Supporting Information

for

Photo-responsive Gels Based on Cyclic/Linear Polymers: Efficient Synthesis and Properties Difference

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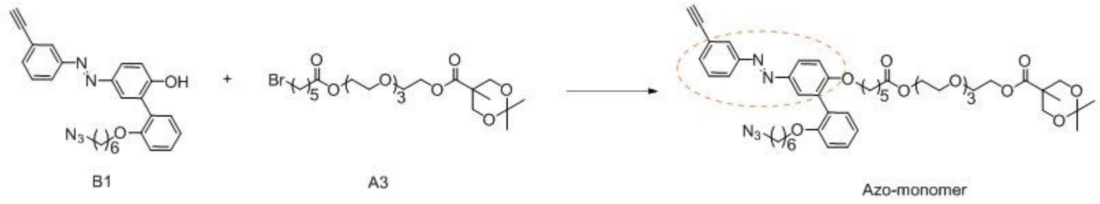
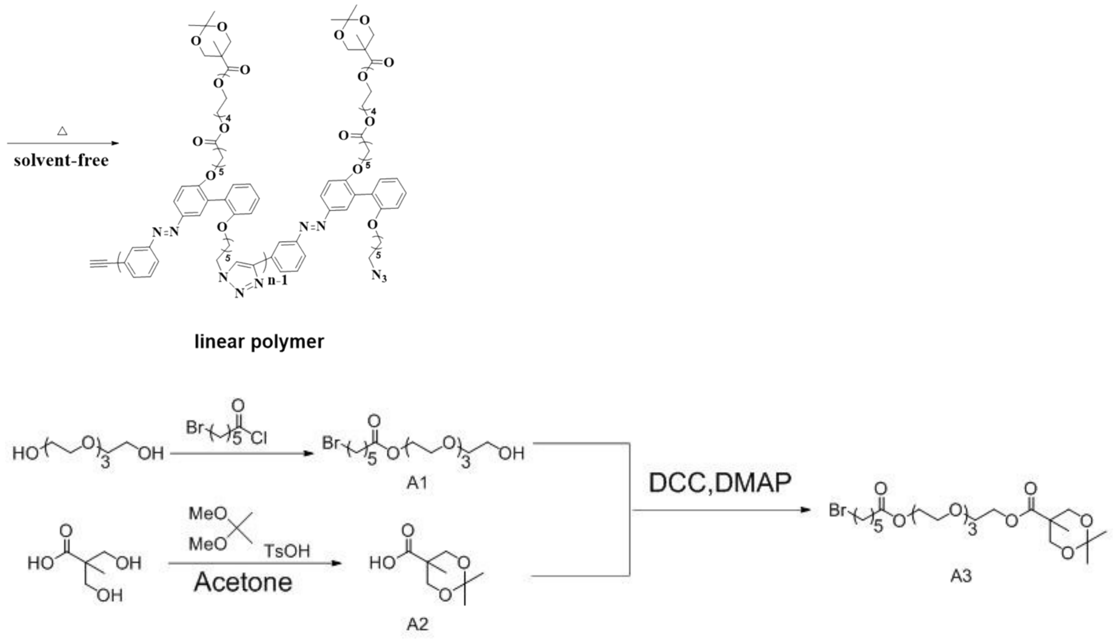
§ The authors have equal contribution to this paper

Experimental Section

Synthesis of azo-monomer





Scheme S1. Synthesis routes of linear polymer precursor consisting of azobenzene and acetonide protected diol.

Synthesis of side chain of containing gacetonide protected diol (A3)

Tetraglycol (10.00 g, 51.5 mmol) and Et_3N (2.00 g, 29.0 mmol) were dissolved in DCM (100 mL) and cooled under 0^{o}C， then a solution of acyl chloride (3.68 g,17.2 mmol) in DCM (20 mL) was added dropwise, and the mixture was stirred at room temperature for 2 h. Filtration and reduced pressure evaporation were used to remove salt and solvent. Eventually the oil like product A1 was obtained after purified by column chromatography (petroleum ether/ethyl acetate = 1/1).

2,2-Dimethylol propionic acid (10.00 g, 74.6 mmol), 2,2-dimethoxypropane (13.8 mL, 111.8 mmol) and p-toluenesulfonic acid monohydrate (0.71 g, 3.7 mmol) were dissolved and stirred in acetone (50 mL) for 2 h at room temperature. 1 mL $NH_3.H_2O/C_2H_5OH$ (1/1) solution was added to neutralize the reaction mixture. The solvent was removed by evaporation. After extracting by DCM (250 mL) and H_2O (20 mL), drying and evaporation, white crystal A2 was got.

A1 (5.00 g, 13.5 mmol), A2 (1.55 g) and dimethylaminopyridine (DMAP) (0.83 g, 6.8 mmol) were dissolved in DCM (50 mL) and cooled under 0^{o}C, then a solution of dicyclohexylcarbodiimide (DCC) (3.34 g, 16.2 mmol) in DCM (15 mL) added dropwise, the mixture was stirred at room temperature for 12 h. Filtration and reduced pressure evaporation were used to remove salt and volatiles. After all, column chromatography (petroleum ether/ethyl acetate = 2/1) was used to purify product. The product A3 was obtained in a yield of 63.7%. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 4.35-4.15, (m, 6H,OCH_2); 3.75-3.60 (m, 12H, OH); 3.44-3.38 (t, 2H, $BrCH_2$); 2.39-2.32 (t, 2H, CH_2OOC-); 1.95-1.45 (m, 6H, CH_2); 1.44-1.37 (b, 6H,CH_3); 1.23-1.20 (s, 3H, CH_3).

Synthesis of compound B1

The azobenzene-containning compound B1 was synthesized according to literature reported by our group (yield : 63.6%).[1] ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.00-7.75, (m, 4H, ArH); 7.65-7.30 (m, 4H, ArH); 7.25-7.01 (m, 3H, ArH); 6.82 (s, 1H, OH); 4.15-4.00 (t, 2H, OCH_2); 3.19-3.14 (t, 2H, N_3CH_2); 3.13 (s, 1H, C≡CH).

Synthesis of azo-monomer

Taking B1 (0.92 g, 2.1 mmol), A3 (1.00 g,1.9 mmol), K_2CO_3 (0.26 g, 1.9 mmol) and catalytic amount KI to dissolve in DMF (100 mL), the mixture was stirred at 70°C for 4 h. Filtration and reduced pressure evaporation were used to remove salt and volatiles. After extracting by ethyl acetate and H_2O, drying, evaporation, and then purified by column chromatography (petroleum ether/ethyl acetate = 1/2), finally a cream like product azo-monomer was got in a yield of 83.4%. ^{1}H NMR (300 MHz, $CDCl_3$), δ (TMS, ppm): 8.00-7.75, (m, 4H, ArH); 7.65-7.20 (m, 4H, ArH); 7.05-6.80 (m, 3H, ArH); 4.40-4.25 (t, 2H, OCH_2); 4.25-4.05 (m, 4H, OCH_2); 4.05-3.75 (m, 4H, OCH_2); 3.75-3.55 (m, 14H, OCH2); 3.19 (t, 2H, CH_2N_3); 3.13 (s, 1H, C≡CH); 2.32-2.21 (t, 2H, CH_2OOC-); 1.95-1.45, 1.37-1.23 (m, 6H,CH_2); 1.44-1.37 (b, 6H, CH_3); 1.23-1.20 (s, 3H, CH_3).

Photoisomerization of the gels formed from the linear- and cyclic-polymer gels

30 mg gels formed from the *linear*- and *cyclic*- polymers at the critical gel point packed in little bottles were irradiated by 365 nm light, then 435 nm visible light until

photostationary states were reached at room temperature.

