Electronic Supplementary Information (ESI)

Stimuli-Responsive Liquid Cell Scaffold: Reversible Viscoelasticity Switching of a Polymer in an Ionic Liquid by Visible-Light

Aya Saruwatari[a, b], Yuji Kamiyama[a], Jun Nakanishi[a, c, d], Ryota Tamate[a], and Takeshi Ueki[a, b]*

[a]Research Center for Macromolecules and Biomaterials, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

[b]Graduate School of Life Science, Hokkaido University, Kita 10, Nishi 8, Kita-ku, Sapporo, Hokkaido 060-0810, Japan.

[c]Graduate School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan

[d]Graduate School of Advanced Engineering, Tokyo University of Science, 6-3-1 Niijuku, Katsushika-ku, Tokyo 125-8585, Japan

*To whom correspondence should be addressed. E-mail: UEKI.Takeshi@nims.go.jp

Experimental

Solubility test for hydrophobic polymers

Poly(methyl methacrylate) (PMMA, norminal weight averaged molecular weight (M_w)= 75 kDa), poly(ethyl methacrylate) (PEMA, M_w = 250 kDa), poly(isopropyl methacrylate)(P(*iso*-Pro)MA, M_w = 100 kDa), poly(*n*-butyl methacrylate) (P(*n*-Bu)MA, M_w = 180 kDa), poly(isobutyl methacrylate) (P(*iso*-Bu)MA, M_w = 260 kDa), poly(*n*-hexyl methacrylate) (P(*n*-Hex)MA, 25.68 wt% solution in toluene), poly(cyclohexyl methacrylate) (P(*c*-Hex)MA)), poly(*n*-dodecyl methacrylate) (P(*n*-Dod)MA, 29.49 wt% solution in toluene), poly(methyl acrylate) (PMA, 35–45 wt% solution in toluene), poly(ethyl acrylate) (PEA, 18–22 wt% solution in toluene), poly(isopropyl acrylate) (P(*iso*-Pro)A, 20–25 wt% solution in toluene), poly(*n*-butyl acrylate) (P(*n*-Bu)A, 25–30 wt% solution in toluene), poly(isobutyl acrylate) (P(*iso*-Bu)A, 20–25wt% solution in toluene), poly(*n*-hexyl acrylate) (P(*n*-Hex)A, 20–25 wt% solution in toluene), poly(*n*-decyl acrylate) (P(*n*-Decy)A, 28–32 wt% solution in toluene), poly(*n*-dodecyl acrylate) (P(*n*-Dod)A, 23–28 wt% solution in toluene), polystyrene (PSt, M_w = 45 kDa), poly(α-methyl)styrene (P(α-MA)St), poly(vinyl toluene) (PVnTol, meta : para = 60 : 40), poly(*p*-*tert*-butyl)styrene (P(*tert*-Bu)St), poly(vinylbenzyl chloride) (PVnBn-Cl, meta : para = 60 : 40, M_w =500 kDa), and poly(2,4,6-tribromo)styrene (P(*tri*-Br)St) were purchased from

Scientific Polymer Products in Methacrylate, Acrylate, and Styrene polymer kits. Poly(benzyl methacrylate) (PBnMA, M_w = 78 kDa) was obtained by general free radical polymerization procedure.

The solubility of polymers in [P8,8,8,8][TFSI] was assessed using a previously reported procedure.[1, 2] Due to high viscosity of ILs, cosolvent evaporation method was commonly used for preparing polymer-IL composites. Initially, the polymer was dissolved in DCM to form a homogeneous mixture. Subsequently, the transparent polymer solution was mixed with [P8,8,8,8][TFSI], and DCM was evaporated overnight at 85 °C. The solubility of the polymer in the IL was evaluated based on the transparency of the solution with naked eye within a temperature range of 4 to 120 °C.

Surface rheological measurements

Surface rheology of P(mAzoA$_{4.5}$-*r*-MMA) solution (2 w/v%) in [P8,8,8,8][TFSI] was investigated by a hybrid rheometer (HR20) (TA Instruments, USA) with a double wall ring geometry (I.D. = 69 mm, O.D. = 71 mm) and a cup (I.D. = 62 mm, O.D. = 79 mm) with a circular channel. The sample was placed in the cup after irradiated with 436 nm or 546 nm light and the ring was lowered, ensuring contact with the surface. Temperature scanning measurements were performed with a shear rate of 1 s^{-1} and a

cooling rate of 0.1 °C min^{-1} in the range from 80 to 10 °C were used under continuous each light irradiation.

The photo switching measurements were also performed with the same shear rate. The sample was placed in the cup of the equipment after irradiated with blue or green light at 85 °C for 1 h and cooled at 30 °C for 30 min, then the surficial viscosity was recorded after 5 min.

FT-IR measurements

Fourier transform infrared (FT-IR) spectroscopy was employed to investigate the potential hydrogen bonding interactions involved in the solvation of PMMA in [P8,8,8,8][TFSI] (IRSpirit, Shimadzu, Japan). Procedure followed as previously reported.[3] Spectra were recorded using the attenuated total reflection (ATR) method for polymer solutions at a concentration of 10 wt%. The C=O stretching vibration band (~1750 cm^{-1}) was compared among three conditions: PMMA fully dissolved in [P8,8,8,8][TFSI] by heating to 50–60 ºC with a hair dryer, PMMA phase-separated from [P8,8,8,8][TFSI], and neat PMMA. The results are shown in **Figure S6**.

