Electronic Supplementary Information (ESI)

Photo/thermoresponsive ABC triblock copolymer-based ion gels: Photoinduced structural transitions

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Calculation procedure of the theoretical elasticity *G* for ABA and ABC ion gels

The theoretical elasticity, G, from classical rubber elasticity theory is expressed as

$$G = nk_{B}T = \rho RT/M_{x} \qquad (1)$$

where n is the number density of network strands, ρ the mass density of the strand, M_x the molecular weight between crosslinks, T the absolute temperature, k_B the Boltzmann constant, and R the gas constant. Here, M_x corresponds to the molecular weight of the B middle block (present ABC: 67 kg/mol, previous ABA[S1]: 33 kg/mol). The mass density of the strand could be calculated as

$$\rho = c\rho_{gel}w_{B} \qquad (2)$$

where c is the polymer concentration (w/w) (ABC: 0.15, ABA: 0.20), ρ_{gel} the mass density of the ion gel (ABC: 1.52 g cm^{-3}, ABA: 1.37 g cm^{-3}), w_B the weight ratio of the B middle block in the triblock copolymer (ABC: 0.68; ABA[S1]: 0.52). Here, we hypothesize that the mass densities of the ion gels are equal to those of the IL solvents ([C_2mim][NTf_2] for ABC, [C_4mim]PF_6 for ABA). The mass densities of the strand (ρ) for ABC and ABA ion gels were calculated by substituting these values into Eq. (2) (ABC: 155 kg m^{-3}, ABA: 144 kg m^{-3}). Finally, by using these values, theoretical elasticity G can be calculated at 25 °C (T = 298.15 K) from Eq. (1) (ABC: 5.71 kPa, ABA: 10.8 kPa).

