

Supporting Information

Constructing Shape Memory Network with Controllable Stability and Dynamic feature through Cation- π Interactions

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Experimental Section

Materials. 8-hydroxypyrene-1,3,6-trisulfonicacidsodiumsalt (Pyranine, 98%), Methyl bromoacetate (98%), Dibutyltin dilaurate (DBTDL, 98%) and Hexamethylene Diisocyanate (HDI, 98%) were purchased from Alfa-Aesar. 2-Amino-2-methyl-1,3-propanediol was provided by TCI. γ -Oxo-1-pyrenebutyric acid (Py-COOH, 98%) was purchased from Aladdin. 2-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 98%), Hydroxybenzotriazole (HOBt, 99%) and N, N-Diisopropylethylamine (DIEA, 98%) were purchased from Innochem. Isopropyl alcohol and Methanol were supplied by Kelong Reagent Corp. All materials and reagents described herein above were used without further purification.

Synthesis of PCL-diol. PCL-diol was synthesized by typical ring open polymerization

(ROP) of ϵ -CL using 1,4-BD as initiator and $\text{Sn}(\text{Oct})_2$ (5 wt% in toluene). To a round flask with magnetic stirrer and the equipment was evacuated and flushed with pure argon three times to exhaust residual water. Then, the purified ϵ -CL, 1,4-BD and $\text{Sn}(\text{Oct})_2$ was added into the flask under argon atmosphere. The mixture was heated to 120 °C under stirring for 12 h. After then, the obtained product was dissolved in chloroform, precipitated in methanol, and dried under vacuum. The molecular weight can be controlled by adjusting the feed ratio of ϵ -CL and 1,4-BD. The molecular weights (M_n) of the PCL prepolymer can be calculated as follows:

$$M_n = \frac{I_h}{I_i} \times 2 \times 114 + 90 \quad (1)$$

Here, I_h and I_i are represents the areas of peaks h and i, respectively. 114 is the molar mass of a ϵ -CL repeat unit, and 90 represents the molar mass of the BD units.

Synthesis of Py-diol. The synthetic route of Py-diol was shown in Scheme S3, the specific synthesis process is as follows: Firstly, Py-COOH (10.00 g, 33 mmol), EDCI (7.75 g, 39.7 mmol), and HOBT (5.36 g, 39.7 mmol) were dissolved and mixed with anhydrous DMF (200 mL) in a round-bottom flask with an ice bath and stirred for 1 h. Then, the ice bath was removed and AMPD (49.7 mmol, 5.21 g) and K_2CO_3 (49.7 mmol, 6.85 g) were added to the reaction solution, respectively. After stirring for 24 h at room temperature, the reaction solution was precipitation in deionized water and filtered. Finally, the collected solids were dried for 24 h in a vacuum of 60 °C, the pure product HO-Py-OH was obtained as a yellow solid.

Synthesis of PCL_{3k}-Py. The synthetic route of PCL_{3k}-Py was shown in Scheme S4, and the synthesis steps are almost the same as those of PCL-Pyr. Firstly, equal molar

amounts of PCL-diols and Py-diol were added into a flask and dried at 80 °C under vacuum for 4 h. Then, dried DMF was injected in to dissolve reactants under argon atmosphere. A predetermined amount of HDI and DBTDL were injected into the reactor and stirred at 80 °C for 4 h. The reaction liquid was then precipitated in a large amount of methanol and the solid was filtered and washed with methanol several times. The residue was dried under vacuum and then dissolved in DMF. The films were prepared by casting solution in a tetrafluoroethylene mold. The solvent was evaporated at 75 °C for 10 h in the reaction kettle, then dried in vacuum at 40 °C for 24 h.