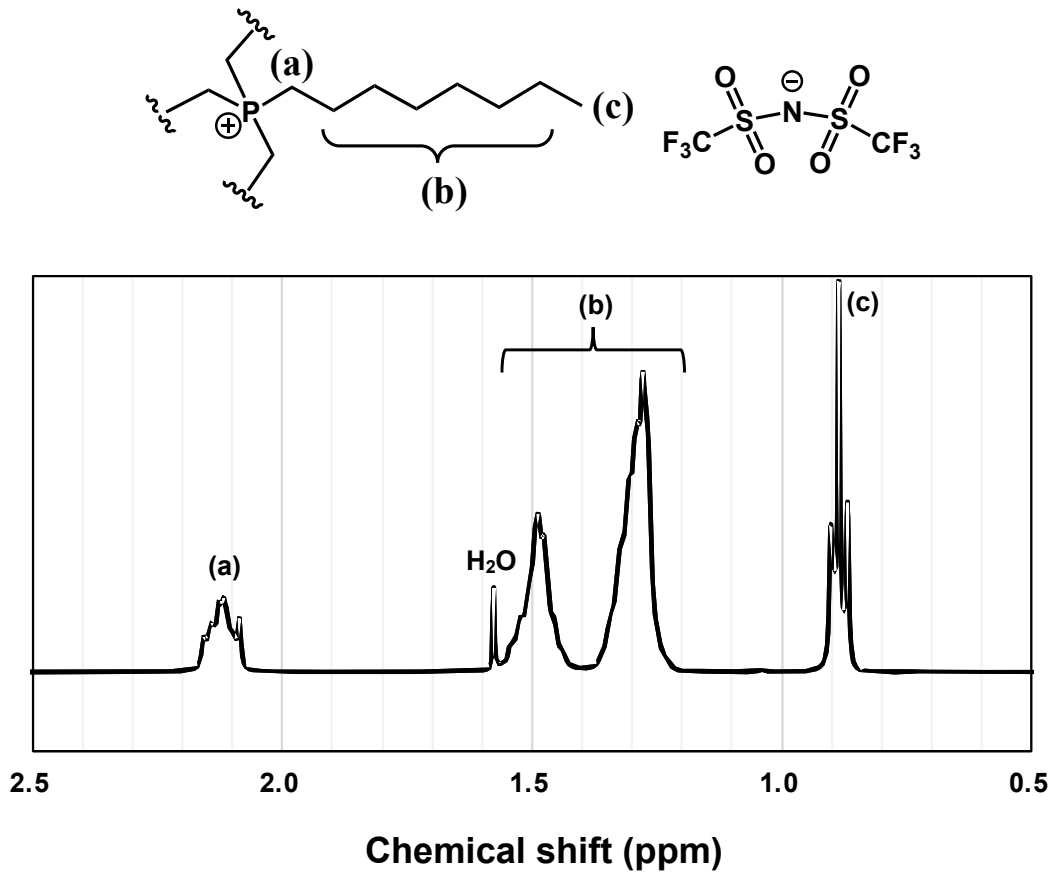
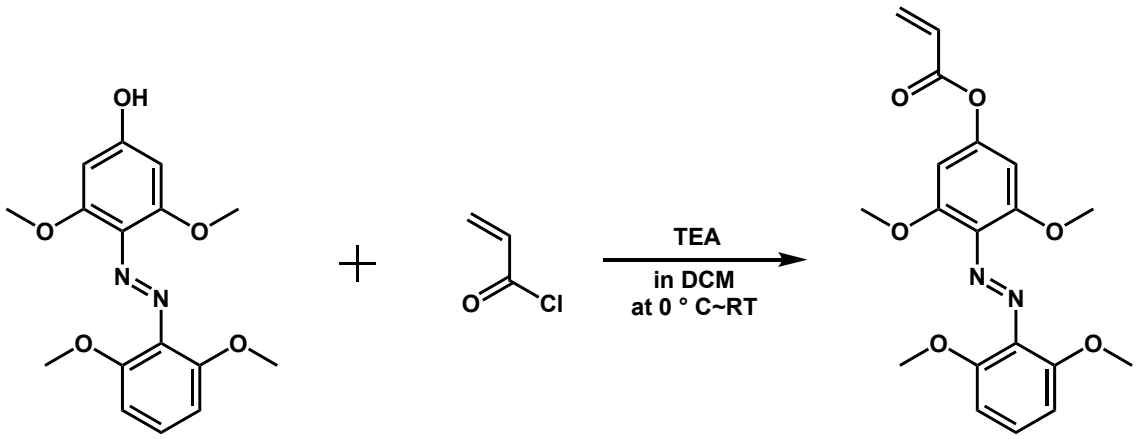
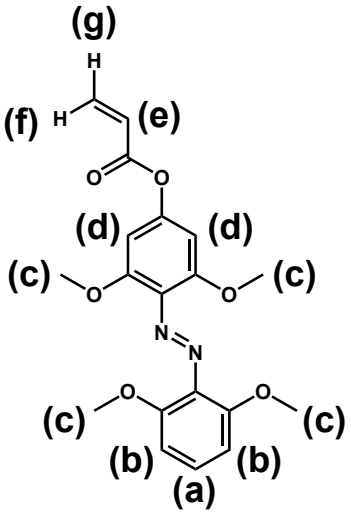
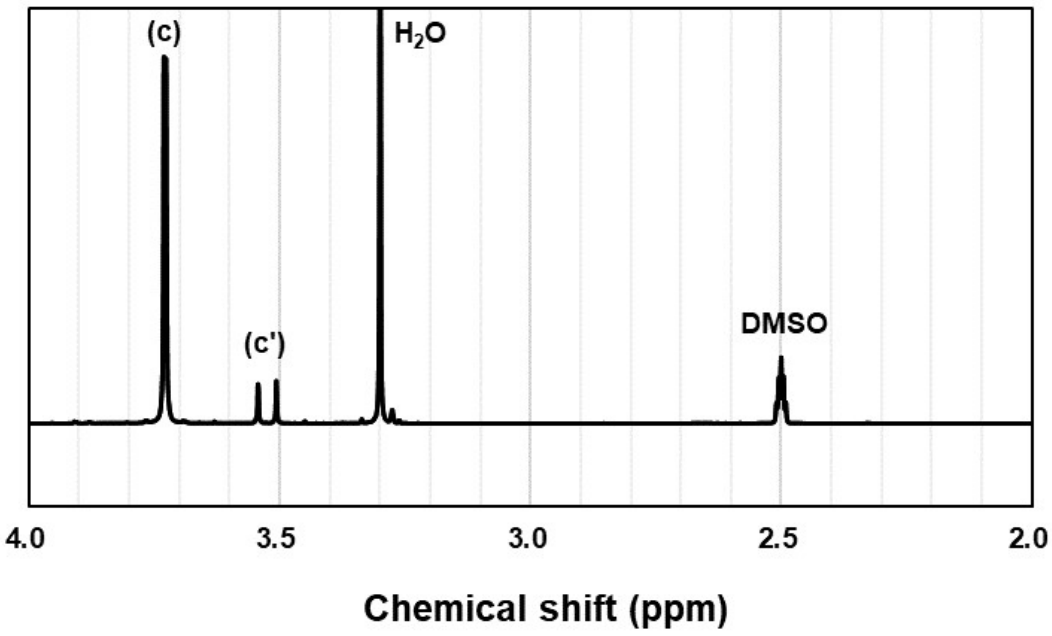


Fig. S1 ^{1}H NMR spectra for [P8,8,8,8][TFSI] in chloroform-*d*.

Scheme S1. Synthesis scheme for mAzoA.




(g)
H
(f)
H
(e)
O
O
(d)
(d)
(c)
O
O
(c)
N
N
(c)
O
O
(c)
(b)
(b)
(a)


(c)
H2O
(c')
DMSO
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3.5
3.0
2.5
2.0
Chemical shift (ppm)