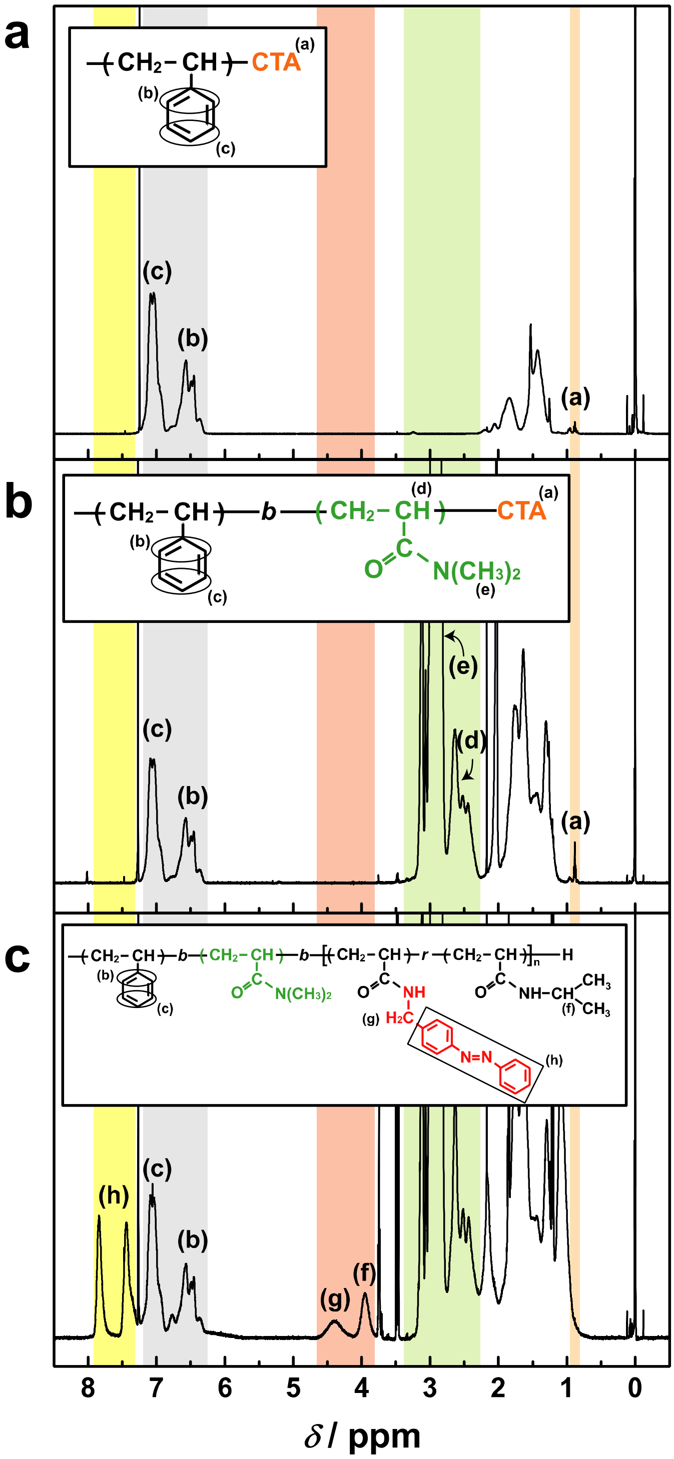

Fig. S1 [1]H-NMR spectra of (a) PS-CTA, (b) PS-*b*-PDMAm-CTA (AB-CTA), and (c) PS-*b*-PDMAm-*b*-P(AzoBnAm-*r*-NIPAm) (ABC(Azo)) in $CDCl_3$.

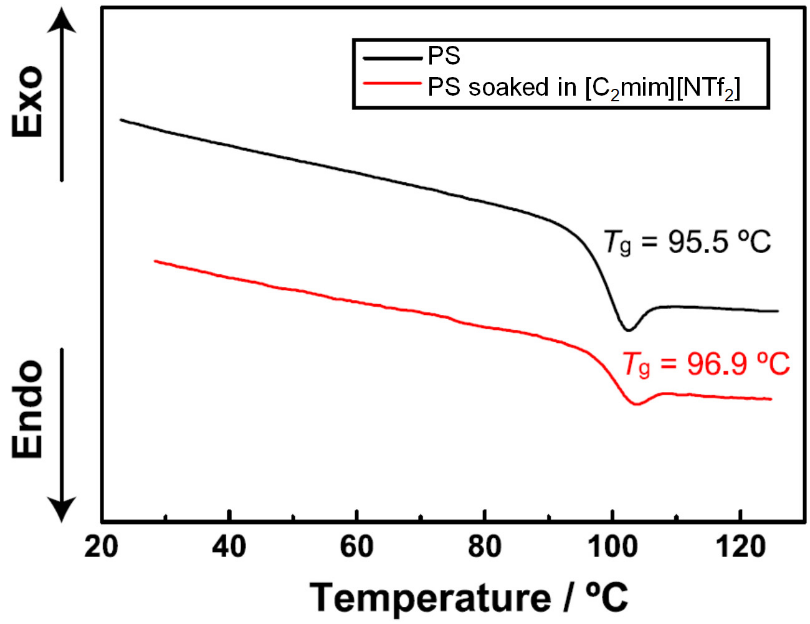

Fig. S2 DSC curves of bulk PS homopolymer and PS homopolymer soaked in [C_2mim][NTf_2] at heating rate 10 ºC min^{-1}. Nearly identical glass transition temperatures (T_g) indicate that the T_g of PS is not affected by the presence of IL, which is consistent with our previous result.[S2]

