Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Adaptable Eu-containing polymeric films with dynamic control of mechanical properties in response to moisture

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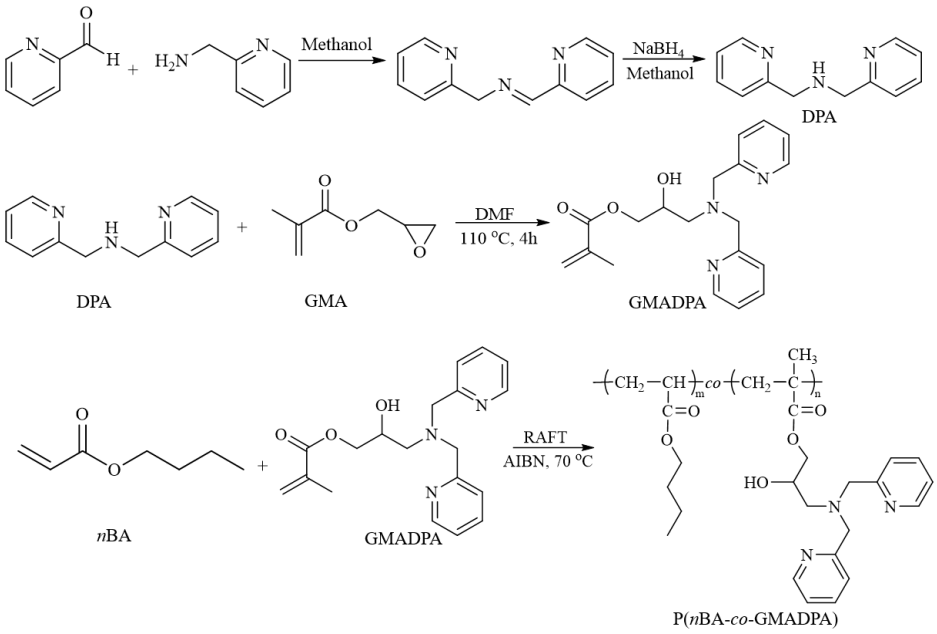

Figure S1. Scheme to illustrate the synthetic route of GMADPA and P(*n*BA-*co*-GMADPA).

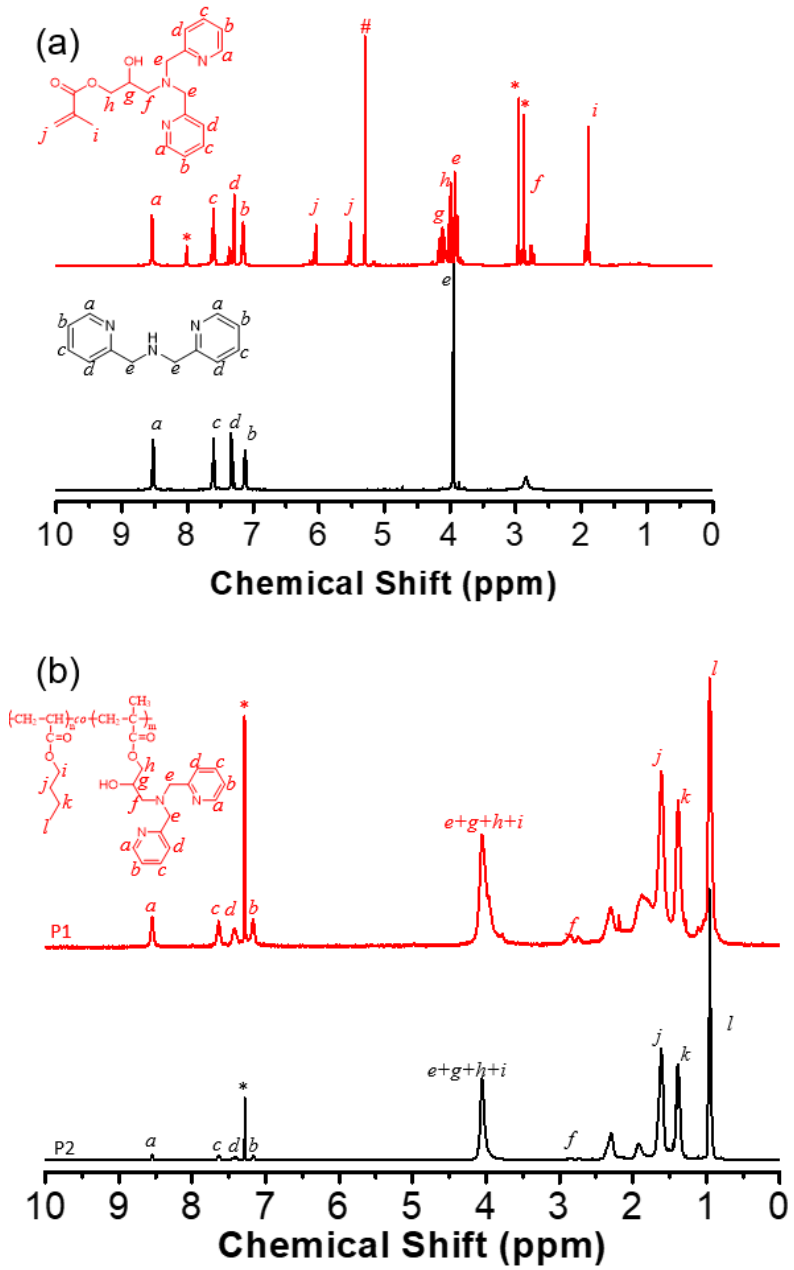

Figure S2. (a) The chemical structures and ^{1}H NMR spectra of DPA ligand (black), GMADPA (red) in $CHCl_3$. * is solvent residue of DMF and # is DCM. (b) ^{1}H NMR spectra of P1 (red) and P2 (black) in $CHCl_3$. * is the solvent $CHCl_3$.

Determination of repeat unit number of random copolymers of P(nBA-co-GMADPA)

The repeat unit number of each polymer was calculate based on the conversion of *n*BA measured using DMF as an internal standard (the solvent). The vinyl protons (CH_2=C*H*-) relative to DMF were integrated before and after polymerization.