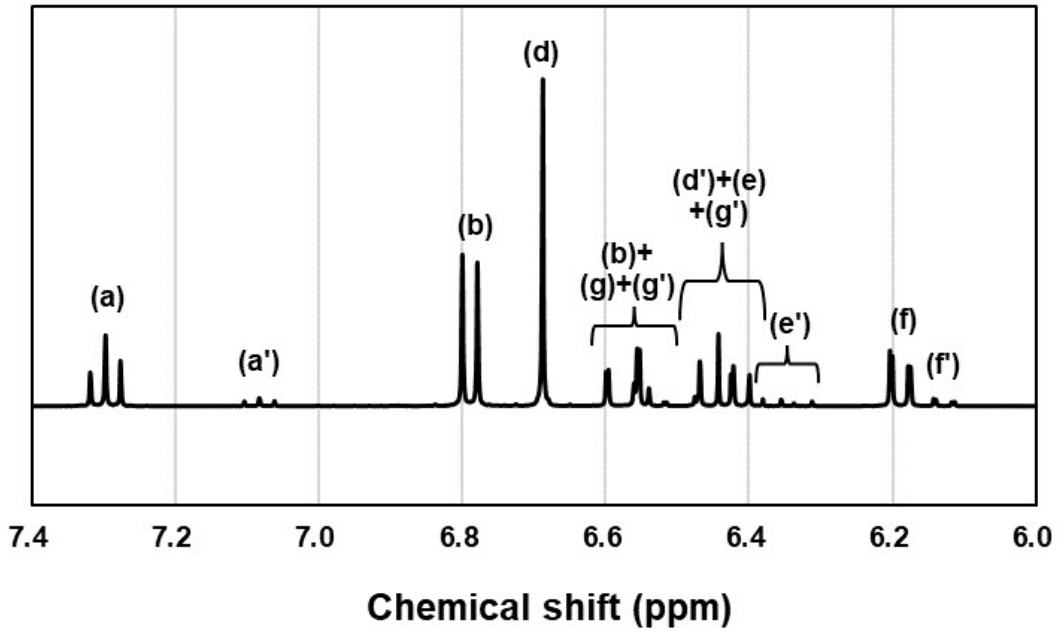
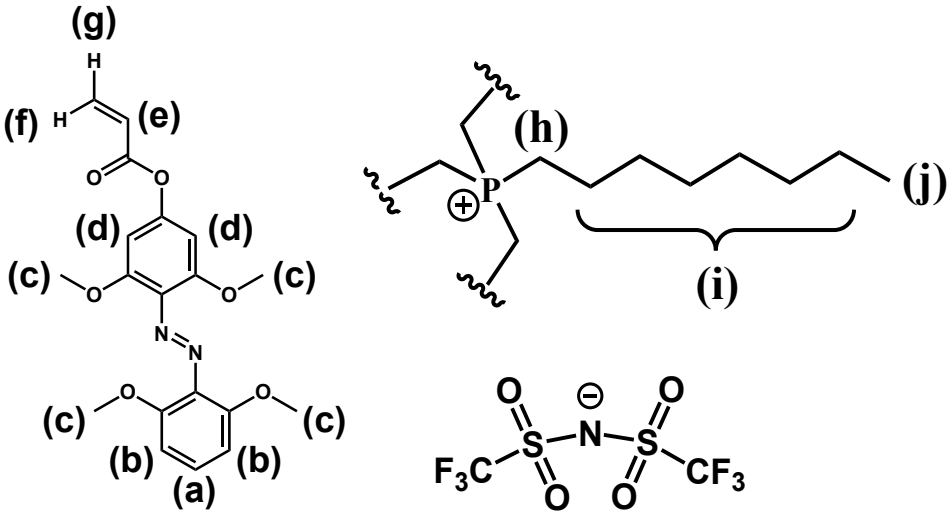
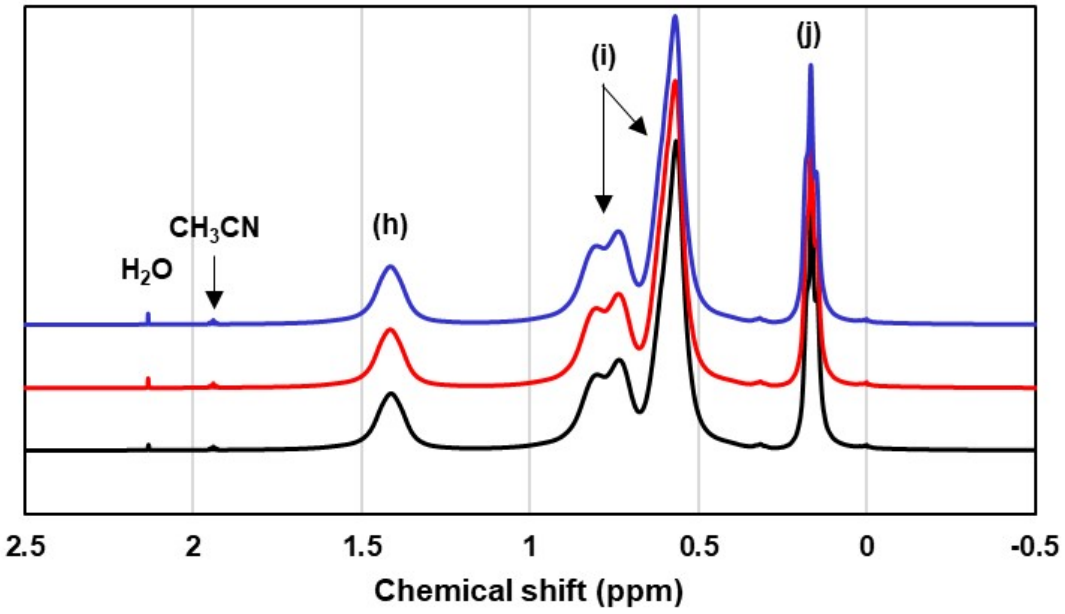


Fig. S2 ^{1}H NMR spectra for mAzoA in dimethyl sulfoxide-d_6. Symbols with quotation marks indicate protons of *cis*-mAzoA, while those without quotation marks indicate protons in the *trans*-form.

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(j)
CH3CN
H2O
(h)
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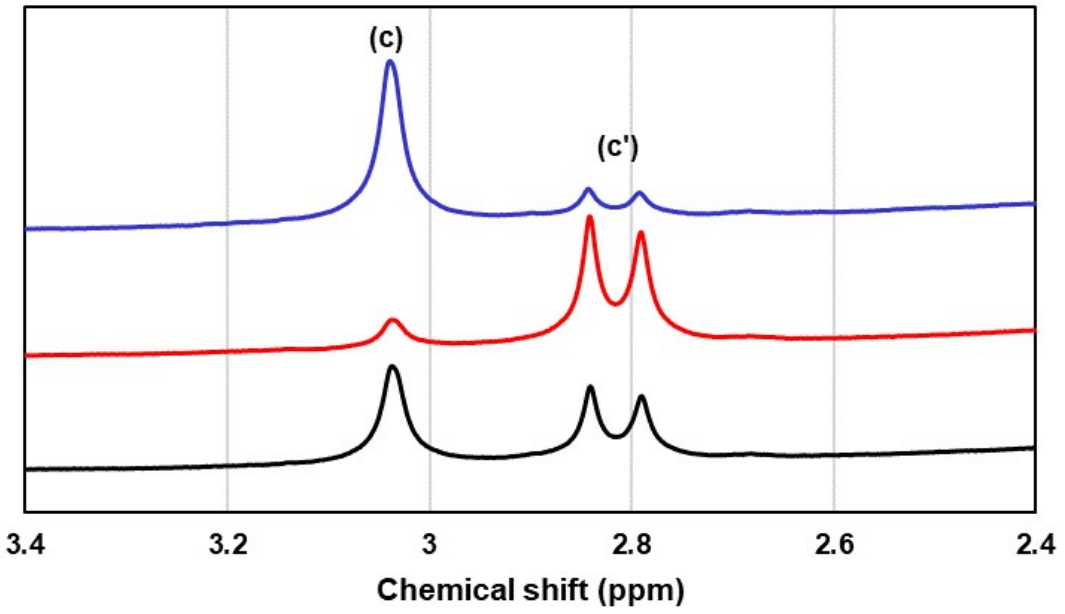
2
1.5
1
0.5
0
-0.5
Chemical shift (ppm)


