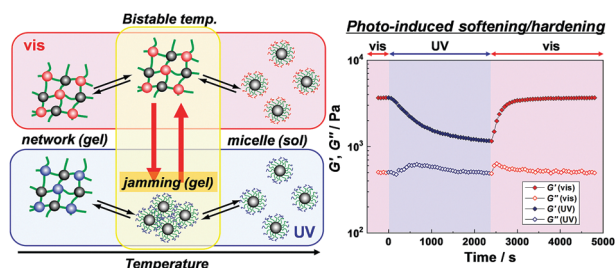# Soft Matter

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

Ryota Tamate, Ryoji Usui, Kei Hashimoto, Yuzo Kitazawa, Hisashi Kokubo and Masayoshi Watanabe*

Photo-induced hardening/softening of an ion gel formed by an ABC triblock copolymer was realized.

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First (given) and middle name(s)	Last (family) name(s)	ResearcherID	ORCID iD
Ryota	Tamate		0000-0002-1704-1058
Ryoji	Usui		
Kei	Hashimoto		
Yuzo	Kitazawa		
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Photo/thermoresponsive ABC triblock copolymer-based ion gels: photoinduced structural transitions†

Ryota Tamate, [ID] Ryoji Usui, Kei Hashimoto, Yuzo Kitazawa, Hisashi Kokubo and Masayoshi Watanabe [ID] *

A photo/thermoresponsive ABC triblock copolymer-based ion gel exhibiting photoinduced structural transitions accompanied by significant rheological changes is newly developed. The ABC triblock copolymer comprises an ionic liquid (IL)-phobic A block, an IL-philic B block, and a photo/thermoresponsive C block containing azobenzene moieties. The IL-phobic A block forms a rigid micellar core in an IL over a wide temperature range and the photo/thermoresponsive C block undergoes upper critical solution temperature (UCST)-type phase transition in ILs. In concentrated polymer solution, the ABC triblock copolymer can form a percolated micellar network at low temperatures through aggregation of A and C blocks as physical crosslinks, bridged by IL-philic B blocks. In contrast, the ion gel undergoes structural transition to jammed micelles at high temperatures due to the disassembly of the thermoresponsive C block, resulting in significant softening of the ion gel. Importantly, the temperature dependences of the viscoelastic properties of the ion gel differed drastically depending on photo-irradiation conditions as the photoinduced isomerization of azobenzene moieties in the C block modulates the affinity between the polymer chain and IL. Utilizing this feature, photoinduced softening/hardening of the ion gel is realized at constant temperature. This study provides a promising strategy to control the rheological properties of nonvolatile soft materials via contactless light irradiation that could be exploited in various applications such as photoresponsive soft actuators and photo-healable soft materials.

Introduction

Polymer gels based on block copolymer self-assembly have attracted attention owing to their versatile and tunable physical properties.[1,2] ABA-type triblock copolymers containing solvatophobic A endblocks and solvatophilic B midblocks can form gels with moderate polymer concentration (typically 10–20 wt%) through the formation of micellar network structures containing aggregated A endblocks as physical crosslinks bridged by B midblock chains.[3–7] ABA triblock copolymer-based hydrogels are being intensively investigated for biomedical applications such as injectable drug delivery systems[8–10] and cell-culture materials.[11–14] However, water evaporation is a serious drawback of hydrogels, restricting their use in open atmospheres. Ion gels—defined as macromolecular networks swollen with ionic liquids (ILs)—exhibit unique properties, including nonvolatility, nonflammability, and high ionic conductivity, endowed by the intrinsic properties of ILs, and are regarded as promising nonvolatile soft electrolytes used in open atmospheres and under harsh conditions.[15–19] Seminal work by Lodge et al. demonstrated that physically crosslinked ion gels can be formed by the self-assembly of ABA triblock copolymers in ILs.[20–22] Taking advantage of the solution processabilities of physically crosslinked gels, applications of ABA triblock copolymer-based ion gels in electric double layer capacitors,[23–25] gel electrolytes for lithium ion batteries,[26] and soft actuators,[27,28] among others, were proposed.

Recently, we reported a new class of photo- and thermoresponsive ion gels based on the self-assembly of ABA triblock copolymers in ILs.[29–31] The A block comprised a random copolymer of N-isopropylacrylamide (NIPAm) and 4-phenylazophenyl methacrylate (AzoMA). The IL-philic B block was poly(ethylene oxide) (PEO). Owing to the upper critical solution temperature (UCST)-type phase transition of the P(AzoMA-r-NIPAm) block in ILs, the ABA triblock copolymer P(AzoMA-r-NIPAm)-b-PEO-b-P(AzoMA-r-NIPAm) underwent gel-

Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.
E-mail: mwatanab@ynu.ac.jp

to-sol transition upon heating. Notably, the sol–gel transition temperature (T_{gel}) was modulated under photo-irradiation conditions, attributable to the *cis–trans* isomerization of azobenzene moieties introduced in the A block. T_{gel} under UV light (*cis*-T_{gel}) was lower than that under visible light (*trans*-T_{gel}). As a result, at a temperature intermediate between *cis*-T_{gel} and *trans*-T_{gel}, reversible photoinduced sol–gel transitions were observed by switching light sources.[29] Furthermore, by exploiting photoinduced sol–gel transition, the damaged part of the ion gel was observed to be photo-healed by sequential irradiation with UV and visible light.[30]

Herein, we describe a new class of photo/thermoresponsive ion gels based on an ABC triblock copolymer that shows significant softening/hardening of ion gels upon irradiation driven by photoinduced transition between the jammed micelle state and the percolated micellar gel state (Fig. 1a). The ABC triblock copolymer contains an IL-phobic A block, an IL-philic B block, and a photo/thermoresponsive C block (Fig. 1b). As the ABC architecture prevents looped chains that do not contribute to the elasticity of the polymer network, a high elastic modulus is realized with lower polymer concentration than with the ABA architecture.[32–35] Furthermore, compared to the ABA triblock copolymer containing azobenzene moieties at both endblocks, the ABC triblock copolymer contains azobenzene moieties only in the C endblock, which enables introduction of a large azobenzene content without impairing the transmittance of UV light. Consequently, the ABC triblock copolymer shows a large rheological difference under irradiation conditions,

which can be exploited to induce photoinduced drastic rheological changes due to the structural transition between jammed micelles and percolated micellar networks.

Experimental

Materials

Styrene and *N,N*-dimethylacrylamide (DMAm) were purchased from Wako Pure Chemicals (Japan) and purified by distillation. *N*-Isopropylacrylamide (NIPAm) was kindly donated by KJ Chemicals (Japan) and purified by recrystallization from toluene/*n*-hexane. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Wako Pure Chemicals and recrystallized from methanol. The chain transfer agent (CTA) *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate was synthesized according to a previous report.[36] *N*-Acryloyloxysuccinimide (NAS)[37] and 4-phenylazobenzylamine[38] (azoamine) were synthesized according to the literature. 1-Ethylpiperidine hypophosphite (EPHP) was purchased from Sigma Aldrich (MO, USA) and used as received. Other chemicals were from Wako Pure Chemicals and used as received, unless otherwise noted.

Synthesis of PS-CTA

CTA (1.09 g, 2.99 mmol) and AIBN (98.5 mg, 0.601 mmol) were dissolved in 1,4-dioxane (250 mL), and then styrene monomer (110 mL, 1.01 mol) was added. The solution was bubbled with argon (Ar) for 60 min. Reversible addition–fragmentation chain transfer (RAFT) polymerization was performed at 65 °C for 72 h. The reactant was precipitated into methanol and the polymer was purified twice by reprecipitation from tetrahydrofuran (THF) as good solvent and methanol as poor solvent. Polystyrene-CTA (PS-CTA) was obtained after drying under vacuum at 60 °C.

Synthesis of PS-*b*-PDMAm-CTA (AB-CTA)

PS-CTA (8.31 g, 0.620 mmol) was dissolved in anhydrous dimethylformamide (DMF, 200 mL) and subsequently DMAm (45.1 mL, 0437 mol) was added. The solution was bubbled with Ar at 45 °C for 60 min. Ar-bubbled AIBN (0.0310 mmol) dissolved in DMF (5.09 mL) was added to the solution and RAFT polymerization was performed at 65 °C for 18 h. The polymer solution was precipitated into diethyl ether. The polymer was further purified twice by reprecipitation with THF as good solvent and diethyl ether as poor solvent. The diblock copolymer PS-*b*-PDMAm-CTA (AB-CTA) was obtained after drying under vacuum at 60 °C.

Synthesis of PS-*b*-PDMAm-*b*-P(NAS-*r*-NIPAm)-CTA (ABC(NAS)-CTA)

AB-CTA (10.7 g, 0.134 mmol), NAS (2.17 g, 12.8 mmol), and NIPAm (5.81 g, 51.4 mmol) were dissolved in anhydrous DMF followed by Ar bubbling at 45 °C for 60 min. Ar-bubbled AIBN (6.68 μmol) dissolved in DMF (2.19 mL) was then added to the solution. RAFT polymerization was allowed to proceed at 65 °C for 20.5 h. The polymer solution was precipitated into diethyl
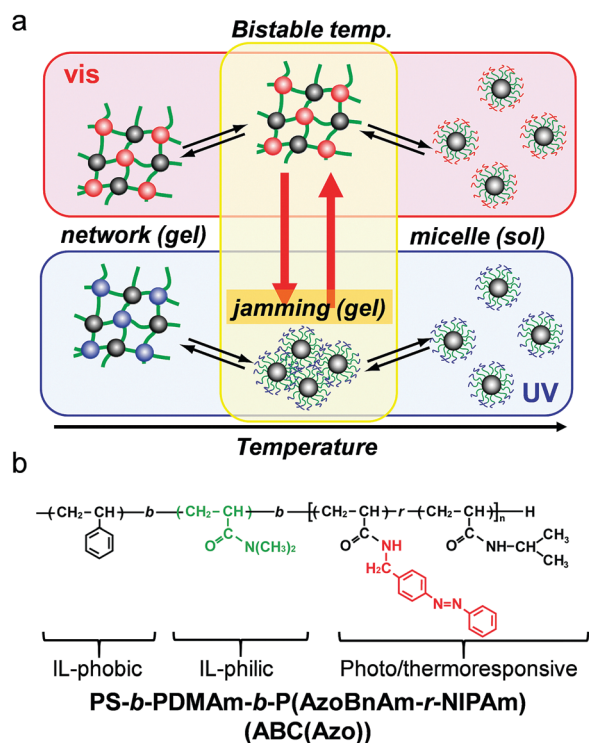

