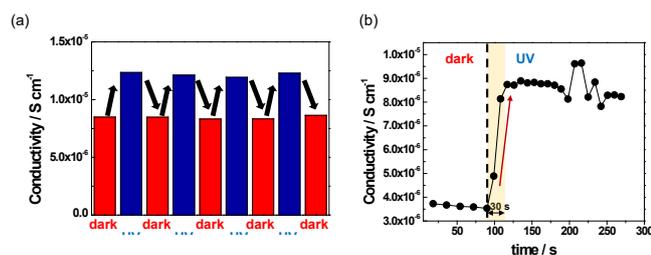


Figure 5. (a) Change in ionic conductivity and (b) time evolution of the ionic conductivity of the NON/[Azobim][NTf₂]/[C₂mim][NTf₂] ion gel upon UV irradiation.

Finally, the correlation between the structural change and ionic conductivity was investigated. The variation in ionic conductivities is shown in **Figure 5(a)**. We repeatedly measured the ionic conductivity at 117 °C, first under dark conditions and then upon UV irradiation. The ionic conductivity increased upon UV irradiation and then decreased again under dark conditions; this highly reversible change in the ionic conductivity was maintained for at least four cycles. This was due to the structural change caused by the UV irradiation and the linking of the conduction paths. **Figures S7(a)** and **(b)** show the ionic conductivity of the [Azobim][NTf₂]/[C₂mim][NTf₂] IL mixture (weight ratio: 4:96) at 117 °C and the NON/[Azobim][NTf₂]/[C₂mim][NTf₂] ion gel (weight ratio: 80:4:16) at 150 °C. These systems did not undergo any morphological changes and exhibited no change upon UV irradiation, suggesting that the phase-separated structural change is a critical factor in modulating the ionic conductivity. However, the ionic conductivity under dark conditions is rather high and of the order of 10⁻⁶ S cm⁻¹. If the phase-separated structure shown in **Figure 3(a)** is distinct, i.e., continuous PNIPAm without the IL mixture and isolated spherical PEO domains with the dissolved IL mixture, the conductivity in the dark should be much lower. However, as suggested by the SAXS measurements, the PNIPAm segment is not completely isolated from the IL mixture; it dissolves the IL to some extent, especially around the sol-gel transition temperature.

Figure 5(b) shows the time dependence of the ionic conductivity. Immediately after UV irradiation, the ionic conductivity rapidly increased and attained saturation in 30 s, similar to the variation in the rheological properties. This indicated that the structural change in ion-path was complete in 30 s. In this system, the polymer concentration was remarkably high (~80 wt%). This could result in a low diffusion rate of the polymer. In the previously reported ion gel systems, the time scale of the transition was generally large (over 10 min).^[12, 17] Thus, the time scale of the change in the ionic conductivity is too small compared to the diffusion rate of the polymer. The rapid response implies that the sol-gel transition is mainly induced by the diffusion of the cation or anions (solvents) and not by that of the polymer. We measured the self-diffusion coefficients of the IL using pulsed-field-gradient (PFG)-NMR spectroscopy. The experimental details are available in our previous reports^[12, 17]. The measurement was performed on the PEO/[C₂mim][NTf₂] solution, which has the same composition as that of the soft segment of the ion gel at 117 °C. The measured self-diffusion coefficients were 6.50 × 10⁻⁷ cm² s⁻¹ (cation) and 2.94 × 10⁻⁶ cm² s⁻¹ (anion). Considering the three-dimensional random walk model for ionic diffusion, the

average diffusion length (l) can be obtained from the relation $l = (6Dt)^{0.5}$, where D and t are the diffusivity and diffusion time, respectively. The ionic diffusion length in the 30-s window was calculated to be 108 μm (cation) and 230 μm (anion). These values are much higher than the aggregate size obtained by AFM analysis (< 100 nm). Of course, for the gel-to-sol transition (**Figure 3**) to be mainly driven by the diffusion of the ions, the IL ions must swell and penetrate the PNIPAm segments. However, the fast ion diffusion and the moderate swelling of PNIPAm in the IL mixture induce the morphological changes within 30 s. The fast diffusion of IL also distributes *cis*-[Azobim][NTf₂] throughout the sample even with the low penetration length (9.5 μm, see Supporting Information). Thus, we concluded that the fast diffusion of the IL induced the rapid modulation of the mechanical and ion transport properties.

In summary, ion gels undergoing sol-gel transition upon UV irradiation have been successfully prepared from UCST-type block copolymer and photoresponsive IL. The microphase-separated structure was directly observed by AFM, and the phase separation structure was found to change with the sol-gel transition. The ionic conductivity increased two-fold due to the structural change. Immediately after the start of the UV irradiation, the ionic conductivity rapidly increased and attained saturation in 30 s, similar to the variation in the rheological properties. Even at a high polymer concentration, the fast diffusion of the IL induced the structural change. For the first time, we have directly observed the photo-induced reversible changes in a block copolymer self-assembly containing an azobenzene IL.

Acknowledgements

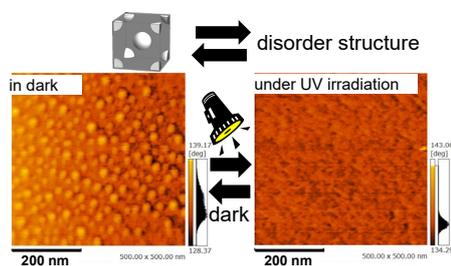
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Keywords: block copolymer • ionic liquid • microphase-separated structure • sol-gel transition • AFM • photoresponsiveness

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Using atomic force microscopy, we directly observed the photo-induced reversible changes in a block copolymer self-assembly containing an azobenzene ionic liquid that underwent sol-gel transition. The sol-gel transition was accompanied by an order-to-disorder structural change, leading to an alteration of the ionic conductivity. Surprisingly, the photo-induced ionic conductivity and rheological changes were rapid (~ 30 s).