(c)
(c')
3.4
3.2
3
2.8
2.6
2.4
Chemical shift (ppm)

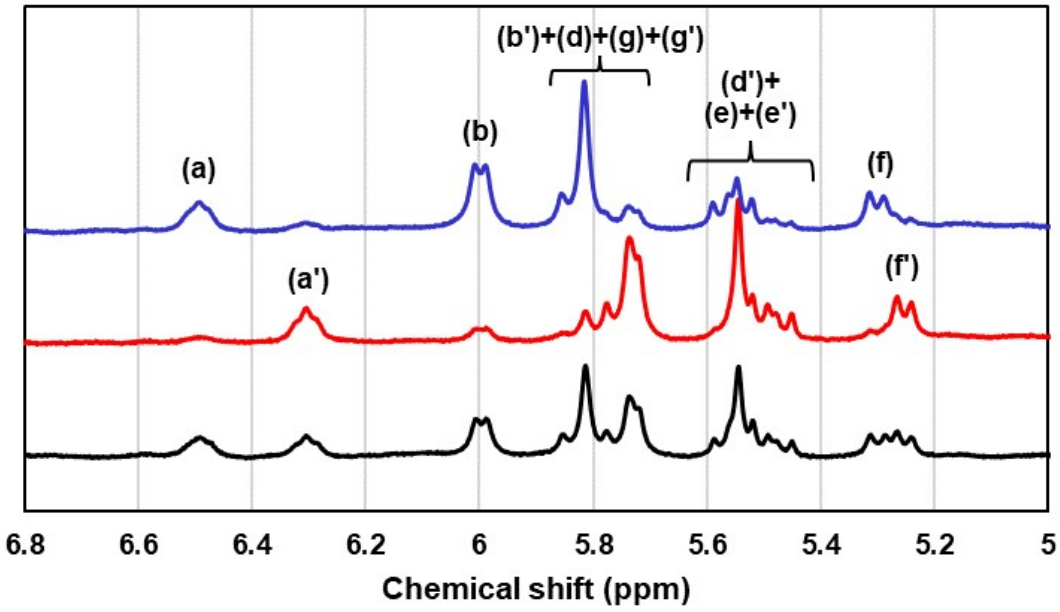


Fig. S3 ^{1}H NMR spectra for mAzoA solution in [P8,8,8,8][TFSI]. Measurements were conducted using a double NMR tube technique[4] to avoid solvation of mAzoA by CD_3CN. 10 mM mAzoA solution in [P8,8,8,8][TFSI] and CD_3CN containing tetramethylsilane were separately introduced into inner tube and outer tube. The pristine sample (black) was exposed to 546 nm light (red) or 436 nm light (blue). Symbols with quotation marks indicate protons of *cis*-mAzoA, while those without quotation marks indicate protons in the *trans*-form.

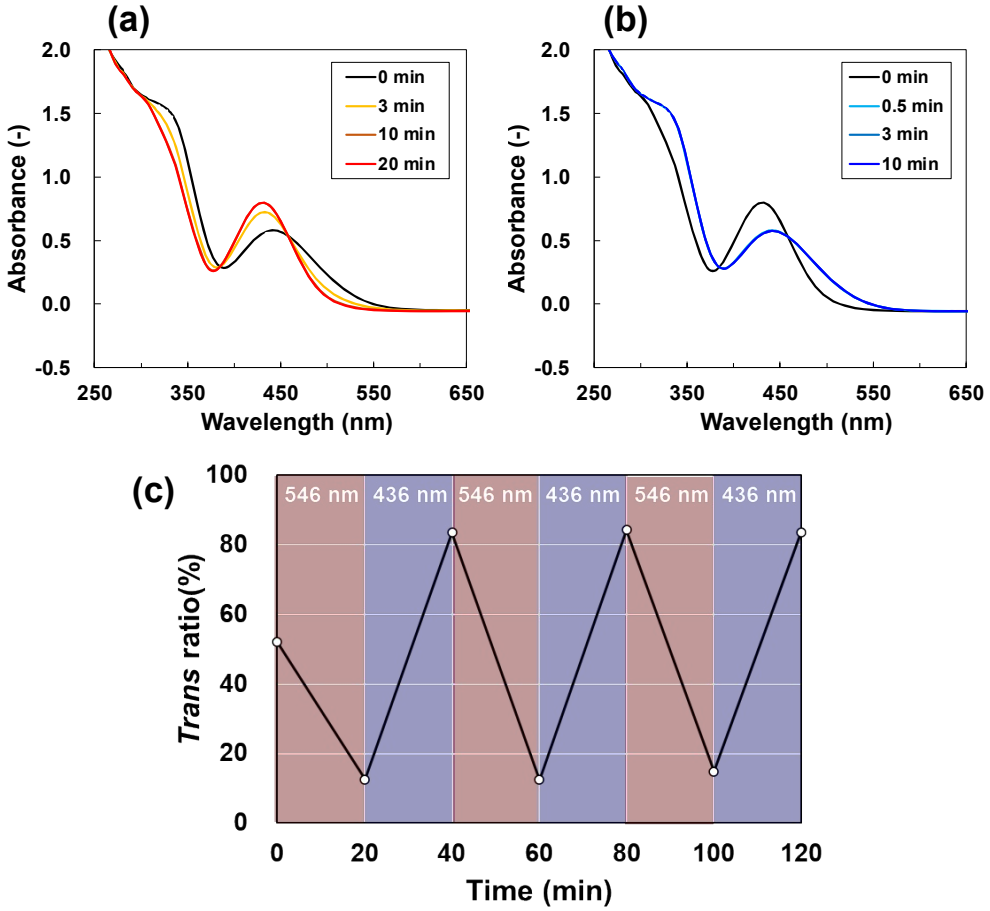


Fig. S4 Absorbance of 0.01 wt% mAzoA solution in [P8,8,8,8][TFSI] at 25 °C under (a) 546 nm and (b) 436 nm. (c) Three cycles of photoswitching of 10 mM mAzoA in [P8,8,8,8][TFSI] with alternating green (546 nm) and blue (436 nm) light for 20 min each. *Trans* ratio was calculated from the integral ratio of *trans*- and *cis*-form obtained from ^{1}H NMR spectra. To avoid the influence of deuterated solvent addition on the photoisomerization reaction, measurements were conducted using NMR double tubes to separate CD_3CN and mAzoA monomer solution.