The number of repeated units (n) and the number-average molecular weight ($M_{n,NMR}$) of cyclic and linear polymers were determined from their ^{1}H NMR spectra by the Formulae S1 and S2:

$$n = (I_{4.24\text{-}4.30}/2)/(I_{3.00\text{-}3.11}/3) \qquad \text{Formula S1}$$

$$M_{n,NMR} = n \times M_{mon} \qquad \text{Formula S2}$$

$I_{4.25\text{-}4.35}$: the integrations at 4.25-4.35 ppm in ^{1}H NMR relative to the signals of -OCOCH$_2$O-(2H) at TEG side chains of the cyclic and linear polymers.

$I_{3.00\text{-}3.11}$: the integrations at 3.00-3.11 ppm in ^{1}H NMR relative to the signals of the terminal alkynyl protons at 3.07-3.11 ppm (d, 1H, -C≡CH) and the characteristic signals at 3.00-3.07 ppm (c, 2H, -CH$_2$N$_3$) adjacent to the terminal azide group in linear samples.

M_{mon}: the molecular mass of monomer.

The calculation of crosslinking densities of the gels

The crosslinking densities of gels formed from *linear*- and *cyclic*-polymer were calculated by equilibrium swelling method.

The test method is as follows: The linear and cyclic polymer gels was conducted at 1:1 molar ratio of crosslinking group. First, the initial mass and volume of the dry gels formed from the *linear*- and *cyclic*-polymer were recorded, then the equilibrium swelling was conducted with THF. After 10 min of swelling, the mass of gels were recorded every 1 min until it was no longer changed, then the mass and volume of swollen gels were recorded. The data were put into the following formula, where the density of linear and cyclic polymers were assumed to be 1.0 g /mL, and the parameter of action of Flory polymer - solution in THF was 0.42.

Calculation results for the approximate crosslinking densities of gels from linear and cyclic polymers were shown in Table 2.

The moles of chain segments, moles of cross-links and concentration of cross-links in the *linear*- and *cyclic*-polymer gels were calculated by the Formula S3-S5:

$$\upsilon_e = -\frac{v_d}{v_1}\frac{[ln(1-\upsilon_{2,s})]+\upsilon_{2,s}+\chi\upsilon_{2,s}^2}{\upsilon_{2,r}\left[\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)^{1/3}-\frac{1}{2}\left(\frac{\upsilon_{2,s}}{\upsilon_{2,r}}\right)\right]} \qquad \text{Equation S3}$$

$$\mu_e = \upsilon_e\left(\frac{2}{f}\right) = \upsilon_e\left(\frac{2}{4}\right) \qquad \text{Equation S4}$$

$$\mu = \mu_e/V_0 \qquad \text{Equation S5}$$

In Equations S3-S5:

υ_e = moles of elastically active chains in the network

υ_d = volume of polymer in the network (mass/density)

υ_1 = molar volume of swelling agent (solvent)

$\upsilon_{2,r}$ = polymer volume fraction in the preparation state, after cross-linking but before swelling

$\upsilon_{2,s}$ = polymer volume fraction in the equilibrium swollen state

χ = Flory polymer-solvent interaction parameter (the reasonable value of 0.42 was used)

μ_e = moles of cross-links in the network

V_0 = gel volume in the preparation state, after cross-linking (mL)

μ = concentration of cross-links (mol/mL)

The first-order rate constant k_e of *trans*-to-*cis* photoisomerization was determined by the Formula S6:

$\mathrm{Ln}[(A_\infty-A_t)/(A_\infty-A_0)] = -k_e t$ Formula S6

Where A_∞, A_t, and A_0 are absorbance at about 365 nm corresponded to the π-π* transition of trans isomers of azobenzene at infinite time, time t and time zero with irradiation of 365 nm UV light (0.55 mW/cm^2) at room temperature, respectively.

The first-order rate constant k_H of cis-to-trans recovery was determined by the Formula S7:

$\mathrm{Ln}[(A_\infty-A_t)/(A_\infty-A_0)] = -k_H t$ Formula S7

Where A_∞, A_t, and A_0 are absorbance at about 365 nm corresponded to the π-π* transition of trans isomers of azobenzene at infinite time, time t and time zero with irradiation of 435 nm visible light (0.70 mW/cm^2) at room temperature, respectively.

Photo-healing procedure of the gels formed from the linear and cyclic polymer

The gel samples from linear and cyclic polymers (30 w.t % of THF or 50 w.t % of THF) were molded into cycloid sheet with 0.1 mm thickness, and the center part in the gels was cut with a razor blade. Then the gel sample with wounds was irradiated with UV light directly to the cut portion by using a photomask at 25^{o}C, and then visible light irradiation was applied to gels for 1 min, and recorded the degree of self-healing by photographs. Another contrasting experiment of the photo-healing was conducted by placing the gel sample with wounds for same time with irradiation time in the darkness at 25^{o}C, and recorded the degree of self-healing by photographs.

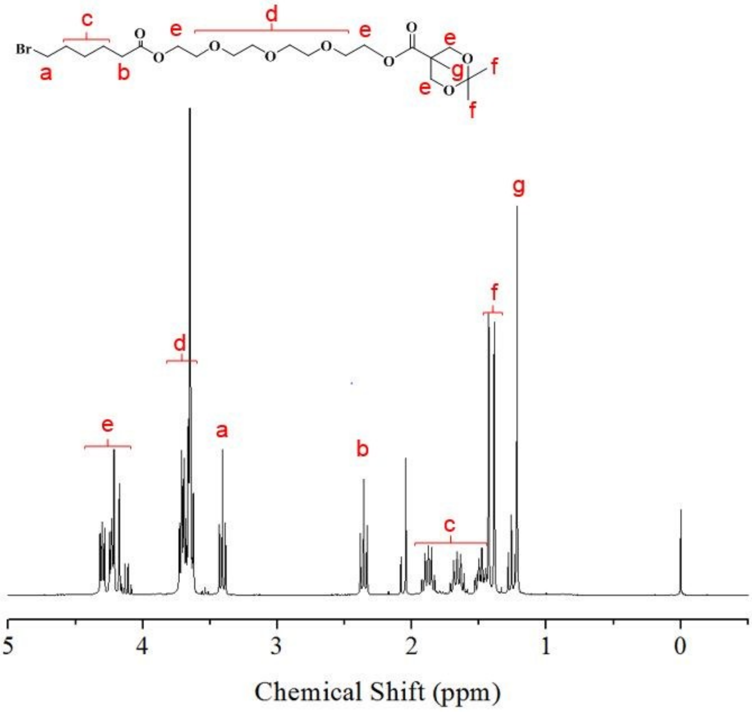


Figure S1. ^{1}H NMR spectrum of A3.

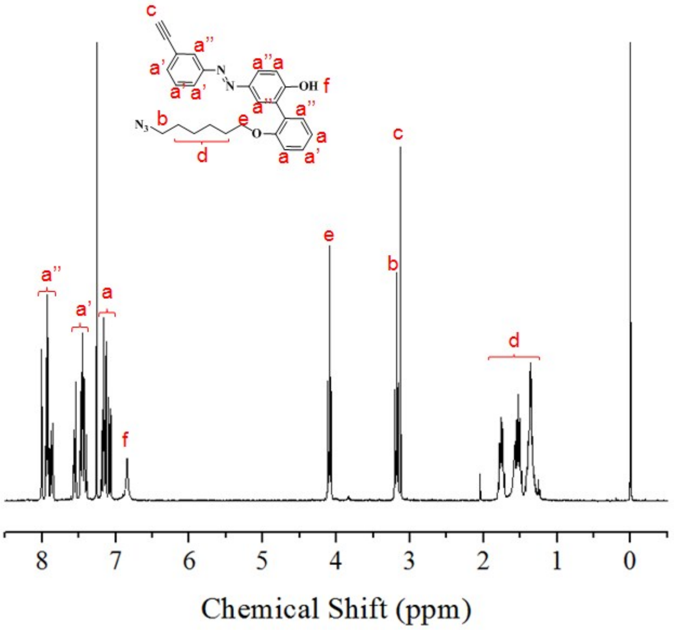


Figure S2. ^{1}H NMR spectrum of compound B1.

