Supporting Information for:

Shape-Memory and Self-Healing Polyurethanes Based on Cyclic Poly(ε-caprolactone)

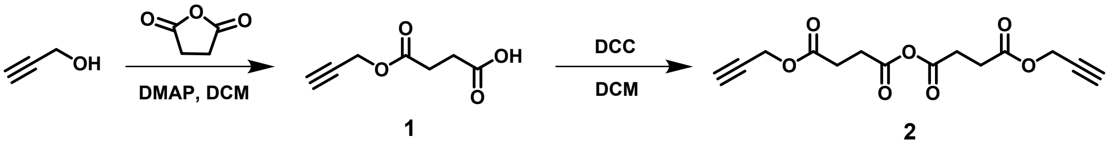
Wei Chen, Yanyan Zhou, Ying Li, Jun Sun, Xiangqiang Pan, Qian Yu, Nianchen Zhou, Zhengbiao Zhang* and Xiulin Zhu

State and Local Joint Engineering Laboratory for Novel Functional Polymeric Materials, Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, China.

* Correspondence: zhangzhengbiao@suda.edu.cn

Synthesis

Synthesis of micromolecules



Scheme S1. Synthesis of compound **2**.

Synthesis of compound 1

Succinic anhydride (9.3 g, 93.0 mmol) and DMAP (2.6 g, 21.4 mmol) were dissolved in 20 mL of anhydrous DCM. Then propargyl alcohol (6.0 g, 107.0 mmol) was dissolved in DCM (10 mL) and added dropwise to the above suspension, which was stirred for 36 h subsequently at ambient temperature. After the reaction, the mixture was diluted with 50 mL of DCM, and washed three times with 10% $NaHSO_4$ (3×20 mL), followed by washing three times with water (3×20 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford a white solid (10.0 g, 68.9% yield).

Synthesis of compound 2

Compound **2** (8.0 g, 51.3 mmol) was dissolved in 40 mL of anhydrous DCM and the solution was cooled to

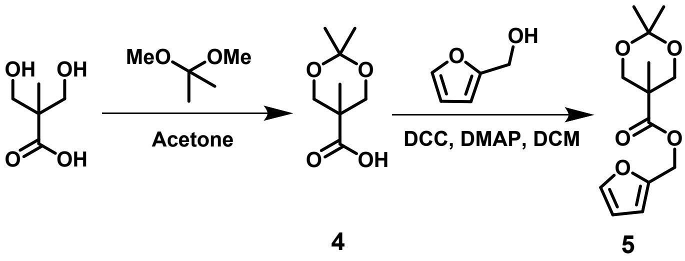
0 °C. Then DCC (5.5 g, 26.6 mmol) was dissolved in DCM (20 mL) and added dropwise to the above mixture. After 1 h at 0 °C, the reaction was left to reach room temperature and stirred for 24 h. The reaction mixture was then filtered to remove all solids. After evaporation under reduced pressure, the final product was obtained as a white solid (7.5 g, 99% yield) (**Figure S1**).

3

Scheme S2. Synthesis of compound **3**.

Synthesis of compound 3

A mixture of 1,4-butanediol diglycidyl ether (3.0 g, 14.8 mmol), NaN_3 (4.8 g, 78.0 mmol) and NH_4Cl (4.0 g, 74.0 mmol) were added in 30 mL of DMF, stirred at 50 °C for 24 h. The reaction mixture was cooled to room temperature and then dissolved in 300 mL of DCM and washed three times with water (3×50 mL) to remove DMF. The organic layer was then dried with anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford a white solid (3.7 g, 86.4% yield) (**Figure S2**).



4

5

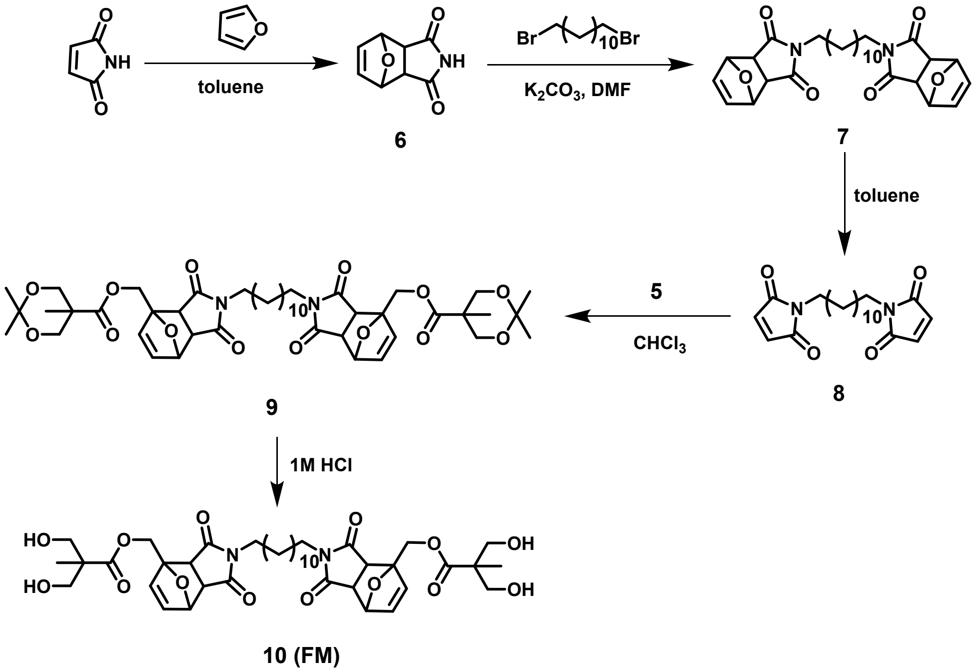
Scheme S3. Synthesis of compound **5**.

Synthesis of compound 4

Bis-MPA (10.0 g, 74.5 mmol) , 2,2-dimethoxypropane (13.8 mL , 111.8 mmol) and p-Toluenesulfonic acid monohydrate (0.7 g , 3.7 mmol) were dissolved in 50 mL of acetone. The reaction mixture was stirred for 2 h at room temperature. After the catalyst was neutralized by adding approximatively 1mL of a NH_3/EtOH (50/50) solution, then evaporated under reduced pressure to remove the solvent. The residue was then dissolved in DCM of 250 mL and washed three times with water (3×20 mL). The organic phase was dried over anhydrous $MgSO_4$, filtered and evaporated under reduced pressure to afford a white crystals (12.0 g, 92.0% yield) as compound **4**.

Synthesis of compound 5

Compound **4** (6.0 g, 34.5 mmol) was dissolved in 50 mL of DCM. Furfuryl alcohol (4.1 g, 41.4 mmol) and DMAP (0.5 g, 4.0 mmol) was added to the reaction mixture in that order. After stirring for 5 min at room temperature, DCC (8.3 g, 40.0 mmol) dissolved in 20 mL of DCM was added slowly. The mixture was stirred overnight at room temperature and urea byproduct was filtered. Then, reaction mixture was dissolved in 200 mL of DCM and washed two times with water (2×40 mL). The organic layer was then dried with anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford crude product. Then, the product was purified by silica gel column chromatography eluting with petroleum ether / ethyl acetate (v/v = 6/1) to afford a pale yellow oil (6.4 g, 73.1% yield) (**Figure S3**).



Scheme S4. Synthesis of compound **10** (**FM**).

Synthesis of compound 6

Maleimide (40.0 g, 0.4 mol) and furan (60 mL, 0.8 mol) were dissolved in 800 mL of toluene, sealed with a rubber plug and heated at 90 °C for 12 h. The product precipitated as a white solid during the process. After cooling the mixture to room temperature, the product was filtered and washed two times with cold toluene (2×10 mL) to remove the unreacted maleimide and obtained a white solid (62 g, 91.2% yield) as compound **6**.

