

Supplementary Information

Self-Healable Polymer Gels with Multi-Responsiveness of Gel-Sol-Gel Transition and Degradability

Ruixue Chang, Heng An, Xu Li, Ruyi Zhou, Jianglei Qin,* Yuelan Tian and Kuilin Deng

College of Chemistry and Environmental Science, Hebei University, 180 East Wusi Road, Baoding 071002, China.

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Fig. S7 Polymer gels prepared from $\text{P}(\text{NIIPAM}_{344}\text{-co-FPA}_8)$ and PEO_{90} di-acylhydrazine with gelator concentration of 10 wt% in DMF. No acetic acid was added in (a) and acetic acid concentration for (b) is 10%.

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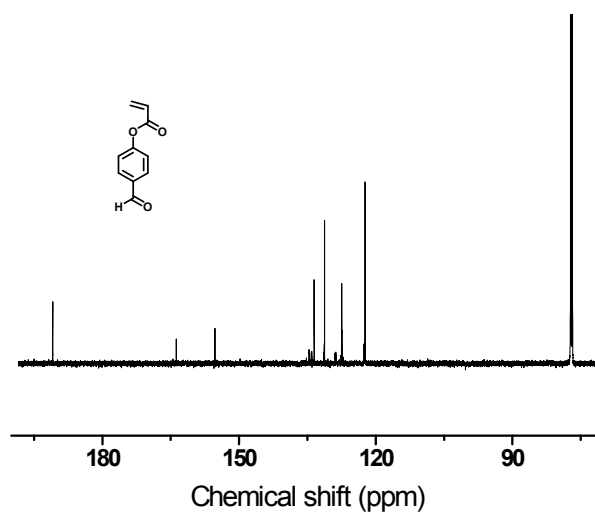


Fig. S1 ^{13}C NMR of FPA in CDCl_3 .

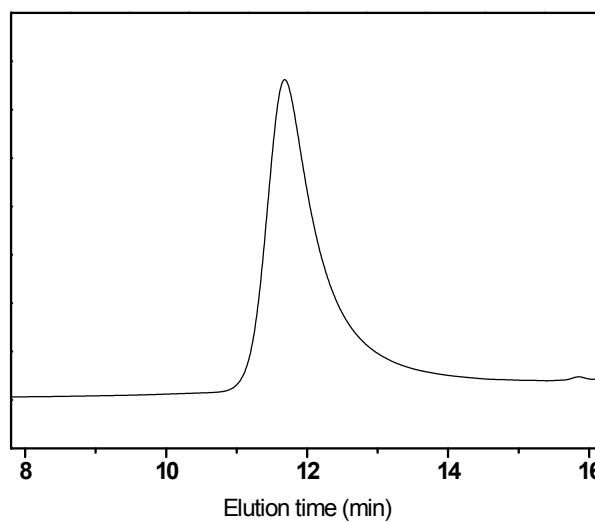


Fig. S2 GPC curve of $\text{P}(\text{NIPAM}_{179}\text{-co-FPA}_9)$.

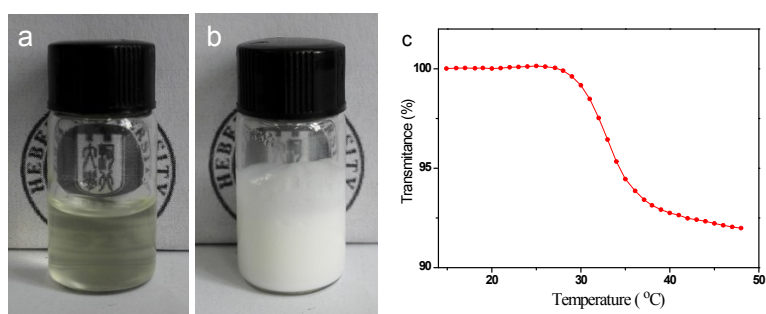


Fig. S3 The 8% $\text{P}(\text{NIPAM}_{344}\text{-co-FPA}_8)$ water solution (a) , after warmed in hand for 3 min (b) and transmission change upon heating (c) (0.5% concentration). (Credit from Hebei University)

