

Supporting information

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

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Experimental section

1. Materials

Poly(ethylene oxide) (PEO; number-average molecular weight, $M_n = 4.6$ kDa) was purchased from Aldrich (USA), dissolved in toluene, and dried under reduced pressure at 50 °C to remove water prior to use. A chain transfer agent (CTA), viz. 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid, was purchased from Aldrich (USA) and used without further purification. *N*-Isopropyl acrylamide (NIPAm) was purchased from Wako Chemicals (Japan) and purified by repetitive recrystallization using toluene as a good solvent and hexane as a poor solvent. A radical initiator, viz. 2,2'-azobis(isobutyronitrile) (AIBN), was purchased from Wako Chemicals (Japan) and purified by repetitive recrystallization using methanol as the solvent. Dichloromethane, toluene, tetrahydrofuran (THF), hexane, and 1,4-dioxane (super dehydrated) were purchased from Wako Chemicals (Japan). Oxalyl chloride was purchased from Tokyo Chemical Industry (Japan). These reagents were used without further purification.

2. Synthesis

2.1. Synthesis of PEO-CTA bifunctional macroinitiator

CTA (2.75 g, 7.52 mmol) and oxalyl chloride (0.97 mL, 12.7 mmol) were dissolved in dichloromethane (40 mL) in an Ar-filled flask. The solution was stirred at 30 °C for 2 h. Following this, CO₂ gas and solvent were removed from the mixture under reduced pressure, and a solution of PEO (4.6 kDa, 3.47 g, 0.753 mmol) in dichloromethane (12 mL) was added to the residue. The solution was stirred at 30 °C for 12 h. The reaction mixture was precipitated in excess hexane, and the resulting polymer was collected by filtration. The polymer was purified by repetitive precipitation using THF (good solvent)

and hexane (poor solvent) and dried overnight under vacuum at 40 °C. The purified PEO-CTA macroinitiator was obtained as a pale yellow powder.

2.2. Synthesis of ABA-type triblock copolymer

The synthesized PEO-CTA macroinitiator (4.6 kDa, 0.75 g, 0.163 mmol) and NIPAm (7.5 g, 66.2 mmol) were put in an Ar-filled flask. Then, AIBN/1,4-dioxane solution (15 mg/30 mL), from which dissolved oxygen was removed by Ar bubbling, was poured into the flask. The polymerization reaction was conducted at 70 °C for 20 h with stirring. Subsequently, the reaction was quenched using liquid nitrogen and exposed to air. The polymer was then purified by precipitation in excess diethyl ether and collected by filtration. The polymer was purified by repetitive precipitation using THF (good solvent) and diethyl ether (poor solvent) and dried overnight under vacuum at 40 °C. The purified CTA-PNIPAm-*b*-PEO-*b*-PNIPAm-CTA mixture was obtained as a pale yellow powder. CTA was removed by the reaction with excess AIBN in 1,4-dioxane at 80 °C for one day. Then, the polymer was purified by precipitation again and dried overnight under vacuum at 40 °C. The purified PNIPAm-*b*-PEO-*b*-PNIPAm mixture was obtained as a white powder. **Figure S1** shows the ¹H NMR spectra of PNIPAm-*b*-PEO-*b*-PNIPAm. **Table S1** shows the M_n , polydispersity index (PDI), and volume fraction of the PNIPAm block (f_{PNIPAm}) of NON.

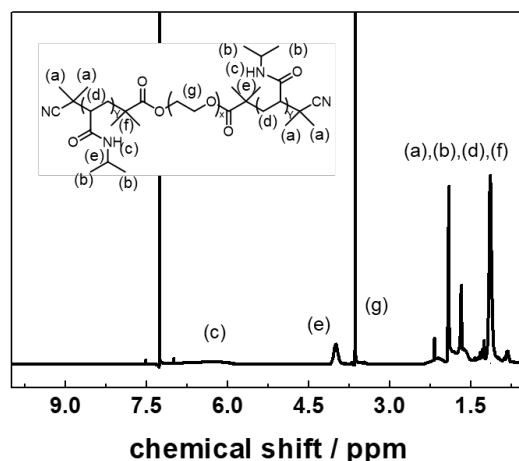


Figure S1 ¹H NMR spectra of PNIPAm-*b*-PEO-*b*-PNIPAm in CDCl₃.