Fig. 1 (a) Schematic illustration of photoinduced transition between a jammed micellar ion gel and a network ion gel. (b) Chemical structure of an ABC triblock copolymer.

ether and further purified by reprecipitation with THF as good solvent and diethyl ether as poor solvent. After vacuum drying at 60 °C, the ABC triblock copolymer PS-*b*-PDMAm-*b*-P(NAS-*r*-NIPAm)-CTA (ABC(NAS)-CTA) was obtained.

Removal of CTA residues

The dodecyl trithiocarbonate terminal group derived from CTA was removed using the following method. ABC(NAS)-CTA (8.00 g, 0.0808 mmol) and EPHP (58.9 mg, 0.329 mmol) were dissolved in anhydrous DMF (60 mL) and bubbled with Ar at 45 °C for 30 min. Ar-bubbled AIBN (0.0211 mmol) dissolved in DMF (6.92 mL) was then added to the polymer solution. The reaction was conducted at 100 °C for 3 h. The solution was precipitated into diethyl ether and purified twice by reprecipitation with THF/diethyl ether. After vacuum drying at 60 °C, the ABC triblock copolymer PS-*b*-PDMAm-*b*-P(NAS-*r*-NIPAm) (ABC(NAS)) was obtained as a white powder.

Synthesis of PS-*b*-PDMAm-*b*-P(4-phenylazobenzyl acrylamide-*r*-NIPAm) (PS-*b*-PDMAm-*b*-P(AzoBnAm-*r*-NIPAm); ABC(Azo))

The ABC(NAS) triblock copolymer (5.00 g, 0.0505 mmol) was dissolved in THF (40 mL) and azoamine (1.00 g, 4.44 mmol) dissolved in THF (10 mL) was added to the solution. The reaction was carried out at 40 °C for 24 h. The solution was precipitated into diethyl ether. The polymer was dissolved in methanol (40 mL) and diethyl ether (400 mL) was added dropwise to the solution. The precipitated polymer was collected by centrifugation and further purified with THF/diethyl ether several times. After vacuum drying at 60 °C, the target ABC triblock copolymer PS-*b*-PDMAm-*b*-P(AzoBnAm-*r*-NIPAm) (ABC(Azo)) was obtained.

Polymer characterization

Characterization of the synthesized polymers was performed by ^{1}H-NMR measurements and gel permeation chromatography (GPC). The GPC columns were calibrated with PS standards and DMF containing 0.01 M LiBr was used as eluent. The degree of polymerization of each segment and the [AzoBnAm]/[NIPAm] ratio were calculated from ^{1}H-NMR spectra (Fig. S1, ESI†). The polydispersity index (PDI) of each polymer was measured by GPC (Fig. 2).

Preparation of ion gels and polymer solutions in ILs

Ion gels and polymer solutions dissolved in ILs were prepared by the cosolvent method.[29] First, appropriate amounts of polymers and ILs were weighed and dissolved in THF with stirring. THF was completely removed by vacuum drying at 80 °C.

Dynamic light scattering (DLS) measurements

The polymer solution was passed through a 0.2 μm filter prior to use. Dynamic light scattering (DLS) measurements were performed on an Otsuka Electronic DLS-6500 (Otsuka Electronics, Japan) combined with an ALV correlator (ALV, Germany). A He–Ne laser (632.8 nm) was used as a light source. The second-order autocorrelation function $g_2(q,t)$ was recorded at a scattering angle of 90° for 100 s. The distribution of R_h was
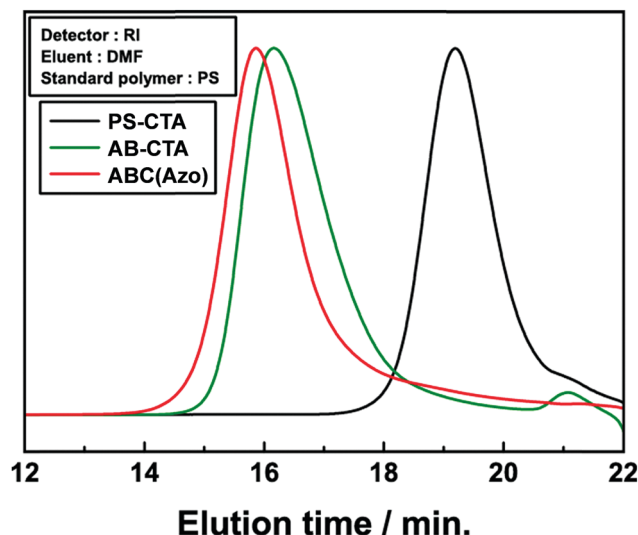