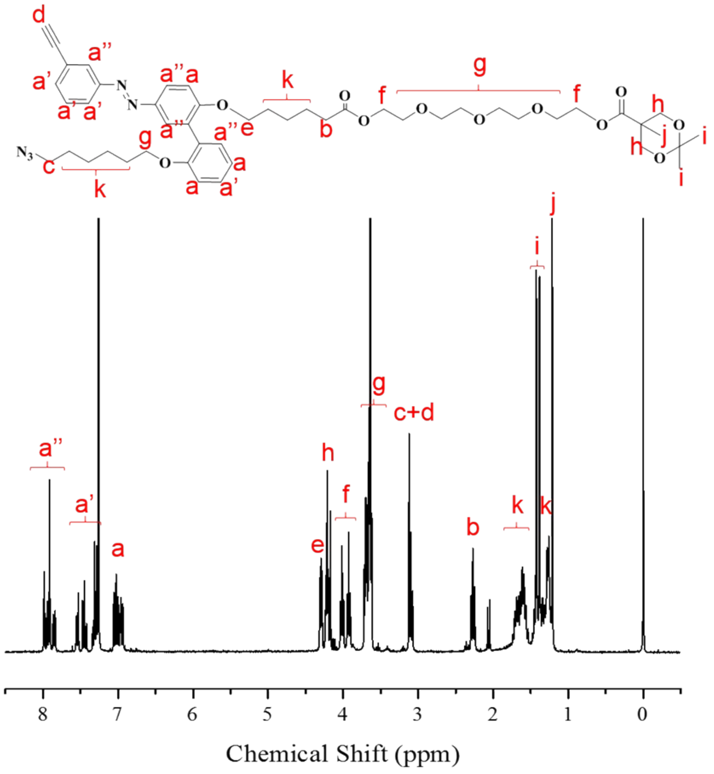


Figure S3. ^{1}H NMR spectrum of monomer (azo-monomer) consisting of azobenzene and acetonide protected diol in $CDCl_3$.

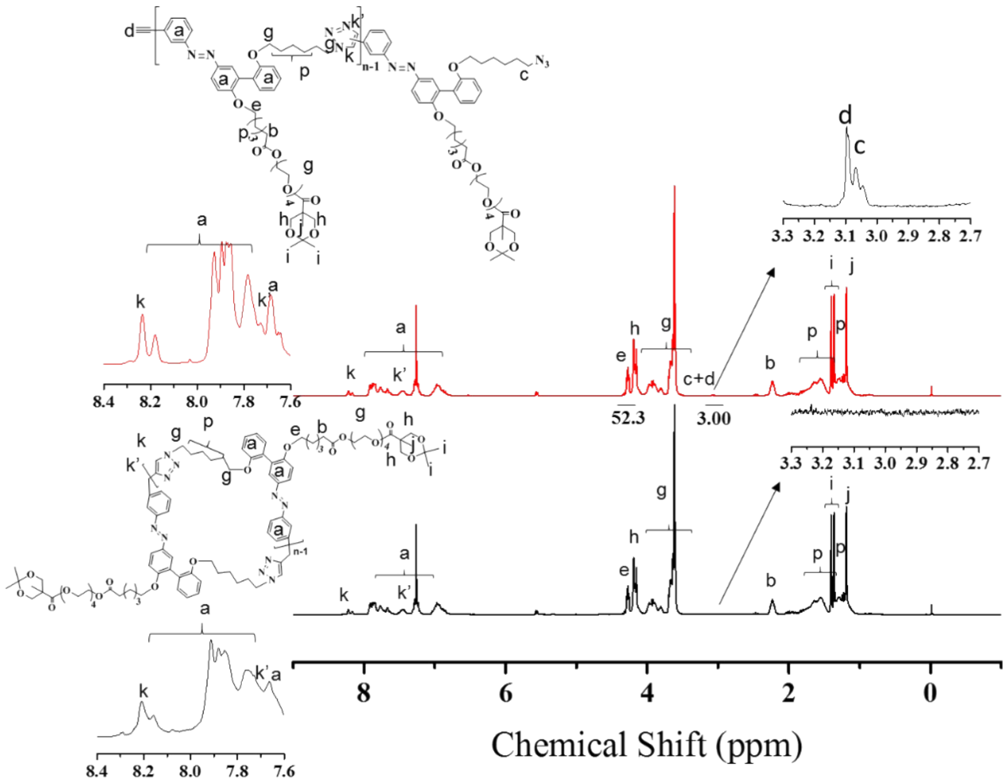


Figure S4. ^{1}H NMR spectra of linear polymer (L2) and cyclic polymer (C2) in $CDCl_3$.

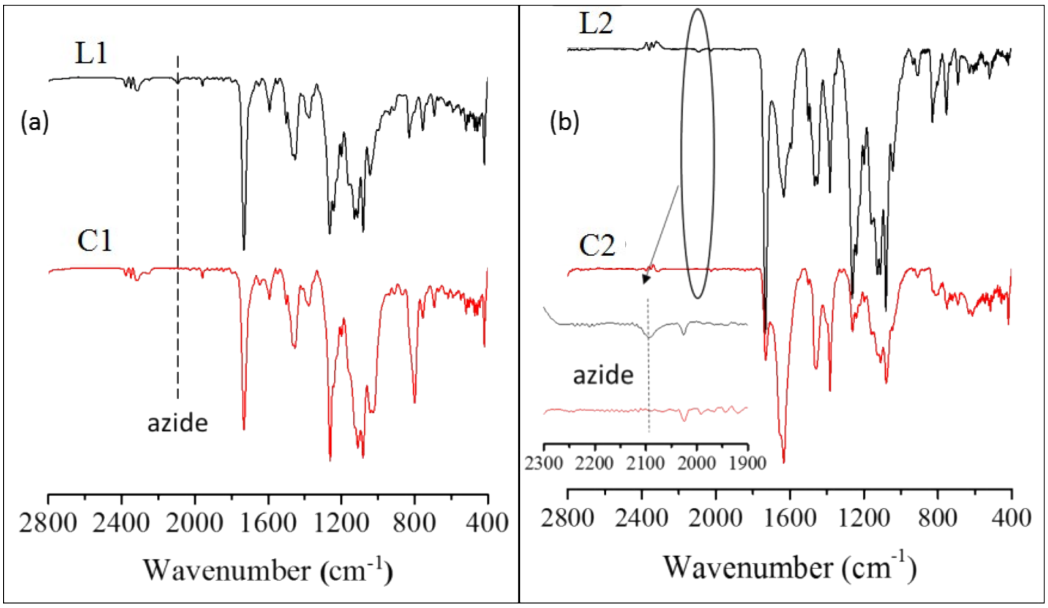


Figure S5. The FT-IR spectra of (a) linear polymer (L1) and cyclic-polymer (C1), (b) linear polymer (L2) and cyclic-polymer (C2).