Table S1 M_n , PDI, and f_{PNIPAm} of NON.

Polymer	M_n (PNIPAm- <i>b</i> -PEO- <i>b</i> -PNIPAm) / kDa ¹⁾	PDI ²⁾	f_{PNIPAm} (%) ³⁾
NON	21.5-4.6-21.5	1.25	92.1

1) Calculated from conversion.

2) Calculated from GPC curves.

3) Calculated from the density of PNIPAm and PEO.

2.3. Synthesis of [Azobim][NTf₂]

[Azobim][NTf₂] was synthesized and dried prior to use, according to a previously reported method.^[S1] **Figure S2** shows the ¹H NMR spectra of [Azobim][NTf₂]. ¹H NMR (500 MHz, CDCl₃): δ 9.30 (s, 1H), 7.87 (d, 4H), 7.69-7.66 (m, 2H), 7.45-7.52 (m, 4H), 7.34 (s, 1H), 5.45 (s, 2H), 4.10 (s, 2H), 1.85-1.30 (m, 4H), 0.89 (s, 3H).

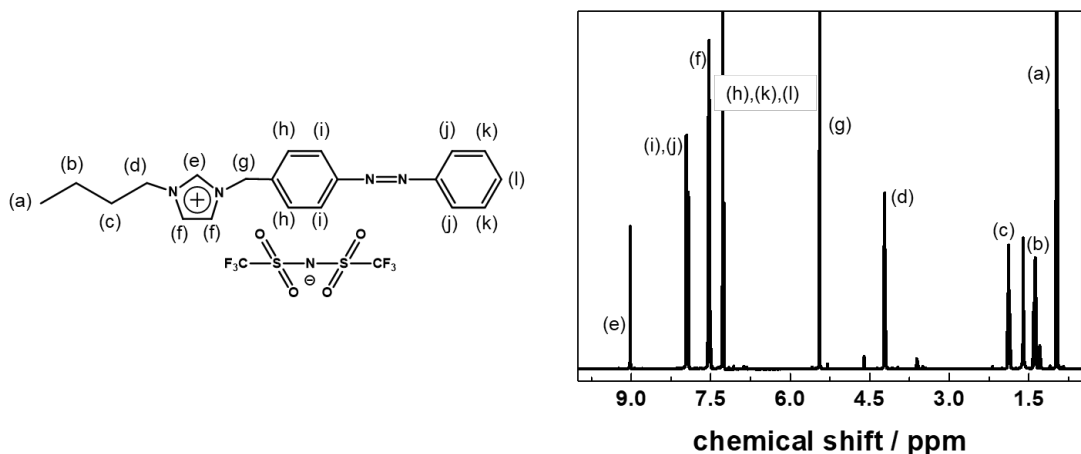


Figure S2 ^1H NMR spectra of [Azobim][NTf₂] in CDCl₃.

2.4. Preparation of NON/[Azobim][NTf₂]/[C₂mim][NTf₂] ion gel

The solution of [C₂mim][NTf₂], [Azobim][NTf₂], and NON in THF (cosolvent) was cast into a mould, and THF was gradually evaporated to obtain an ion gel. The obtained gel was annealed at 180 °C for one day to obtain a well-equilibrated microstructure.

3. Measurements

3.1. UV source

A 500-W high-pressure mercury lamp (Ushio Optical Modulex BA-H500) was used to irradiate the samples at a tuned intensity and wavelength using glass filters (UV light: 366 nm, $\Delta\lambda \approx 30$ nm, intensity = 8 mW cm⁻²; visible light: 437 nm; $\Delta\lambda \approx 23$ nm, intensity = 4 mW cm⁻²). For all photoirradiation measurements, a heat-absorbing filter was used to dissipate the heat generated by the mercury lamp.

