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Supporting Information

Redox- and pH-Responsive Polymer Gels with Reversible Sol-Gel Transitions and Self-Healing Properties

Ping Zhang[1], Fengyang Deng[1], Ya Peng[1], Hongbiao Chen[1*], Yong Gao[1], Huaming Li[1, 2*]

[1] College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, P. R. China

[2] Key Laboratory of Polymeric Materials & Application Technology of Hunan Province, and Key Laboratory of Advanced Functional Polymeric Materials of College of Hunan Province, Xiangtan 411105, Hunan Province, P. R. China

*Corresponding author. Tel.: +86 731 58298572; Fax: +86 731 58293264.

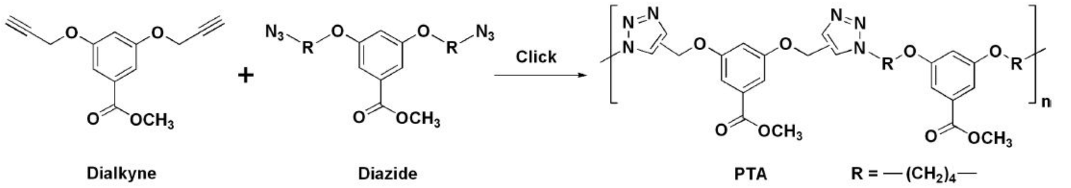
E-mail address: lihuaming@xtu.edu.cn (H. Li), chhb606@163.com (H. Chen).

S1. Materials and Instruments

1,4-Dibromobutane was dried over anhydrous $MgSO_4$, distilled under reduced pressure. Methyl 3,5-dipropargyloxylbenzoate and methyl 3,5-bis(4-azidobutoxy)benzoate were prepared according to the procedure reported by our group.[1] 4-Hydroxybenzaldehyde and 1,4-dithiothreitol (DTT) were purchased from Aladdin Co., Shanghai, China. All other chemicals and solvents were of reagent grade quality and used without further purification unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded with a Bruker AV-400 NMR spectrometer. FTIR spectra were recorded on a ThermoFisher NICOLET 6700 FTIR spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEXeIII mass spectrometer using a nitrogen laser (337 nm) and an accelerating potential of 20 kV. The molecular weight and polydispersity index of polymer were determined by a PL-GPC120 setup equipped with a PL HTRI RI detector, and a column set consisting of two PL gel 5 μm mixed-D columns (7.5 × 300 mm, effective molecular weight range of 0.2-400.0 kg/mol) using DMF that contained 1.0 g/L LiBr as an eluent at 80 °C and a flow rate of 1.0 mL/min. The molecular weights of the polymers were calculated relative to linear polystyrene standards. Rheological behavior of the samples was characterized with a TA ARES rheometer, equipped with a parallel plate of 25 mm in diameter. The values of the strain amplitude were checked to ensure that all measurements were carried out within the linear viscoelastic regime. Both elastic modulus (G') and loss modulus (G") of the gels were monitored as a function of frequency to characterize the viscoelastic properties. The compression tests were performed on mechanical test equipment (Model: Instron 5943), under uniaxial compression using a parallel plate geometry. Test parameters were as follows: load cell 1 kN, crosshead speed 1 mm/min. Before loading on to the Instron the samples were equilibrated at room temperature for 48 h. Mechanical compression data were averaged over three samples.

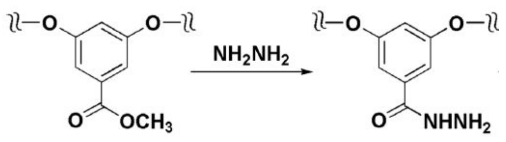
S2. Synthesis of PTB

S2.1. Synthesis of poly(triazole)s (PTAs)



To a 250 mL erlenmeyer flask equipped with a magnetic stir bar, was added methyl 3,5-dipropargyloxylbenzoate (8.00 g, 32.8 mmol), methyl 3,5-bis(4-azidobutoxy)benzoate (11.87 g, 32.8 mmol), and CH_2Cl_2 (50 mL). After stirring at room temperature for 30 min, the mixture was concentrated at 80 °C to dryness. The flask was backfilled with nitrogen and immersed in an 80 °C oil bath for 36 h. The resultant polymer was redissolved in CH_2Cl_2 (20 mL) and fractionated into four fractions using a multistep precipitation method. Four different precipitating agents (500 mL each, dichloromethane/acetone (1/1, v/v), acetone, acetone/ethyl acetate (1/1, v/v), ethyl acetate) were used to precipitate polymer. The polymer fraction were collected by filtration, and dried under vacuum at 60 °C for 24 h.