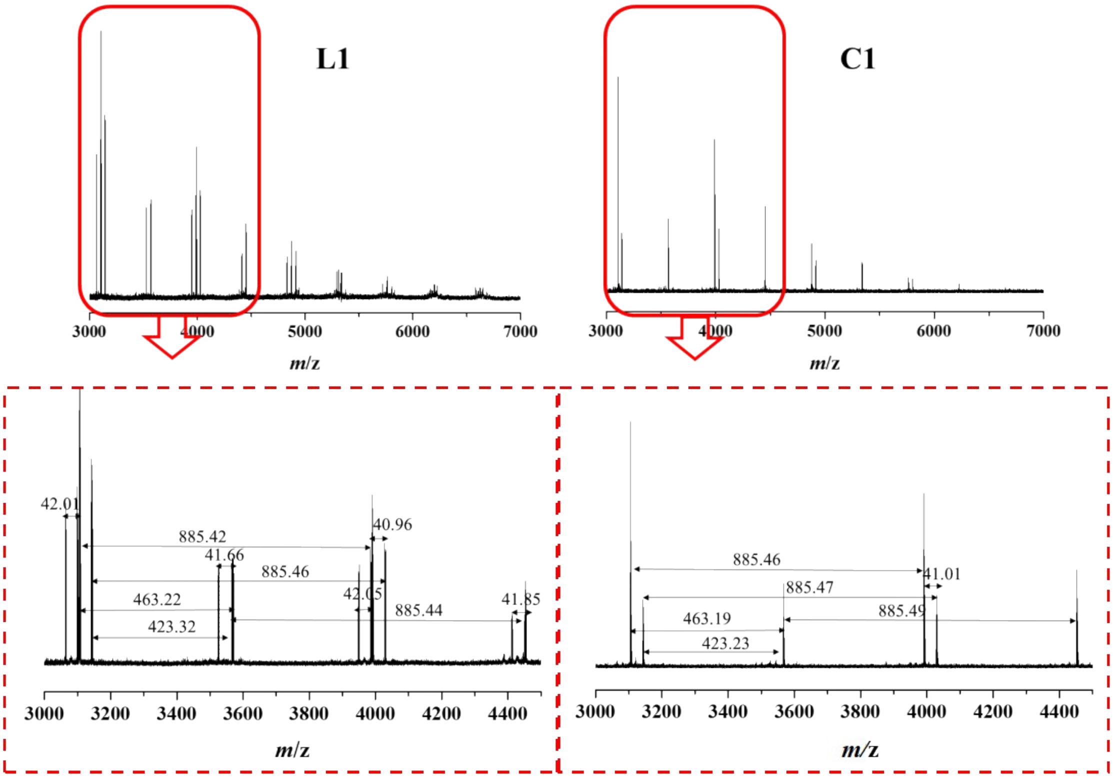


Figure S6. MALDI-TOF mass spectra of linear polymer (L1) and cyclic-polymer (C1).

Table S1. Relevant data corresponding to mass peaks in MALDI-TOF mass spectra (Figure S6) of L1 and C1.

Entry	**Calcd.(L1)$^+$ [Da]**	**Obesd.(L1)$^+$ [*m*/*z*]**	**Calcd.(C1)$^+$ [Da]**	**Obesd.(C1)$^+$ [*m*/*z*]**	**n**
1^{a1}	3564.80	3564.73	3564.80	3565.01	4
1^{a2}	3522.79	3523.07			
1^{b1}	3101.54	3101.51	3101.54	3101.78	
1^{b2}	3059.53	3059.51			
1^{c1}		3142.43		3142.78	
1^{c2}		3099.87			
2^{a1}	4450.25	4450.17	4450.25	4450.49	5
2^{a2}	4408.24	4408.32			
2^{b1}	3987.00	3986.93	3987.00	3987.27	

2^{b2}	3944.98	3944.88			
2^{c1}		4027.89		4028.28	
2^{c2}		3985.87			
3^{a1}	5335.70	5335.52	5335.70	5335.99	6
3^{a2}	5293.68	5293.49			
3^{b1}	4872.45	4872.28	4872.45	4872.79	
3^{b2}	4830.43	4830.18			
3^{c1}		4913.20		4912.76	
3^{c2}		4871.19			
4^{a1}	6221.16	6220.99	6221.16	6221.41	7
4^{a2}	6178.97	6178.85			
4^{b1}	5757.91	5757.75	5757.91	5758.26	
4^{b2}	5715.89	5715.84			
4^{c1}		5797.83		5798.22	
4^{c2}		5755.42			
5^{a1}	7106.61	7106.30	7106.61	7106.72	8
5^{a2}	7064.59	7064.13			
5^{b1}	6643.36	6643.31	6643.36	6643.63	
5^{b2}	6601.34	6601.32			
5^{c1}		6683.56		6683.57	
5^{c2}		6641.33			

Calcd. (L1 and C1): calculated molecular mass (Da);

Obsed. (L1 and C1): molecular mass obtained from MALDI-TOF mass spectra (m/z);

a1: Calcd. (L1) = M_{mon} (885.45) × n + M_{Na} (22.99);

Calcd. (C1) = M_{mon} (885.45) × n + M_{Na} (22.99);

a2: Calcd. (L1) = M_{mon} (885.45) × n + M_{Na} (22.99) - M_{N3} (42.02);

b1: Calcd. (L1) = M_{mon} (885.45) × n + M_{Na} (22.99) - $M_{\mathrm{C22H39O10}}$ (463.25);

Calcd. (C1) = M_{mon} (885.45) × n + M_{Na} (22.99) - $M_{\mathrm{C22H39O10}}$ (463.25);

b2: Calcd. (L1) = M_{mon} (885.45) × n + M_{Na} (22.99) - $M_{\mathrm{C22H39O10}}$ (463.25) - M_{N3} (42.02);

c1: Calcd. (L1) = M_{mon} (885.45) × n + M_{Na} (22.99) – M_{unknown} (423.23);

Calcd. (C1) = M_{mon} (885.45) × n + M_{Na} (22.99) – M_{unknown} (423.23);

c2: Calcd. (L1) = M_{mon} (885.45) × n + M_{Na} (22.99) – M_{unknown} (423.23) - M_{N3} (42.02);

The M_{N3} for 42.02 can be assigned to the expulsion of N_3 of the linear polymers with azide end group during testing procedure, resulting in the mass was 42.02 g/mol smaller than that of corresponding cyclic polymers with the same repeat units.

The $M_{C22H39O10}$ for 463.25 can be assigned to the expulsion of the side chain $C_{22}H_{39}O_{10}$ in during testing procedure, resulting in the mass was 463.25 g/mol smaller than that of corresponding linear or cyclic polymers with the same repeat units.

The M_{unknown} for 423.23 can be assigned to the expulsion of something during testing procedure, resulting in the mass was 423.23 g/mol smaller than that of corresponding linear or cyclic polymers with the same repeat units.

M_{mon} : the molecular mass of monomer;

M_{Na} : the molecular mass of Na;

M_{N3} : the molecular mass of N_3;

n : the number of repeat units of monomer.

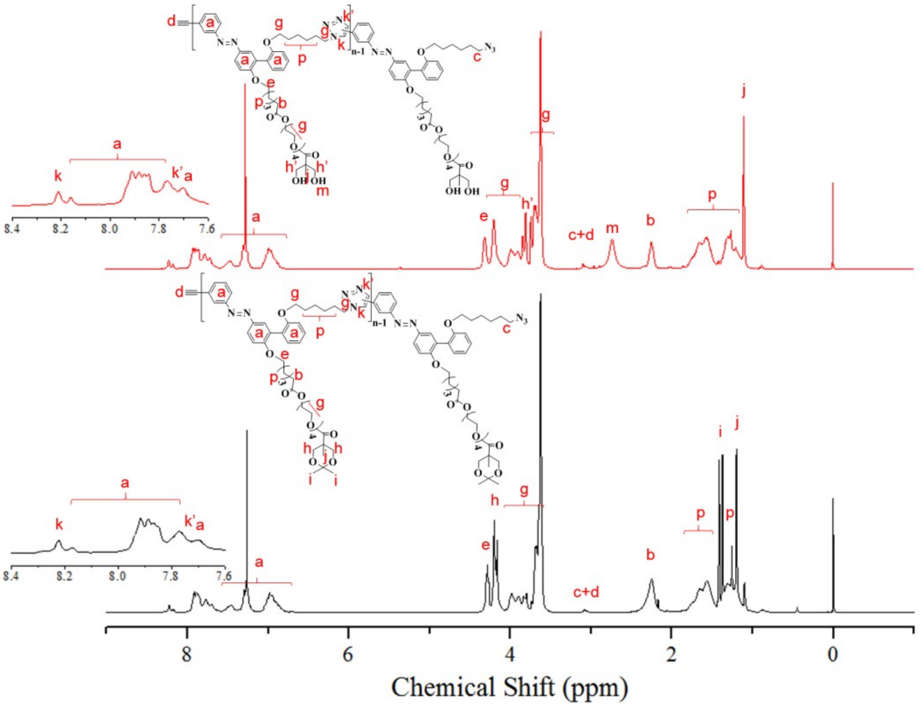


Figure S7. ^{1}H NMR spectra of linear polymer (L1) before and after deprotection in

$CDCl_3$.