Synthesis of H-PCL_{6.5k}. The synthetic route of H-PCL_{6.5k} was shown in Scheme S5, and the synthesis steps are almost the same as those of PCL-Pyr. Firstly, PCL-diol was added into a flask and dried at 80 °C under vacuum for 4 h. Then, dried DMF was injected in to dissolve reactants under argon atmosphere. Equal molar amount of HDI and appropriate amount DBTDL were injected into the reactor and stirred at 80 °C for 4 h. The reaction liquid was then precipitated in a large amount of methanol and the solid was filtered and washed with methanol several times. The residue was dried under vacuum and then dissolved in DMF. The films were prepared by casting solution in a tetrafluoroethylene mold. The solvent was evaporated at 75 °C for 10 h in the reaction kettle, then dried in vacuum at 40 °C for 24 h.

Characterization methods

¹H Nuclear Magnetic Resonance (¹H-NMR). ¹H-NMR was performed on Bruker Corporation AC-P 400 MHz NMR spectrometer at room temperature in CDCl₃ or

DMSO-*d*₆. The chemical shifts are represented in δ (ppm) with tetramethylsilane (TMS) as an internal reference.

Gel Permeation Chromatography (GPC). GPC analysis of copolymers was performed on Waters 1515 GPC apparatus equipped with a refractive index detector, using Polymethylmethacrylate (PMMA) standards to obtain a calibration curve. The elution solvent used was N, N-dimethylformamide (DMF) at a flow rate of 0.4 mL/min at 40 °C.

Fluorescence Testing. Fluorescence emission spectra of samples at 345-800 nm were measured by F-7000 FL spectrophotometer. The excitation wavelength was 345 nm, the scanning speed was 1200 nm/min, and the incident and exit slits were both 5 nm.

Reaction Efficiency of Pyr. Firstly, the copolymer was purified by dialysis. Then, to determine the actual content of Pyr-diol in product copolymers, we use the absorption peaks of 393, 374 and 365 nm in the spectra of Pyr-diol solution to make the C_{Pyr} -Absorbance standard curve and fit the linear regression equation. The UV-Vis spectra of the samples were recorded on a Varian Cary 50 spectrophotometer using DMF as solvent at room temperature with the scanning speed of 1200 nm/min. And the absorbance is calculated as concentration of Pyr-diol from working curve. Finally, the reaction efficiency can be calculated by the following equation:

$$RE(\%) = \frac{m_{\text{Pyr, UV}}}{m_{\text{Pyr}}} \times 100\% \quad (2)$$

Here, $m_{\text{Pyr,UV}}$ and m_{Pyr} are represents the actual weight and feeding weight of Pyr-diol in copolymers, respectively.

Swelling Test. The samples were cut into small slices and swelled in CH_2Cl_2 for 24 h,

and then dried to constant weight in vacuum oven. The mass of the original sample (m_0), the swelled extracted sample (m_1) and the dried extracted sample (m_2) were recorded. The gel content (G (%)) and the degree of swelling (S (%)) were calculated by the following equations:

$$G(\%) = \frac{m_2}{m_0} \times 100\% \quad (3)$$

$$S(\%) = \frac{m_1}{m_2} \times 100\% \quad (4)$$

Differential Scanning Calorimetry (DSC). DSC measurements were carried out on TA Instruments DSC-Q200 calorimeter. Each sample was heated to 130 °C to eliminate the thermal history and cooled down at 10 °C/min to -60 °C. And then, the samples were heated to 130 °C at the same rate.

Stress-Strain Experiment. The stress-strain experiment was performed on Instron Model 3366 universal testing machine with the strain rate of 100 mm/min at the room temperature. The tensile strength (σ_m), and elongation at break (ϵ_b) were obtained with at least three identical specimens and reported as the averaged value.

Dynamic Mechanical Analysis (DMA). The thermomechanical properties of samples were measured on TA Instruments DMA Q200 in the “Multi-Frequency Strain” mode with a heating rate of 3 °C/min from -70 to 90 °C and a frequency of 1 Hz. The storage modulus (E') were recorded. And stress relaxation experiments were performed using the “Stress Relaxation” mode. The samples were stretched 20% at different temperature and kept at this position for 30 min, while the stress was measured.