3.2. Rheological measurement

Rheological measurements were performed on disk-shaped ion gels (thickness: 0.2

mm) using a Physica MCR102 (Anton Paar, Austria) rheometer. A temperature controlling hood (H-PTD200) was attached to it for stabilizing the measurement temperature. A parallel plate (diameter: 12.5 mm) was employed. The frequency (f) was 1 Hz and the strain (γ) was 3%. The temperature dependencies of storage and loss moduli (G' and G'' , respectively) were recorded at the first heating and cooling steps. The cooling/heating rate was 1 °C min⁻¹.

3.3 Ionic conductivity

The ionic conductivity of the ion gel (thickness: 0.2 mm) was calculated from complex impedance measurements over a frequency range from 5 Hz to 13 MHz (amplitude: 10 mV) using a Hewlett-Packard 4192A LF impedance analyser. The ion gels were examined using a comb-shaped Au electrode (BAS, Japan). The measurements were conducted at 117 °C. Prior to impedance measurement, the temperature was equilibrated for at least 1 h to stabilize the sample temperature.

3.4. AFM

An SPM9700-HT (Shimadzu, Japan) instrument equipped with a silicon cantilever (spring constant: 26 N m⁻¹) was employed. The ion gel (thickness: 0.5 mm) was soaked into liquid nitrogen and cleaved. At room temperature, the cleaved surface of the sample was observed using AFM in the tapping mode to obtain the height and phase images.

3.5. SAXS

Small-angle X-ray scattering (SAXS) measurements were conducted on the BL-10C beamline (Photon Factory, Japan) with a monochromated X-ray beam (wavelength $\lambda = 1.00$ Å) using a detector (PILATUS3 2M, Dectris) at a sample-to-detector distance of 3.1 m. X-rays were directly irradiated onto the sample. The measurements were performed at room temperature for an exposure time of 60 s. The obtained SAXS profiles were

corrected for exposure time, dark current, background scattering, and transmittance. The profiles were presented as a function of the scattering vector ($q = (4\pi/\lambda) \sin 2\theta$, where 2θ is the scattering angle).

4. Figures

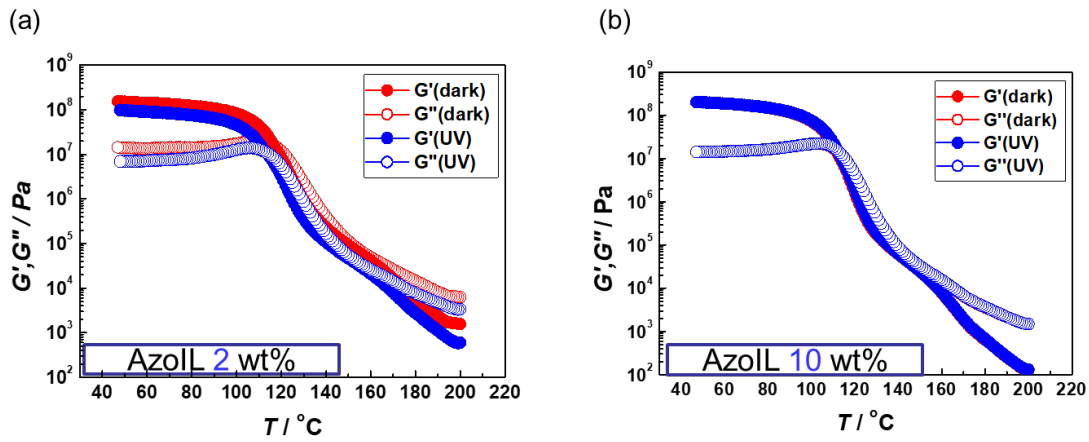


Figure S3. Temperature sweep measurements of G' and G'' for (a) NON/[Azobim][NTf₂]/[C₂mim][NTf₂] (weight ratio: 80:4:16) and (b) NON/[Azobim][NTf₂]/[C₂mim][NTf₂] (weight ratio: 80:10:10) ion gels.