Fig. 2 GPC traces for PS-CTA, AB-CTA, and ABC(Azo).

obtained by CONTIN analysis. The hydrodynamic radius (R_h) was calculated using a cumulant method[39] for unimodal distributions and a double exponential method[40] for bimodal distributions.

Rheological measurements

The rheological behaviours of ion gels were investigated with an Anton Paar Physica MCR 301 (Anton Paar, Austria). A standard cell for irradiation (P-PTD200/GL) was used to measure the viscoelasticity of the ion gels under irradiation. A parallel plate geometry with a diameter of 25 mm and a gap spacing of ∼0.2 mm were used for all measurements. Irradiation was conducted using a 500 W high-pressure mercury lamp Optical Modulex BA-H500 (Ushio Inc., Japan) with a heat-absorbing filter HA-50 (HOYA Co., Japan). The intensity and wavelength of the light were adjusted with color filters (UV light: λ = 366 nm, 8 mW cm^{-2}, visible light: λ = 437 nm, 4 mW cm^{-2}) (Toshiba Glass Co., Japan).

Results and discussion

The ABC triblock copolymer PS-*b*-PDMAm-*b*-P(AzoBnAm-*r*-NIPAm) (denoted ABC(Azo)) was synthesized by living radical polymerization and subsequent post-modification of the activated esters (Scheme 1). First, the precursor ABC triblock copolymer PS-*b*-PDMAm-*b*-P(NAS-*r*-NIPAm) (ABC(NAS)) was synthesized by sequential RAFT polymerization. The activated ester group of the NAS segment was reacted with azoamine by which azobenzene moieties were introduced in the thermoresponsive C block. The degree of polymerization for each step was confirmed by ^{1}H-NMR (Fig. S1, ESI†). The molar ratio of azobenzene to NIPAm ([AzoBnAm]/[NIPAm]) in the C block was calculated by ^{1}H-NMR as 25.9/74.1, which was more than twice the azobenzene content over NIPAm in our previous report for an ABA triblock copolymer ([AzoMA]/[NIPAm] = 10.4/89.6).[29] The PDIs of the synthesized polymers were measured by GPC
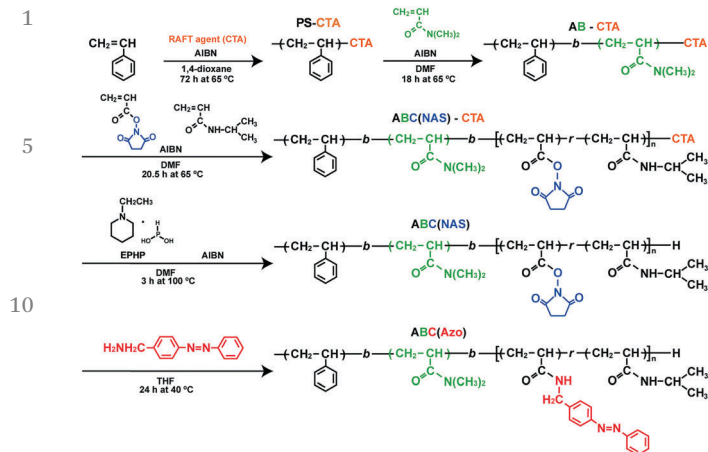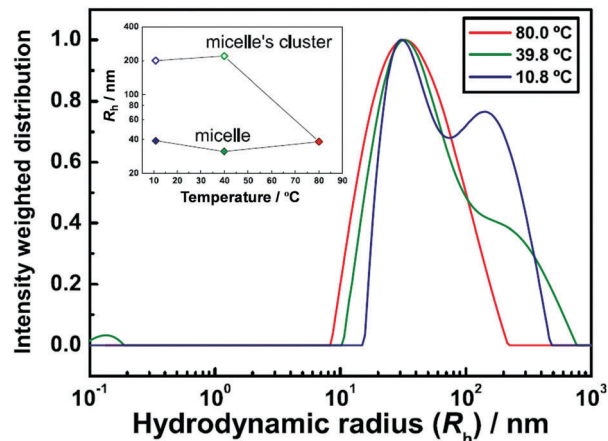
Scheme 1 Synthesis scheme for the ABC(Azo) triblock copolymer.