Synthesis of compound 8

Compound **6** (6.4 g, 38.8 mmol) and K_2CO_3 (6.0 g, 43.4 mmol) were added in 80 mL of DMF, the mixture was stirred under argon flow and heated to 60 ^{o}C for 1 h. Then, 1,12-Dibromodecane (4 g, 12.3 mmol) was added and the mixture was stirred for 24 h. The reaction mixture was cooled to room temperature and then diluted with 300 mL of ethyl acetate, washed with water and brine (3×50 mL). The organic layer was dried with anhydrous $Na_2SO_{4,}$ filtered and evaporated under reduced pressure to afford crude product compound **7**. Compound **7** was dissolved in 300 mL of toluene in an open flask, the reaction mixture was stirred at 110 ^{o}C overnight. Then, toluene was evaporated under reduced pressure. The product was purified by silica gel column chromatography eluting with petroleum ether / $CHCl_3$ (v/v, 1/2) to afford a white solid (3.5 g, 79.5% yield) (**Figure S4**).

Synthesis of compound 9

Compound **5** (6.0 g, 23.6 mmol) and compound **8** (3.0 g, 8.3 mmol) were dissolved in 20 mL of $CHCl_3$. The reaction mixture was stirred at 55 ^{o}C for 7 days. Then, the product was purified by silica gel column chromatography eluting with petroleum ether / ethyl acetate (v/v, 2/1) to afford a pale yellow solid (2.2 g, 30.6% yield) as compound **9**.

Synthesis of compound 10 (FM)

Compound **9** was dissolved in a mixture of 10 mL of THF and 10 mL of 1 M HCl. Then reaction mixture was stirred for 2 h at room temperature. Then, the reaction mixture was evaporated under reduced pressure to remove THF and dissolved in 200 mL of DCM to remove water. The organic layer was then dried with anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford crude product. Hexane was added to the reaction mixture, and it was kept in deep freeze overnight to give a pale yellow solid (1.9 g, 95.0% yield) (**Figure S5**).

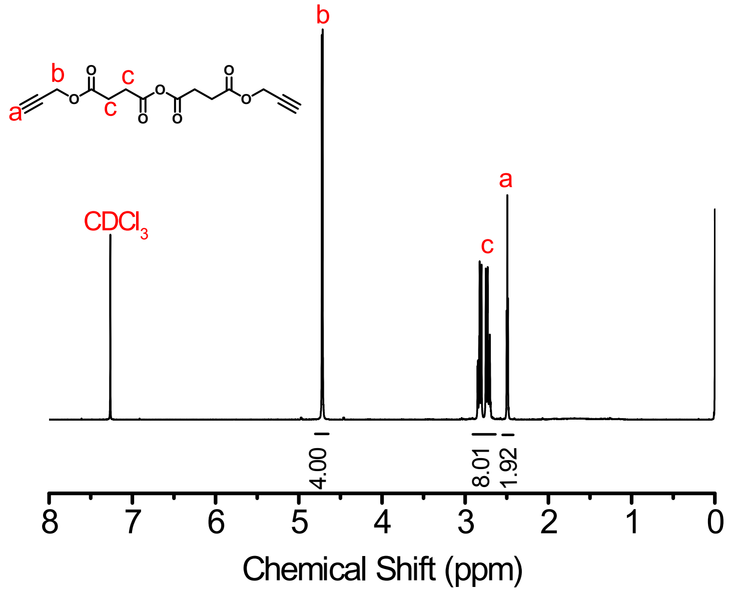


Figure S1. 300 MHz ^1H NMR spectra in $CDCl_3$ of compound **2**.

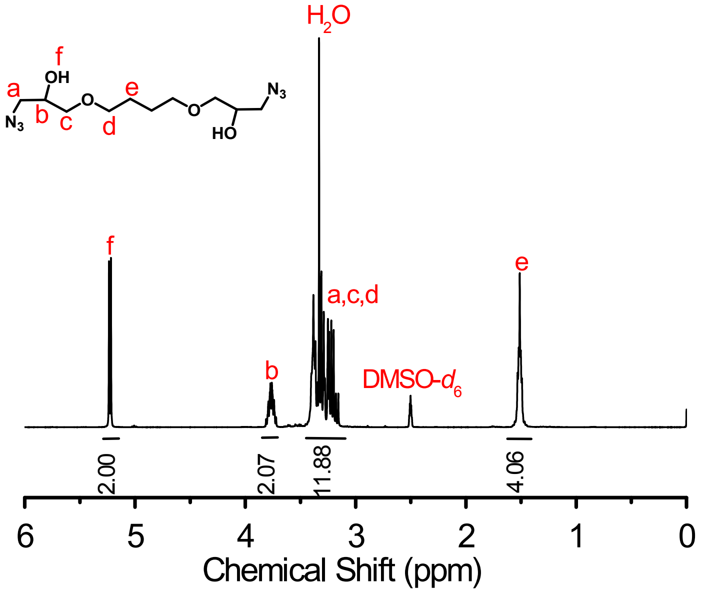


Figure S2. 300 MHz ^1H NMR spectra in DMSO-d_6 of compound **3**.

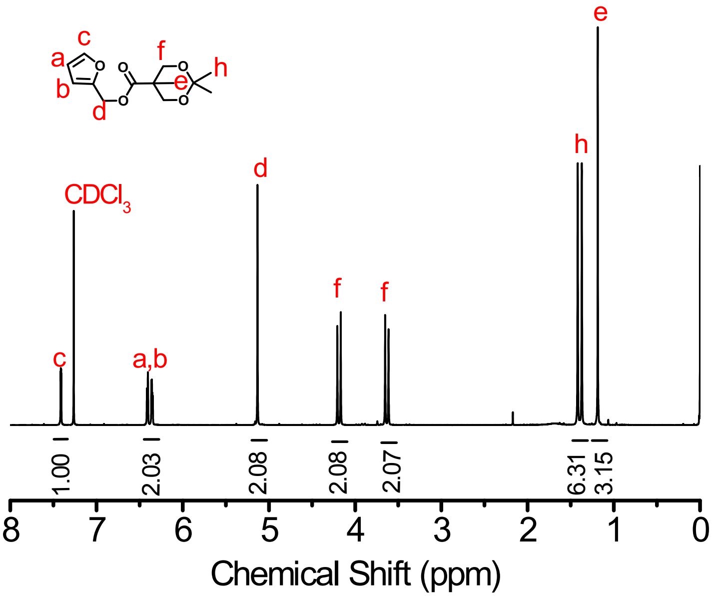


Figure S3. 300 MHz ^{1}H NMR spectra in $CDCl_3$ of compound **5.**

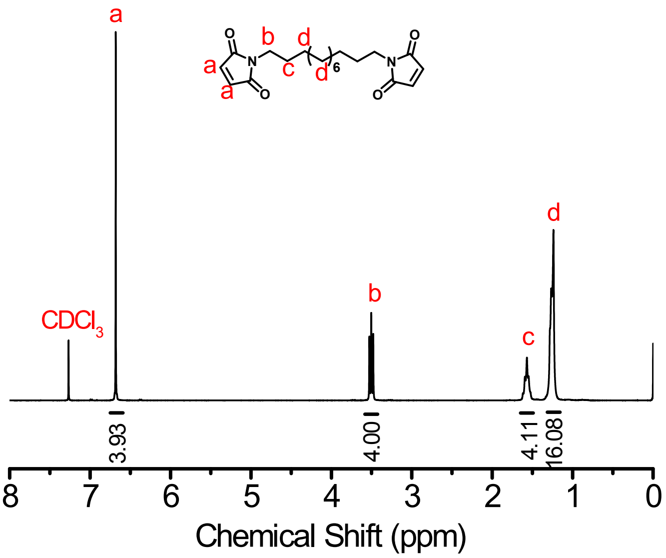


Figure S4. 300 MHz ^{1}H NMR spectra in $CDCl_3$ of compound **8**.