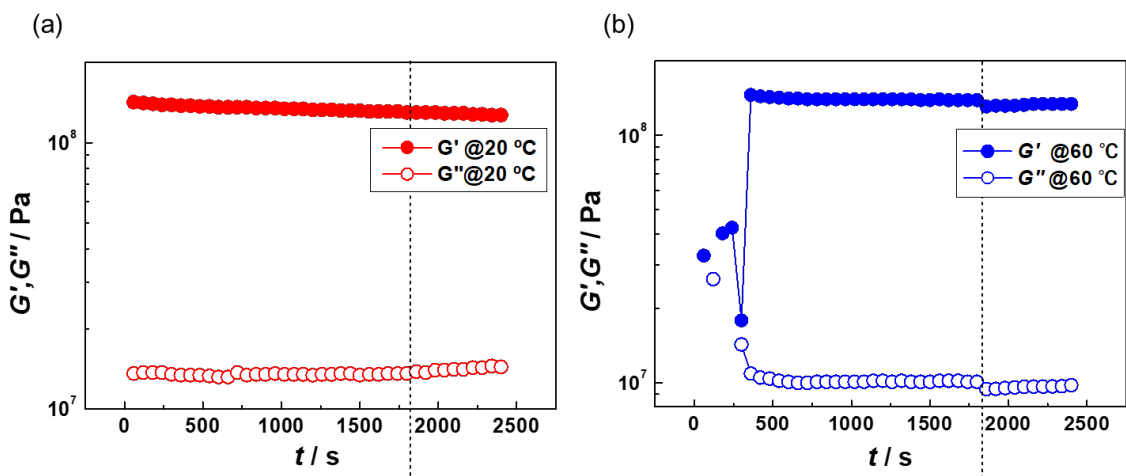


Figure S4. Time sweep measurements of the elastic moduli of the ion gels of NON/[Azobim][NTf₂]/[C₂mim][NTf₂] at 20 °C and 60 °C. The broken lines correspond to the starting time of UV irradiation.