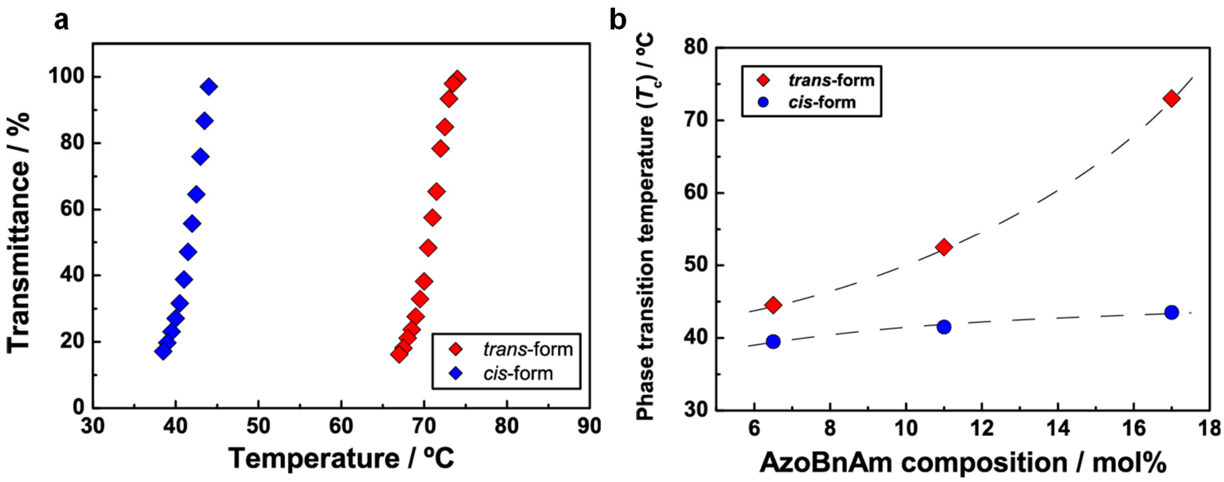

Fig. S3 (a) Temperature dependence of optical transmittance at 500 nm for 3 wt% P(AzoBnAm-*r*-NIPAm) random copolymer in [C_2mim][NTf_2] in the dark (*trans*-form) and under UV light irradiation (*cis*-form). [AzoBnAm]/[NIPAm] = 17/83. (b) Effect of the AzoBnAm composition in P(AzoBnAm-*r*-NIPAm) on UCST type phase transition temperatures for 3 wt% P(AzoBnAm-*r*-NIPAm) solutions in [C_2mim][NTf_2].