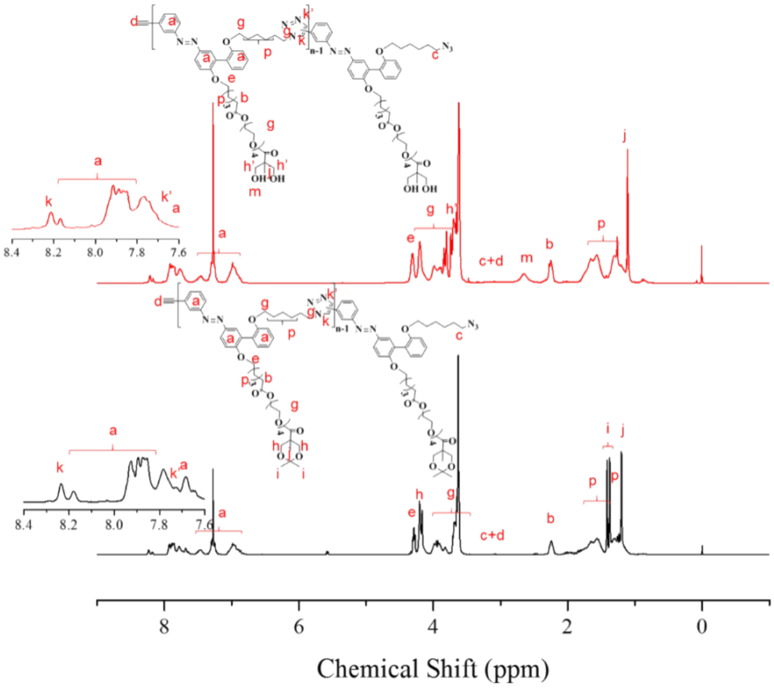


Figure S8. ^{1}H NMR spectra of linear polymer (L2) before and after deprotection in $CDCl_3$.

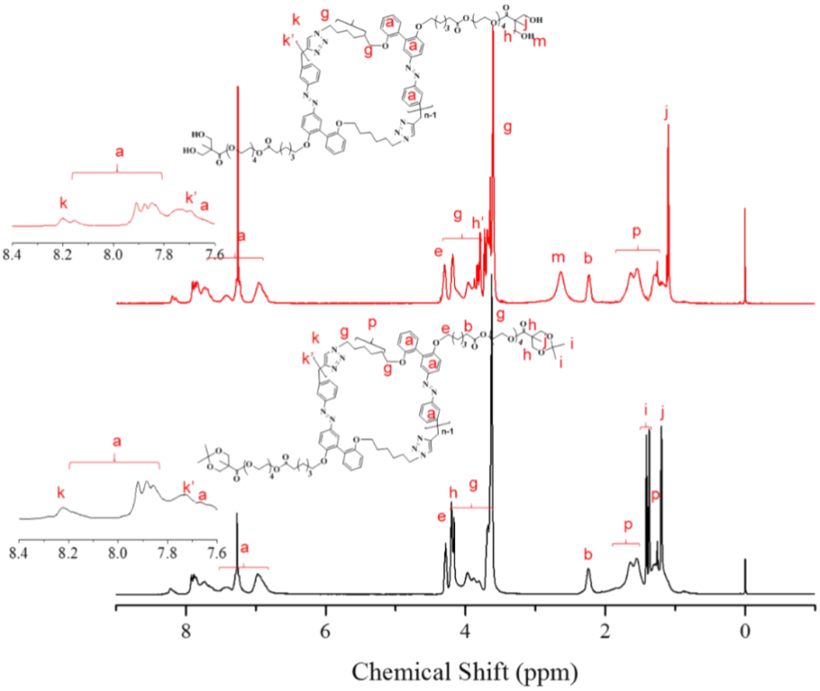


Figure S9. ^{1}H NMR spectra of the cyclic polymer (C1) before and after deprotection in $CDCl_3$.

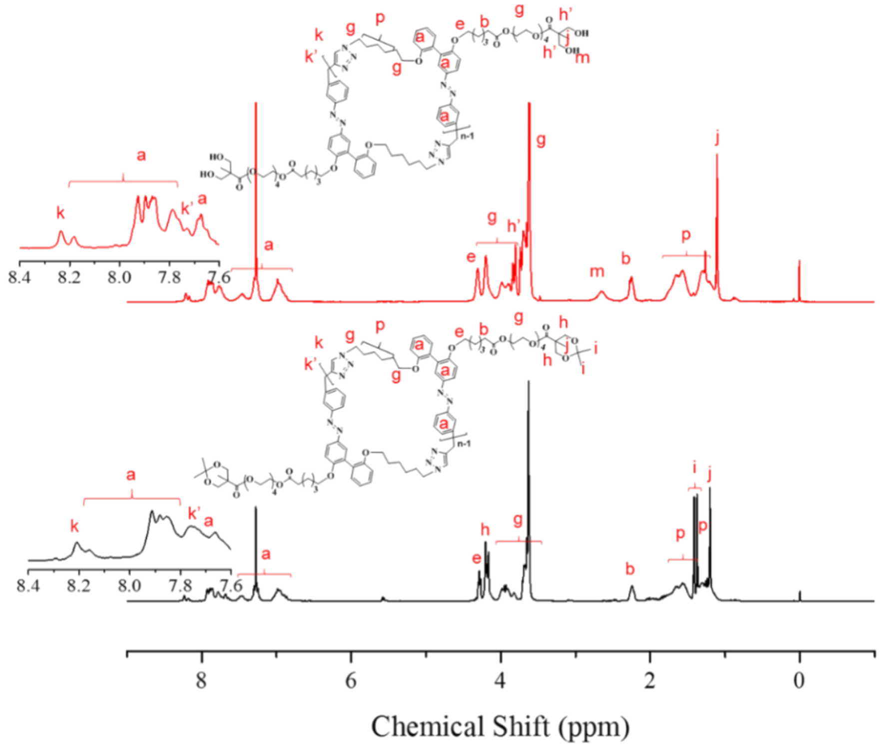


Figure S10. ^1H NMR spectra of the cyclic polymer (C2) before and after deprotection in $CDCl_3$.