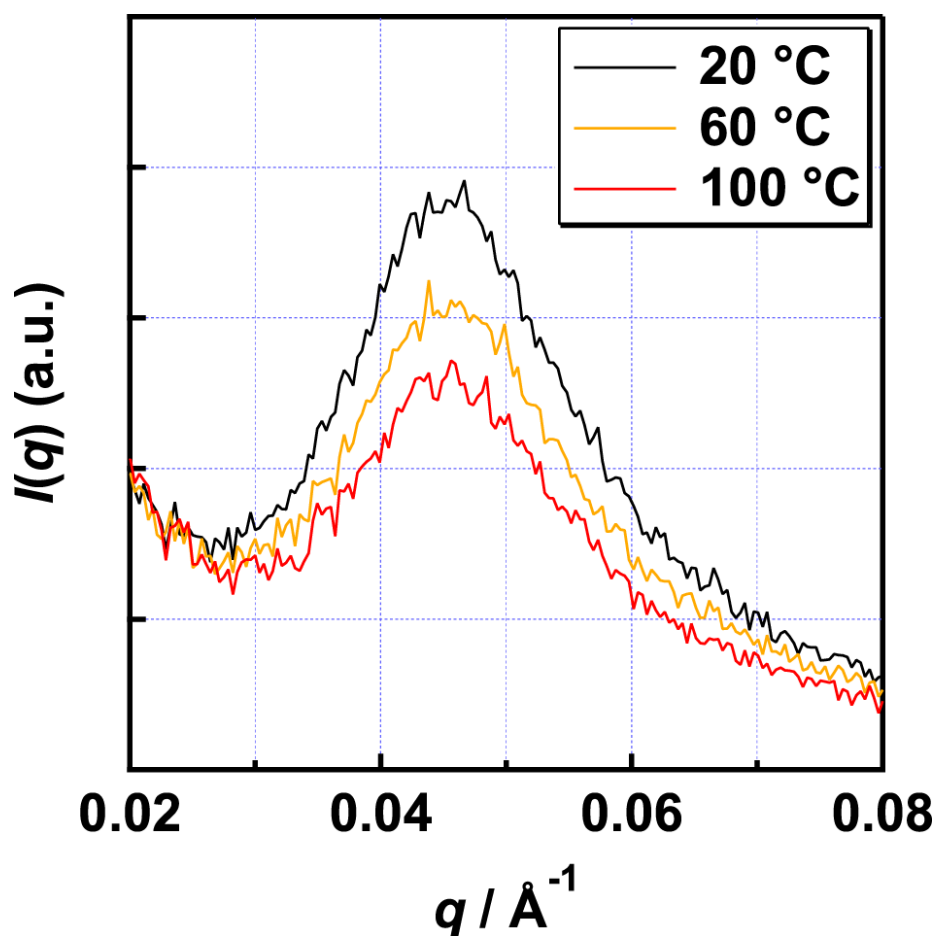


Figure S5. Temperature variation of the SAXS profiles for NON/[Azobim][NTf₂]/[C₂mim][NTf₂].

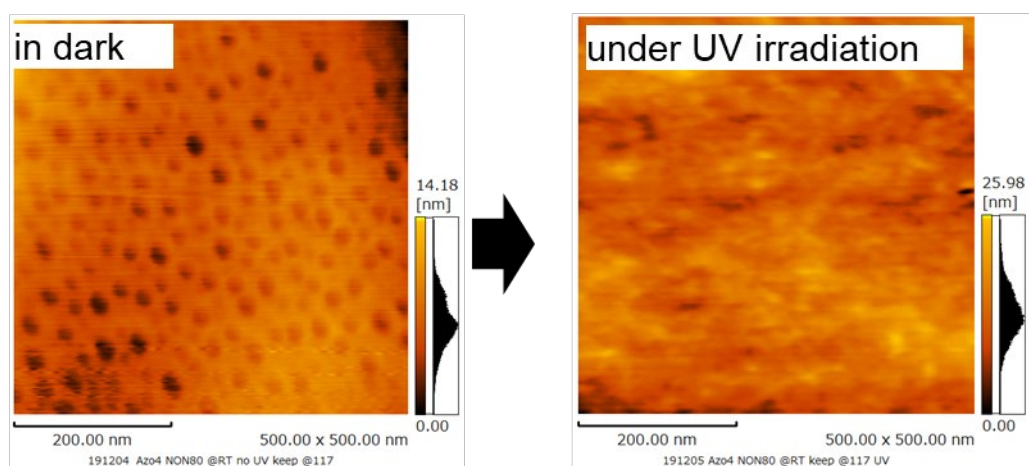


Figure S6. AFM height images of NON/[Azobim][NTf₂]/[C₂mim][NTf₂].

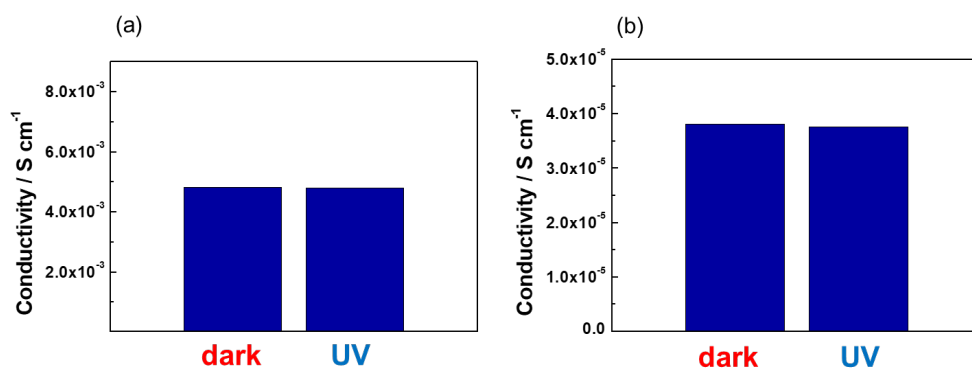


Figure S7. Change in ionic conductivity of (a) [Azobim][NTf₂]/[C₂mim][NTf₂] (weight ratio: 4:96) at 117 °C and (b) NON/ [Azobim][NTf₂]/ [C₂mim][NTf₂] (weight ratio: 80:4:16) ion gel at 150 °C.