Fig. 3 Distribution of R_h for 1 wt% ABC(Azo) triblock copolymer in $[C_2mim][NTf_2]$ at different temperatures in the dark. (inset) The temperature dependence of R_h values calculated from double exponential fit for bimodal distributions and cumulant fit for unimodal distributions.

and the narrow GPC curves indicate successful RAFT polymerization and subsequent post-modification reaction (Fig. 2). The characterization results are summarized in Table 1.

The thermoresponsive behaviour of a dilute solution of the ABC(Azo) triblock copolymer in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide $([C_2mim][NTf_2])$ in the dark was investigated by DLS measurements. Fig. 3 shows the distributions of hydrodynamic radii (R_h) at different temperatures. At a high temperature of 80 °C a unimodal R_h distribution with a peak around 40 nm was obtained, indicating that the ABC triblock copolymer formed micelles. The broad R_h distribution ranging from 10 nm to 200 nm indicates that there might exist a small amount of large micelle aggregates.[29] From differential scanning calorimetry (DSC) analysis, the glass transition temperature of the PS homopolymer remained unchanged when it was soaked in $[C_2mim][NTf_2]$ (Fig. S2, ESI†). It means that the PS is completely immiscible with the IL. Therefore, the micelle at high temperature was composed of aggregated PS chains as the micelle core and PDMAm-b-P(AzoBnAm-r-NIPAm) chains as the micelle corona. Considering the much higher molecular weight of the coronal PDMAm-b-P(AzoBnAm-r-NIPAm) chains than that of the core PS chains, the morphology of the micelle is expected to be spherical micelles.[41,42] When the measurement temperature was decreased to 40 °C, another peak with a large R_h value at ∼200 nm appeared. The bimodal distribution indicates that partial micelles participate in the formation of micellar aggregates. It was previously reported that an aqueous dilute solution of thermoresponsive ABC triblock copolymers underwent micelle-to-micelle aggregate transition upon temperature

change.[43] As the P(AzoBnAm-r-NIPAm) block showed UCST-type phase transition in ILs, it was considered that the phase transition from micellar dispersion to micellar aggregates occurred with a decrease in temperature. By further decreasing the temperature from 40 to 10 °C, the fraction of the peak at ∼200 nm increased. This suggested that a larger number of micelles participated to form micellar aggregates at lower temperatures.

The rheological properties of concentrated polymer solutions of the ABC(Azo) triblock copolymer were investigated under light. The temperature dependences of the storage (G') and loss (G'') moduli for 15 wt% ABC(Azo) triblock copolymer in $[C_2mim][NTf_2]$ under UV and visible light are shown in Fig. 4. For both light irradiation conditions, the G' values continuously decreased with increasing temperature. This could be attributed to the UCST-type phase transition of the P(AzoBnAm-r-NIPAm) block. Fig. S3a (ESI†) shows the temperature dependence of the optical transmittance for the P(AzoBnAm-r-NIPAm) random copolymer in $[C_2mim][NTf_2]$ with or without UV irradiation. The P(AzoBnAm-r-NIPAm) random copolymer exhibited UCST-type phase transition in $[C_2mim][NTf_2]$. Notably, the UCST phase transition temperature determined by the cloud point (50% transmittance temperature) significantly changed by UV irradiation, probably due to the difference in polarity between the cis-form (under UV) and trans-form (in the dark) of azobenzene.[44] The difference in UCSTs increased upon increasing the AzoBnAm composition (Fig. S3b, ESI†). The UCSTs of the cis-P(AzoBnAm-r-NIPAm) (under UV) were around

Table 1 Characterization results of the polymers synthesized

Sample	Polymer formula	$M_n{}^a$ (kDa)	PDI^b	[AzoBnAm]/[NIPAm]^a (mol%)
	PS-CTA	13	1.27	—
AB-CTA	PS-b-PDMAm-CTA	13–67	1.35	—
ABC(Azo)	PS-b-PDMAm-b-P(AzoBnAm-r-NIPAm)	13–67–19	1.49	25.9/74.1

^{a} The number-averaged molecular weight (M_n) of each block and the molar ratio of the azobenzene content to the NIPAm segment were calculated by ^{1}H-NMR. ^{b} The PDI of each polymer was measured by GPC.
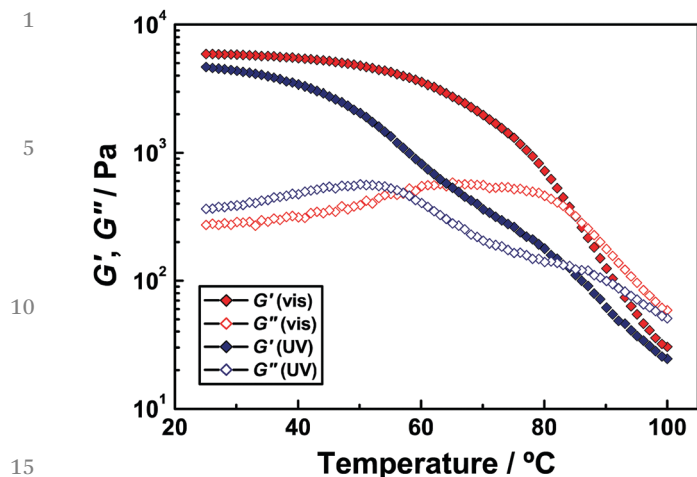
Fig. 4 Variations in G' and G'' values for 15 wt% ABC(Azo) triblock copolymer in [C₂mim][NTf₂] under UV and visible light as functions of temperature at frequency ω = 0.1 rad s⁻¹, strain amplitude γ = 1%, and a cooling rate of 0.2 °C min⁻¹.

