

Multi-shape Memory Effect of Polyimides with Extremely High Strain

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Supporting information

Preparation of Crosslinked Polyimides

1. Materials

2,2'-Bis[4-(3-aminophenoxy)phenyl]hexafluoropropane (m-6FBAPP), 4,4'-(hexafluoroisopropylidene) (6FDA) were supplied by Changzhou Sunlight Pharmaceutical Co., Ltd. 1,1',1''-Tri(4-hydroxyphenyl)ethane, 1-fluoro-4-nitrobenzene, potassium carbonate (K_2CO_3), 5% palladium on charcoal (Pd/C), and 80% hydrazine monohydrate were obtained from Acros and used as received. N,N-dimethylacetamide (DMAc) were purified by vacuum distillation over CaH_2 and stored over 4 Å molecular sieves prior to use.

2. Preparation of 1,1',1''-tris[4-(aminophenoxy)phenyl]ethane (TAPE)

The TAPE was synthesized according the literature.¹ The route of triamine was shown in Scheme S1.

A 250 mL flask containing 1,1',1''-tri(4-hydroxyphenyl)ethane (5.00 g, 16.48 mmol), 1-fluoro-4-nitrobenzene (8.14 g, 57.69 mmol), 90 mL DMF, and potassium carbonate (7.97 g, 57.69 mmol) was fitted with a mechanical stirrer, condenser, nitrogen inlet and thermometer. The mixture was stirred at 75 °C for 6 h, then, the reaction mixture was cooled and poured into 500 ml of distilled water. The precipitated product was filtered off and washed with water until it was neutral. The crude product 1,1',1''-tris[4-(aminophenoxy)phenyl]ethane (TNPE) was recrystallized from DMF/water and then dried under vacuum at 80 °C for 10 h to yield 8.1 g (73%).

Under nitrogen protection, a mixture of 2 g (2.99 mmol) of TNPE, 0.15 g of Pd/C catalyst, and 30 mL of dioxane was placed into a 100 mL three-necked flask equipped with a dropping funnel, and reflux condenser. The mixture was stirred under reflux for 30 min, and then 10 mL of hydrazine hydrate was added dropwise over 2 h, followed by 6 h of reflux. The resulting mixture was filtered while hot to remove the catalyst and the filtrate was subsequently concentrated and poured into 500 mL of deionized water to produce a precipitate, which was washed with water. After recrystallization from dioxane/water, the product TAPE was dried under vacuum at 80 °C for 10 h to yield 1.4 g (81%).

TAPE Melting point: 223°C (DSC peak). ¹H NMR (DMSO, ppm): 6.96 (d, H_b, 6H), 6.93 (d, H_c, 6H), 6.76 (m, H_e, 6H), 6.74 (m, H_d, 6H), 4.97 (s, H_a, 6H), 2.02 (m, H_f, 6H); HRLC-MS (ESI): 579.6 (M+H)⁺, Calcd 580.5 for C₃₈H₃₃N₃O₃.

3. Preparation of polyimide films

The synthesis of PI-0.5 (m-6FBAPP/6FDA/0.5%mol TAPE) is used as an example to illustrate the general synthetic route as shown in Scheme S2. 1.7770 g 6FDA was added to a solution of 2.0427 g m-6FBAPP in 10 g DMAc with stirred under nitrogen. The reaction mixture stirred at room temperature for 24h to afford a viscous poly(amic acid) (PAA) solution. 0.0232 g TAPE as triamine crosslinker (equimolar with functional groups) and additional 5.4 g DMAc was added to the mixture with stirring for another 12h. The solid concentration of the reaction system was controlled at 20%wt. PI films were prepared by pouring the PAA onto the glass plates and then heated in air oven with a temperature procedure (50 °C/24h, 80 °C/24h) to remove the solvent. In addition, the materials were fully imidized at 100 °C/2h, 150 °C/2h, 200 °C/1h, 250 °C/1h, and 300 °C/1h under vacuum. The films were stripped from the plate by soaking into the distilled water they were cooled to room temperature, and the thickness is about 150 μm.

Instruments and Measurements

1. Hydrogen nuclear magnetic resonance (^1H NMR) spectra were determined using a BRUKER-300 spectrometer (Massachusetts, USA) at 300 MHz DMSO- d_6 .
2. FTIR spectra were recorded using a FT-IR measurements were performed using a Bruker Vector 22 spectrometer (Massachusetts, USA) in the range of 400-4000 cm^{-1} , with the samples in the form of thin films (PIs).
3. High resolution liquid chromatography-mass spectroscopy (HRLC-MS) data were obtained using an Agilent 1290-microTOF-QII (Bruker, Massachusetts, USA) high resolution mass spectrometer.
4. Gel content was measured by submerging the films in DMAc for 24h at room temperature.

$$\text{Gel Content (wt\%)} = \frac{\text{Undissolved PI}}{\text{Crosslinked PI}} \quad (1)$$