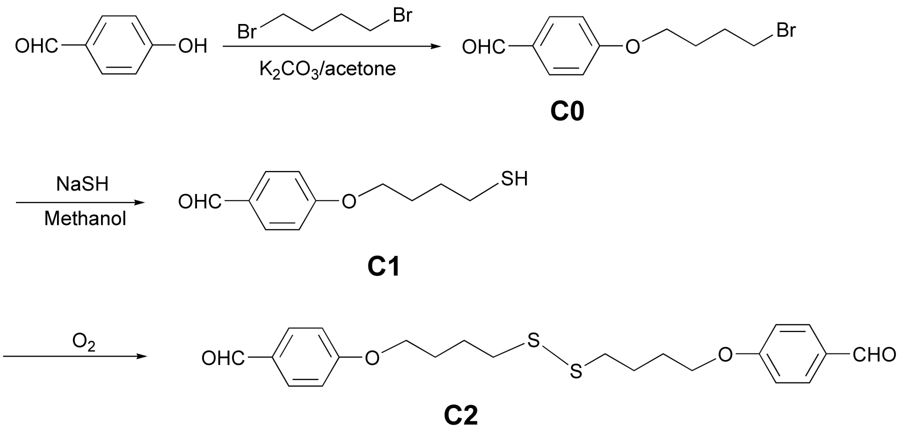
S2.2. Synthesis of PTB



To a solution of PTA (5.00 g, 8.25 mmol based on the repeating unit) in 100 mL DMF, a mixture of 50 mL hydrazine hydrate (80 wt% in water) in 50 mL of DMF was added dropwisely. The reaction mixture was refluxed at 80 °C for 24 h. After completion of reaction, most of the solvent was evaporated under vacuum and then poured into 500 mL of water to precipitate polymer. The benzohydrazide-containing poly(triazole) (PTB) was collected by filtration, washed several times with water and dried under vacuum at 80 °C for 48 h.

S3. Synthesis of C2

Scheme S1. Synthesis of 4,4-[4,4'-dithiobis(1-butoxyl)]diphenylformaldehyde (**C2**)



S3.1. Synthesis of ***C0*** [2]

4-Hydroxybenzaldehyde (2.00 g, 16.4 mmol), K_2CO_3 (50 g), 1,4-dibromobutane (5.29 g, 24.5 mmol), and dried acetone (100 mL) were added into an 250 mL round-bottom flask, equipped with a Teflon coated stir bar. The mixture was stirring for 12 h at room temperature. The resulting mixture was diluted with 500 mL water. After extraction with ethyl acetate (4 × 100 mL), the combined organic phase was dried with anhydrous $MgSO_4$ overnight. Filtration and concentration by evaporation of all but the last 10 mL solvent and the crude product was subsequently purified by silica gel chromatography using petroleum ether/ethyl acetate (20/1, v/v) as the eluent to yield a brown solid **C0** (2.77 g, yield: 66%). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H (ppm): 9.90 (1H, s, Ar-*CHO*), 7.86 (2H, q, J = 8.40 Hz, Ar-*H*), 7.01 (2H, d, J = 8.4 Hz, Ar-*H*), 4.11 (2H, t, J = 6 Hz, CH_2*CH_2*O), 3.51 (2H, d, J = 6.8 Hz, CH_2*CH_2*Br), 2.05 (2H, m, CH_2*CH_2*). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si) δ_C (ppm): 190.81, 163.92, 132.22, 130.15, 114.91, 67.23, 33.46, 29.54, 27.75.

S3.2. Synthesis of ***C2***

To a 25 mL round-bottom Schlenk flask equipped with a magnetic stir bar was charged with $Na_2S·9H_2O$ (6.30 g, 80.7 mmol), deionized H_2O 8.0 mL, stirring till $Na_2S·9H_2O$ was dissolved. The hydrochloric acid (6.0 mL, 6.0 mol/L) was added dropwisely while stirring at room temperature for 30 min to give a yellow solution of sodium hydrosulfide.

To a solution of 4-(4-bromobutoxy)benzaldehyde **C0** (2.0 g, 7.8 mmol) in 30 mL methanol, a freshly prepared solution of sodium hydrosulfide was added. The mixture was stirred for 10 h at room temperature. The resulting mixture was diluted with 100 mL water, extracted with ethyl acetate (3 × 50 mL), the combined organic phase was washed with brine (4 × 60 mL) and dried with anhydrous $MgSO_4$ overnight and filtered. The filtrate was concentrated and purified by a silica gel column using petroleum ester/ethyl acetate (20/1, v/v) as the eluent to yield a smelly, light golden solid **C2**. ^1H NMR (400 MHz, $CDCl_3$, Me_4Si) δ_H (ppm): 9.92 (2H, s, Ar-C*H*O), 7.88 (4H, d, J = 8.8 Hz, Ar-*H*), 7.04 (4H, d, J = 8.4 Hz, Ar-*H*), 4.11 (4H, t, J = 5.6 Hz, CH_2CH_2O), 2.82 (4H, t, J = 6.4 Hz, CH_2S), 1.97 (8H, m, CH_2CH_2). ^{13}C NMR (400 MHz, $CDCl_3$, Me_4Si) δ_C (ppm): 190.64, 163.99, 131.96, 114.76, 67.79, 38.55, 27.84, 25.69.