Shape Memory Effect. 1W and 2W-SME of samples were conducted by cyclic

thermal mechanical tested with a TA Instruments DMA Q800 in a force-controlled mode.

For 1W-SME, the procedures were carried out as follows. Firstly, the temperature of sample is equilibrium at 70 °C and isothermal for 10 min. At this time, the strain of the sample is denoted as the initial strain (ε_0). Then, the sample was deformed under external stress, followed by cooling it to 0 °C and keeping for 5 min to get a temporary strain (ε_m). Next, removing the external stress, and the fixed strain ($\varepsilon_{f(N)}$) was obtained. Finally, the temperature was raised to 70 °C and isothermal for 25 min, and then the sample recovered to its original strain with a residual strain ($\varepsilon_{p(N)}$). The shape memory cycles were conducted for four or five cycles and value of 2-5 were taken. The average shape fixity ratio (R_f) and shape recovery ratio (R_r) were calculated by the following equations:

$$R_f = \frac{\varepsilon_{f(N)} - \varepsilon_{p(N-1)}}{\varepsilon_{d(N)} - \varepsilon_{p(N-1)}} \quad (5)$$

$$R_r = \frac{\varepsilon_{f(N)} - \varepsilon_{p(N)}}{\varepsilon_{f(N)} - \varepsilon_{p(N-1)}} \quad (6)$$

For 2W-SME, the procedures were performed as follows. Firstly, the sample was heated to 70 °C and isothermal for 10 min. Applying a constant stress and keeping the station for 30 min to get the initial strain (ε_{low}). Then, the temperature was cooled to -20 °C and isothermal for 10 min to make the PCL segment fully crystallization. At this point, the temporary strain (ε_{high}) was obtained. Finally, reheating to 70 °C and isothermal for 10 min, the sample recovered to its original strain. The shape memory cycles were conducted for four or five cycles and value of last three cycles were taken.

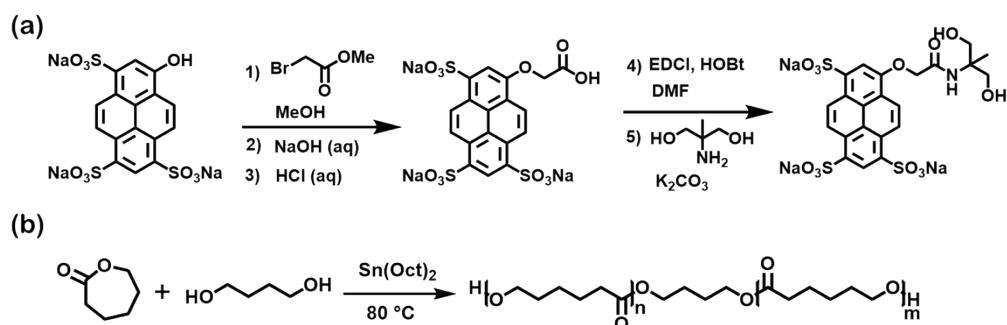
The average actuation magnitude ($R_{act(\sigma)}$) and recovery magnitude ($R_{rec(\sigma)}$) were calculated by the following equations:

$$R_{act(\delta)} = \varepsilon_{high} - \varepsilon_{low} \quad (7)$$

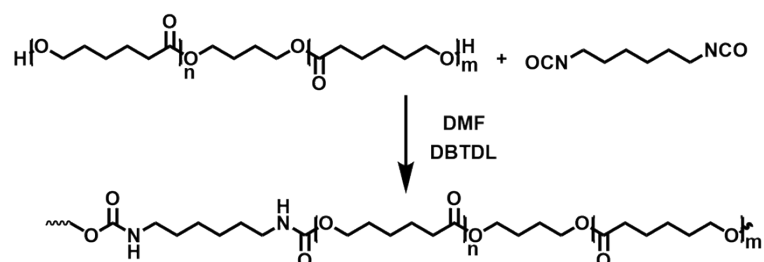
$$R_{rec(\delta)} = \frac{\varepsilon_{high(N)} - \varepsilon_{low(N+1)}}{\varepsilon_{high(N)} - \varepsilon_{low(N)}} \quad (8)$$