An example to calculate the molecular weight of the copolymer P1 is given below. Using the peak at 6.4 ppm

$$\text{Conversion of nBA} = \frac{A_i \text{ (before polymerization)} - A_i \text{ (after polymerization)}}{A_i \text{ (before polymerization)}} = 0.63$$

Where A_i is the peak area of one vinyl proton at 6.4 ppm (-C*H*=*C*H$_2$) of *n*BA.

The feeding mole ratio of *n*BA relative to the RAFT agent is 280: 1. Therefore, the repeat unit number of *n*BA is, 0.63×280 = 176.4 ≈ 176. After purifying, the number of GMADPA units was calculated to be 32 based on the repeat unit number of *n*BA.

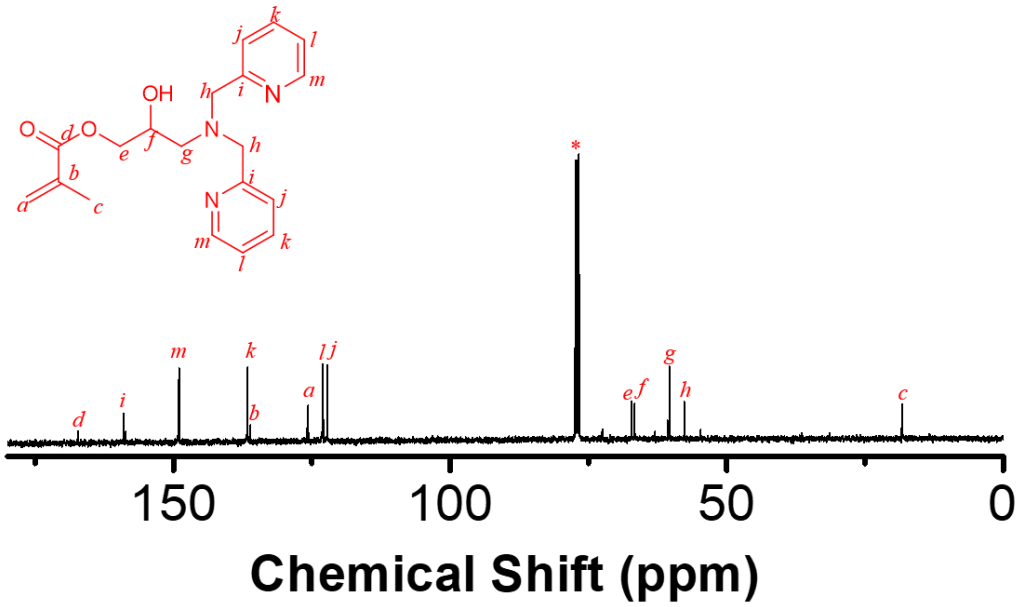

Figure S3. (a) The chemical structures and ^{13}C NMR spectra of GMADPA (red) in $CHCl_3$. * is solvent residue of $CHCl_3$.

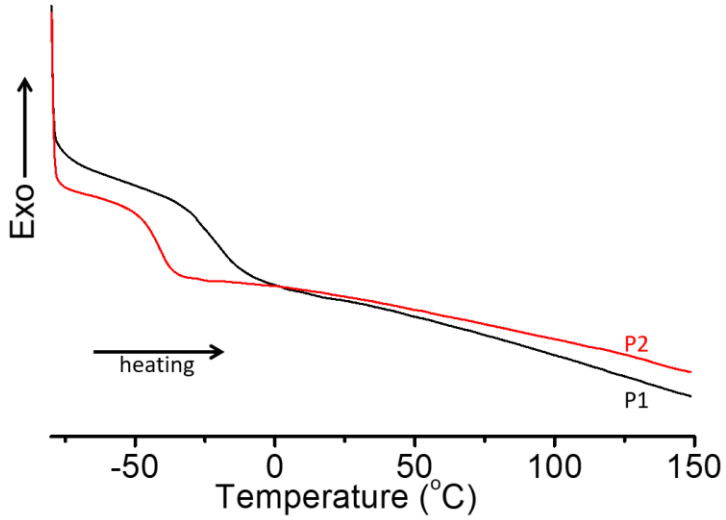

Figure S4. DSC heating curves of copolymer of P1(black) and P2(red) All heating curves are collected from the second heating scanning.