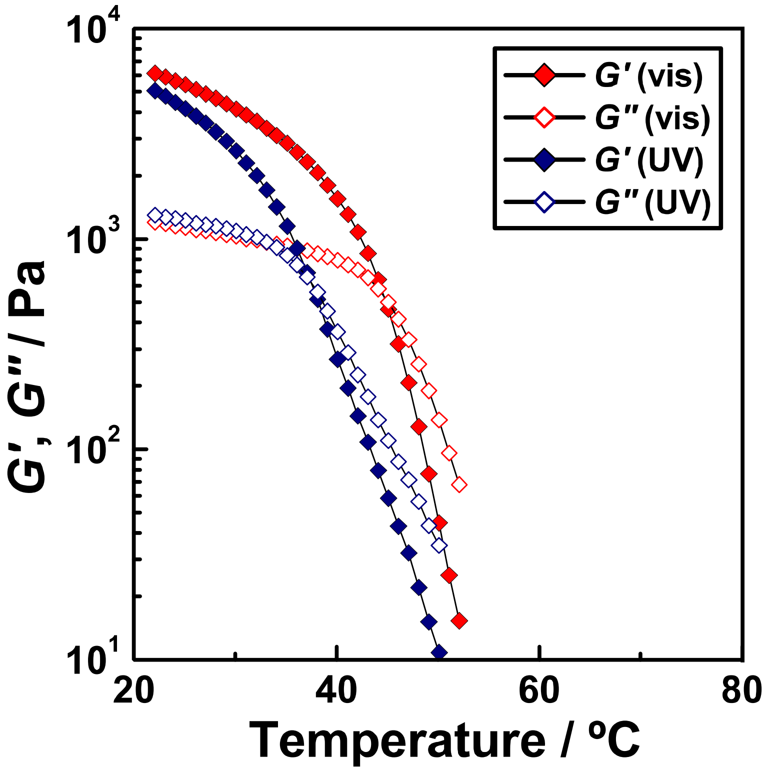

Fig. S4 Variations in *G′* and *G″* values for 20 wt% ABA triblock copolymer P(AzoMA-*r*-NIPAm)-*b*-PEO-*b*-P(AzoMA-*r*-NIPAm) in $[C_2mim][NTf_2]$ under UV and visible light irradiations as functions of temperature at frequency $\omega = 0.1$ rad s^{-1}, strain amplitude $\gamma = 1$ %, and cooling rate 0.2 ºC min^{-1}.

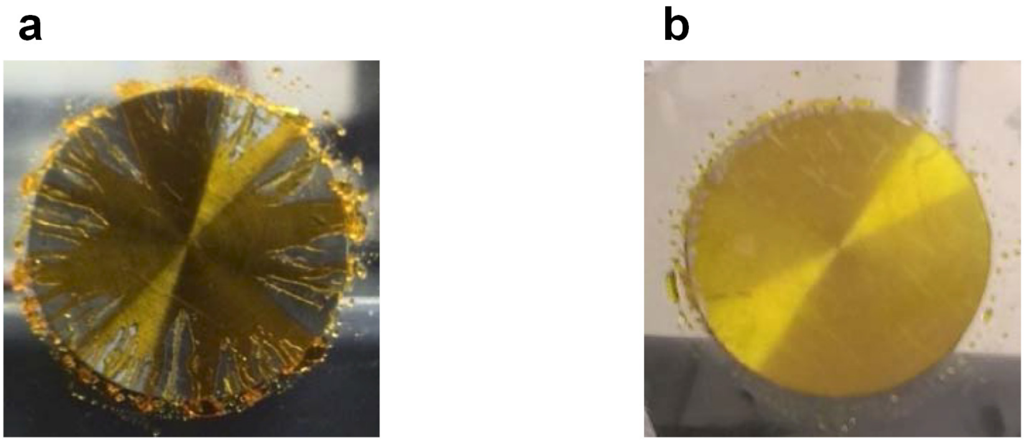

Fig. S5 (a, b) Appearances of 15 wt% ABC(Azo) ion gel after strain sweep measurements under visible light (a) and UV light (b).