Table S1. Effect of different catalysts, catalyst contents, –NH_2/–CHO molar ratio, and gelator concentrations on the gelation time in DMF.[a]

Run	Catalysts	Cat. Content (wt%)	–NH_2/–CHO (mol/mol)	Gelator Concn. (wt%)	Gelation Time (h or min)
1	None	0	10/1	15	17 h
2	HOAc	5	10/1	15	20 min
3	HOAc	10	10/1	15	9 min
4	HOAc	15	10/1	15	4 min
5	HOAc	20	10/1	15	2 min
6	$PhNH_2$	10	10/1	15	9 h
7	HOAc	10	20/1	15	Sol
8	HOAc	10	12.5/1	15	14 min
9	HOAc	10	10/1	15	13 min
10	HOAc	10	7/1	15	7 min
11	HOAc	10	5/1	15	6 min
12	HOAc	10	7/1	5	Sol
13	HOAc	10	7/1	8	20 min
14	HOAc	10	7/1	10	13 min
15	HOAc	10	7/1	15	7 min
16	HOAc	10	7/1	20	4 min

[a] –NH_2/–CHO represents the molar ratio of benzohydrazide to aldehyde moieties.

Table S2. Redox responsive reversible sol−gel transitions of polymer gels.

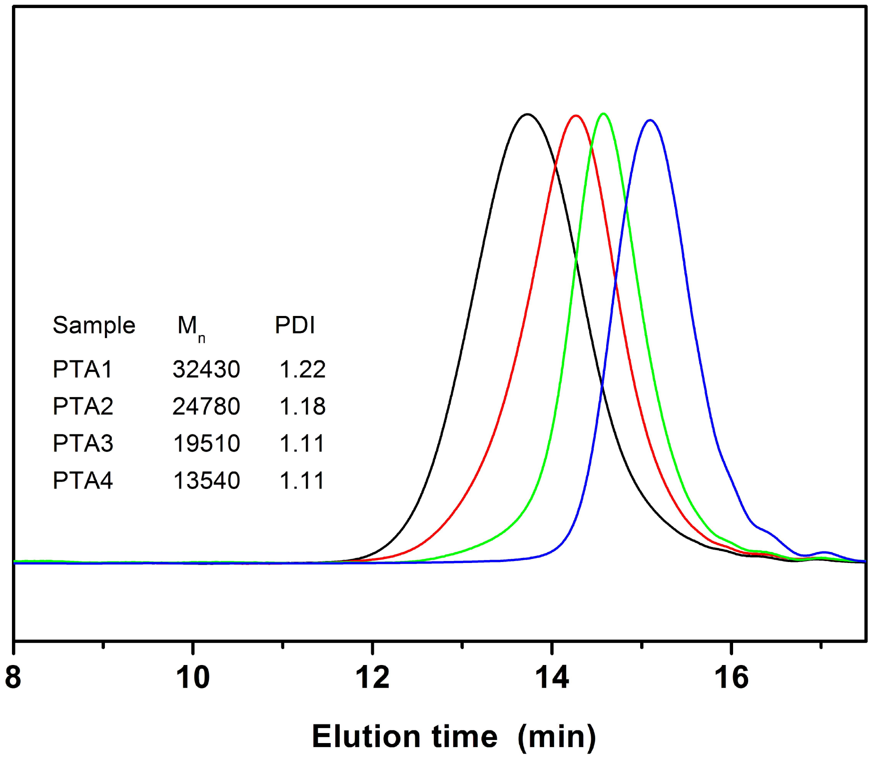
Sample	Transition Cycle	Gel to sol			Sol to gel	
		DTT (mg)	Et_3N (μL)	t (h)	BPO (mg)	t (min)
Table S1 Run 1	1	30	20	1	50	3
	2	30	20	4	50	5
	3	30	20	24	50	4
Table S1 Run 3	1	30	50	0.7	50	5
	2	30	20	5	50	6
	3	30	20	26	50	5
Table S1 Run 6	1	30	20	1	50	2
	2	30	20	3.5	50	3
	3	30	20	23	50	3

Table S3. Modulus data from dynamic rheology and compressive stress *vs.* strain studies for polymer gels with different gelator concentrations (–NH_2/–CHO = 10/1, HOAc concn. = 10 wt%).

Modulus	Gelator Concn.			
	8 wt%	10 wt%	15 wt%	20 wt%
G' (kPa) [a]	51.9	74.1	163.8	248.6
E (kPa) [b]	11.8	21.9	76.0	181.9

[a] The values of G' are determined from the average G' over the plateau region of the frequency sweep in Fig. 2c.

[b] The values of E are determined from the linear region (6–18%) of the stress–strain curves in Fig. 3.