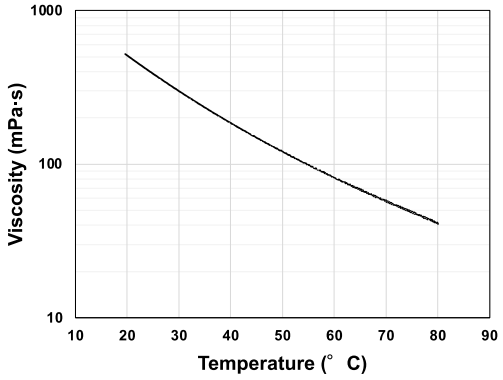


Fig. S5 Viscosity of [P8,8,8,8][TFSI] as a function of temperature. (390 mPa s at 25 °C and 214 mPa s at 37 ºC)

Table S1 Results of solubility tests for poly(meth)acrylates and polystyrenes in [P2,2,2,5][TFSI],[5] [P4,4,4,1][TFSI],[5] [P6,6,6,14][TFSI],[5] and [P8,8,8,8][TFSI] as solvents. The solutions were obtained using the co-solvent evaporation method, and transparency was evaluated visually. Yes: Transparent, homogeneous mixture with a range from 4 °C to 100 °C. No: Turbid phase separation within a range from 4 °C to 100 °C. UCST: UCST type phase transition within a range from 4 °C to 100 °C. LCST: LCST type phase transition within a range from 4 °C to 100 °C.

	PMMA	PEMA	P(*iso*-Pro)MA	P(*n*-Bu)MA	P(*iso*-Bu)MA	P(*c*-Hex)MA	P(*n*-Hex)MA	P(*n*-Dod)MA	PBnMA
[P2,2,2,5][TFSI]	Yes	Yes	Yes	Yes	Yes	No	No	No	No
[P4,4,4,1][TFSI]	Yes	Yes	Yes	Yes	Yes	No	No	No	No
[P6,6,6,14][TFSI]	Yes	Yes	Yes	Yes	Yes	No	No	No	No
[P8,8,8,8][TFSI]	UCST	Yes	Yes	Yes	Yes	Yes	Yes	No	No
	PMA	PEA	P(*iso*-	P(*n*-Bu)A	P(*iso*-	P(*n*-	P(*n*-	P(*n*-	

			Pro)A		Bu)A	Hex)A	Decy)A	Dod)A
[P2,2,2,5][TFSI]	Yes	Yes	Yes	Yes	Yes	No	No	No
[P4,4,4,1][TFSI]	Yes	Yes	Yes	Yes	Yes	No	No	No
[P6,6,6,14][TFSI]	Yes	Yes	Yes	Yes	Yes	No	No	No
[P8,8,8,8][TFSI]	No	Yes	Yes	Yes	Yes	Yes	LCST	No

	PSt	P(*α*-Me)St	PVnTol	P(*tert*-Bu)St	PVnBn-Cl	P(*tri*-Br)St
[P2,2,2,5][TFSI]	No	No	No	No	No	No
[P4,4,4,1][TFSI]	No	No	No	No	No	No
[P6,6,6,14][TFSI]	No	No	No	No	No	No
[P8,8,8,8][TFSI]	No	No	No	No	No	No

Table S2 Characterization of PMMA.

Polymer	M_w **[g mol^{-1}]**	M_w/M_n
M-1	1.1×10^5	2.23
M-2	5.0×10^5	1.02
M-3	8.9×10^5	1.07

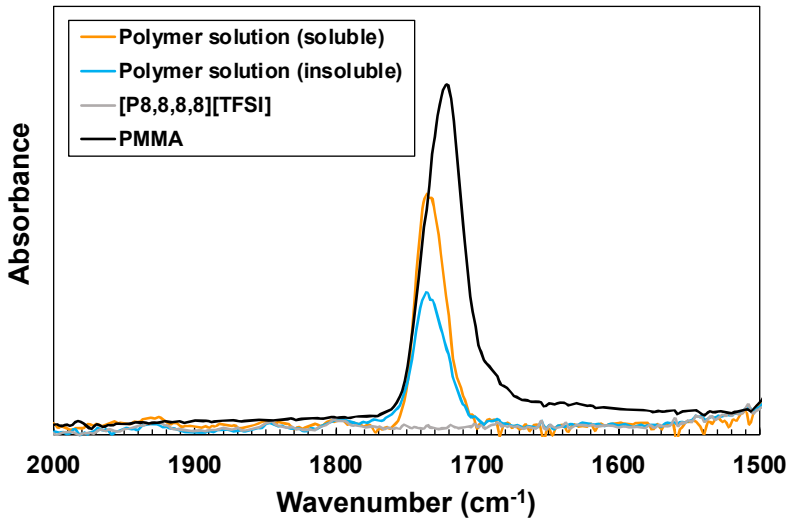


Fig. S6 FT-IR spectra of [P8,8,8,8][TFSI] (gray), PMMA (black), and 10 wt % PMMA solution in [P8,8,8,8][TFSI] heated (orange) and unheated (light blue).

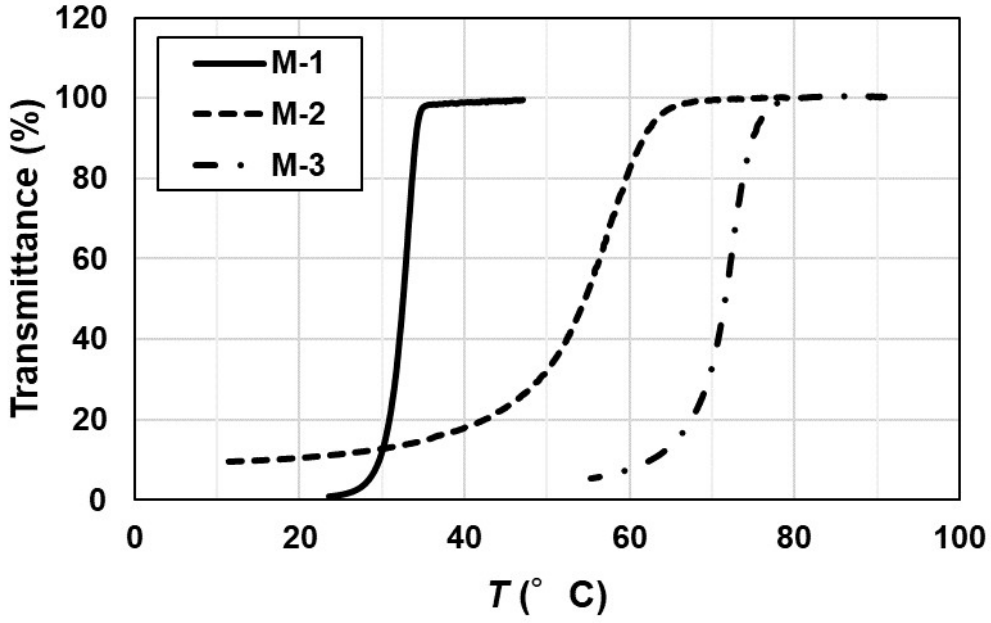
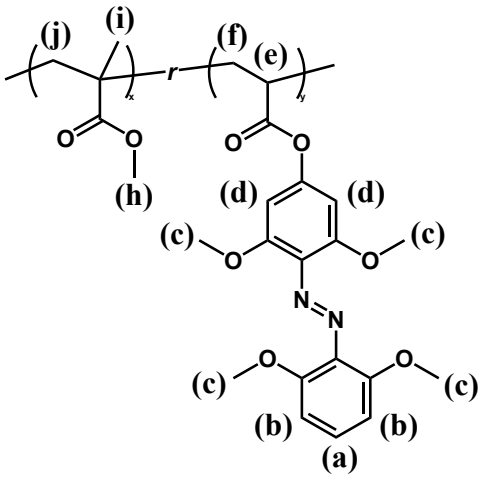


Fig. S7 Temperature dependence of transmittance at 700 nm for 2 w/v% PMMA solution in [P8,8,8,8][TFSI]. The transmittance of the solutions was monitored at 700nm with a cooling rate of 0.1 °C min^{-1}.