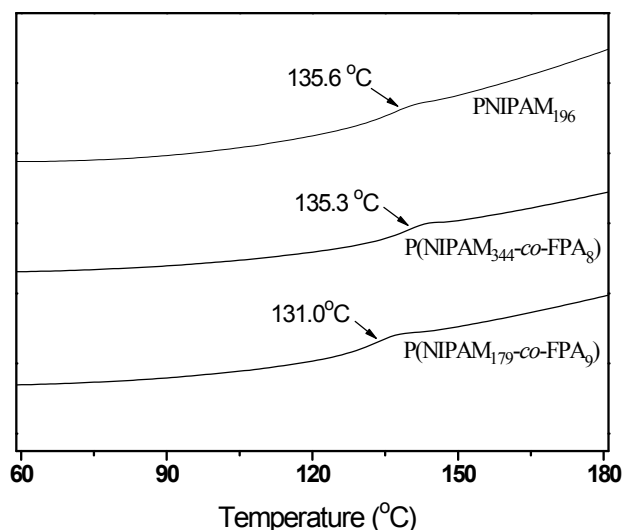


Fig. S4 DSC curves of P(NIPAM-*co*-FPA) compared with homopolymer.

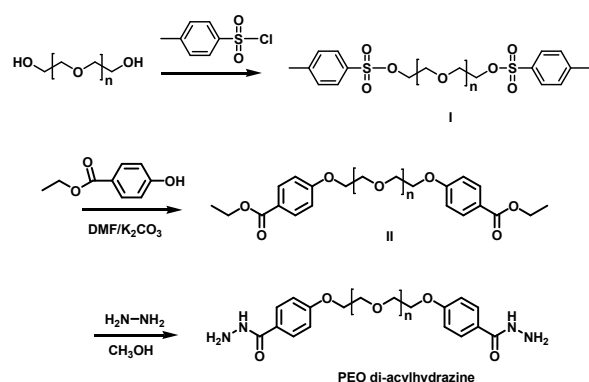
Synthesis of acylhydrazine-terminated PEO (PEO di-acylhydrazine).

The synthesis of PEO with two acylhydrazine-terminal groups was carried out according to literature as shown in Scheme S1. [1] PEO (DP=23, 90 and 227 respectively) was dried by azeotropic distillation in toluene. The synthesis of procedure was carried out with PEO₉₀ as an example. 20 g (5 mmol) PEO₉₀ was dissolved in 40 mL dry dichloromethane (CH₂Cl₂) in a 250 mL flask and the solution was cooled to 0 °C in an ice bath. Then triethylamine (5.5 mL, 40 mmol) and 4-toluene sulfonyl chloride (7.6 g, 40 mmol) were added successively. After stirred for 2 h at 0°C, the temperature was increased to room temperature gradually and stirred for another 24h. The reaction mixture was dilute by CH₂Cl₂ and extracted by 300 mL saturated NaHCO₃ solution three times (100mL for each extraction). The organic phase was dried by anhydrous MgSO₄ and the 4-toluene sulfonyl terminated PEO₉₀ (I) was collected by precipitating in petroleum ether (Yield 90%).

4-toluene sulfonyl terminated PEO₉₀ (I) (10 g, 2.5 mmol) and 4-ethyl hydroxybenzoate(3.3 g, 20 mmol) were dissolved in DMF(40 mL), then K₂CO₃ (27 g, 20 mmol) was added into the solution. The mixture was stirred for 72 h days at 80°C. After cooled to room temperature, the mixture was diluted by 100 mL water, and the solution was extracted with 150 mL CH₂Cl₂ (5 times, 30 mL each). The organic layer was washed by Na₂CO₃ and dried by anhydrous MgSO₄. The product of ethyl benzoate-terminated PEO (II) was obtained by precipitating in petroleum ether twice (yield 85%).

Synthesis of acylhydrazine-terminated PEO. 8 g (4mmol) 4-ethyl benzoate-terminated PEO (II)

was dissolved in 40 mL methanol, then 20 mL hydrazine hydrate (80% in water, w/w) was added into the solution. The reaction mixture was refluxed for 72 h at 80 °C. After cooled to room temperature, the methanol was removed by rotary evaporation and the solution was diluted with 100 mL water. The solution was extracted with 150 mL CH₂Cl₂ (5 times, 30 mL each). The CH₂Cl₂ solution was washed with saturated NaCl solution 3 times and dried over by MgSO₄. The product of PEO di-acylhydrazine was collected by precipitating in petroleum ether and dried under vacuum (yield: 70%). ¹H NMR is shown in Figure S3.