5. UV measurements

5.1. Estimation of molar absorption coefficient and penetration length

The UV-vis spectra of [Azobim][NTf₂] in [C₂mim][NTf₂] were recorded using a UV-2700 UV-vis spectrophotometer (Shimadzu, Japan) in the wavelength range of 200–700 nm. The solutions were stored in the dark for 12 h before measurement. The solution was sealed in a quartz cell with an optical path length of 0.1 mm. UV light was irradiated to the sample at room-temperature or 117 °C for 1 h.

To obtain the molar absorption coefficient of [Azobim][NTf₂] in [C₂mim][NTf₂], we calculated molar concentration of the solutions. The densities of [Azobim][NTf₂] in [C₂mim][NTf₂] solutions were measured using a viscometer (SVM 3000, Anton Paar) at 30 °C, as shown in **Figure S8**. The molar concentration of [Azobim][NTf₂] was calculated and listed in **Table S2**.

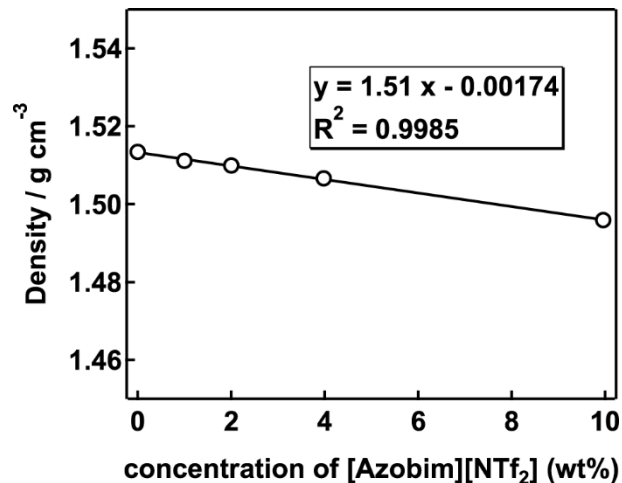


Figure S8. The concentration dependency of the densities of [Azobim][NTf₂] in [C₂mim][NTf₂] solutions.

Table S2 Molar concentration of [Azobim][NTf₂] in [C₂mim][NTf₂] solutions.

[Azobim][NTf ₂] in [Azobim][NTf ₂] (wt%)	Concentration / M
10	0.47
4.0	0.19
2.0	0.095
1.0	0.047
0.50	0.024
0.25	0.012
0.094	0.0045
0.051	0.0024