(j)
(i)
(f)
(e)
r
x
y
O
O
O
O
(h)
(d)
(d)
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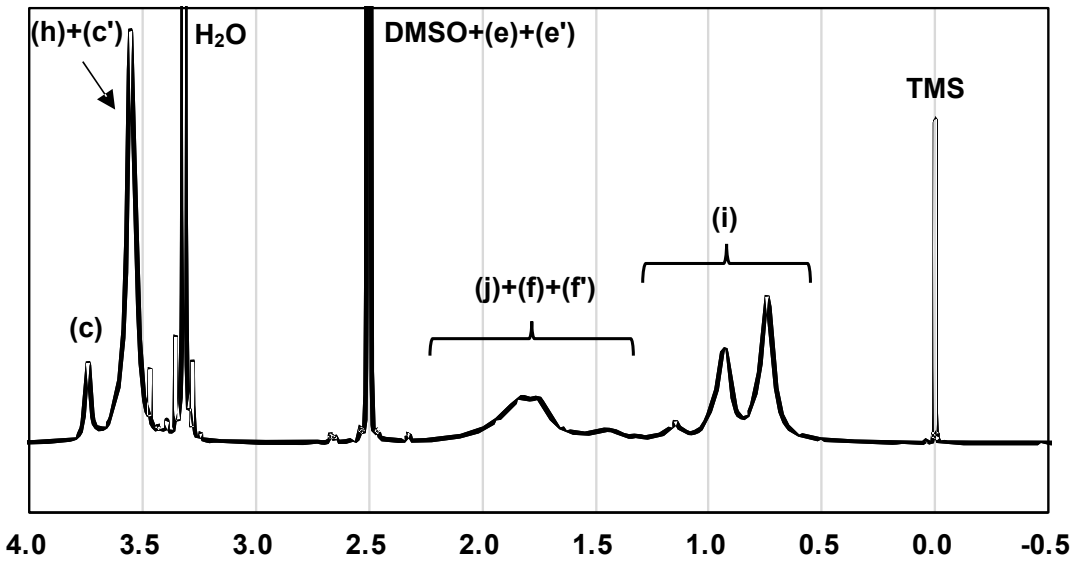
(c)
O
O
(c)
(b)
(b)
(a)


(h)+(c')
H2O
DMSO+(e)+(e')
TMS
(i)
(j)+(f)+(f')
(c)
4.0
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3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
Chemical shift (ppm)

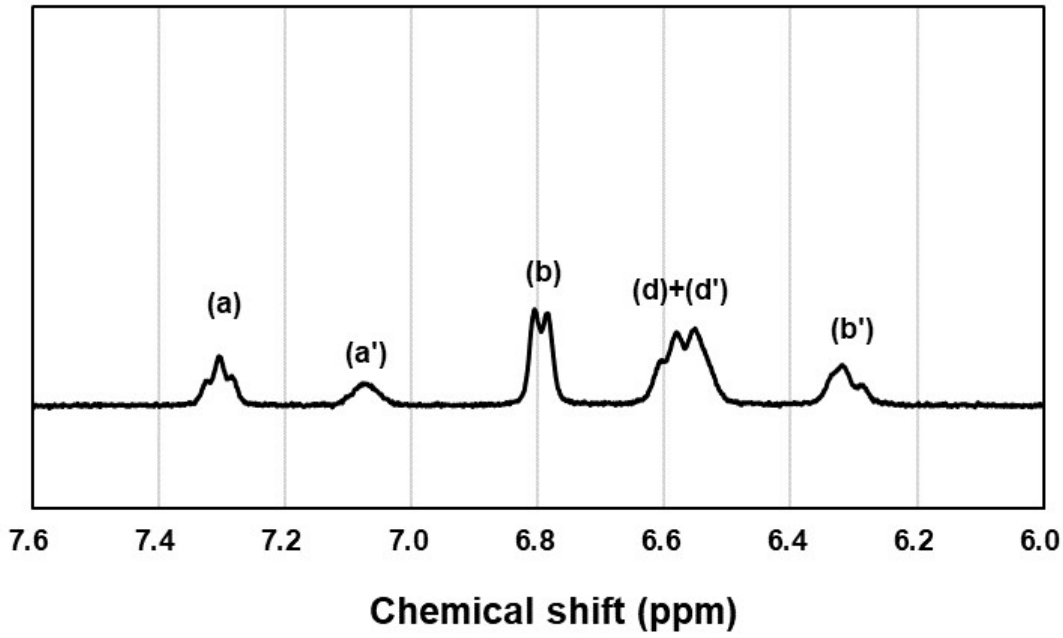

Fig. S8 ^{1}H NMR spectra for P(mAzoA$_{2.4}$-*r*-MMA) in dimethyl sulfoxide-d$_6$. Symbols with quotation marks indicate protons of *cis*-mAzoA, while those without quotation marks indicate protons in the *trans*-form.

Table S3 The integrated intensity ratio of polymers, evaluated from ^{1}H NMR.

Polymer	The integrated intensity ratio [a]			
	(a)+ (a')	(f)+(f')	(i)+(j)+(f)+(f')	(i)+(j)
P(mAzoA$_{2.4}$-*r*-MMA)	1.000	2.000	201.5	199.5
P(mAzoA$_{4.5}$-*r*-MMA)	1.000	2.000	108.7	106.7
P(mAzoA$_{7.3}$-*r*-MMA)	1.000	2.000	65.49	63.49

a) Each symbol corresponds to the respective ^{1}H of P(mAzoA-*r*-MMA) shown in **Fig. S8**. The value of (f)+(f') was obtained by doubling the sum of (a)+(a').

Table S4 Characterization of polymers.

Polymer	M_w [g mol^{-1}] [a]	M_w/M_n [a]	[mAzoA]/[MMA] [b]
P(mAzoA$_{2.4}$-*r*-MMA)	1.5×10^5	2.25	2.4/97.6
P(mAzoA$_{4.5}$-*r*-MMA)	1.7×10^5	2.23	4.5/95.5
P(mAzoA$_{7.3}$-*r*-MMA)	1.1×10^5	2.21	7.3/92.7

a) Obtained from GPC (eluent: DMF, standard: PMMA, detector: RID).

b) Calculated by ^{1}H NMR. [mAzoA]/[MMA] was obtained from the ratio of the integrated intensity ratio of the mAzoA peaks ((a)+(a')) and the MMA peaks ((i)+(j)) shown in **Table S3**.