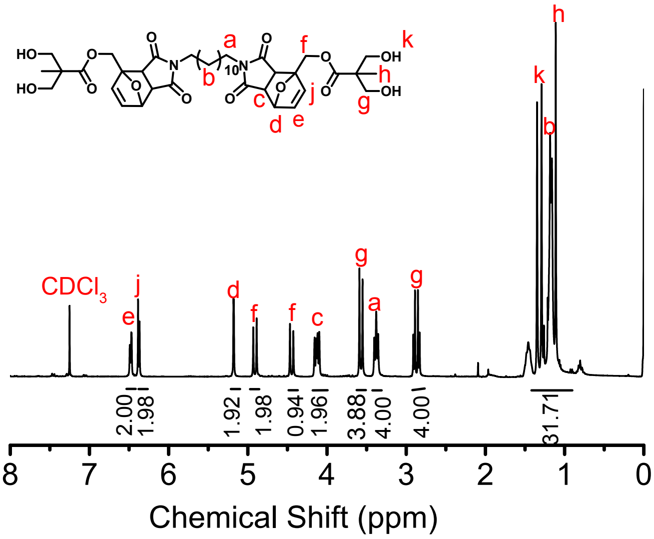
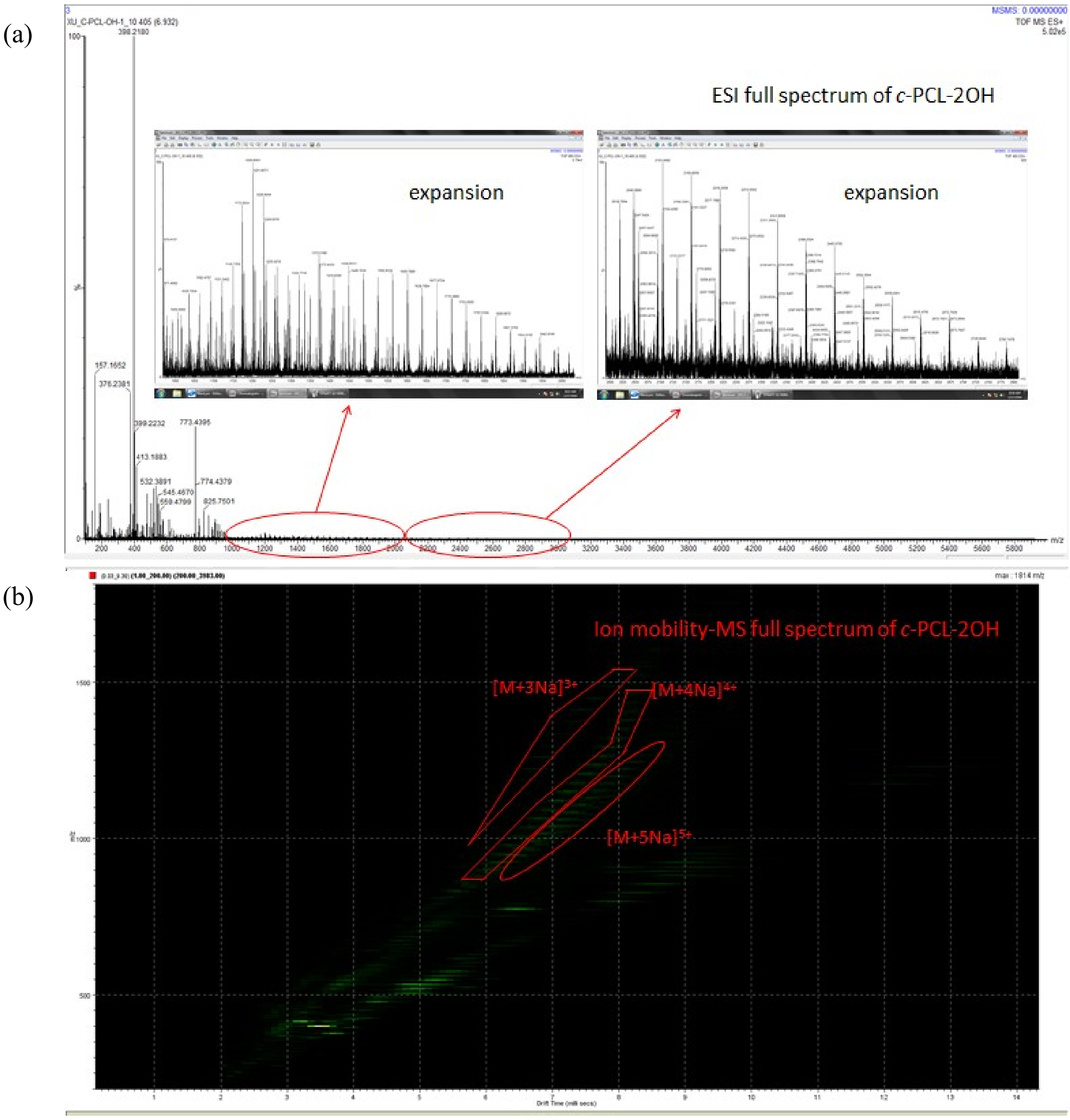


Figure S5. 300 MHz ^{1}H NMR spectra in CDCl$_3$ of compound **10** (**FM**).