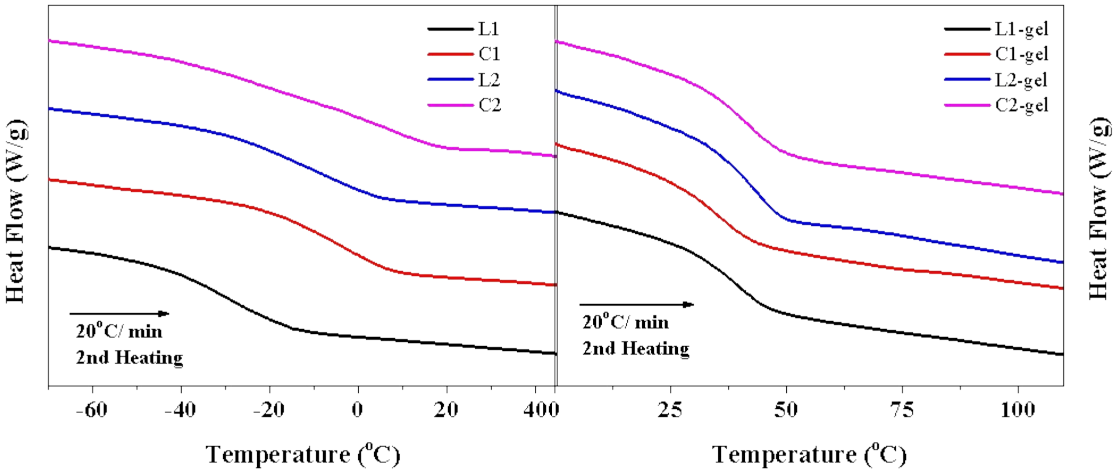


Figure S11. Second DSC heating curves of the linear polymers (L1 and L2), cyclic polymers (C1 and C2) and dried gels (crosslinking ratio 1:1) formed from linear and cyclic polymers.

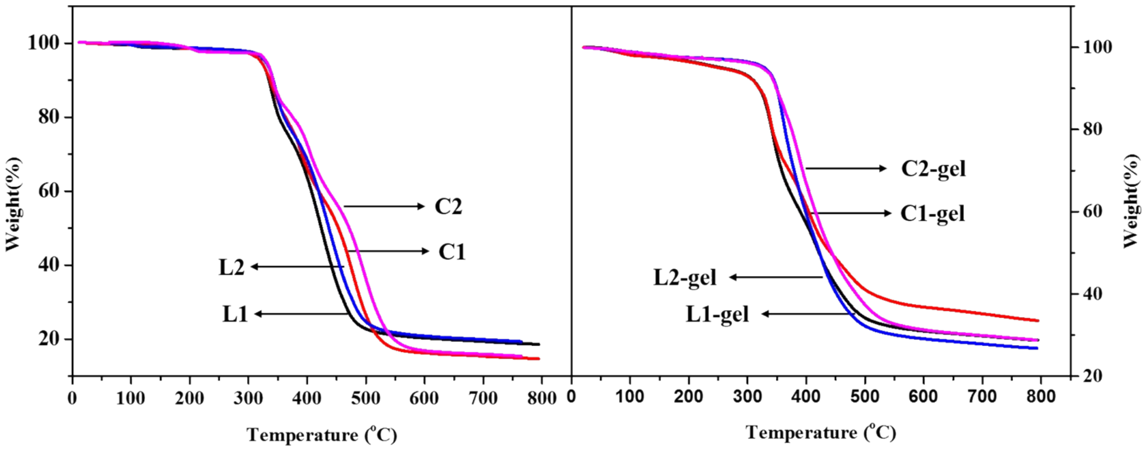


Figure S12: Thermo gravimetric analysis of polymers L1, L2, C1, C2 and gels L1-gel, L2-gel, C1-gel, C2-gel. Determined by TGA. T_d: decomposition temperature, the temperatures for 5% weight loss of initial weight, averaging the values of three times.

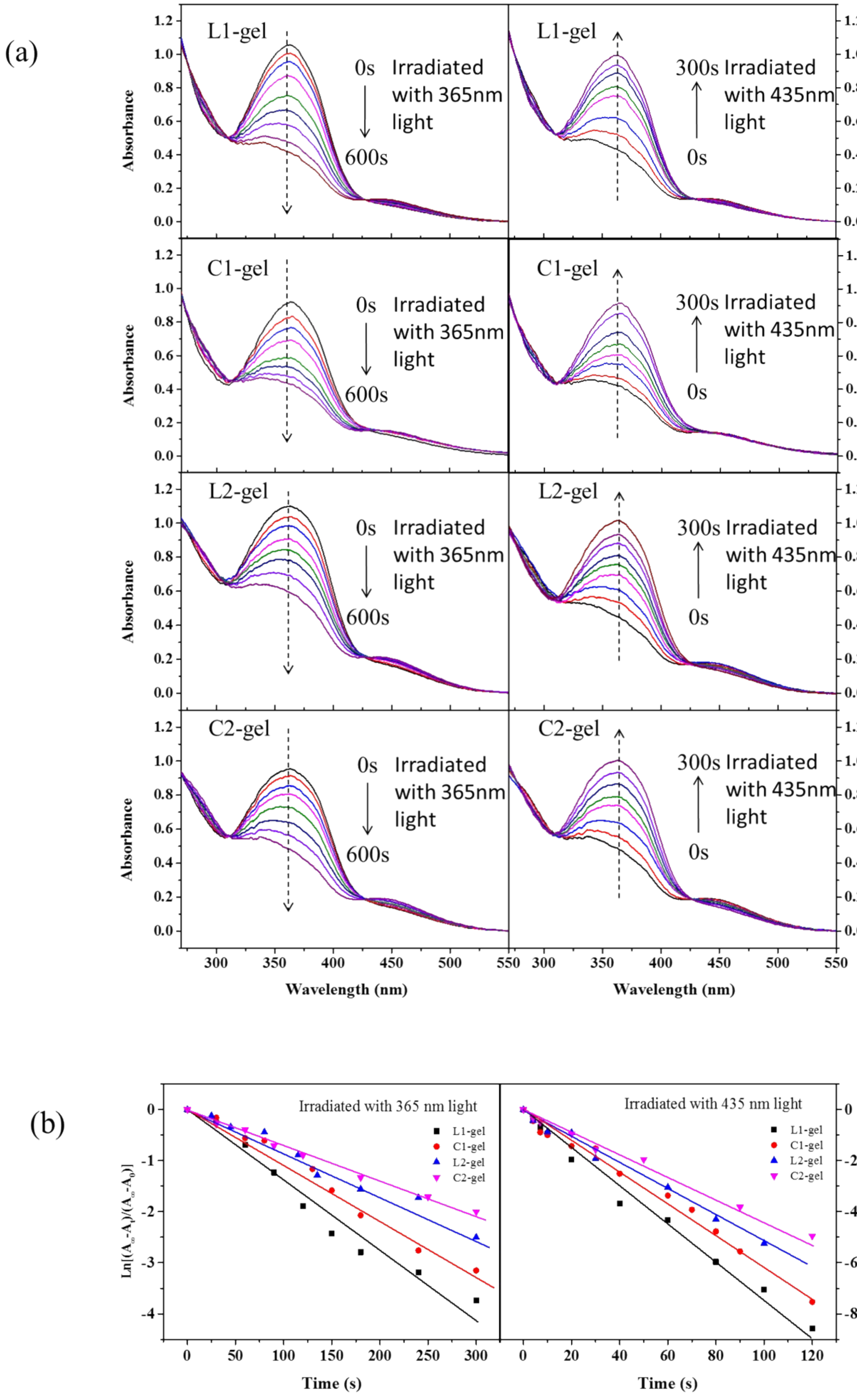
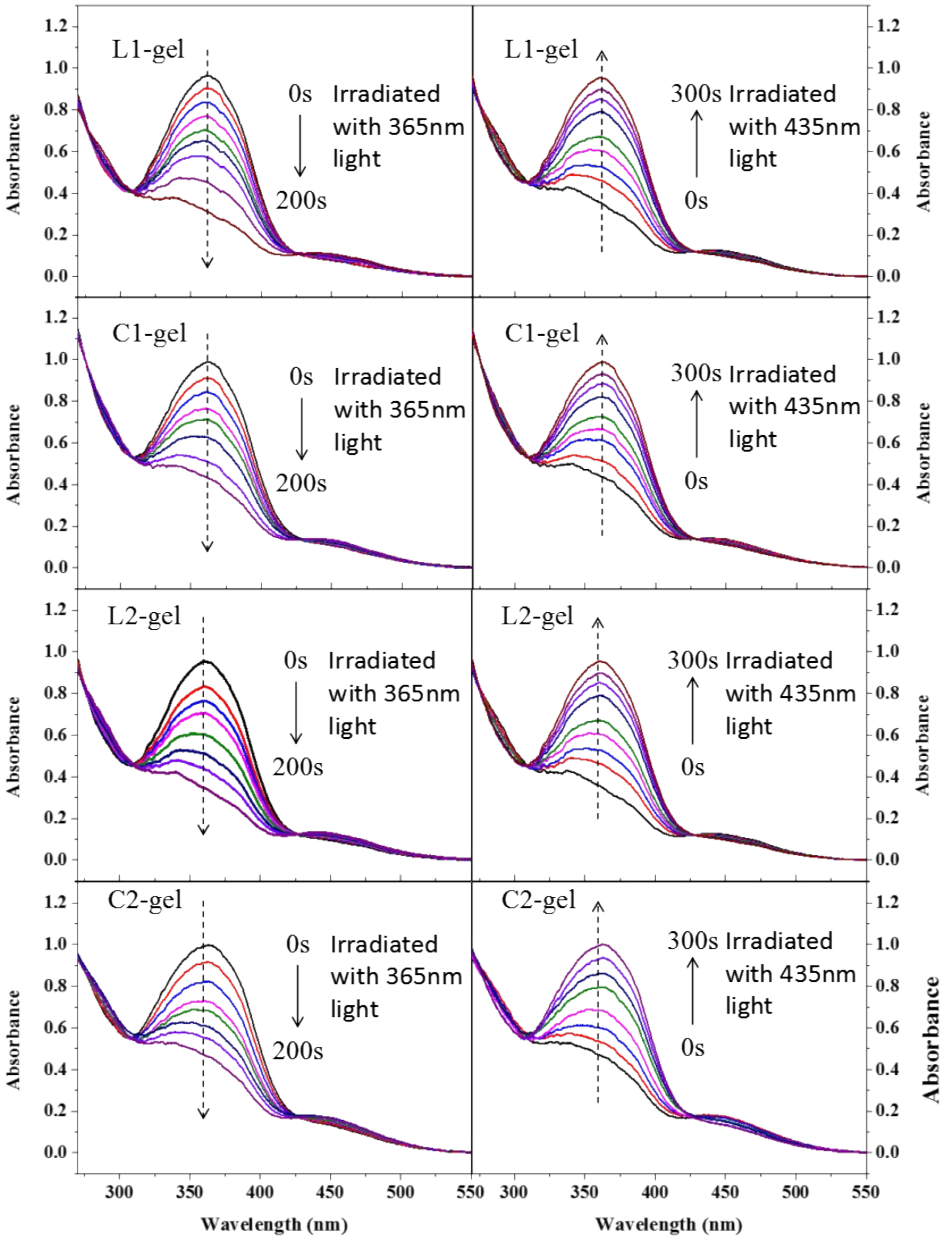