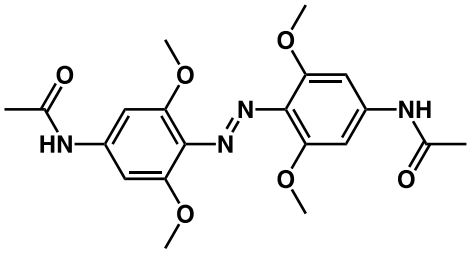

Fig. S9 Chemical structure of mAzoDA synthesized and studied by Woolley *et al*. [6]

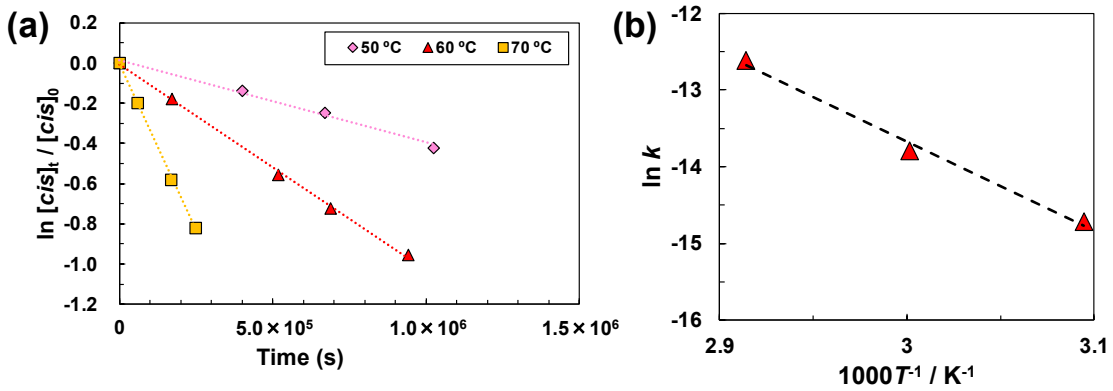

Fig. S10 (a) Time course of first-order reaction for thermal *cis*-to-*trans* isomerization of mAzoA in DMSO at 50 °C (pink diamonds), 60 °C (red triangles), and 70 °C (orange squares). (b) Arrhenius plot of the first order rate constants for thermal isomerization.

Table S5 Activation energy, frequency factor of *cis*-to-*trans* thermal isomerization and half-life of *cis* isomer at 37 °C for azobenzene in various organic solvents and ILs.

	Solvent	E_a **[kJ mol^{-1}]**	A **[s^{-1}]**	$\tau_{1/2}$ **[h]** [b]
Ref. [7]	[C_4mim][TFSI]	89.5±2.1	4.8×10^{9}	48
Ref. [7]	[C_5mim][TFSI]	104.5±3.1	1.3×10^{12}	60
Ref. [7]	[C_6mim][TFSI]	94.4±4.7	3.5×10^{10}	44
Ref. [8]	Hexane	91.1 [a]	4.26×10^{10} [a]	10.0
Ref. [8]	chlorobenzene	88.3 [a]	9.73×10^{10} [a]	1.47
Ref. [8]	*o*-dichlorobenzene	84.4 [a]	9.73×10^{10} [a]	0.281
Ref. [9]	heptane	95.4	7.53×10^{12}	0.303
Ref. [9]	toluene	97.1	1.07×10^{13}	0.407
Ref. [9]	benzene	97.5	1.26×10^{13}	0.408

Ref. [9]	nitrobenzene	98.3	1.69×10^{13}	0.422
Ref. [9]	decanol	96.9	8.83×10^{12}	0.457
Ref. [9]	hexanol	99.2	2.00×10^{13}	0.494
Ref. [9]	ethyl acetate	97.1	8.28×10^{12}	0.529
Ref. [9]	butanol	100	2.44×10^{13}	0.606
Ref. [9]	dioxane	98.7	1.43×10^{13}	0.588
Ref. [9]	aniline	100	2.55×10^{13}	0.628
Ref. [9]	acetone	99.2	1.54×10^{13}	0.639
Ref. [9]	ethanol	102	3.67×10^{13}	0.711
Ref. [9]	nitromethane	101	2.66×10^{13}	0.834
Ref. [9]	methanol	104	5.22×10^{13}	1.04
Ref. [9]	acetonitrile	100	1.46×10^{13}	0.937
Ref. [10]	cyclohexanone	114	5.6×10^{13}	61
Ref. [10]	*o*-dichlorobenzene	114	1.5×10^{14}	23
Ref. [10]	benzene	99.2	4.5×10^{11}	22
Ref. [10]	chloroform	100	7×10^{11}	19
Ref. [10]	tetrachloromethane	98.3	4.1×10^{11}	17
Ref. [10]	cyclohexane	94.6	8.7×10^{10}	19
Ref. [10]	chlorobenzene	105	5.45×10^{12}	15

[a] Calculated from the rate constants at each temperature listed in the literature. [b] Calculated from activation energy and frequency factors.

Table S6 Activation energy, frequency factor of *cis*-to-*trans* thermal isomerization and half-life of *cis* isomer at 37 °C for mAzoA in DMSO and [P8,8,8,8][TFSI].

Solvent	mAzo derivative	E_a [kJ mol^{-1}]	A [s^{-1}]	$\tau_{1/2}$ [h]
DMSO	mAzoDA [6]	80.2	6.5×10^{7}	97
DMSO	mAzoA	96.4	1.5×10^{9}	2233
[P8,8,8,8][TFSI]	mAzoA	106	4.0×10^{10}	2911

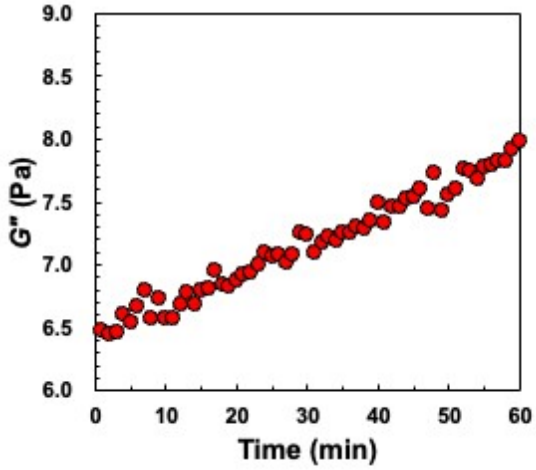

Fig. S11 Time course of loss modulus under illumination with 546 nm light in the 1st cycle.