Evaluation of the thermal-responsive 2W SME. The investigation of thermal-responsive 2W SME: firstly, a straight sample with 500 g weight was heated above T_c which result in the sample elongated. Then, after the sample with weight was transferred to the refrigerator for cooling to $-10\text{ }^\circ\text{C}$, the sample elongation again because of crystallization induced elongation. Finally, reheating the sample with a blow drier, we could find that the sample contract with the heating on and the sample elongate with the heating off.

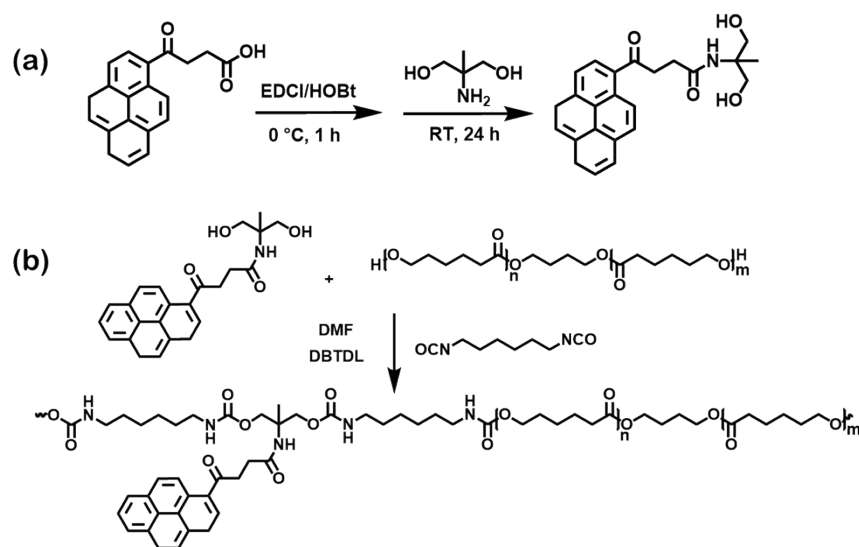
Supporting Schemes and Figures



Scheme S1 (a) Synthetic route of Pyr-diol; (b) Synthetic route of PCL prepolymer.



Scheme S2 Synthetic route of H-PCL_{6.5k}.



Scheme S3 (a) Synthetic route of Py-diol; (b) Synthetic route of PCL_{3k}-Py.

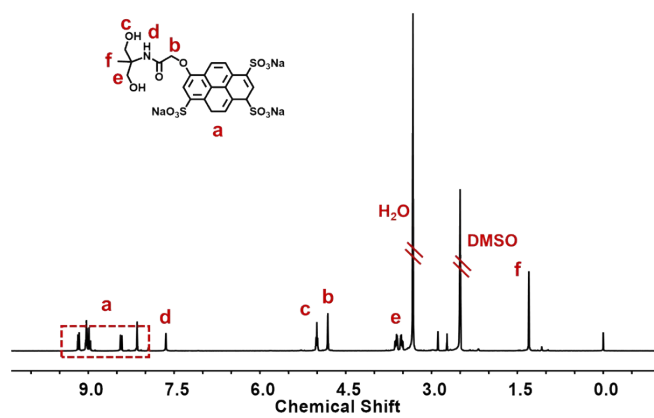


Figure S1 ¹H-NMR spectrum of Py-diol in DMSO-d₆.