5. Thermo gravimetric analysis (TGA) was measured by a TA 2050 (Delaware, USA), with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under nitrogen.
6. Differential scanning calorimetric (DSC) analyses were performed using a TA instrument, DSC Q100 (Delaware, USA), at a scanning rate of 20 $^{\circ}\text{C}/\text{min}$ under a nitrogen flow of 50 mL/min.
7. Differential mechanical analysis (DMA) were performed using a TA instrument, DMA Q800 (Delaware, USA), at a scanning rate of 5 $^{\circ}\text{C}/\text{min}$ from 50 to 400 $^{\circ}\text{C}$, an amplitude of 10 μm , and a load frequency of 1 Hz in film tension geometry. T_g was regarded as the peak of $\tan \delta$.
8. Shape memory test:

The shape memory properties of polyimides were conducted on TA Instruments Q800. The samples were prepared in a rectangular mode (20mm \times 5.0mm \times 0.15mm). All the shape memory cycles were performed by tension clamps in controlled force mode. The detail test setup was listed below:

The polyimide films was first heated to T_d (deformation temperature) at 8 $^{\circ}\text{C}/\text{min}$; then the sample was stretched from $\epsilon_{(N-1)}$ to a elongation at T_d , where N gives the number of the cycle. The sample was kept for 5min at $\epsilon_{\text{load}(N)}$ and afterward cooled under load to 120 $^{\circ}\text{C}$ with a cooling rate of 8 $^{\circ}\text{C}/\text{min}$. After unloading, the sample was in the temporary shape $\epsilon_{(N)}$. Then the recovery procedure was heating the sample back to T_d to get the $\epsilon_{\text{re}(N)}$

Thermal-induced shape-memory behaviour of polyimides was evaluated by the shape fixity (R_f) and the shape recovery (R_r) based on the following equations:²

$$R_f = \frac{\epsilon_{(N)} - \epsilon_{(N-1)}}{\epsilon_{\text{load}(N)} - \epsilon_{(N-1)}} \times 100\% \quad (2)$$

$$R_r = \frac{\epsilon_{(N)} - \epsilon_{\text{re}(N-1)}}{\epsilon_{(N)} - \epsilon_{(N-1)}} \times 100\% \quad (3)$$

where ϵ_{load} represents the maximum strain in the deformation procedure under load, ϵ is the fixed strain after cooling and unloading the applied force, ϵ_{re} is the corresponding strain after recovering, and N is the step number in one shape memory cycle.

9. Crosslink densities³⁻⁵

According to the Mooney-Rivlin equation

$$\sigma_N = (2C_1 + \frac{2C_2}{\lambda}) \cdot (\lambda - \frac{1}{\lambda^2}) \quad (4)$$

The samples of different crosslinker content were measured using a DMA Q800 in the mode of film tension. An increment force of 0.01N was applied for 20 min at a constant temperature of 220 °C to achieve a constant value of λ for the certain force. This procedure was repeated until the strain beyond the DMA detection limits. In addition, the Mooney-Rivlin equation was converted

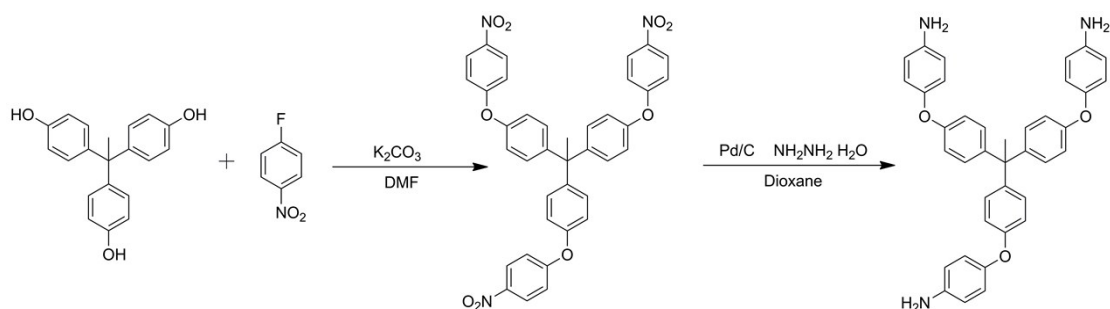
to a linear relationship by the $\frac{\sigma_N}{\lambda - \lambda^{-2}}$ and the $\frac{1}{\lambda}$. The coefficients $2C_1$ and $2C_2$ were obtained by linear fit, and the $1.5 < \lambda < 2.5$. The value of $2C_2$, which can be related to the number of the elastically effective trapped entanglements. The constant C_1 is related to the shear modulus G in the following way