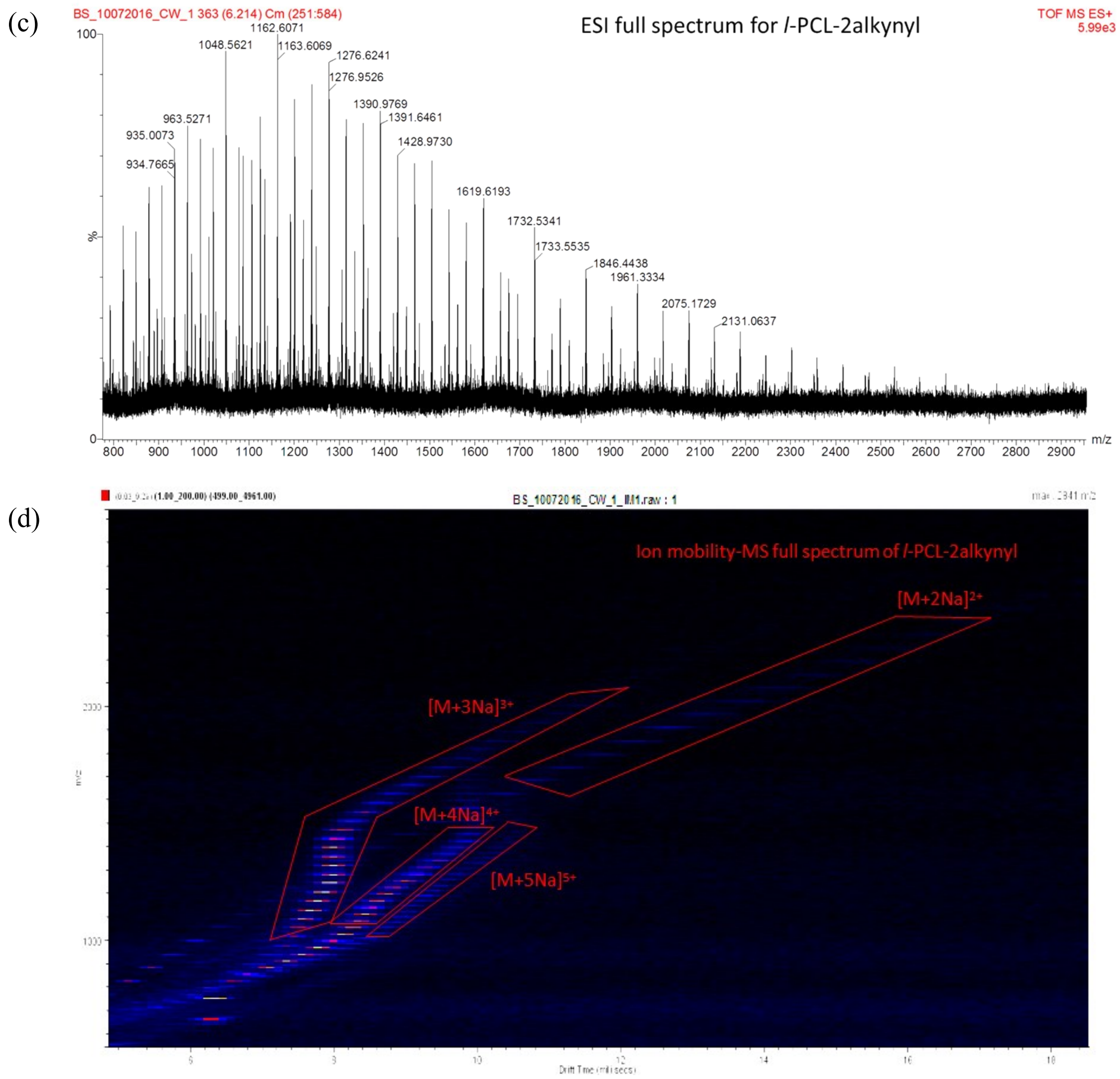


Figure S6. (a) ESI full spectrum of ***c*-PCL-2OH**, (b) Ion mobility-MS full spectrum of ***c*-PCL-2OH**, (c) ESI full spectrum of ***l*-PCL-2alkynyl**, (d) Ion mobility-MS full spectrum of ***l*-PCL-2alkynyl.** The signal with different charge states were marked on the IM-MS spectrum in red.

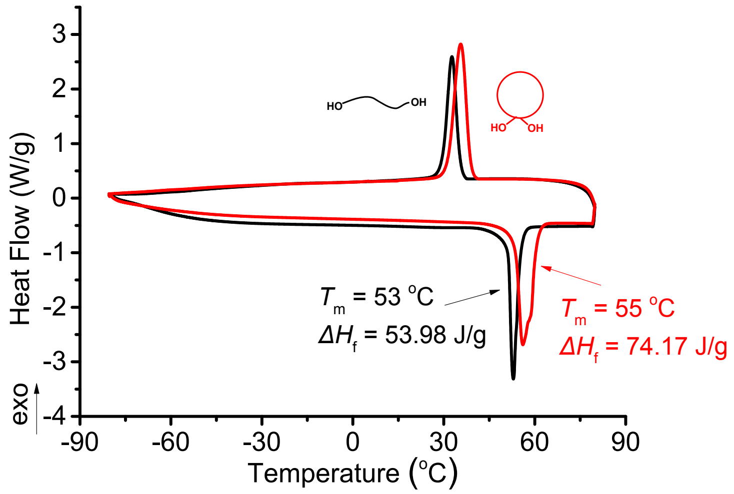


Figure S7. DSC thermograms of ***l*-PCL-2OH** and ***c*-PCL-2OH**. The heating rate was 10 °C /min from -80 °C to 80 °C under a nitrogen flow.

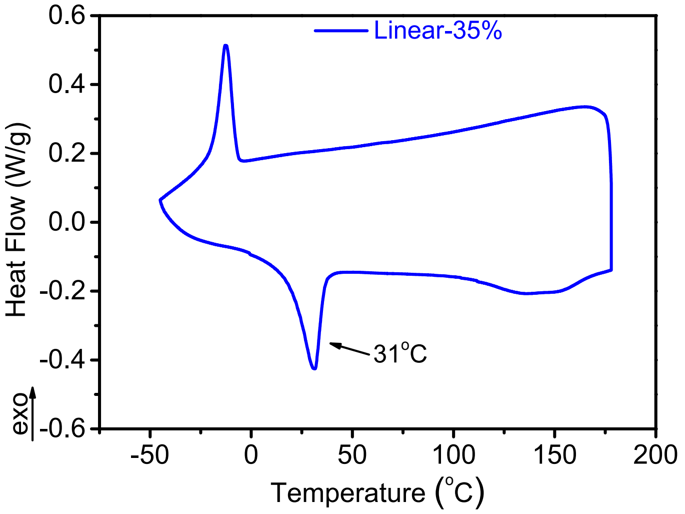


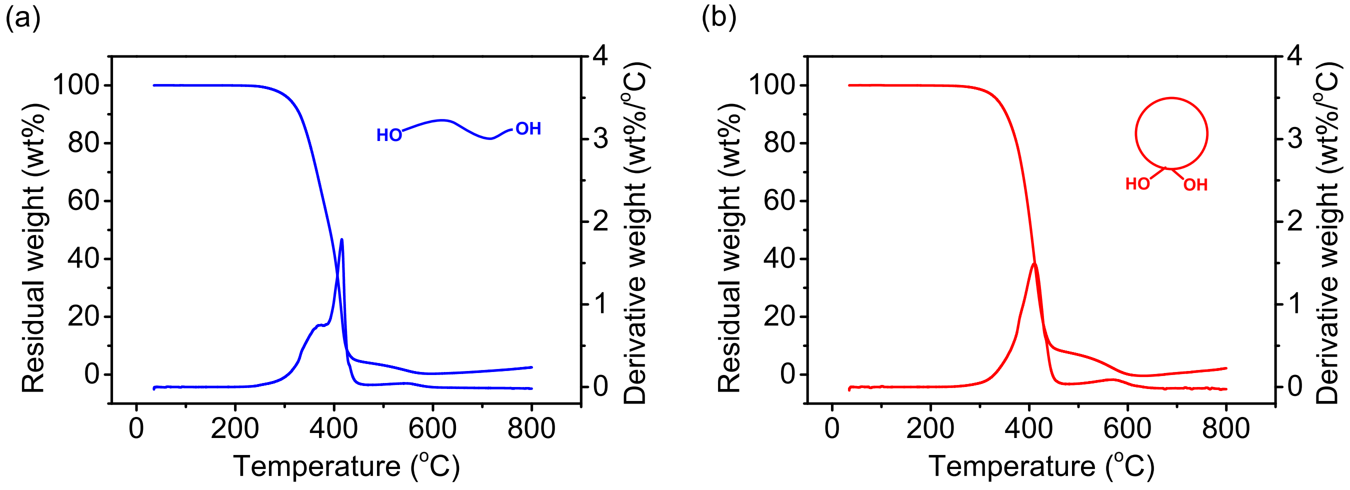
Figure S8. DSC thermograms of **Linear-35%**. The heating rate was 10 °C /min from -50 °C to 180 °C under a N_2 atmosphere.

Table S1. Analysis of TGA curves about **FM** (a), ***l*-PCL-2OH** (b), ***c*-PCL-2OH** (c) and PUs (d,e,f).

Sample	T_{di}[a] （°C）	T_{max}[b] （°C）
l-PCL-2OH	311	415
c-PCL-2OH	335	410
FM	158	205
Linear-35%	283	330
Cyclic-50%	274	405
Linear-50%	272	330
Cyclic-70%	271	420
Linear-70%	274	350

[a] T_{di}, the temperature at which the initial weight loss is 5 wt%.

[b] $T_{max,}$ the temperature of the maximum decomposition rate.