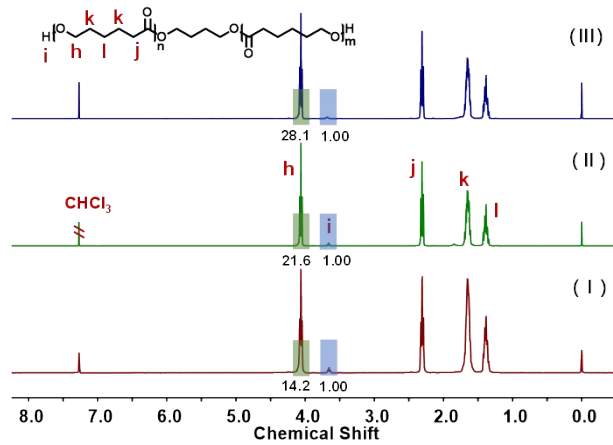


Figure S2 $^1\text{H-NMR}$ spectra of PCL-diol with different molecular weights of 3 k (I), 5 k (II) and 6.5 k (III) in CDCl_3 .

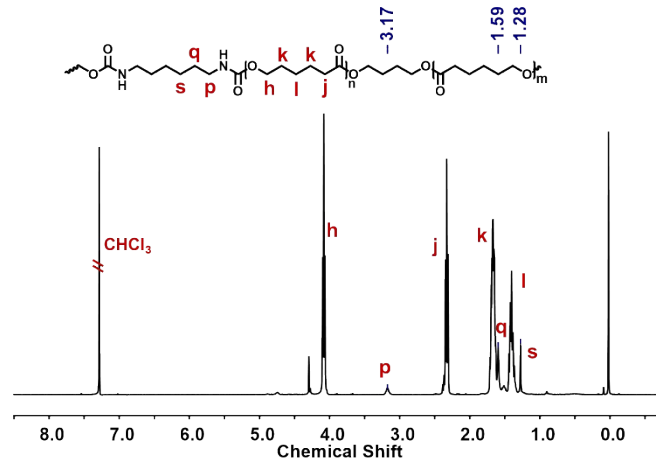


Figure S3 $^1\text{H-NMR}$ spectrum of $\text{H-PCL}_{6.5\text{k}}$ in CDCl_3 .

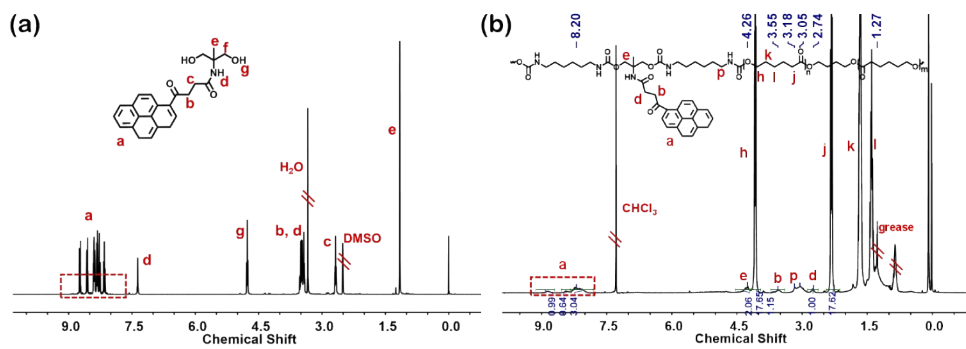


Figure S4 $^1\text{H-NMR}$ spectrum of Py-diol in DMSO-d_6 (a) and $\text{PCL}_{3\text{k}}\text{-Py}$ in CDCl_3 (b).