Figure S13. (a) The UV-vis absorption spectra of gel films formed by the linear and cyclic polymer at the critical gel point under irradiation with 365 nm UV light (0.55 mW/cm^2) and 435 nm visible light (0.70 mW/cm^2) at different time intervals at room temperature. (b) First-order kinetic curves for the *trans*-to-*cis* and *cis*-to-*trans* photoisomerization of gel films correspond to the UV-vis absorption spectra. The L1-gel and C1-gel is corresponding to the gel film of the *linear* polymer (L1) and *cyclic* polymer (C1) at the critical gel point. The gels were diluted by THF, and then the gel films were prepared by spinning-coated the solution of gels. The critical gel point of linear gels and cyclic gels is shown in Table S4 and Table S5, respectively.

(a)



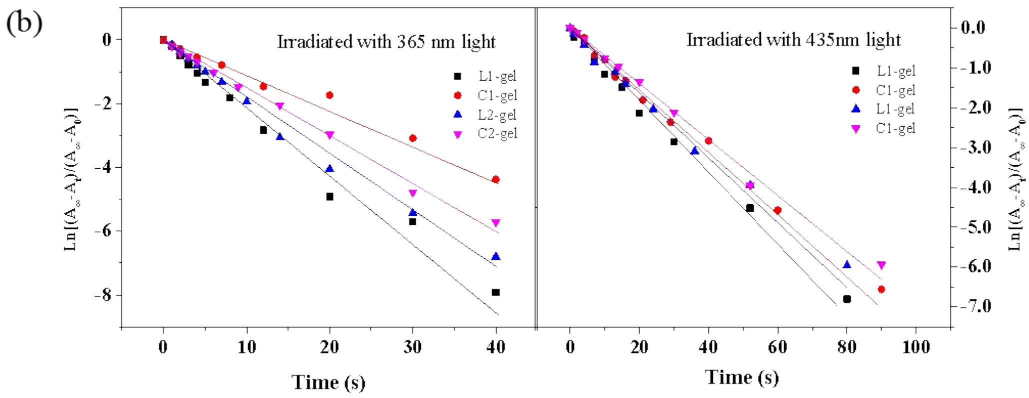


Figure S14. (a) The UV-vis absorption spectra of gel films formed by the *linear*- and *cyclic*-polymer at 1:1 molar ratio of crosslinking group under irradiation with 365 nm UV light (0.55 mW cm^{-2}) and 435 nm visible light (0.70 mW cm^{-2}) at different time intervals at room temperature. (b) First-order kinetic curves for the *trans*-to-*cis* and *cis*-to-*trans* photoisomerization of gel films correspond to the UV-Vis absorption spectra. L1-gel and C1-gel, L2-gel and C2-gel is corresponding to the gel film formed by the linear polymer (L1) and cyclic polymer (C1), linear polymer (L2) and cyclic polymer (C2), respectively; The gels were diluted by THF, and then the gel films were prepared by spinning-coated the solution of gels.

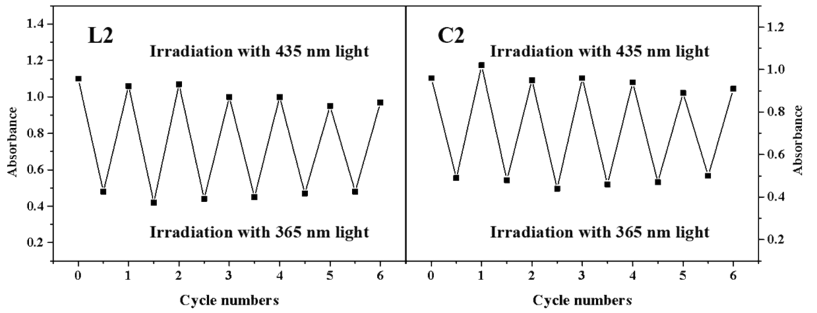


Figure S15. The photoisomerization cycles of the linear gel formed from linear polymer (L2) and cyclic gel formed from cyclic polymer (C2) at the critical gel point corresponding to Figure S13. In each cycle, the gel was irradiated alternately under 365 nm UV light (0.55 mW cm^{-2}) and 435 nm visible light (0.7 mW cm^{-2}) at room temperature.