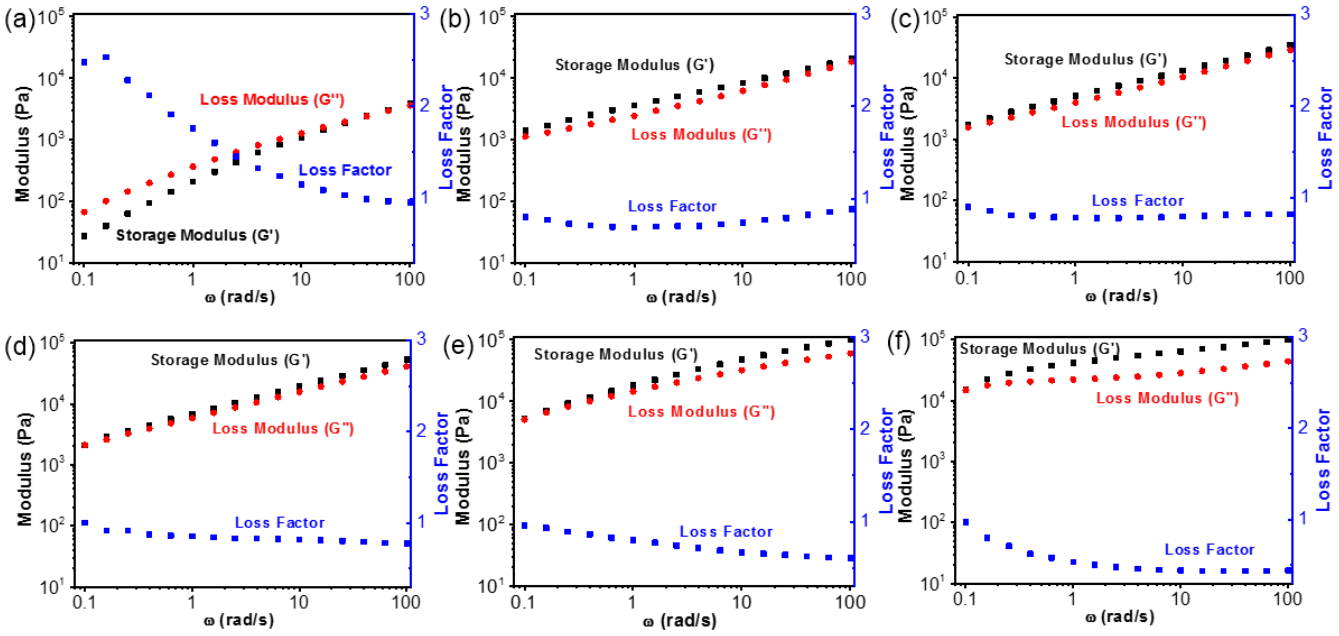

Figure S5. The rheological studies of the copolymer P1 with different Eu-to-DPA ratios: (a) P1; (b-f) P1 with Eu-to-DPA ratios of 1/7 (b) ;1/5 (c); 1/4 (d); 1/3 (e); 1/2 (f).

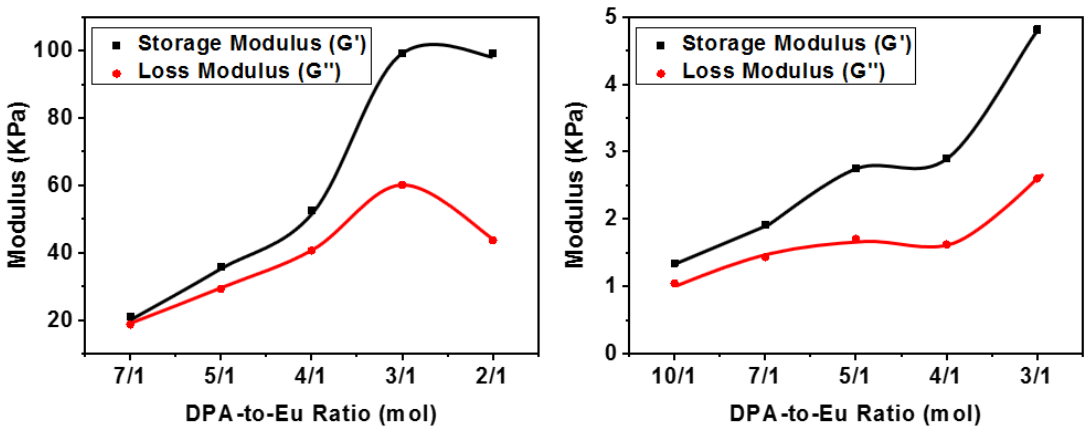

Figure S6. Storage modulus (G′) and loss modulus (G″) plotted against the Eu-to-DPA ratio at ω = 100 rad s^{-1} (a) P1; (b) P2.

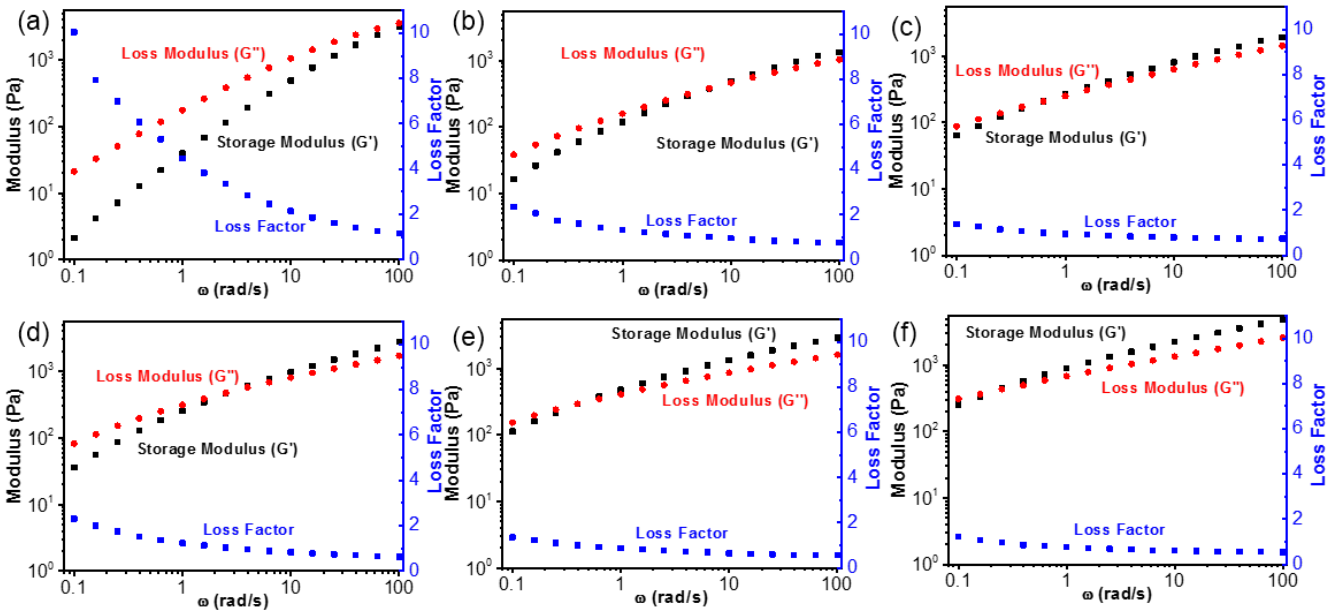

Figure S7. The rheological studies of the copolymer P2 with different Eu-to-DPA ratios: (a) P2; (b-f) P2 with Eu-to-DPA ratios of 1/10 (b) ;1/7 (c); 1/5 (d); 1/4 (e);1/3 (f).