40 °C independent of the AzoBnAm composition, whereas those of the *trans*-P(AzoBnAm-*r*-NIPAm) (in the dark) increased upon increasing the AzoBnAm composition, which was consistent with the previous result.[45] From these results, it is speculated that at lower temperature than the UCST of the P(AzoBnAm-*r*-NIPAm) block, the ABC triblock copolymer forms multicompartmentalized micellar networks with PS and P(AzoBnAm-*r*-NIPAm) cores bridged by PDMAAm chains. The large viscoelastic difference of the ABC(Azo) triblock copolymer in the IL under visible and UV light could be explained by the large difference of UCSTs between the *cis*-form and *trans*-form, as the AzoBnAm composition in the ABC(Azo) triblock copolymer is high ([AzoBnAm]/[NIPAm] = 25.9/74.1). However, the sol–gel transition temperatures of the ABC(Azo) triblock copolymer under UV light (*cis*-T_{gel}) and visible light (*trans*-T_{gel}), defined as the crossover point of G' and G'', were almost the same at *ca.* 85 °C. Although it is difficult to precisely determine the UCST of the P(AzoBnAm-*r*-NIPAm) block in the ABC(Azo) triblock copolymer, the result in Fig. S3b (ESI†) implies that the UCST of the *cis*-P(AzoBnAm-*r*-NIPAm) block exists around 40 °C. This strongly suggests that the *cis*-T_{gel} did not correlate with the UCST-type phase transition of the *cis*-P(AzoBnAm-*r*-NIPAm) block. At high polymer concentration, polymer micelles could form gels by jamming of micelles.[46,47] Therefore, it is suspected that the UCST-type phase transition of the *cis*-P(AzoBnAm-*r*-NIPAm) block at around 40 °C caused the transition from the percolated micellar network to the jammed micelles. More significant softening of the *cis*-form ABC triblock copolymer than the *trans*-form ABC triblock copolymer with increasing temperature could be explained by the phase transition from percolated micellar networks to jammed micelles induced by the UCST-type phase transition of the *cis*-P(AzoBnAm-*r*-NIPAm) block. This assumption is also supported by the strain sweep data for the *cis*- and *trans*-ion gels at 60 °C shown in the later discussion (Fig. 5). The sol–gel transition under visible light
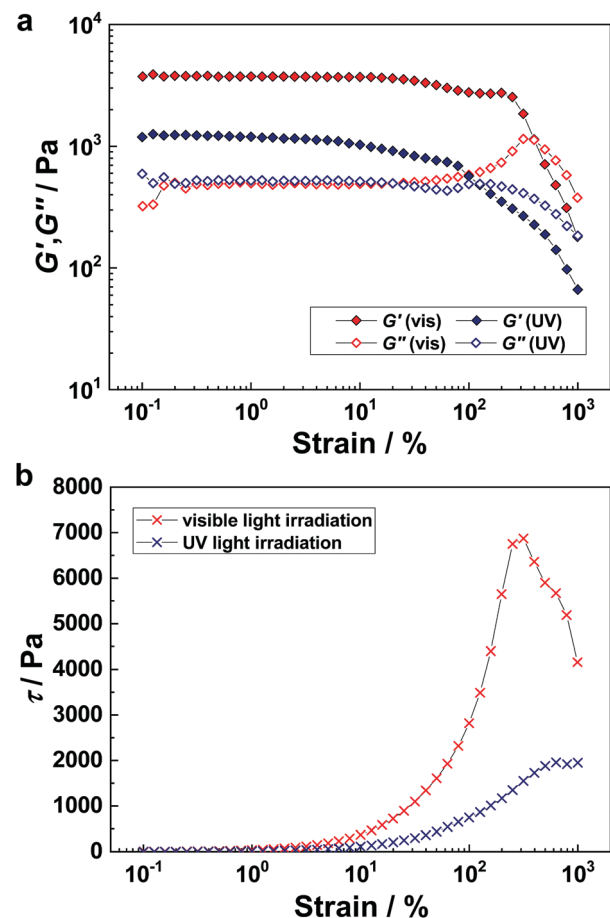