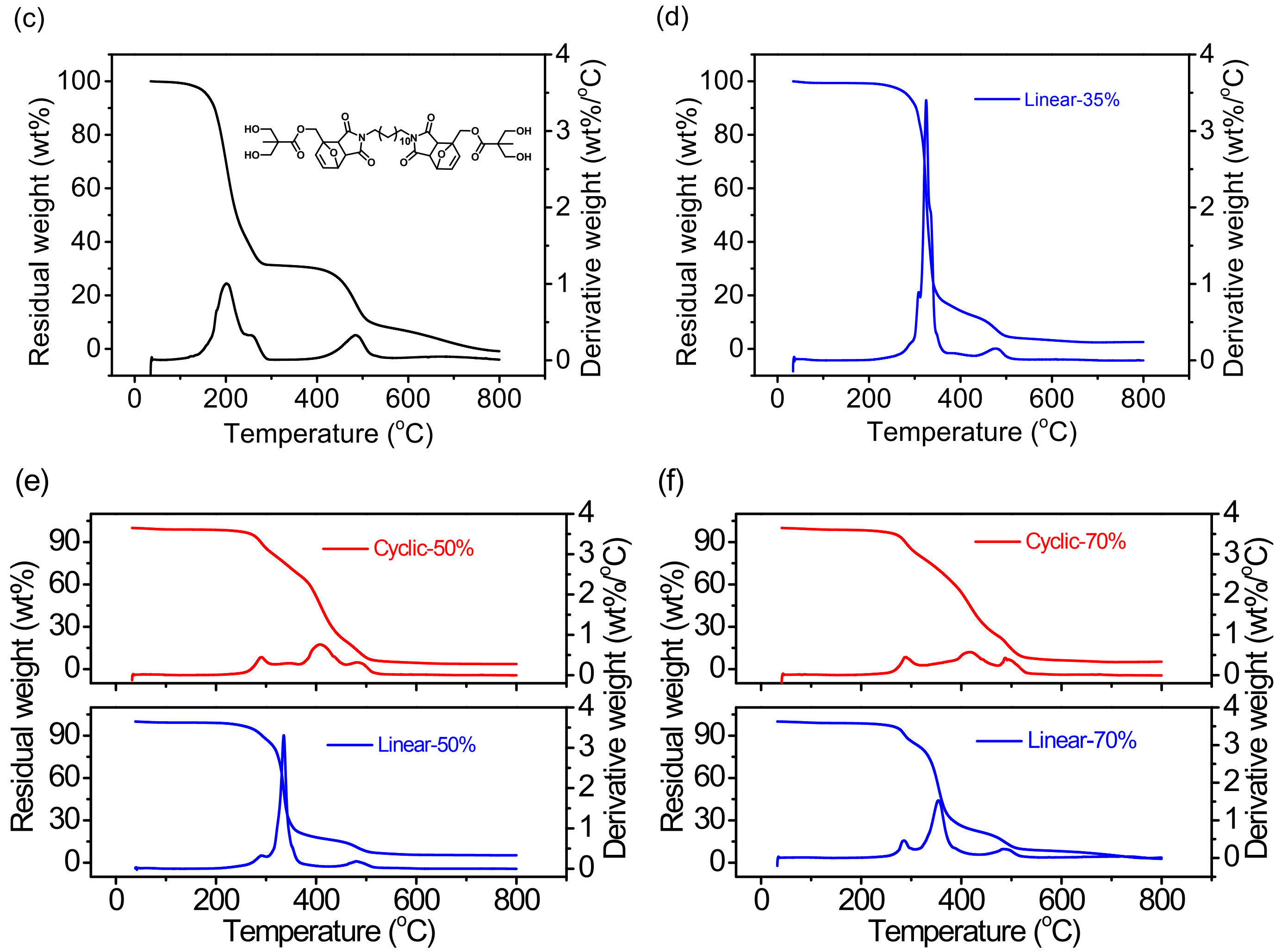


Figure S9. (a) TGA curves of ***l*-PCL-2OH**, (b) ***c*-PCL-2OH**, (c) **FM** and (d,e,f) PUs. The heating rate was 10 °C /min from room temperature to 800 °C under a N_2 atmosphere.

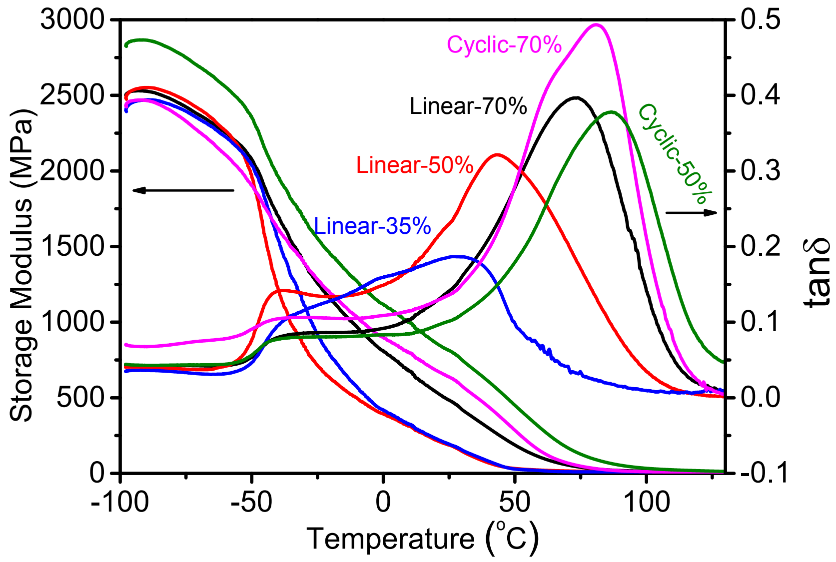


Figure S10. DMA curves of PUs. The heating rate was 3 °C/min from -100 °C to 130 °C.

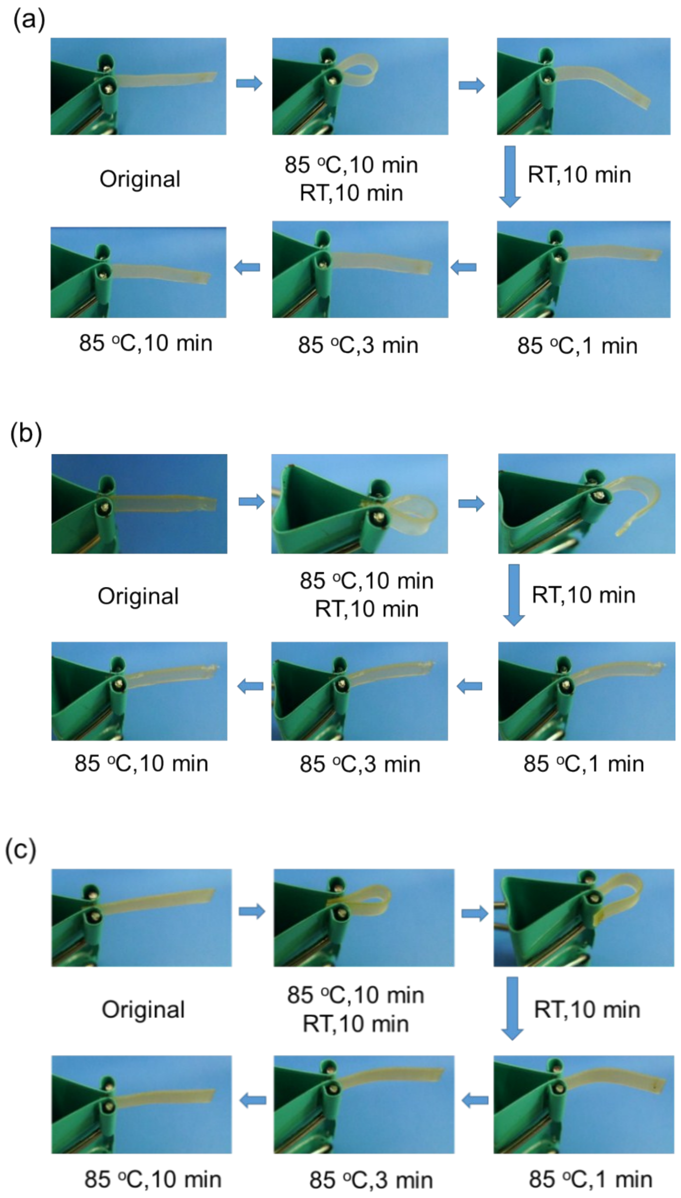


Figure S11. Pictures showing the shape memory properties of (a) **Linear-35%**, (b) **Linear-70%** and (c) **Cyclic-70%**.