Sample	M_n	PDI
PTA1	32430	1.22
PTA2	24780	1.18
PTA3	19510	1.11
PTA4	13540	1.11

Figure S1. GPC traces of synthesized PTAs.

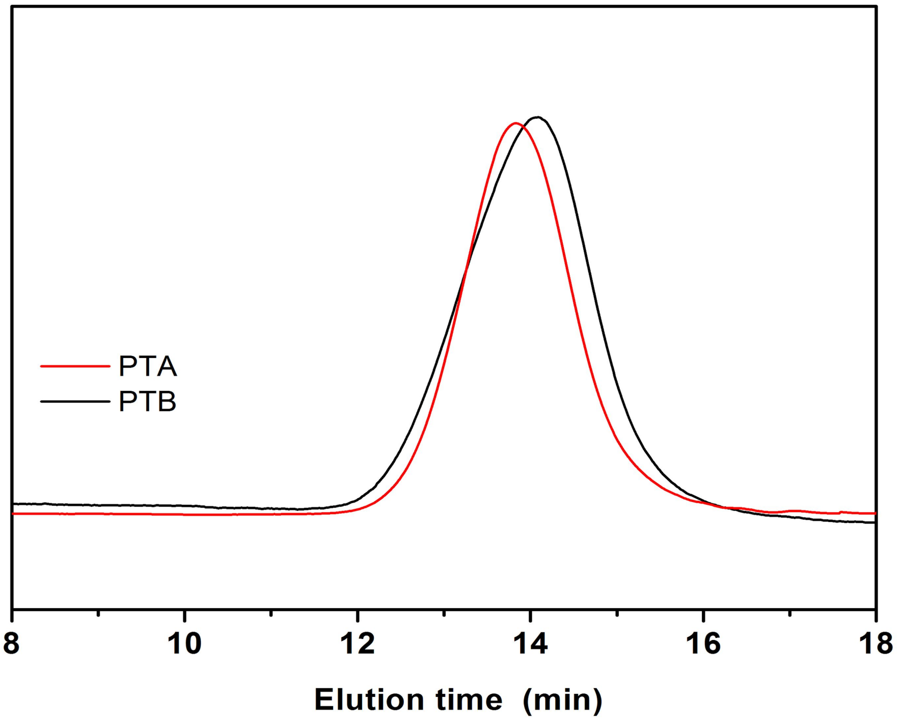


Figure S2. GPC traces of PTA and PTB.

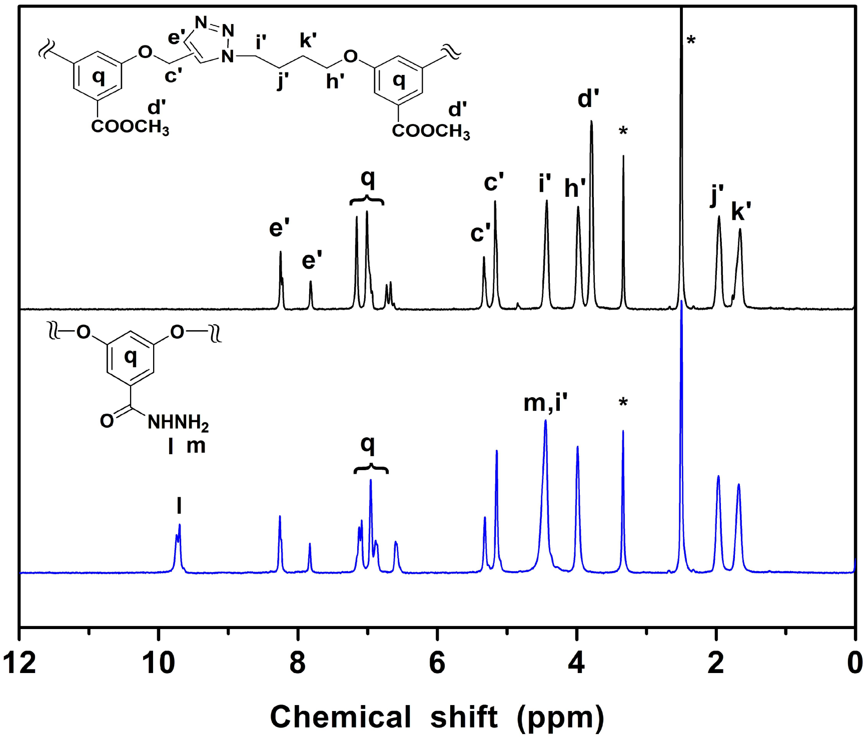


Figure S3. ^{1}H NMR spectra of PTA and PTB.