Fig. 5 (a and b) Strain dependences of (a) the G' and G'' values and (b) shear stress for 15 wt% ABC(Azo) triblock copolymer in [C₂mim][NTf₂] under UV or visible light irradiation at 60 °C with frequency ω = 0.1 rad s⁻¹.

irradiation at *ca.* 85 °C could be understood as the phase transition from jammed micelles to free-flowing micelles, attributed to the increased thermal fluctuation of micelles with increasing temperature.[48] From Fig. S3b (ESI†), on the other hand, the UCST of the *trans*-P(AzoBnAm-*r*-NIPAm) block would be over 80 °C. Thus, the *trans*-ABC triblock copolymer might form jammed micelles in the narrow temperature region, or directly undergo phase transition from the percolated micellar network to the micelle solution.

Remarkably, the rheological difference between the *cis*-ion gel and *trans*-ion gel of the ABC triblock copolymer existed over a wider temperature range than that of the previously reported 20 wt% P(AzoMA-*r*-NIPAm)-*b*-PEO-*b*-P(AzoMA-*r*-NIPAm) ABA triblock copolymer-based ion gel (Fig. S4, ESI†).[29] One of the possible reasons was the larger azobenzene content introduced in the photo/thermoresponsive block (25.9 mol% in the present ABC triblock copolymer and 10.4 mol% for the previous ABA triblock copolymer), causing a large difference in the UCST-type phase transition temperature of the photo/thermoresponsive block between the *cis* and *trans* states, *i.e.*, a large bistable temperature region. This large bistable temperature region would induce a significant rheological difference depending on the isomerization state. The differences in the physical

properties of azobenzene between the *cis* and *trans* states such as hydrogen bonding and π–π interaction abilities might also directly contribute to the rheological change.[49] Furthermore, as the ABC ion gel contained low polymer concentration and the azobenzene structure was only introduced in one endblock, the concentration of azobenzene moieties in the ABC ion gel was lower than that in the previous ABA ion gel (ABC: 0.074 M, ABA: 0.11 M). It was recently reported by Lodge *et al.* that the strong absorption of azobenzene in the UV region induced the spatial inhomogeneity of the isomerization state of azobenzene moieties introduced into polymer chains in ILs.[50] Therefore, the lower concentration of azobenzene in the ABC ion gel might contribute to the good penetration of UV light into the ABC ion gel, which led to more efficient *trans*-to-*cis* isomerization of the ion gel.

As the multicompartment structure significantly suppresses the looped chains that frequently occur in ABA triblock copolymer-based micellar networks, ABC triblock copolymer-based gels form more efficient network structures.[32,33] The ion gel at a polymer concentration of 15 wt% in this system showed a comparable storage modulus to the previous ABA triblock copolymer-based ion gel at a polymer concentration of 20 wt%.[29] A simple discussion of rubber elasticity indicated that the ABC ion gel had a more efficient polymer network without looped chains than the ABA ion gel (Table 2). The theoretical elasticity (G) from classical rubber elasticity theory is expressed as $G = nk_{B}T = \rho RT/M_{x}$, where n is the number density of network strands, ρ the mass density of the strands, M_{x} the molecular weight between crosslinks, T the absolute temperature, k_{B} the Boltzmann constant, and R the gas constant. Calculation details of the G values for the ABC and ABA ion gels are described in the ESI.† When these values were compared to the experimental G' values at 25 °C obtained from temperature sweep measurements (Fig. 4 and Fig. S4, ESI†), the ABC ion gel showed almost the same G' value as the ideal theoretical elasticity, whereas the experimental G' value of the ABA ion gel was only half the ideal theoretical elasticity. This implied that the ABC ion gel contained almost no loop chains that did not contribute to the network elasticity. The ABA ion gel contained about 50% loop chains, which was consistent with previous studies.[20,51–53] However, it should be noted that the above discussion is very simplified and rough as many factors such as differences in ILs, the chemical compositions of

polymer chains, polymer concentrations, and the relaxation of physical crosslinks also affect gel elasticity.

The percolated micellar network and the jammed micelle structure were expected to have been formed at an intermediate temperature under visible and UV light, respectively (Fig. 1a). The strain sweep measurements at 60 °C shown in Fig. 5 demonstrate that the ion gels under UV and visible light irradiation showed drastically dissimilar strain dependences. Under visible light, the ion gels exhibited clear critical strains at which G' and shear stress suddenly decreased. This behaviour was typical of physically crosslinked gels, indicative of the destruction of physically crosslinked networks under high amplitude strain.[7,54] On the other hand, under UV light no clear critical strain was observed. Instead, G' continuously decreased up to a strain of 1000%. In addition, the shear stress gradually increased and yielding behaviour did not occur. As the jammed micelle structure did not have a percolated network but only kinetically frozen micelles, strain-induced fluidization occurred at high strain amplitudes, resulting in non-yielding behaviour. The appearances of the ion gels after strain sweep measurements also demonstrated that the breakdown of the gel network was induced for the ion gels under visible light, whereas the ion gel was not broken under UV light (Fig. S5, ESI†).