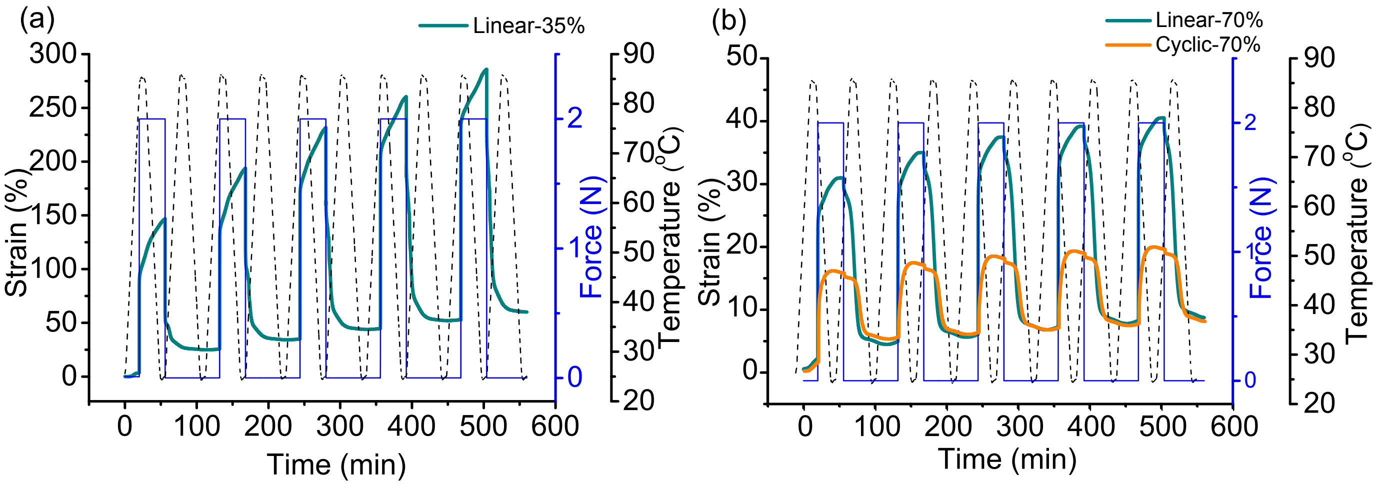


Figure S12. (a) Shape memory experiment for **Linear-35%** and (b) **Cyclic-70%** and **Linear-70%** showing five cycles. The material was heated to 85 °C, and a force of 2 N was applied to stretch the sample. The sample was then cooled to 25 °C. The force was removed, and the degree of fixing was measured. The sample was then heated to 85 °C and allowed to cool again to 25 °C, and the degree of recovery was measured for one cycle.

Table S2. Polyurethane (PU) prepared without any cyclic or linear PCL.

Sample	HDI : FM /(molar ratio)	Hard segment content (HS) /(wt)%
FM-100%	2.1 : 1	100

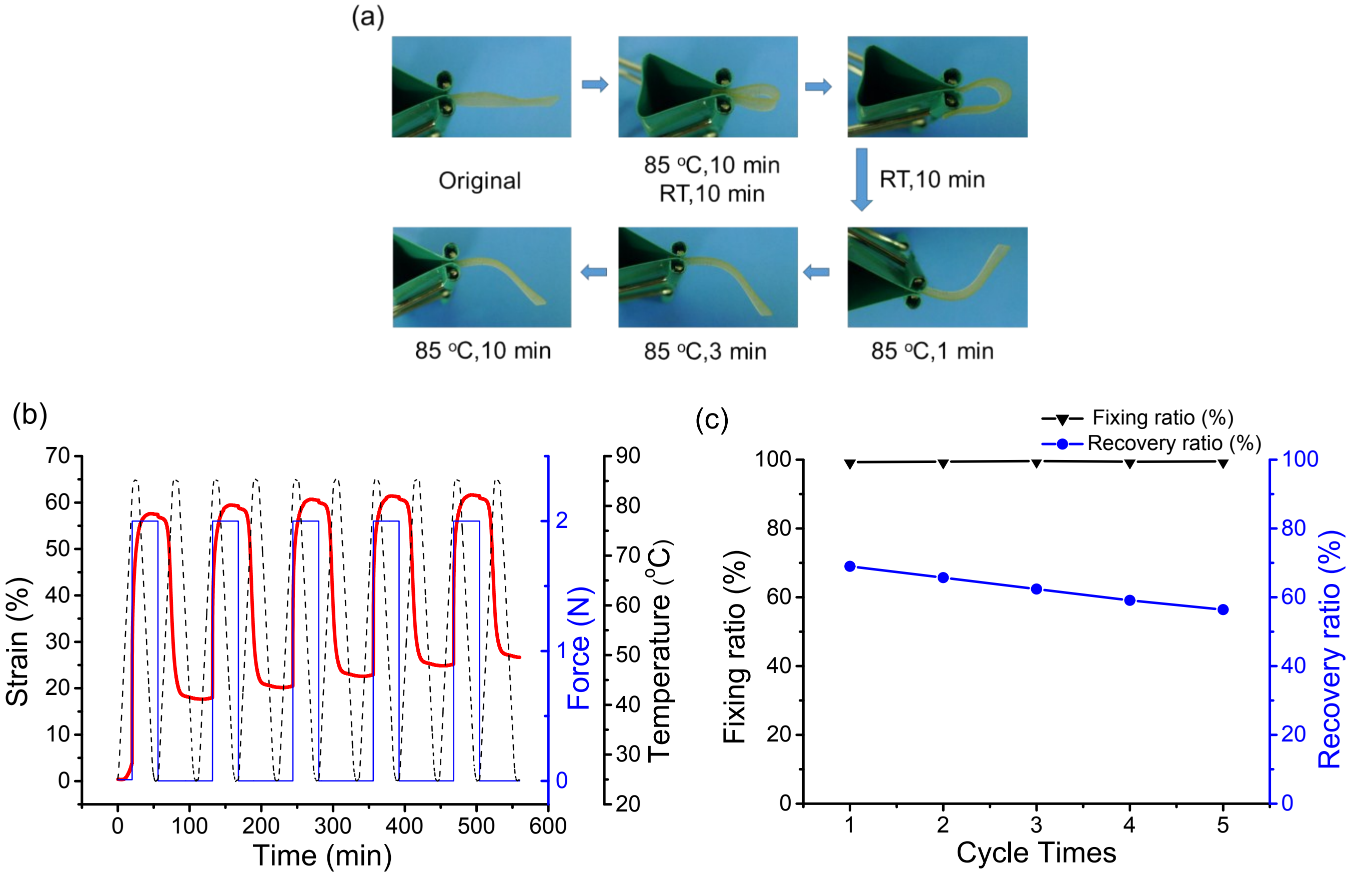


Figure S13. (a) Pictures showing the shape memory properties of **FM-100%**. (b) Shape memory experiment for **FM-100%** showing five cycles. The material was heated to 85 °C, and a force of 2 N was applied to stretch the sample. The sample was then cooled to 25 °C. The force was removed, and the degree of fixing was measured. The sample was then heated to 85 °C and allowed to cool again to 25 °C, and the degree of recovery was measured for one cycle. (c) Fixing ratio and Recovery ratio for **FM-100%**.