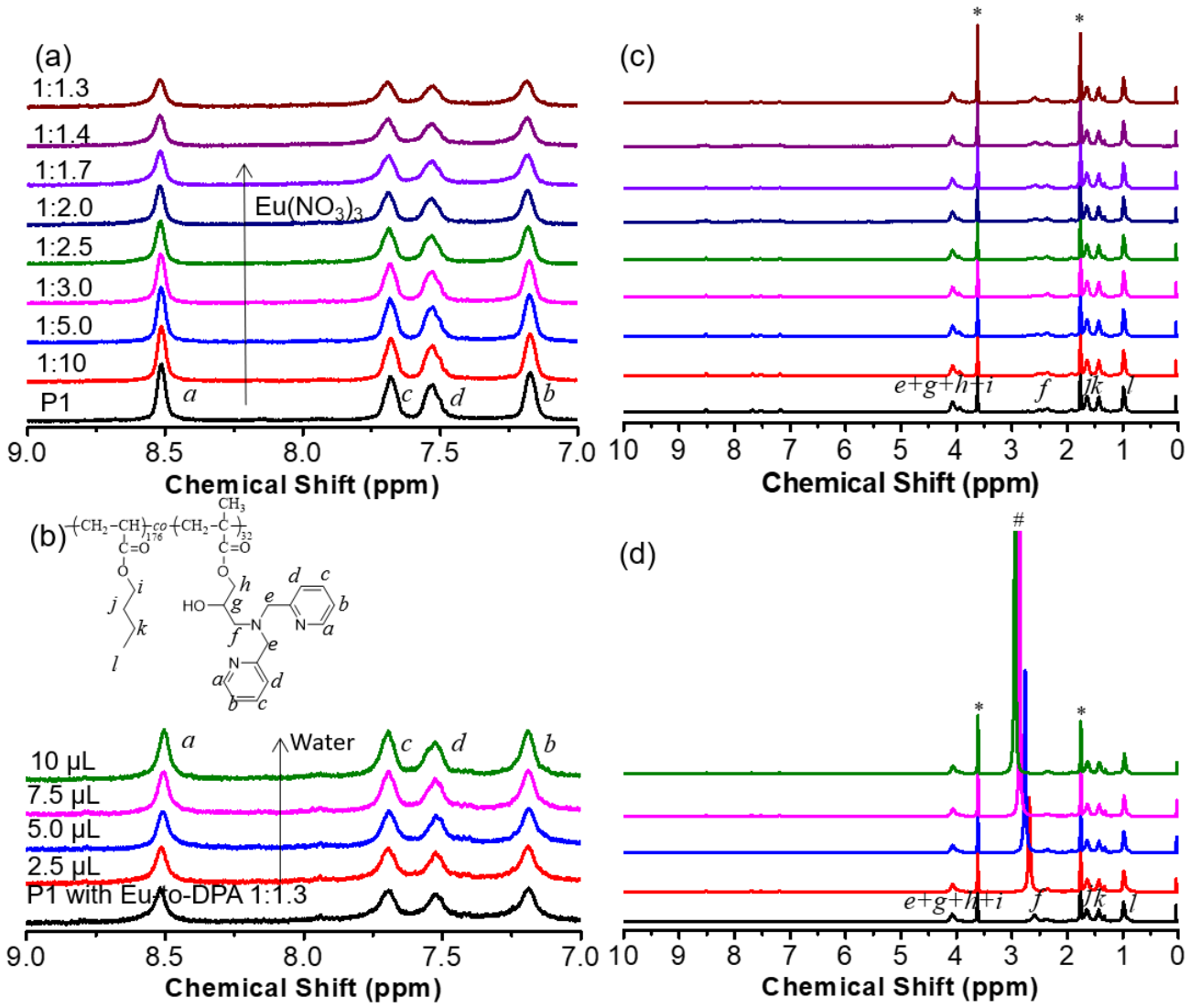

Figure S8. (a) ^{1}H NMR spectra of the copolymer P1 (black, bottom) and its titration spectra with $Eu(NO_3)_3$ in the range of 6.9 to 9.0 ppm. (b) ^{1}H NMR reverse titration using water to an Eu-to-DPA ratio of 1:1.3 in the range of 6.9 to 9.0 ppm. (c) Full ^{1}H NMR spectra of the copolymer P1 (black, bottom) and its titration spectra with $Eu(NO_3)_3$. (d) Full ^{1}H NMR spectra reverse titration using water: pure P1 with an Eu-to-DPA ratio of 1:1.3 (black, bottom), All spectra were measured in d_8-tetrahydrofunan (*). # is the peak for water.