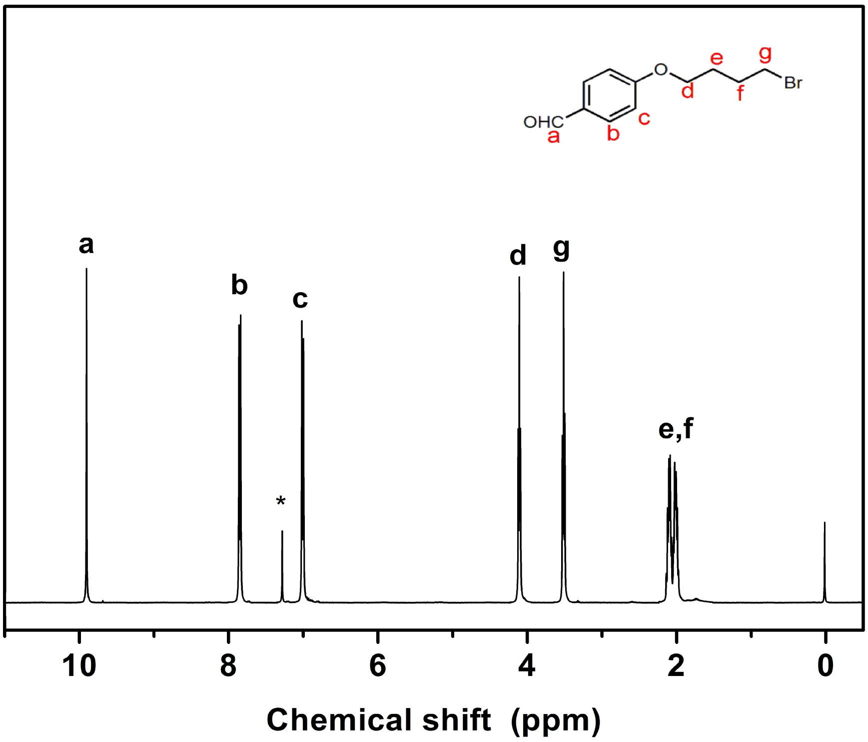


Figure S4. ^{1}H NMR spectrum of **C0**.

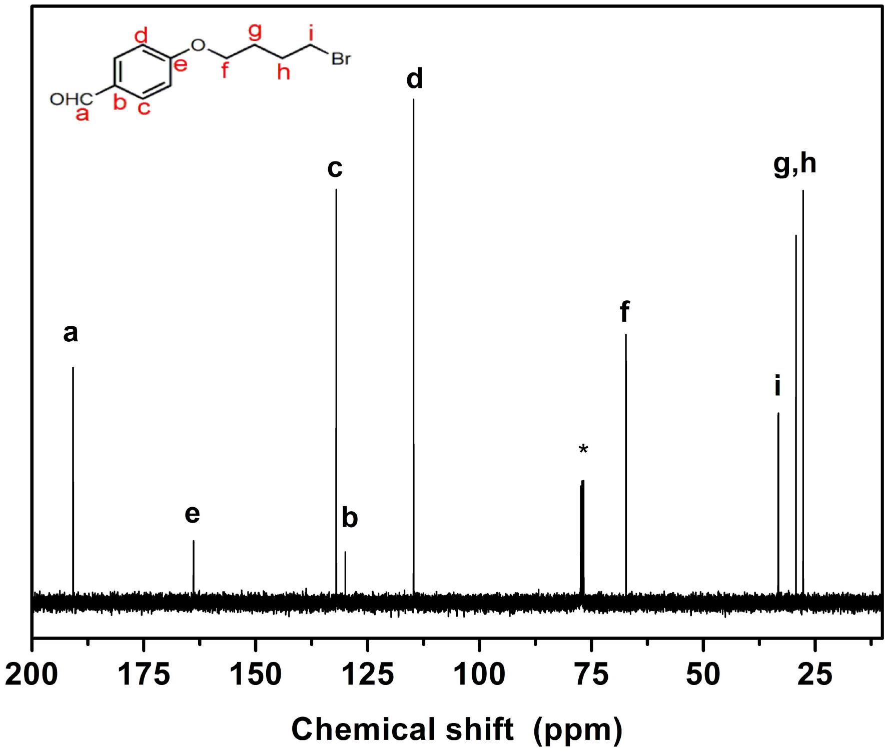


Figure S5. ^{13}C NMR spectrum of **C0**.