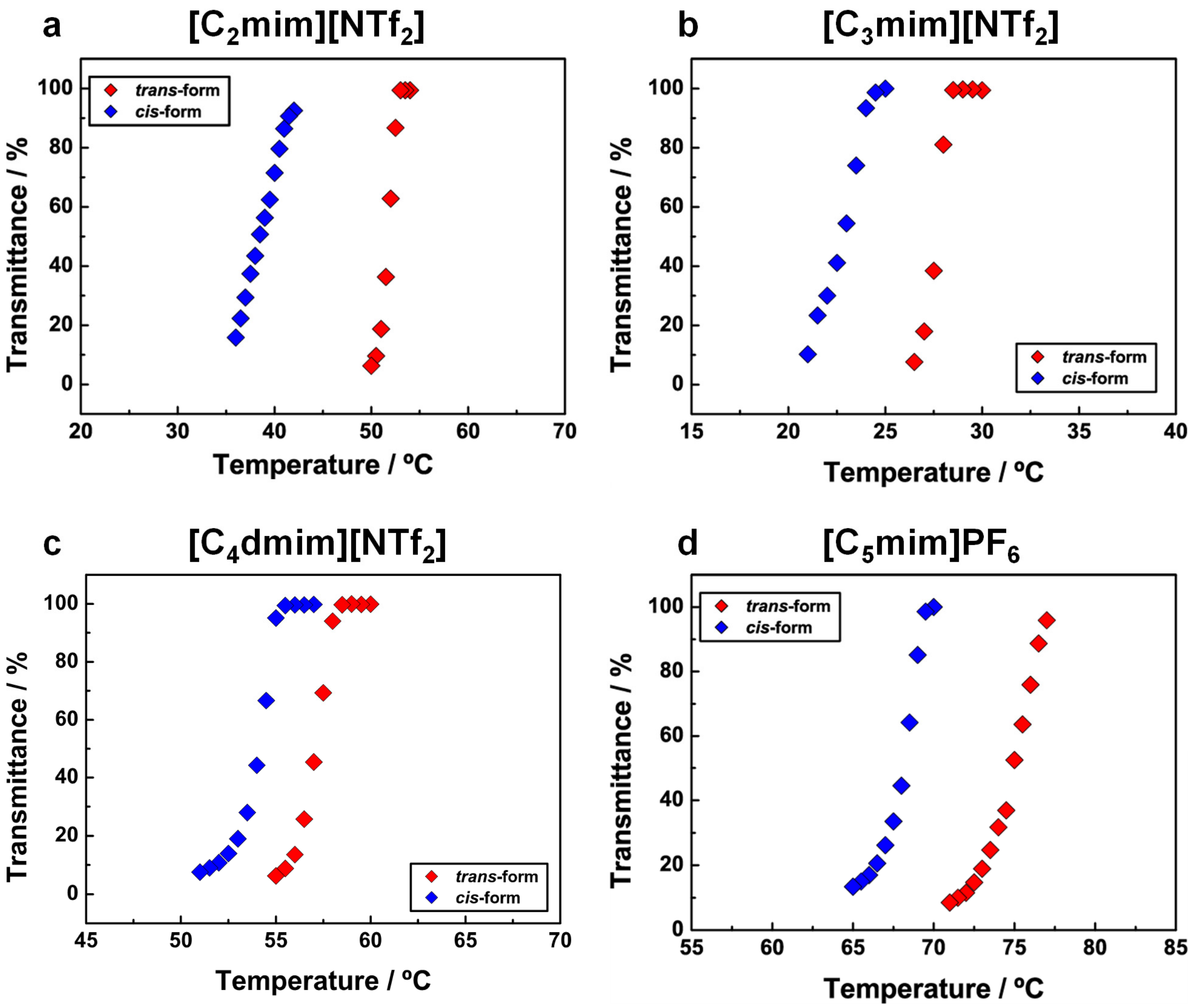

Fig. S6 Temperature dependence of optical transmittance for 3 wt% P(AzoBnAm-*r*-NIPAm) random copolymer ([AzoBnAm]/[NIPAm] = 11:89) in (a) $[C_2mim][NTf_2]$, (b) 1-methyl-3-propylimidazolium ($[C_3mim]$) $[NTf_2]$, (c) 1-butyl-2,3-dimethylimidazolium ($[C_4dmim]$) $[NTf_2]$, and (d) 1-methyl-3-pentylimidazolium ($[C_5mim]$) PF_6 under UV light irradiation (*cis*-form) and in the dark (*trans*-form).

Table S1 Cloud points (T_cs) for 3 wt% P(AzoBnAm-*r*-NIPAm) random copolymer ([AzoBnAm]/[NIPAm] = 11:89) in several imidazolium-based ILs under UV light irradiation or in the dark.

IL	$T_c(trans)$ / ºC	$T_c(cis)$ / ºC	ΔT_c / ºC
[C_2mim][NTf_2]	53	42	11
[C_3mim][NTf_2]	28	24	4
[C_4dmim][NTf_2]	58	55	3
[C_5mim]PF_6	77	69	8

Supporting References

S1 T. Ueki, R. Usui, Y. Kitazawa, T. P. Lodge and M. Watanabe, *Macromolecules*, 2015, **48**, 5928–5933.

S2 S. Imaizumi, H. Kokubo and M. Watanabe, *Macromolecules*, 2012, **45**, 401–409.