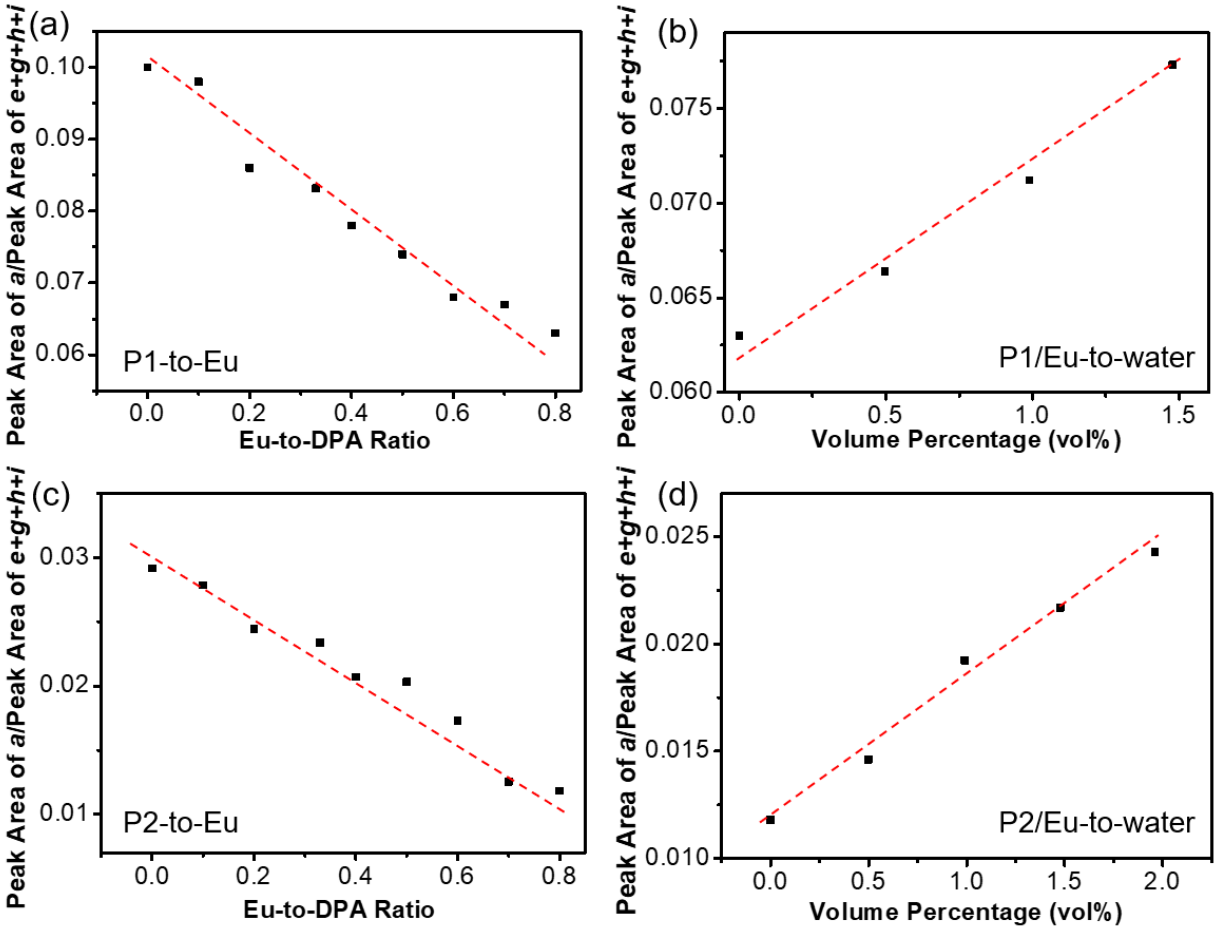

Figure S9. The plot of relative integrals of peak *a* and peak *e*+*g*+*h*+*i* *vs* the molar ratio of Eu-to-DPA. Eu titration with P1 (a) and P2 (c). The plot of relative integrals in ^{1}H NMR spectra of peak *a* and peak *e*+*g*+*h*+*i* *vs* water. Water titration with Eu-P1 (d) and (c) Eu-P2.