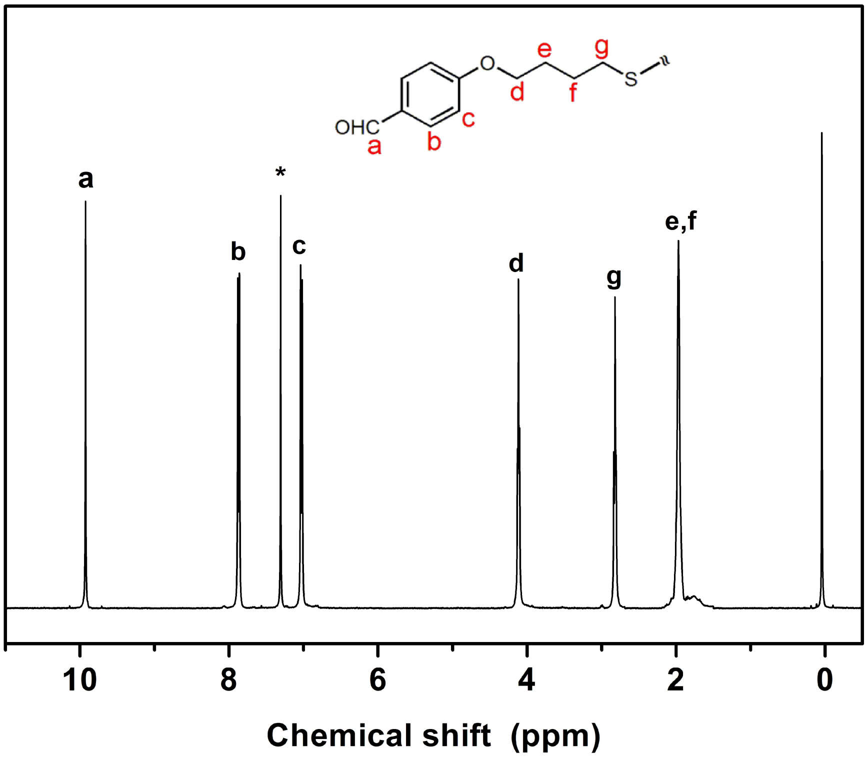


Figure S6. ^{1}H NMR spectrum of **C2**.

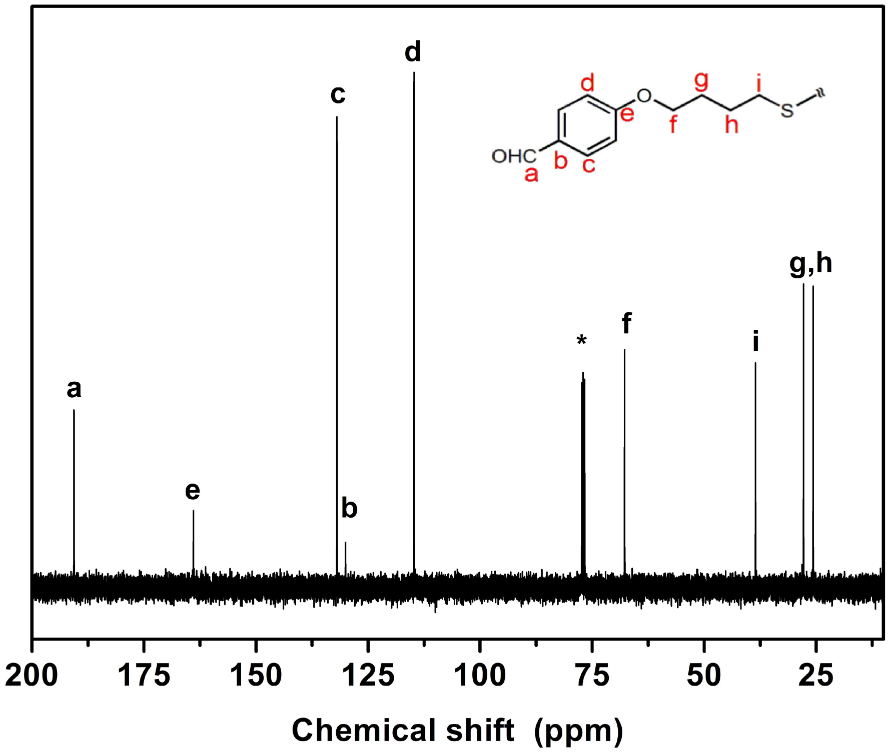


Figure S7. ^{13}C NMR spectrum of **C2**.