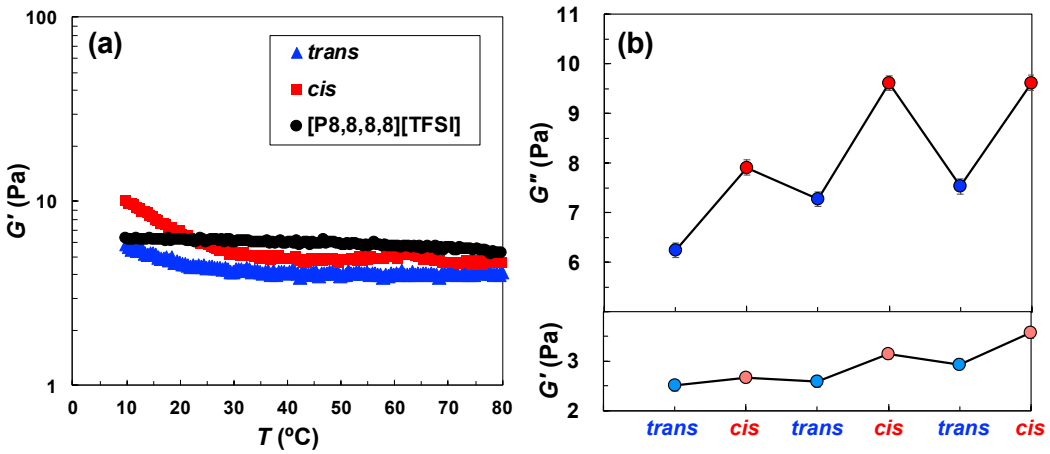

Fig. S12 (a) Temperature-dependent storage modulus (G') of 2 w/v% P(mAzoA$_{2.4}$-*r*-MMA) in [P8,8,8,8][TFSI] (red: 546 nm, bule: 436 nm) and neat [P8,8,8,8][TFSI] (black) at a frequency ω = 10 rad s^{-1} and strain amplitude γ = 10%. Samples were cooled at a rate of 0.1 °C min^{-1} under continuous light irradiation. (b) Cyclic changes in storage modulus (G') and loss modulus (G'') of the polymer solution at 25 °C under alternate illumination with 436 nm light (blue) and 546 nm light (red). After observing the viscoelastic response in *cis*-type, the sample was heated to achieve full miscibility, cooled to 25 °C, and then re-irradiated with 436 nm light to regenerate *trans*-type.

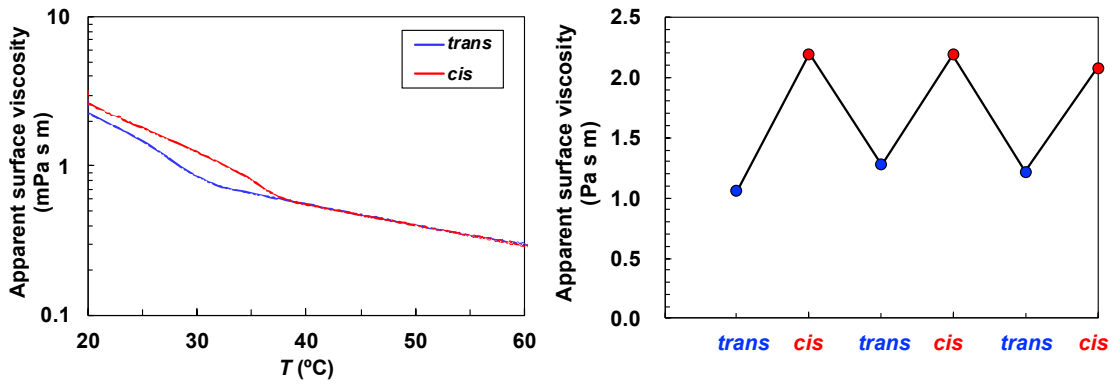

Fig. S13 (a) Apparent surface viscosity for 2 w/v% P(mAzoA$_{4.5}$-*r*-MMA) in [P8,8,8,8][TFSI] solution as a function of temperature at shear rate 10 s^{-1}. The sample was exposed to 546 nm light (red) or 436 nm light (blue) and cooled at 0.1 °C min^{-1}. (b) Cyclic changes in apparent surface viscosity of the polymer solution at 30 °C by illuminating 436 nm light (blue plot) and 546 nm light (red plot). Between each observation, the polymer solution was heated to be fully compatible, irradiated with 436 nm or 546 nm, and cooled to 30 °C.

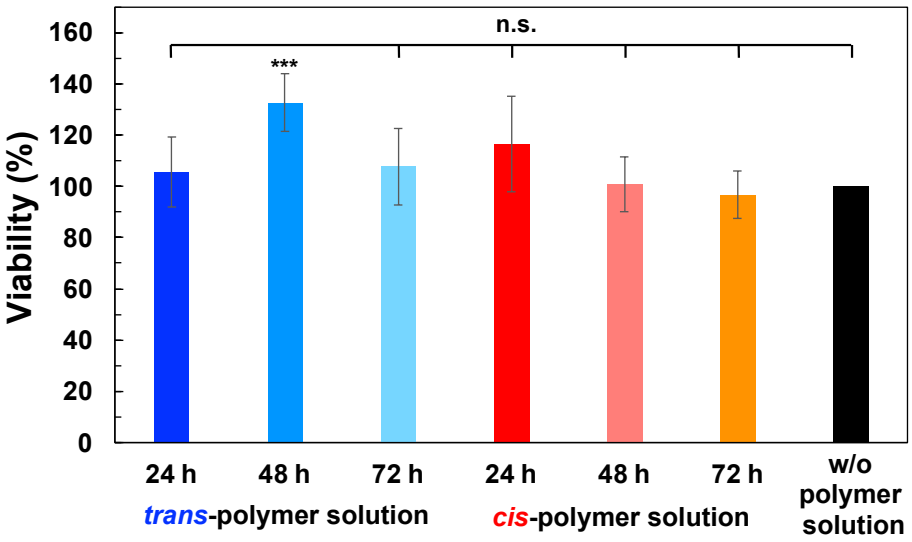

Fig. S14 Cell viability of MDCK cells after 24, 48, and 72h incubation in medium saturated with P(*trans*-mAzoA$_{2.4}$-*r*-MMA) or P(*cis*-mAzoA$_{2.4}$-*r*-MMA) in [P8,8,8,8][TFSI], evaluated using the WST-8 assay. Viability was calculated relative to cells cultured in standard medium without polymer solutions. Error bars represent standard deviation (n = 3). ***P < 0.05 (two-tailed Student's t test).

Table S7 Validation data for phototoxicity tests in **Fig. 6(a)**.

	Viability (%)			
	365 nm	436 nm	546 nm	w/o light
	1.56	110	102	100
	0.651	93.2	111	100
	70.0	114	104	100
	-0.699	80.8	69.0	100
	0.995	91.7	94.6	100
	1.34	110	81.3	100
	0.287	87.9	125	100

	0.404	75.9	120	100
Average	9.31	95.4	101	100
SD	24.5	14.3	19.0	0.00

Table S8 Validation data for phototoxicity tests in **Fig. 6(b)**.

	Viability (%)			
	trans-polymer solution	*cis*-polymer solution	[P8,8,8,8][TFSI]	w/o polymer solution
	89.9	100	108	100
	112	113	96.9	100
	115	137	95.5	100
Average	106	117	100	100
SD	13.6	18.6	6.55	0.00

Table S9 Validation data for phototoxicity tests in **Fig. S14**.

	Viability (%)						
	trans-polymer solution			*cis*-polymer solution			w/o polymer solution
	24 h	48 h	72 h	24 h	48 h	72 h	
	89.9	136	118	100	111	91.5	100
	112	142	90.6	113	89.9	91.2	100
	115	120	114	137	101	108	100
Average	106	133	108	117	101	96.8	100
SD	13.6	11.3	14.9	18.6	10.7	9.36	0.00

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