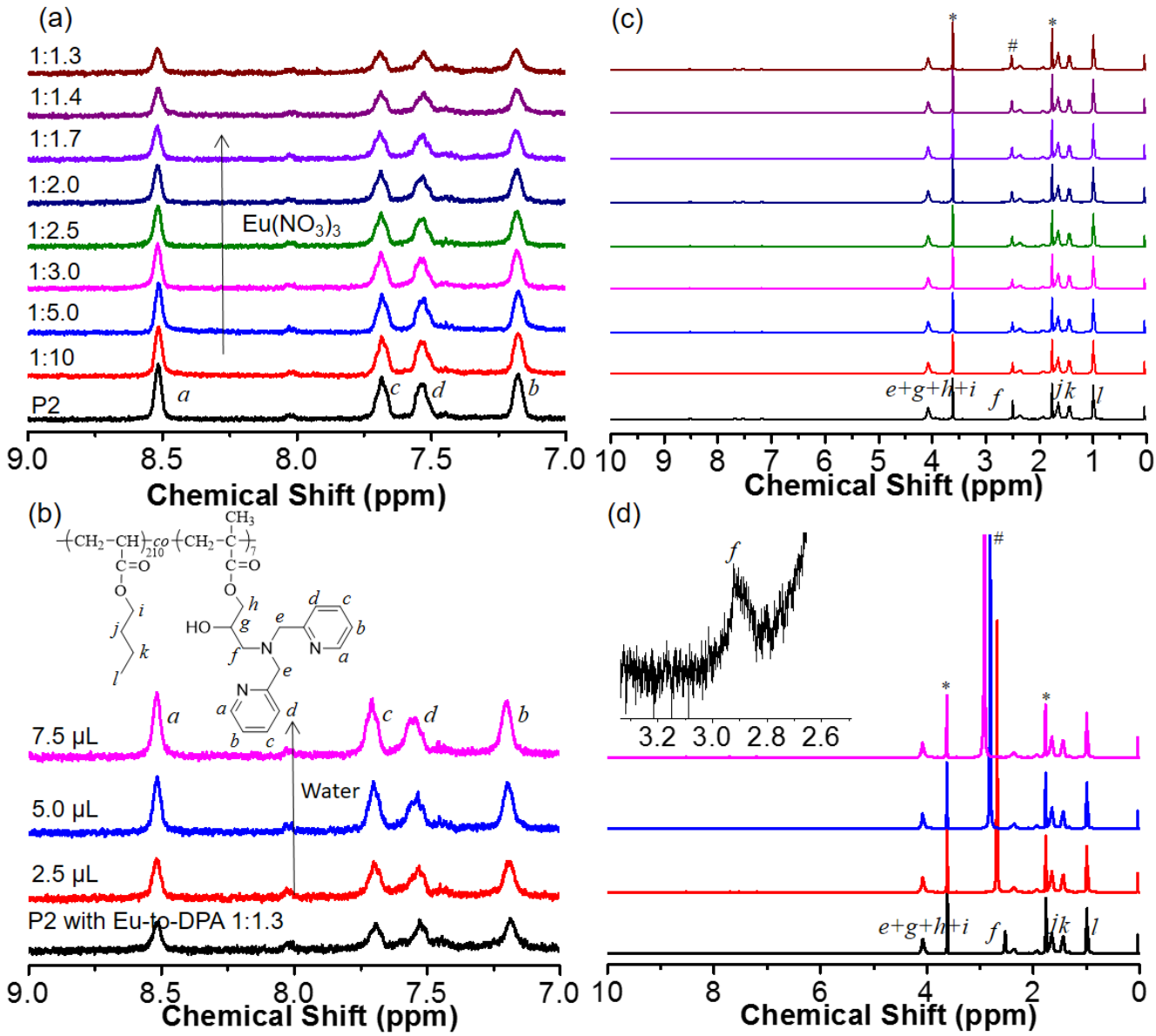

Figure S10. (a) ^{1}H NMR spectra of the copolymer P2 (black, bottom) and its titration spectra with $Eu(NO_3)_3$ in the range of 6.9 to 9.0 ppm. (b) ^{1}H NMR reverse titration using water to an Eu-to-DPA ratio of 1:1.3 in the range of 6.9 to 9.0 ppm with 2.5 μL of water (red), 5 μL of water (blue) and 7.5 μL of water (pink). (c) Full ^{1}H NMR spectrum of the copolymer P2 (black, bottom) and its titration spectra with $Eu(NO_3)_3$. (d) Full ^{1}H NMR spectra reverse titration using water: P2 with an Eu-to-DPA ratio of 1:1.3 (black, bottom). All spectra were measured in d_8-tetrahydrofunan (*). # is the peak for water. The inset in (d) is to show the methylene peak *f* at 2.9 ppm.

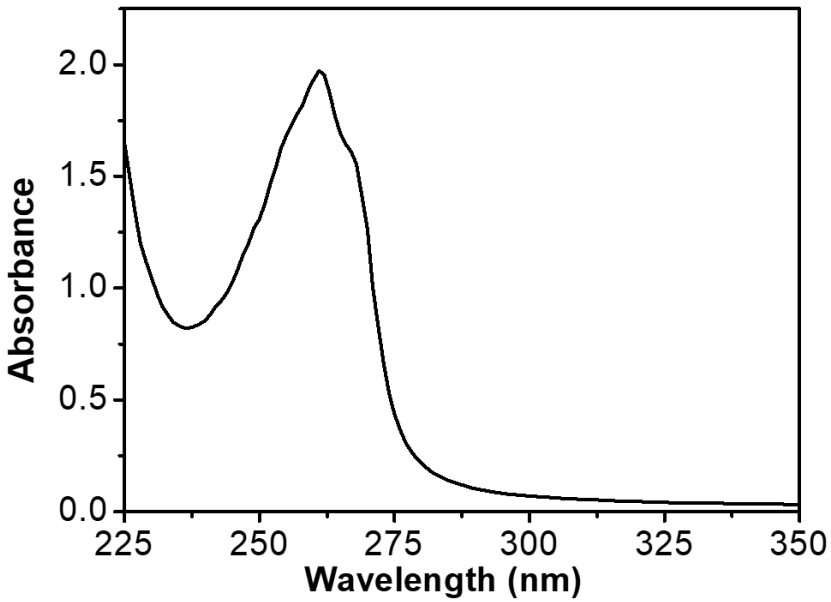

Figure S11. UV-vis spectrum of GMADPA in water.

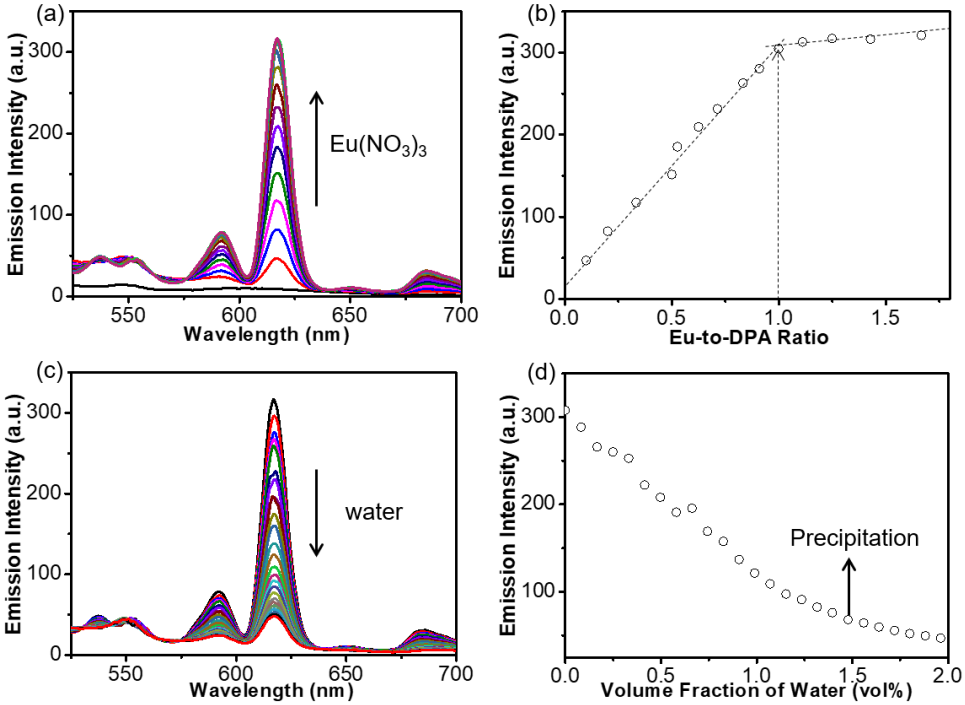

Figure S12. (a) Fluorescent titration experiments of the copolymer P2 in THF (1.67 mg/mL) using $Eu(NO_3)_3$ as a titrant. (b) The plot of emission intensity at 617 nm *vs.* Eu-to-DPA ratio. (c) The fluorescent titration of Eu-containing P2 by adding water/THF (1/1, vol). The initial sample is the Eu-containing P2 solution from (a) (Eu-to-DPA ratio = 1:1.3). The spectrum was collected by stepwise adding 5 μL of water/THF each time. (d) The emission intensity at 617 nm plotted with the volume fraction of water (vol%) recorded in (c) and the arrow indicate the polymer precipitated in the solution. All the emission spectra were collected with an excitation at 272 nm.