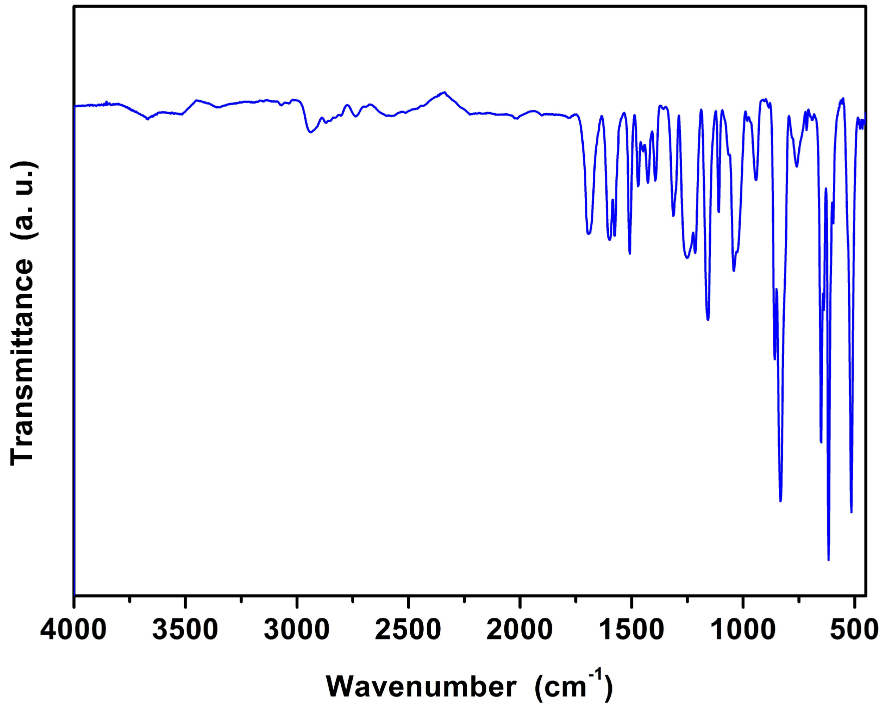


Figure S8. FTIR spectrum of **C2**.

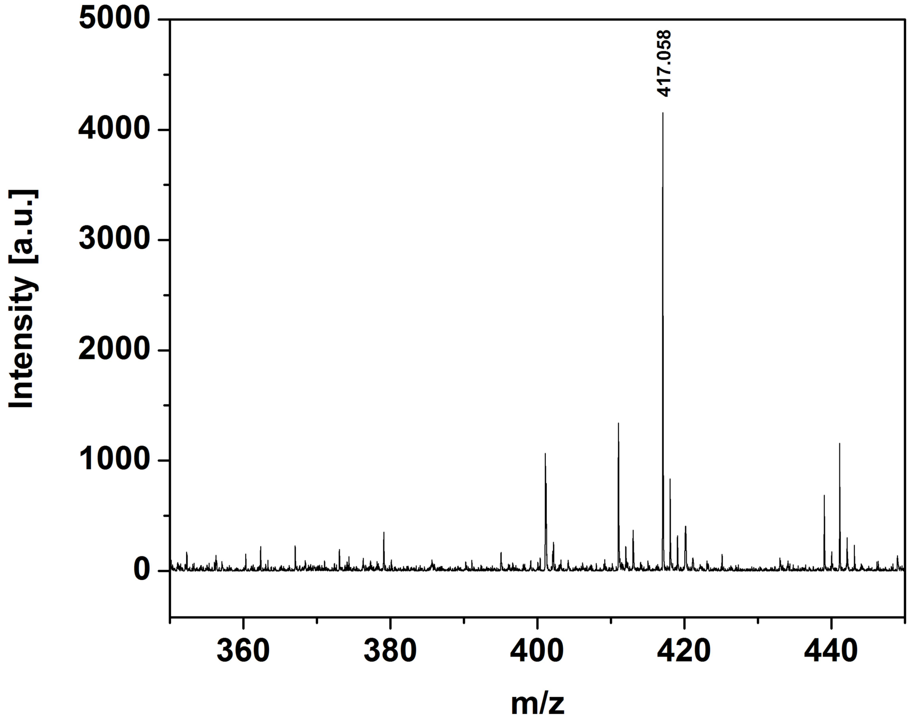


Figure S9. MS spectrum of **C2**.

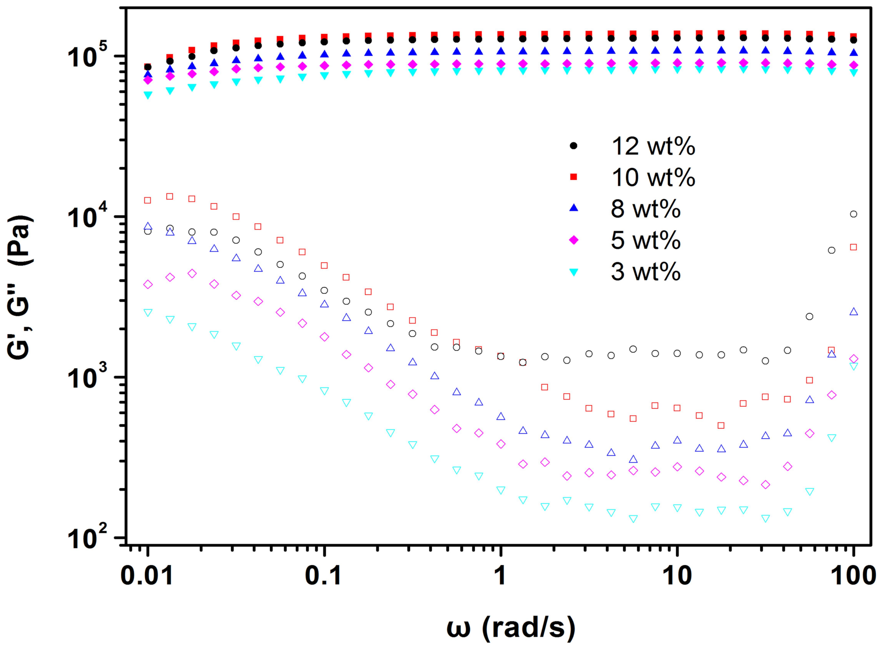


Figure S10. G' (solid symbol) and G"(open symbol) against frequency (ω) for polymer gels with different HOAc contents, $–NH_2/–CHO = 10/1$, gelator concn. = 15 wt%.