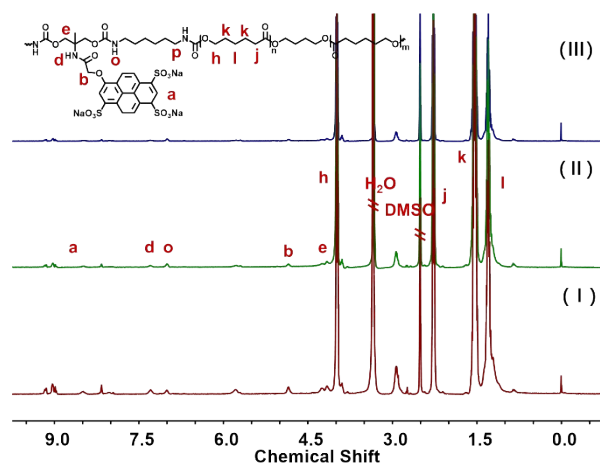


Figure S5 $^1\text{H-NMR}$ spectra of PCL_{3k}-Pyr (I), PCL_{5k}-Pyr (II) and PCL_{6.5k}-Pyr (III) in DMSO-d₆.

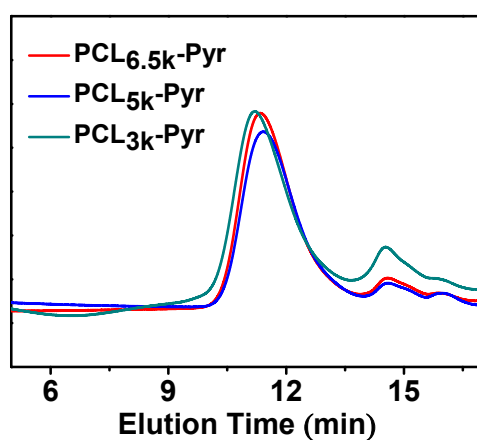


Figure S6 GPC traces of PCL-Pyr copolymers with DMF as eluent .

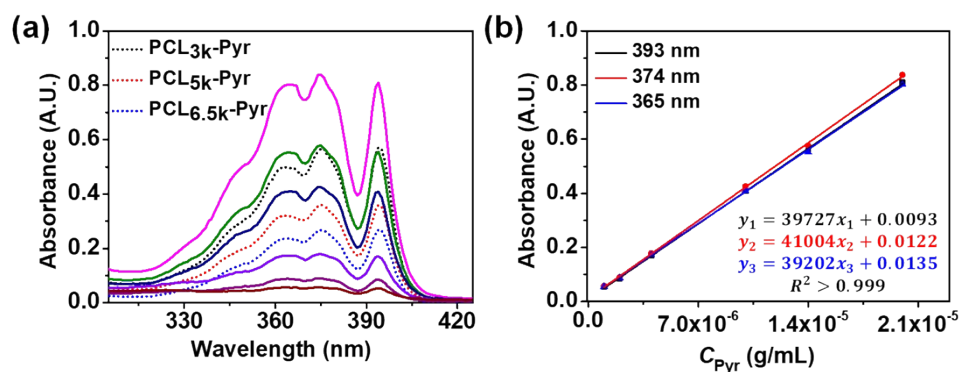


Figure S7 UV-Vis spectra of PCL-Pyr copolymers solutions ($1 \cdot 10^{-4}$ g/mL) and Pyr-diol with different concentrations (From top to bottom: $2 \cdot 10^{-5}$ g/mL, $1.4 \cdot 10^{-5}$ g/mL, $1 \cdot 10^{-5}$ g/mL, $4 \cdot 10^{-6}$ g/mL, $2 \cdot 10^{-6}$ g/mL and $1 \cdot 10^{-6}$ g/mL) (a). The C_{Pyr} -Abs curves and linear regression equation of Pyr-diol (b).