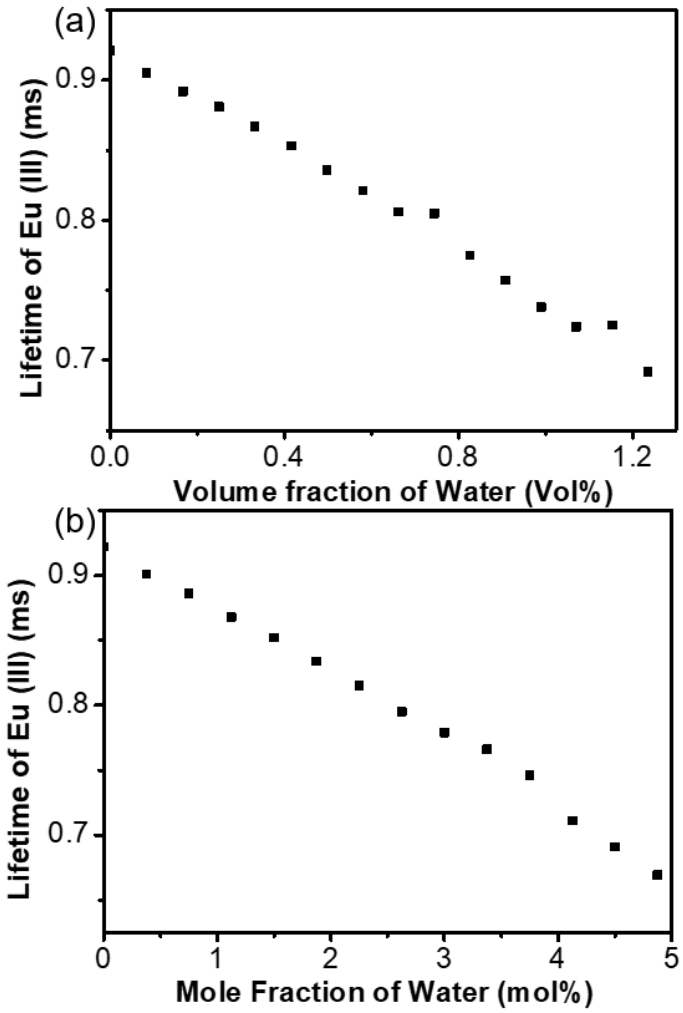

Figure S13. The lifetime of Eu^{3+} ions plotted against (a) volume fraction and (b) mole fraction of water in P2/THF solution. The copolymer P2 (1.67 mg/mL) dissolved into 3 mL of anhydrous THF. The used Eu-to-DPA ratio is 1:3. For each measurement, 5 µL of water/THF mixture (1/1, vol) was added to the P2/Eu^{3+} solution. The lifetime was recorded using an excitation at 272 nm and an emission at 617 nm.

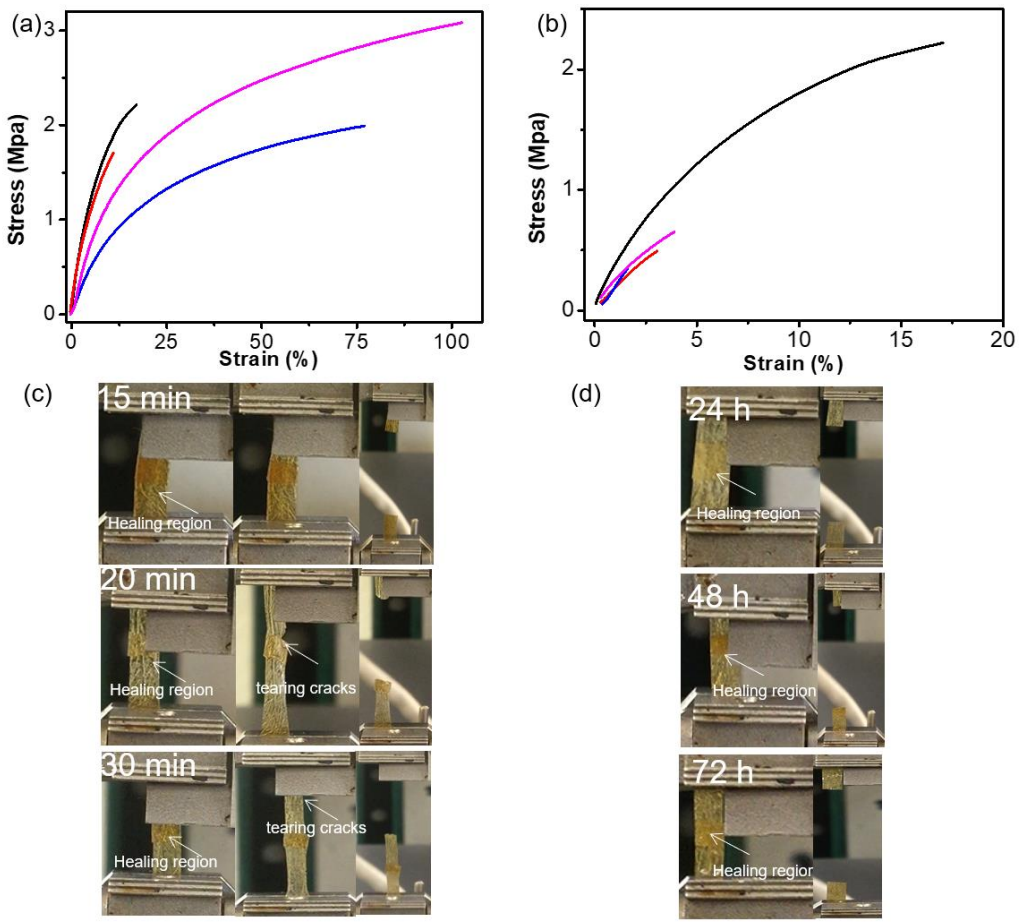

Figure S14. (a). Stress-strain curves of the polymeric film of P1 with an Eu-to-DPA ratio of 1:3 at different moisture treatment time; original copolymer film (black); fractured film at presence of water for 15 min (red); fractured film at presence of water for 20 min (blue); fractured film at presence of water for 30 min (purple). (b) stress-strain curves of the polymeric film of P1 with an Eu-to-DPA ratio of 1:3 after self-healing for 24 (red), 48 (blue) and 72 h (purple). (c) Optical images of stress-strain test for fractured film of polymeric film of P1 with an Eu-to-DPA ratio of 1:3 at different moisture treatment time. (from top to bottom, 15, 20, and 30 min). The left images are the original shape of the films; the white arrows are point to healing regions. The middle images are stretched film and the white arrows are the cracks; the right images are the yielded samples. (d) Optical images of stress-strain test for divided film of copolymer P1 with an Eu-to-DPA ratio of 1:3 with different self-healing time (from top to bottom, 24, 48, and 72 h). The left images are the original shape of the film and the white arrows are overlapped healing regions; the right images are the yielded samples. All the tests were carried out at the room temperature with strain rate of 0.5 N/min.