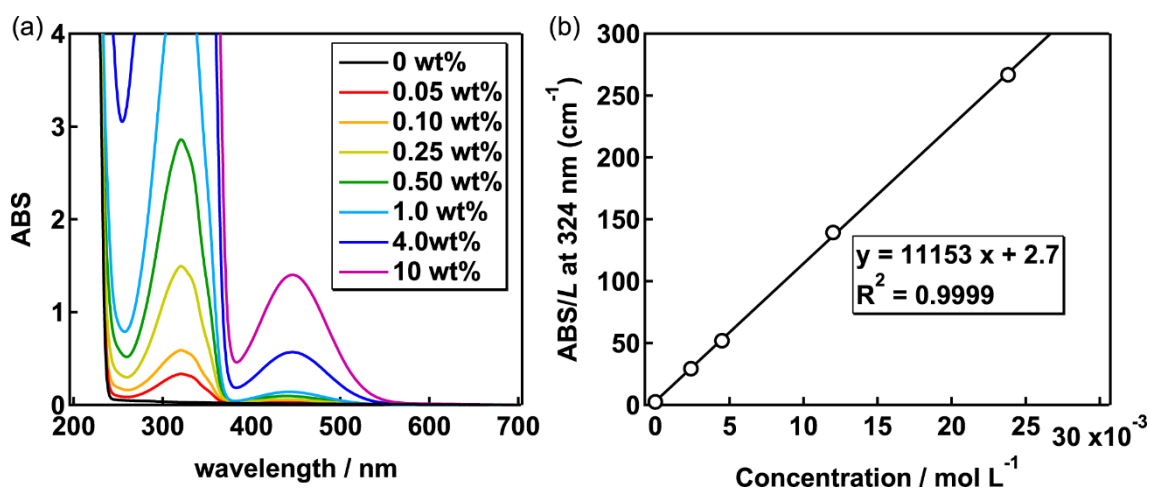


Figure S9. (a) The UV spectra of [Azobim][NTf₂] in [C₂mim][NTf₂] solutions with various [Azobim][NTf₂] concentrations in the dark. (b) The concentration dependence of the absorbance at 324 nm. The absorbance (ABS) was normalized by optical path length ($L = 0.01$ cm).

Figure S9 (a) shows the UV spectra of [Azobim][NTf₂] in [C₂mim][NTf₂] solutions with various [Azobim][NTf₂] concentrations in the dark. The absorption band

corresponds to π - π^* transition of *trans*-[Azobim][NTf₂] was clearly observed at ca. 324 nm at low concentration (< 1 wt%). However, at more than 1 wt%, the UV absorbance was overscaled, indicating that UV light cannot penetrate the sample. We cannot directly evaluate the penetration length at 4% [Azobim][NTf₂] solution due to the overscaled absorbance, thus, we calculated the penetration length from the molar absorption coefficient of [Azobim][NTf₂]. From the concentration dependence of the absorbance at 324 nm divided by optical path length (**Figure S9 (b)**), the molar absorption coefficient was calculated to be 11153 L mol⁻¹ cm⁻¹. From this value, we can estimate the penetration length of UV light. The UV intensity drops to 1% of the incident beam at 9.5 and 3.8 μ m for the 4 and 10 wt% [Azobim][NTf₂] solutions, respectively.

5.2. Estimation of the ratio of *cis*-[Azobim][NTf₂]

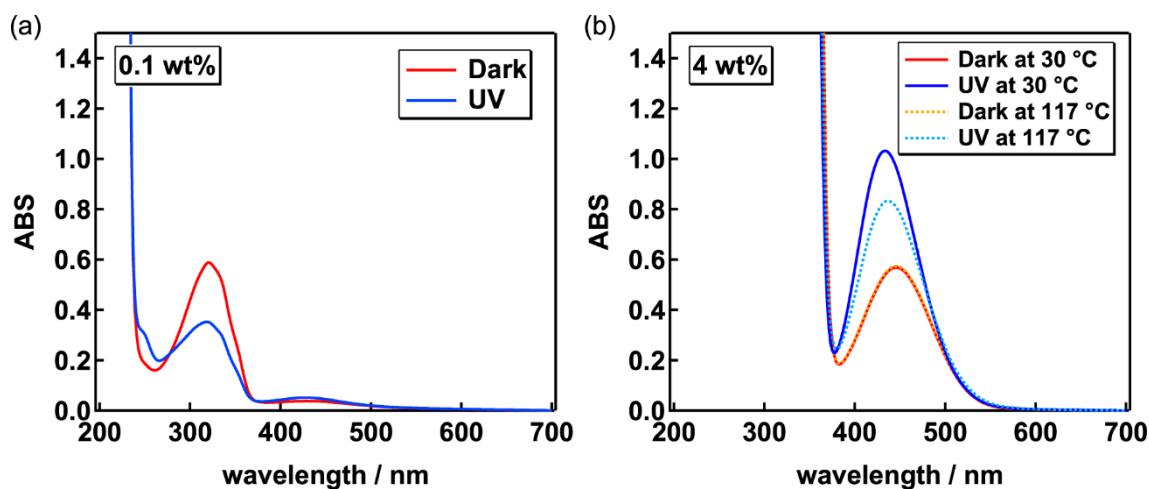


Figure S10. The UV spectra of [Azobim][NTf₂] in [C₂mim][NTf₂] solution in the dark and after UV irradiation (a) at 0.1 wt% and 4 wt% of [Azobim][NTf₂] concentration.