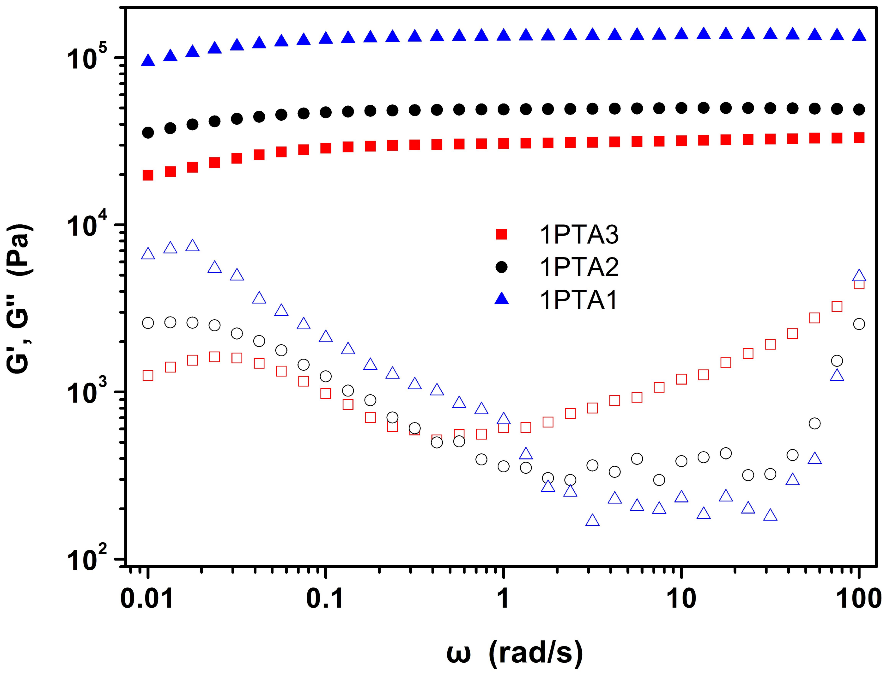


Figure S11. G' (solid symbol) and G"(open symbol) against frequency (ω) for gels prepared from PTB with different M_n (see **Figure S1**), HOAc concn. = 10 wt%, $-NH_2/-CHO$ = 10/1, gelator concn. = 15 wt%.

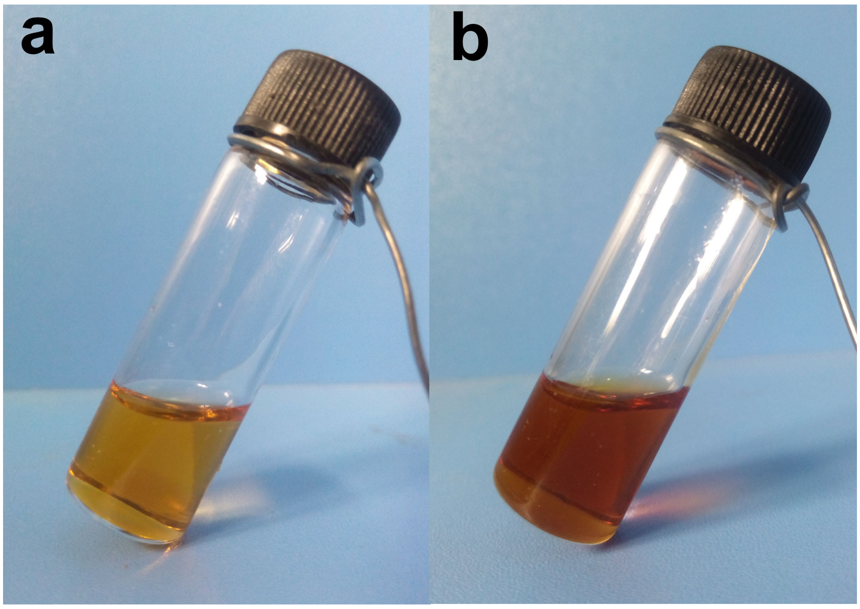


Figure S12. Photographs of PTB solution in DMF before (a) and after opening to air for 10 days (b).

References

1. F. Y. Deng, B. Xu, Y. Gao, Z. Liu, D. G. Yang and H. M. Li, *Journal of Polymer Science, Part A: Polymer Chemistry*, 2012, **50**, 3767-3774.
2. Q. Huang and B. Zheng, *Organic Chemistry International*, 2012, **2012**.