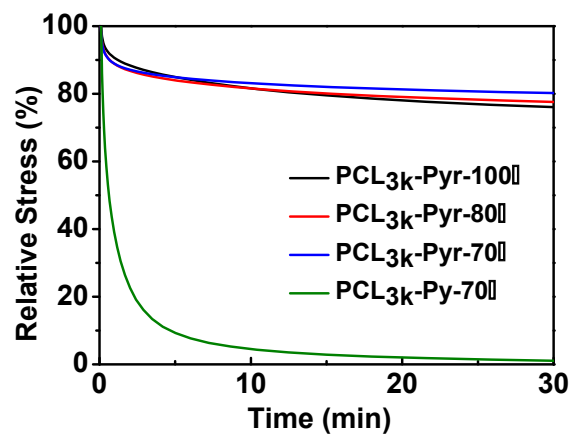


Figure S8 Stress relaxation curves of PCL_{3k}-Pyr (a) and PCL_{3k}-Py (b) at different temperature.

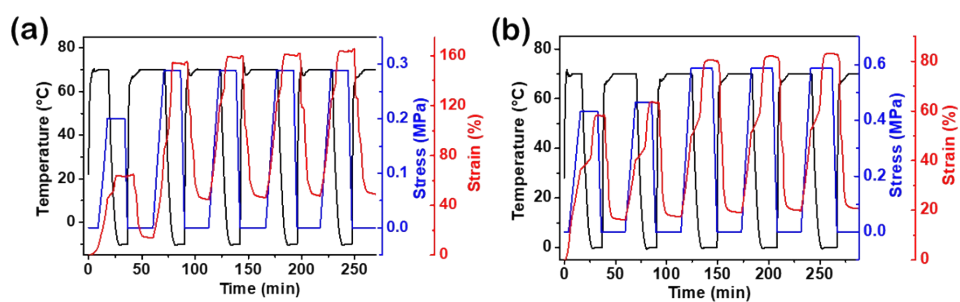


Figure S9 The cyclic tensile shape memory tests of PCL_{3k}-Pyr (a) and PCL_{6.5k}-Pyr (b).