When the wavelength of light was switched at intermediate temperature, photoinduced transitions between the jammed micelles and percolated micellar network could be demonstrated. Fig. 6 shows the time variations of the G' and G'' values of the ABC ion gel under light irradiation, where the light source was switched between UV and visible light. A significant decrease in G' was observed by light switching from visible to UV light ($t = 0$ s), indicating that the ion gel was softened under UV light. This was ascribed to the structural transition from the percolated micellar network to jammed micelles as physical crosslinks formed by aggregation of P(AzoBnAm-*r*-NIPAm) blocks were broken, driven by *trans*-to-*cis* isomerization of the
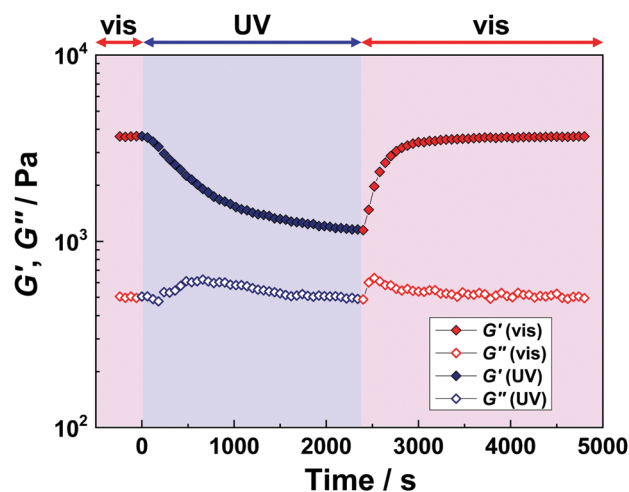
Table 2 Comparison between the ideal rubber elasticities (G) and experimental storage moduli (G') of the ABC and ABA ion gels

	G/kPa	G'/kPa	ρ/kg m^{-3}	M_{x}/kg mol^{-1}
ABC ion gel	5.71	5.89	155	67
ABA ion gel	10.8	5.40	144	33

Theoretical elastic moduli (G), dynamic storage moduli (G'), mass densities of elastic chains (ρ), and molecular weights between cross-linking points (M_{x}) of the ion gels formed by 15 wt% ABC triblock copolymer in [C$_2$mim][NTf$_2$] (ABC ion gel) and 20 wt% ABA triblock copolymer in 1-butyl-3-methylimidazolium hexafluorophosphate ([C$_4$mim]PF$_6$) (ABA ion gel) at 25 °C.

Fig. 6 Variations in the G' and G'' values of 15 wt% ABC(Azo) triblock copolymer in [C$_2$mim][NTf$_2$] by switching UV and visible light irradiation at 60 °C with frequency ω = 0.1 rad s^{-1} and strain amplitude γ = 1%.

azobenzene unit. When the light source was switched from UV to visible light again, G' quickly recovered to the initial value ($t < 0$ s), indicative of the excellent reversibility of the photo-induced rheological transition without structural degradation of the ion gel. During the photoinduced rheological transition, higher G' than G'' values were maintained. In other words, the ABC ion gel retained its solid-like integrity even under UV light irradiation due to the jammed micelle structure with the aid of the IL-phobic PS block. This can be contrasted with previous photoresponsive ion gels based on ABA triblock copolymers where switching of light sources caused photoinduced sol–gel transitions.[29] Since the light-dependent UCST-type phase transition temperatures of the P(AzoBnAm-r-NIPAm) random copolymer were confirmed in several ILs (Fig. S6 and Table S1, ESI†), the photoresponsive rheological behaviour of the ABC triblock copolymer-based ion gel could be modulated by changing ILs, confirming the versatility and tunability of the present strategy.

Conclusions

In this study, we dealt with an ABC triblock copolymer-based ion gel that underwent photoinduced rheological transitions driven by cis–$trans$ isomerization of azobenzene moieties. Introduction of an IL-phobic group enabled structural transition between the jammed micelle structure and the micellar network structure. The ABC architecture suppressed the looped chains that did not contribute to network elasticity. Thus, the ABC ion gel exhibited a superior elastic modulus to the previous ABA ion gel. The temperature dependences of the viscoelastic properties of the ABC ion gel were significantly affected by light irradiation as the cis–$trans$ isomerization of azobenzene moieties modulated the compatibility of the P(AzoBnAm-r-NIPAm) block with the IL. By utilizing the rheological difference depending on the wavelength of light, the photoinduced softening/hardening of the ion gel driven by the structural transition between the jammed micelle structure and the percolated micellar network was demonstrated by switching light sources. The significant rheological change of the non-volatile and ion conducting gel via photo-stimuli presented in this study could be used in various applications such as light-responsive soft actuators and photo-healable soft materials.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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