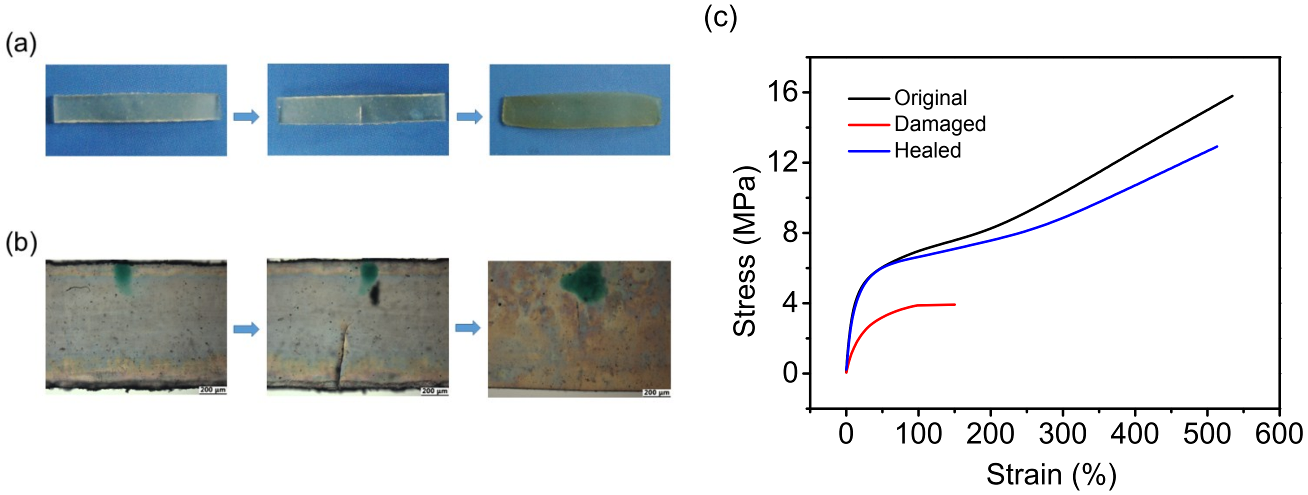


Figure S14. The thermally active self-healing process of a crack in **Linear-35%** and mechanical properties. (a) Digital photos of **Linear-35%**. (b) Optical micrographs of **Linear-35%**. (c) Stress-strain curve for representative original (black curve), damaged (red curve), and healed (blue curve) samples of **Linear-35%**. Tensile tests were executed by DMA in the Controlled Force Stress-Strain mode and conducted at a rate of 1 N/min to 18 N.

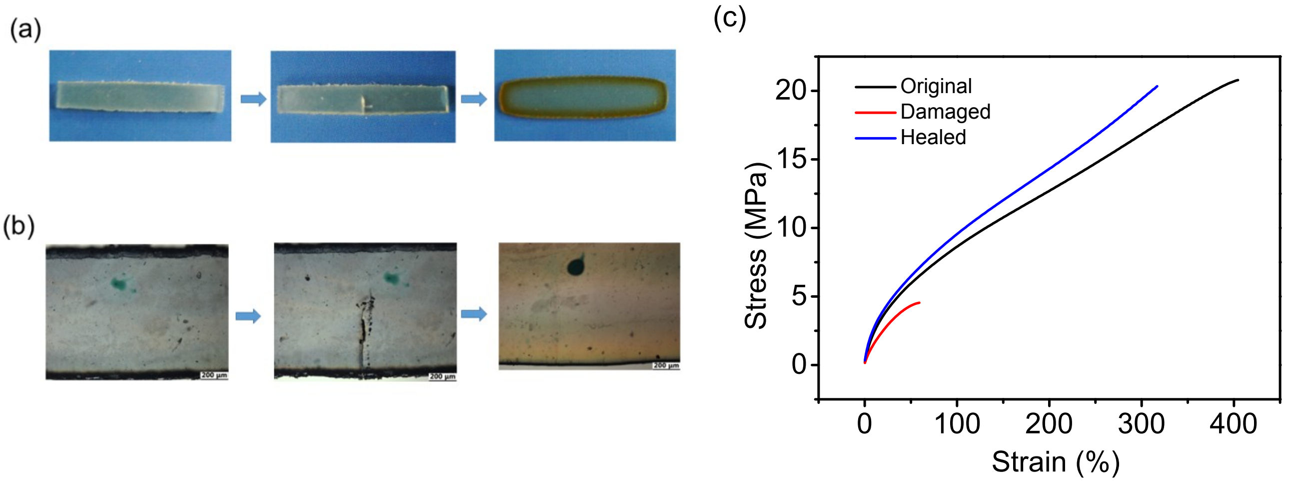


Figure S15. The thermally active self-healing process of a crack in **Linear-50%** and mechanical properties. (a) Digital photos of **Linear-50%**. (b) Optical micrographs of **Linear-50%**. (c) Stress-strain curve for representative original (black curve), damaged (red curve), and healed (blue curve) samples of **Linear-50%**. Tensile tests were executed by DMA in the Controlled Force Stress-Strain mode and conducted at a rate of 1 N/min to 18 N.

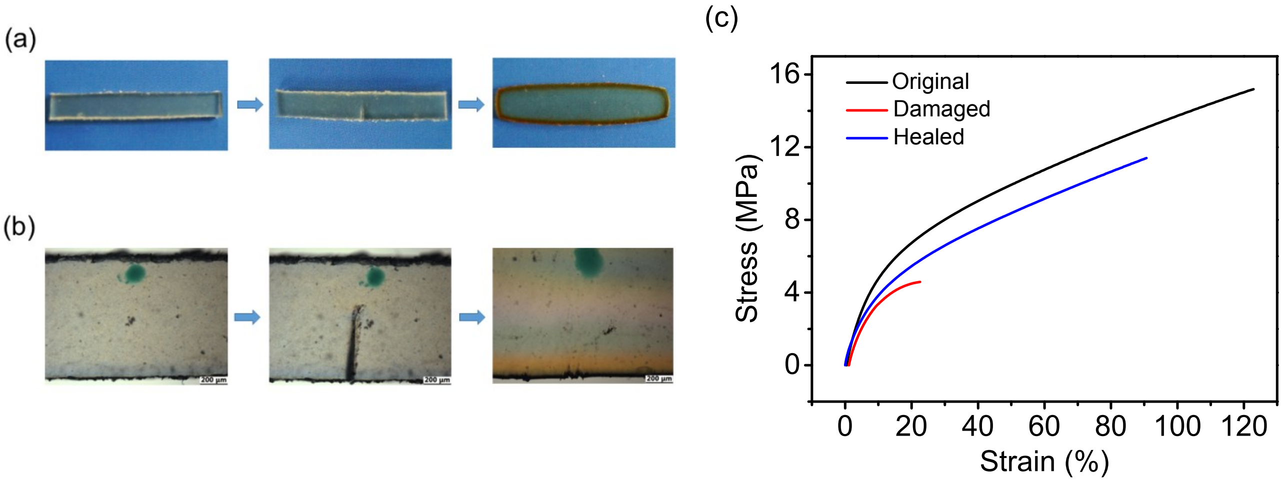


Figure S16. The thermally active self-healing process of a crack in **Linear-70%** and mechanical properties. (a) Digital photos of **Linear-70%**. (b) Optical micrographs of **Linear-70%**. (c) Stress-strain curve for representative original (black curve), damaged (red curve), and healed (blue curve) samples of **Linear-70%**. Tensile tests were executed by DMA in the Controlled Force Stress-Strain mode and conducted at a rate of 1 N/min to 18 N.