Figure S10 (a) shows the UV spectra of 0.1 wt% [Azobim][NTf₂] in [C₂mim][NTf₂] solution in the dark and after 1 h UV irradiation at room-temperature. The absorption peak at ca. 324 nm (*trans* π - π^*) decreased while the peak at ca. 443 nm (*n*- π^*) increased after UV irradiation. **Figure S10 (b)** shows the UV spectra of 4 wt% [Azobim][NTf₂] in

[C₂mim][NTf₂] solution. Unfortunately, the peak intensity at ca. 324 nm is too high to prevent from direct estimation of concentration of *trans*-[Azobim][NTf₂]. However, UV irradiation increases the peak intensity at ca. 443 nm, indicating isomerization from *trans*- to *cis*-state. The UV irradiation at 117 °C also increased the peak, but the intensity was lower than that at room-temperature, indicating higher rate of the thermal relaxation from *cis*- to *trans*-state. The peak intensity at 443 nm can be described as follows;

$$ABS = \varepsilon_{cis} x_{cis} [AzobimNTf_2] + \varepsilon_{trans} (1 - x_{cis}) [AzobimNTf_2]$$

where ABS [cm⁻¹] is the experimental absorbance divided by the cell thickness, x_{cis} [-] is the mole fraction of *cis*-[Azobim][NTf₂], [AzobimNTf₂] [mol L⁻¹] is the molar concentration of [Azobim][NTf₂], ε_{cis} and ε_{trans} [L mol⁻¹ cm⁻¹] are the molar absorption coefficients of *cis*- and *trans*-[Azobim][NTf₂], respectively.

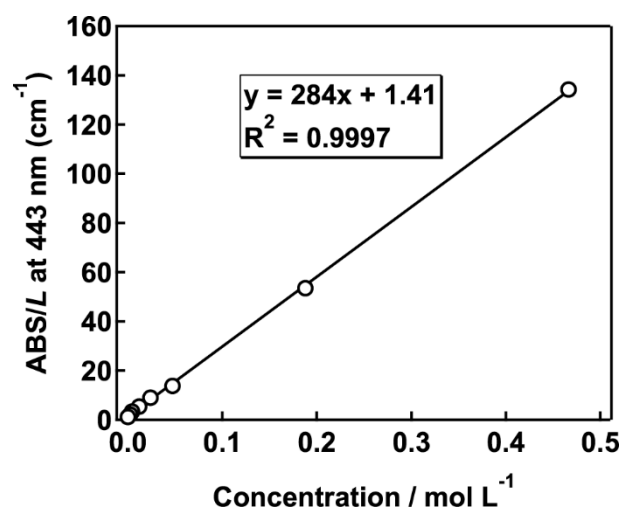


Figure S11. The concentration dependence of the absorbance at 443 nm. The absorbance (ABS) was normalized by optical path length ($L = 0.01$ cm).

According to the previous report,^[S2] 100% of [Azobim][NTf₂] is in *trans*-state in the dark, while 65% of [Azobim][NTf₂] changes into *cis*-[Azobim][NTf₂] after UV

irradiation at low concentration. From **Figure S11**, ϵ_{trans} was estimated to be $284 \text{ L mol}^{-1} \text{ cm}^{-1}$. If we assume that x_{cis} is 0.65 at 0.1 wt% after UV irradiation, we can roughly estimate the ϵ_{cis} to be $1327 \text{ L mol}^{-1} \text{ cm}^{-1}$. Thus, we can estimate the x_{cis} at 4 wt% [Azobim][NTf₂] in [C₂mim][NTf₂] solution to be 0.21 and 0.12 at room-temperature and 117 °C, respectively.

Reference

[S1] C. Wang, K. Hashimoto, R. Tamate, H. Kokubo, K. Morishima, X. Li, M. Shibayama, F. Lu, T. Nakanishi, and M. Watanabe, *Chem. Commun.*, **2019**, 55, 1710-1713.

[S2] C. Wang, X. Ma, Y. Kitazawa, Y. Kobayashi, S. Zhang, H. Kokubo, and M. Watanabe, *Macromol. Rapid Commun.*, **2016**, 37, 1960-1965.