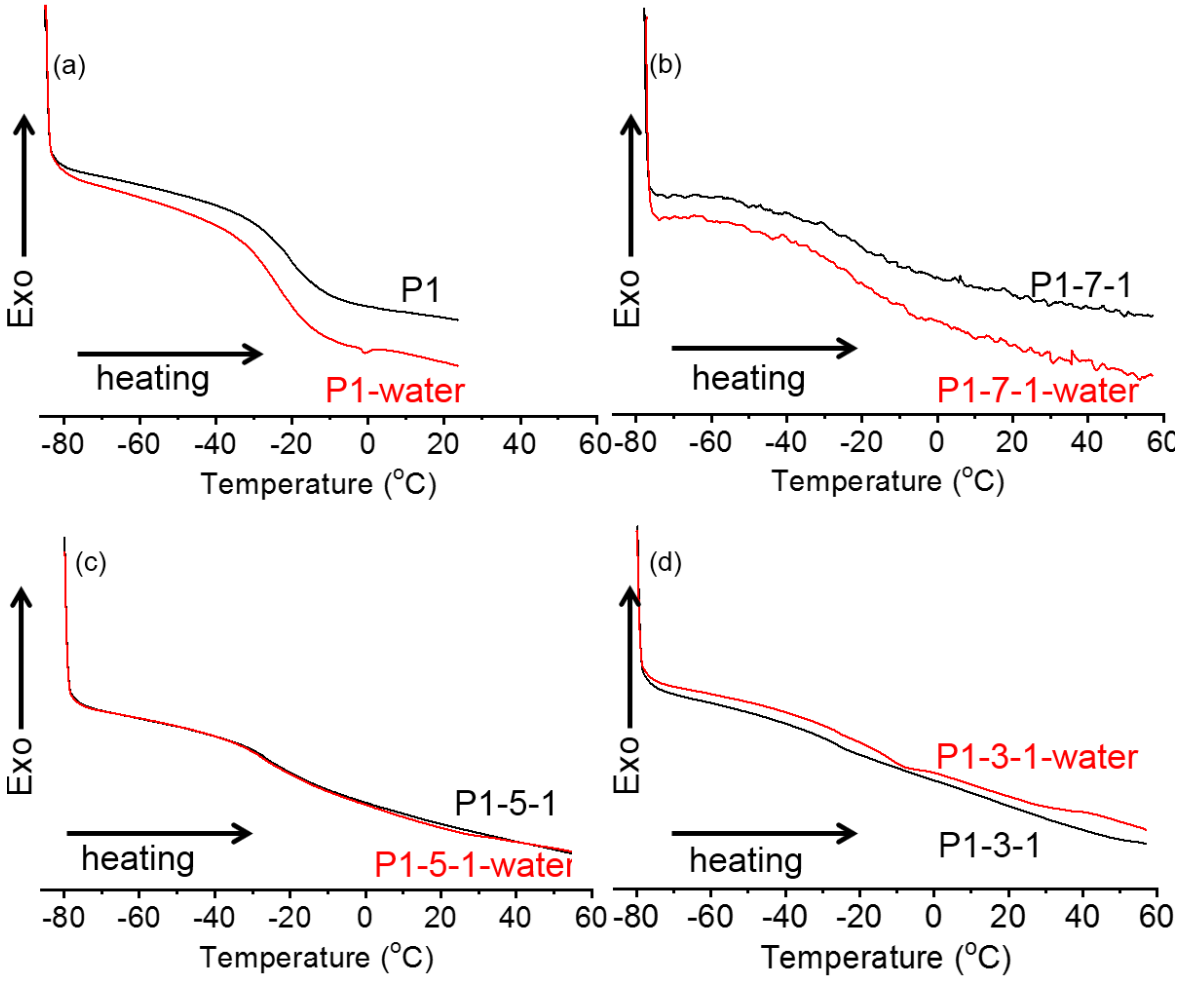

Figure S15. DSC heating curves of copolymer of (a) P1(black) and P1 treated with moisture containing N_2(red); and the Eu containing polymer before (black) and after (red) treated with moisture containing N_2. (b) P1 with DPA-to-Eu of 7:1; (c) P1 with DPA-to-Eu of 5:1;(d) P1 with DPA-to-Eu of 3:1. All heating curves are collected from the second heating scanning.

Table S1. Fracture stress of the P1-Eu film under different healing conditions.

P1 with DPA-to-Eu = 3-1	Fracture stress (MPa)
Original sample	2.29±0.64
15 min water treatment	1.7± 0.17
20 min water treatment	2.0±0.91
30 min water treatment	3.1±0.51
Self-healing 24 h	0.49±0.43
Self-healing 48 h	0.34±0.21
Self-healing 72 h	0.65±0.15

Table S2. The summary of glass transition temperatures of P1, Eu-containing P1 and water treated polymers

Sample	T_g (ºC)
P1	**-32.8**
P1-water	**-27.0**
P1-Eu (7-1)	**-29.8**
P1-Eu (7-1) water	**-31.8**
P1-Eu (5-1)	**-31.6**
P1-Eu (5-1)water	**-34.4**
P1-Eu (3-1)	**-31.9**
P1-Eu (3-1) water	**-28.5**