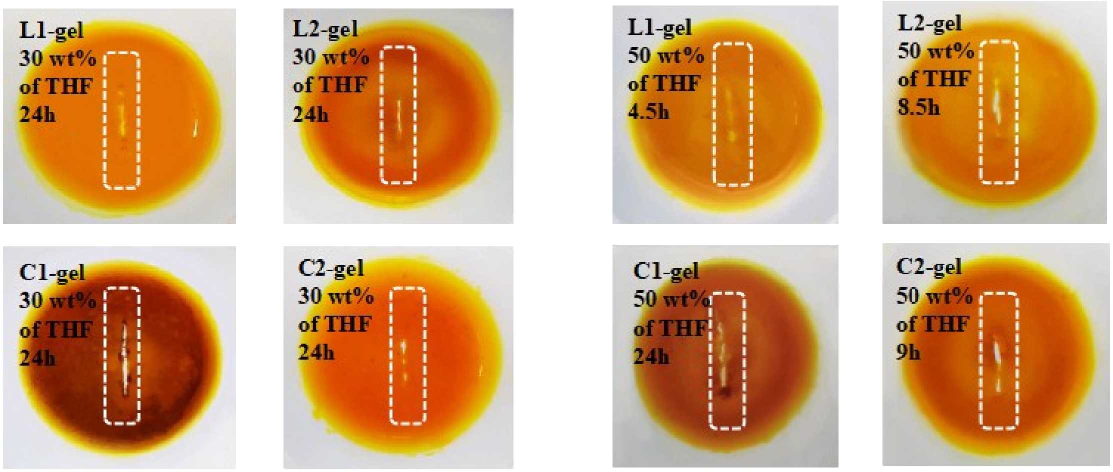


Figure S16 Photographs of the rounded-shaped gels cut at the center in the control group that was placed in the darkness for some time, corresponding to Figure S5 in the main text. L1-gel, C1-gel, L2-gel and C2-gel is corresponding to the gel formed from the linear polymer (L1, L2) and cyclic-polymer (C1, C2) at 3:1 molar ratio of crosslinking group (30 w.t % and 30 w.t % of THF), respectively.

Table S2. The number-average molecular weights ($M_{n,GPC}$, $M_{n,NMR}$) obtained by GPC and ^{1}H NMR spectra, molecular weight distribution (M_w/M_n), and number of repeat units (n) of the *linear* polymers (L1, L2) and *cyclic*-polymers (C1, C2). Glass transition temperatures (T_g)s of the linear and cyclic polymers.

Sample	$M_{n,GPC}$ ^{a} **(g.mol^{-1})**	M_w/M_n	$M_{n,NMR}$ ^{b} **(g.mol^{-1})**	n	T_g/ °C	△T_g/ °C	T_d/ °C
L1	9600	1.24	10600	12	-24		320
C1	8200	1.32	10600	12	-15	9	320
L2	22100	1.30	23900	26	-12		331
C2	17700	1.34	23900	26	-6	6	329

a: The number-average molecular weights ($M_{n,GPC}$) obtained by GPC; **b:** The number-average molecular weights ($M_{n,NMR}$) obtained by ^{1}H NMR spectra.

Table S3 The calculation parameters and results for the moles of chain segments (υ_e), moles of cross-links (μ_e) and concentration of cross-links (μ) in the gels from the linear and cyclic polymers. [a]

Gel sample	υ_e (mol)	μ_e (mol)	μ (mol/mL)
L1-gel	1.59×10^{-6}	7.98×10^{-7}	2.71×10^{-6}
C1-gel	6.54×10^{-7}	3.27×10^{-7}	1.26×10^{-6}
L2-gel	1.89×10^{-6}	9.47×10^{-7}	6.72×10^{-6}
C2-gel	1.17×10^{-6}	5.87×10^{-7}	3.92×10^{-6}

a: the molar ratio of crosslinking group was 1:1; L1-gel: $M_{n,GPC}$ = 9600 g.mol^{-1}, M_w/M_n = 1.24; C1-gel: $M_{n,GPC}$ = 8200 g.mol^{-1}, M_w/M_n = 1.32; L2-gel: $M_{n,GPC}$ = 22100 g.mol^{-1}, M_w/M_n = 1.30 , C2-gel: $M_{n,GPC}$ = 17700 g.mol^{-1}, M_w/M_n = 1.34.

Table S4 Feeding amount of the linear- and cyclic-polymer, cross-linker and weight percentage of THF to prepare the gels at critical gel point from the linear polymer (L1) and cyclic polymer (C1).

sample	**polymer （mg）**	**Crosslinker （mg）**	**Molar ratio of diol and boronic acid**	**THF(mg)**	**THF wt%**	**Sol/Gel (×/√)**
L1-1-gel	30	0.29	10:1	63.2	60	×
L1-2-gel	30	0.37	8:1	63.2	60	×
L1-3-gel	30	0.59	5:1	63.2	60	×
L1-4-gel	30	0.74	4:1	63.2	60	√
L1-5-gel	30	0.59	5:1	52.5	50	√
L1-6-gel	30	0.74	4:1	73.7	70	×
C1-1-gel	30	0.29	10:1	63.2	60	×
C1-2-gel	30	0.37	8:1	63.2	60	×
C1-3-gel	30	0.59	5:1	63.2	60	×
C1-4-gel	30	0.74	4:1	63.2	60	×
C1-5-gel	30	0.98	3:1	63.2	60	√

C1-6-gel	30	0.74	4:1	52.5	50	√
C1-7-gel	30	0.98	3:1	73.7	70	×

L1: $M_{n,GPC}$ = 9600 g/mol, M_w/M_n = 1.24 , C1: $M_{n,GPC}$ = 8200 g/mol, M_w/M_n = 1.32.

Table S5 Feeding amount of the *linear*and *cyclic*-polymer, cross-linker and weight percentage of THF to prepare the gels at critical gel point from the linear polymer (L2) and cyclic polymer (C2).

sample	**polymer（mg）**	**Cross-linker（mg）**	**Molar ratio of diol and boronic acid**	**THF(mg)**	**THF wt%**	**Sol/Gel (×/√)**
L2-1-gel	30	0.29	10:1	63.2	60	×
L2-2-gel	30	0.33	9:1	63.2	60	×
L2-3-gel	30	0.37	8:1	63.2	60	√
L2-4-gel	30	0.33	9:1	52.5	50	√
L2-5-gel	30	0.37	8:1	73.7	70	×
C2-1-gel	30	0.29	10:1	63.2	60	×
C2-2-gel	30	0.33	9:1	63.2	60	×
C2-3-gel	30	0.37	8:1	63.2	60	√
C2-4-gel	30	0.33	9:1	52.5	50	√
C2-5-gel	30	0.59	8:1	73.2	70	×

L2: $M_{n,GPC}$ = 22100 g/mol, M_w/M_n = 1.30 , C2: $M_{n,GPC}$ = 17700 g/mol, M_w/M_n = 1.34.

Table S6 The kinetic parameters for *trans-to-cis* and *cis-to-trans* photoisomerization of linear-polymers and cyclic-polymers in THF.

sample	$k_e \times 10^3$ （S）	$k_H \times 10^3$ （S）	$k_{e\text{-}C}$ / $k_{e\text{-}L}$	$k_{H\text{-}C}/k_{H\text{-}L}$
L1-Solution	14.9	22.4	1.27	1.60
C1-Solution	18.9	35.8		
L2-Solution	13.0	18.7	1.23	1.09
C2-Solution	15.9	20.4		

k_e: Rate constant of *tran-to-cis* photoisomerization under 365 nm light irradiation (light intensity: 0.55 mW/cm^2) at room temperature. k_H: Rate constant of *cis-to-trans* recovery under 435 nm light irradiation (light intensity: 0.70 mW/cm^2) at room temperature.

References

[1] Y. Sun, Z. Wang, Y. Li, Z. Zhang, W. Zhang, X. Pan, N. Zhou and X. Zhu, *Macromol. Rapid Commun*., 2015, **36**, 1341-1347.