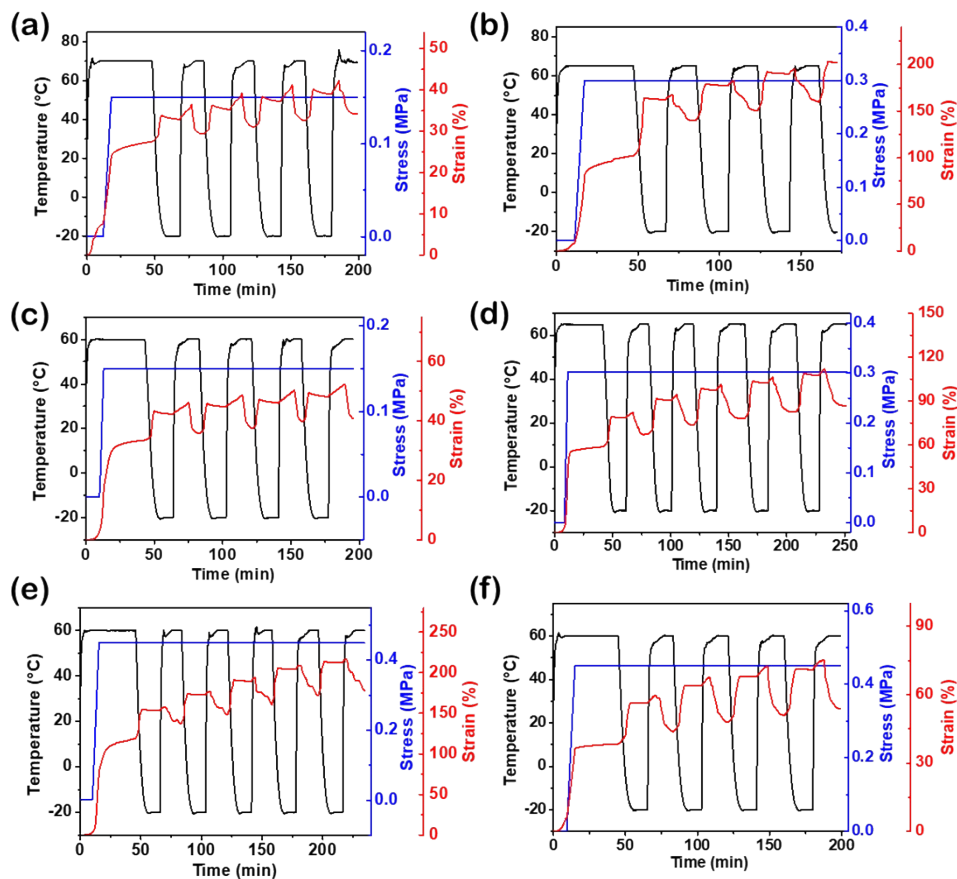


Figure S10 The two-way shape memory properties of PCL-Pyr networks with different applied stress: PCL_{6.5k}-Pyr under 0.15 MPa (a) and 0.30 MPa (b); PCL_{5k}-Pyr under 0.15MPa (c), 0.30MPa (d) and 0.45 MPa (e); PCL_{3k}-Pyr under 0.45 MPa (f).

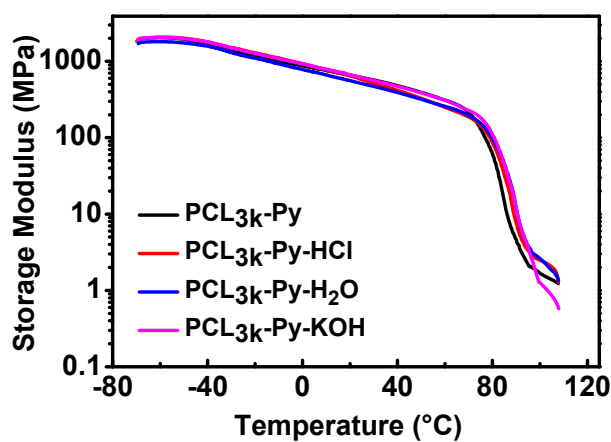


Figure S11 Storage modulus plots of PCL_{3k}-Py and the sample soaked in 0.1M HCl, Up water and 0.1 M KOH for 1 hour.

Supporting Tables:

Table S1 The Molecular Weights of the PCL-Based Samples

Sample	$M_{n, \text{NMR}}^{\text{a}}$ (10^4 g/mol)	$M_{n, \text{GPC}}^{\text{b}}$ (10^4 g/mol)	PDI ^b
PCL _{3k} -diol	0.3	0.4	1.6
PCL _{5k} -diol	0.5	0.6	1.4
PCL _{6.5k} -diol	0.65	0.6	1.4
H-PCL _{6.5k}	-	6.2	1.6
PCL _{6.5k} -Pyr	-	3.2	2.7
PCL _{5k} -Pyr	-	3.5	2.3
PCL _{3k} -Pyr	-	3.8	2.3
PCL _{3k} -Py	-	4.9	1.9

^a Calculated from ¹H NMR spectra.

^b Determined by GPC.

Table S2 Feeding Amounts and Pyr Content of PCL-Pyr Copolymers

Sample	Feed ratio $n_{\text{PCL}}:n_{\text{Pyr}}:n_{\text{HDI}}$	m_{PCL} (g)	m_{Pyr} (g)	m_{HDI} (g)	$m_{\text{Pyr-UV}}$ (g)	RE (%)	Pyr content (wt%)
PCL _{6.5k} -Pyr		3.0	0.30	0.17	0.20	67	5.8
PCL _{5k} -Pyr	1:1:2	3.0	0.40	0.21	0.28	70	7.8
PCL _{3k} -Pyr		3.0	0.66	0.32	0.48	73	12.1

Table S3 DSC Data of PCL-based Samples

Sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
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H-PCL _{6.5k}	20.37	55.59	53.04	49.05
PCL _{6.5k} -Pyr	16.19	45.48	52.83	47.11
PCL _{5k} -Pyr	14.64	40.83	50.21	41.31
PCL _{3k} -Pyr	-3.12	29.59	41.73	33.64