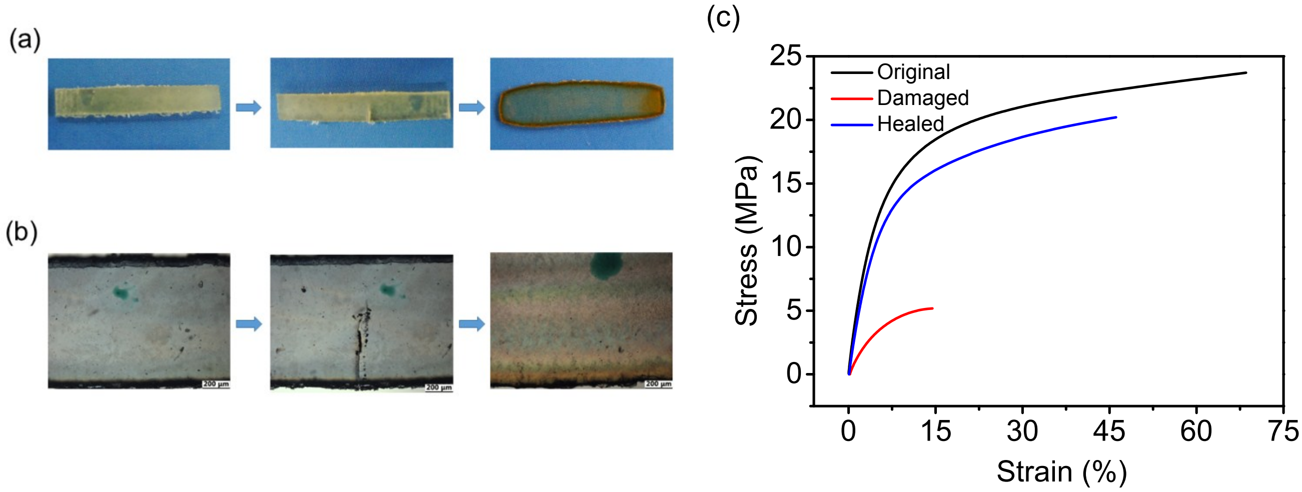
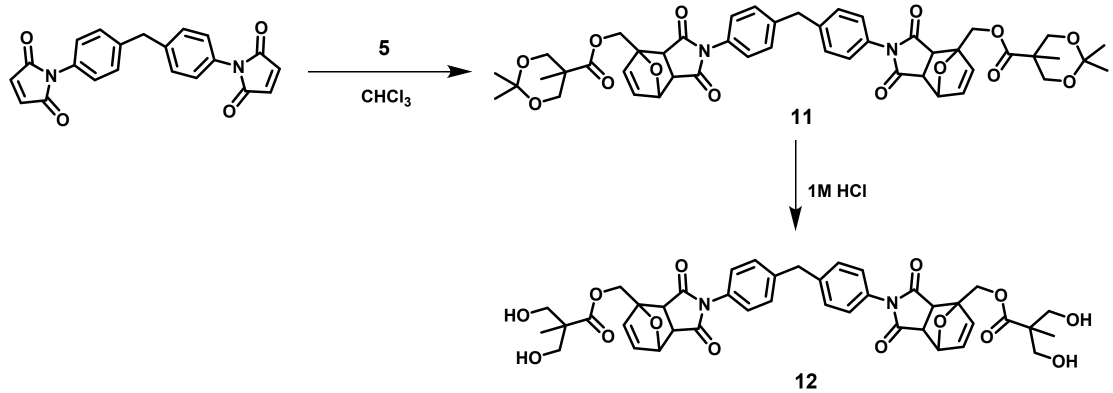


Figure S17. The thermally active self-healing process of a crack in **Cyclic-70%** and mechanical properties. (a) Digital photos of **Cyclic-70%**. (b) Optical micrographs of **Cyclic-70%**. (c) Stress-strain curve for representative original (black curve), damaged (red curve), and healed (blue curve) samples of **Cyclic-70%**. Tensile tests were executed by DMA in the Controlled Force Stress-Strain mode and conducted at a rate of 1 N/min to 18 N.

Additional information



Scheme S5. Synthesis of compound **12**.

Synthesis of compound 11

Compound **5** (3.0 g, 11.8 mmol) and 1,1'-(Methylenedi-4,1-phenylene)bismaleimide (1.4 g, 3.9 mmol) were dissolved in 4 mL of $CHCl_3$. The reaction mixture was stirred at 50 ^{o}C for 7 days. Then, the product was purified by silica gel column chromatography eluting with petroleum ether / ethyl acetate (v/v, 2/1) to afford a pale yellow solid (1.1 g, 32.4% yield) as compound **11**.

Synthesis of compound 12

Compound **11** was dissolved in a mixture of 10 mL of THF and 10 mL of 1 M HCl. Then reaction mixture was stirred for 2 h at room temperature. Then, the reaction mixture was evaporated under reduced pressure to remove THF and dissolved in 200 mL of DCM to remove water. The organic layer was then dried with anhydrous Na_2SO_4, filtered and evaporated under reduced pressure to afford crude product. Hexane was added to the reaction mixture, and it was kept in deep freeze overnight to give pale yellow solid (1.0 g, 98.0% yield) (**Figure S18**).

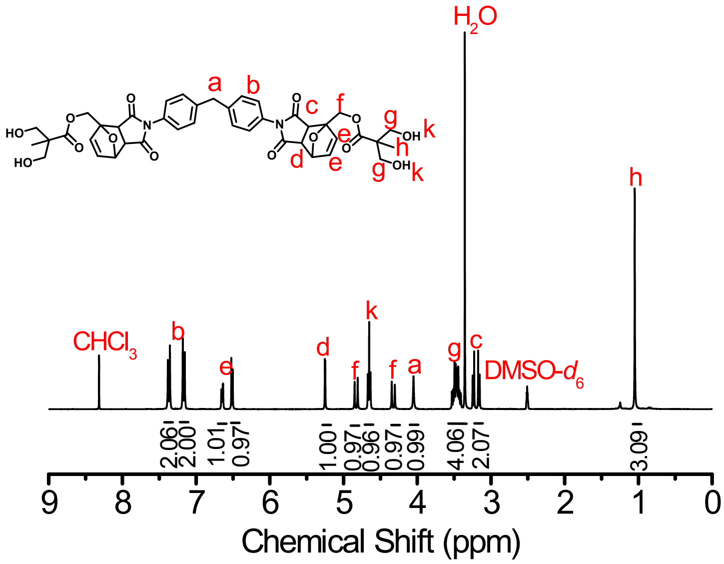


Figure S18. 300 MHz ^{1}H NMR spectra in DMSO-d_6 of compound **12**.

Compound **12** was used to prepare cyclic and linear polyurethanes as crosslinking agent, and their hard segment content were 50%. The PUs based on ***l*-PCL-2OH** had a certain degree of flexibility and could be to a film in good condition. On the contrary, **Figure S19** shows the PU based on ***c*-PCL-2OH** and it is too fragile to be a complete piece. The reason for this phenomenon is that compound **12** is a compound with two benzene ring and would likely be too rigid. Finally, we use FM instead of compound **12** to obtain a series of polyurethanes.

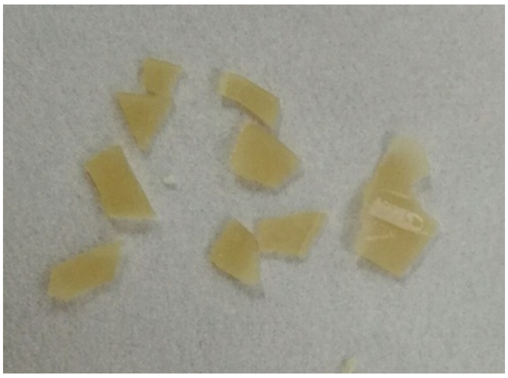


Figure S19. Cyclic-50% based on compound **12**.