Scheme S1. Synthesis of benzaldehyde terminated PEO.

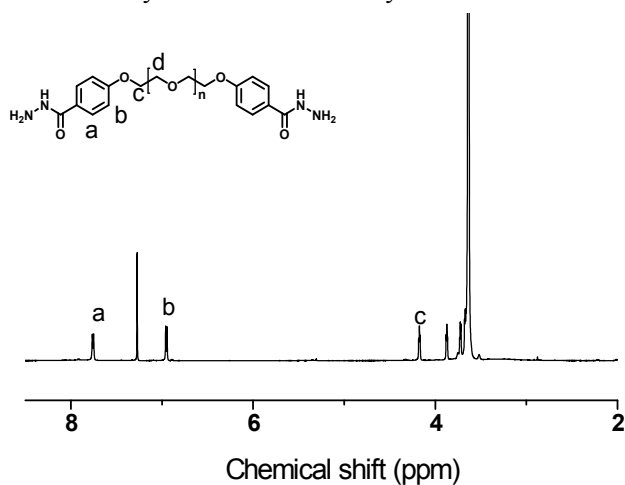


Fig. S5 ¹H NMR spectra of PEO₂₃ di-acylhydrazine.



Fig. S6 Polymer gel prepared from P(NIIPAM₁₇₉-co-FPA₉) and PEO₉₀ di-acylhydrazine with 10 wt% gelator concentration in DMSO did not self-heal in 72 h under 10% acetic acid catalysis. (Credit from Hebei University)

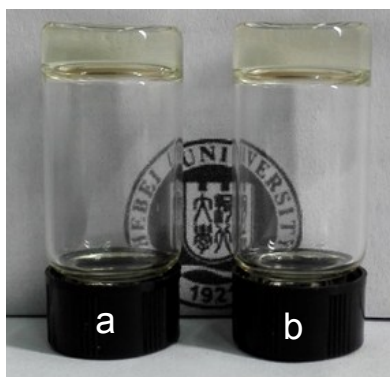


Fig. S7 Polymer gels prepared from P(NIIPAM₃₄₄-co-FPA₈) and PEO₉₀ di-acylhydrazine with gelator concentration of 10 wt% in DMF. No acetic acid was added in (a) and acetic acid concentration for (b) is 10%. (Credit from Hebei University)

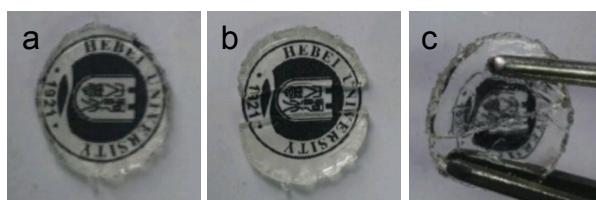


Fig. S8 The self-healing property of polymer gel with 1:1.5 group ratio of aldehyde to acylhydrazine. (a: as prepared; b: cut into 2 pieces; c: self-healed gel under stretching) (Credit from Hebei University)



Fig. S9 Self-healing of organic polymer gel with 5% of gelator concentration and 1:1 group ratio. (Credit from Hebei University)



Fig. S10 Self-healing property of organic polymer gel with 10% of P(NIIPAM₁₇₉-co-FPA₉) and PEO₂₂₇ di-acylhydrazine 1:1 group ratio. (Credit from Hebei University)



Fig. S11 DMF was absorbed by the polymer gel prepared from P(NIIPAM₁₇₉-co-FPA₉) and PEO₂₂₇ di-acylhydrazine in 12 h. (Credit from Hebei University)

[1] G. H. Deng, F. Y. Li, H. X. Yu, F. Y. Liu, C. Y. Liu, W. X. Sun, H. F. Jiang and Y. M. Chen, *Acs Macro Letters* **2012**, *1*, 275-279.