$$2C_1 = G = \frac{\rho_r RT}{M_c} \quad (5)$$

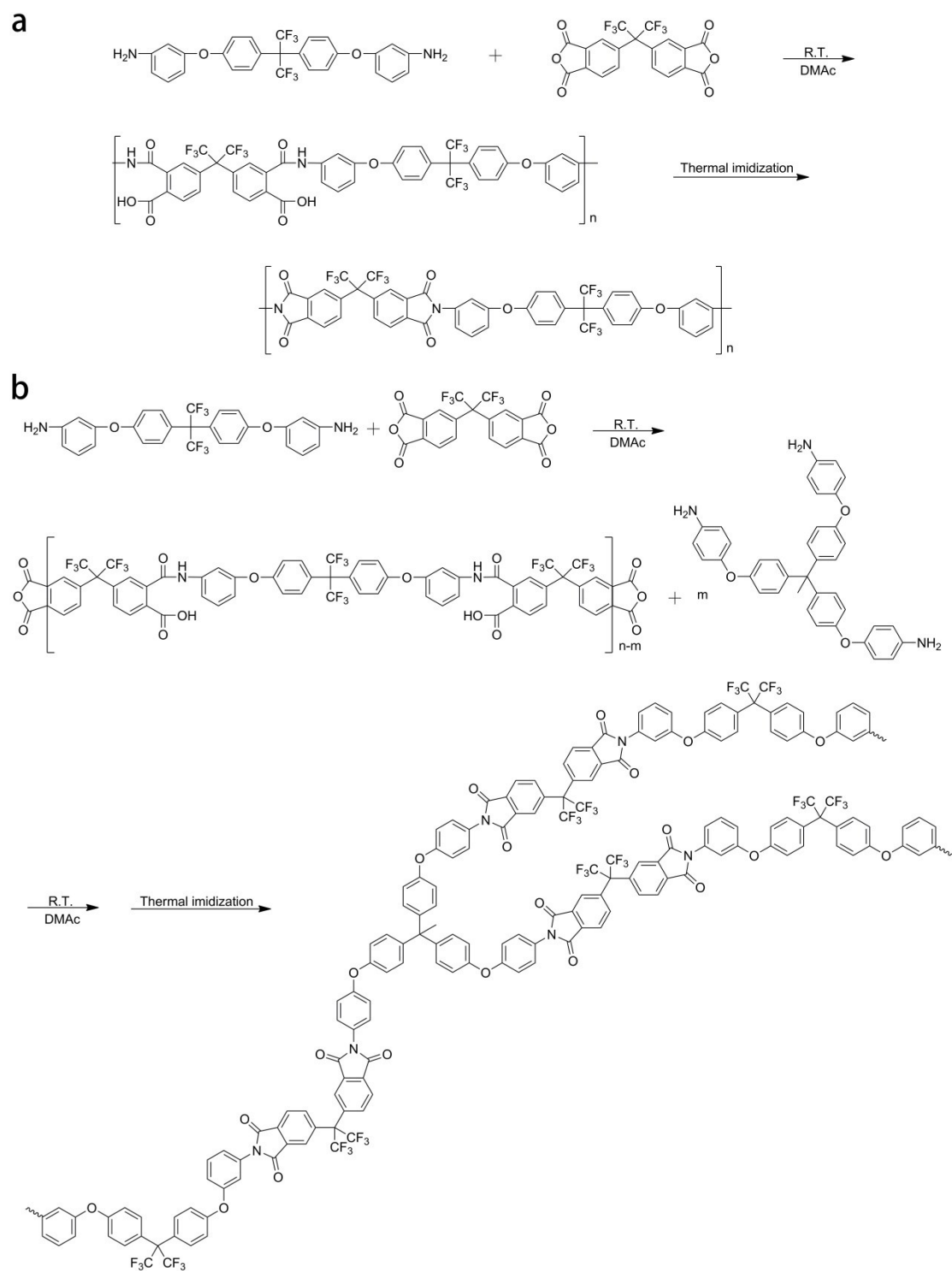
Where T is the absolute temperature, ρ_r is the polymer density, which was measured by pycnometer at 25 °C, and R is the gas constant (8.314 J·mol⁻¹·K⁻¹), M_c is the molecular weights of crosslinked polymers. M_n is the number-average of the molecular weight of the initial polymer. X_c is the crosslink densities of the polymers.

$$X_c = \frac{M_n}{M_c}$$

Figures and Tables



Scheme S1. Synthesis of triamine monomers



Scheme S2. a) Synthesis route of PI-0. b) Synthesis route of crosslinked PI.

Table S1. Physical and thermal properties of the polyimides

	Cross-linker (mol%)	Gel Content (wt%)	Crosslink density (%)	T _g (°C)	T _{5%} (°C) ^a
PI-0	0	0	-	226	529
PI-0.5	0.5	93.4	0.24	227	528
PI-1	1.0	93.9	0.25	225	526

PI-2	2.0	94.2	0.27	226	528
PI-5	5.0	98.5	0.29	225	524

^a 5% weight loss ($T_{5\%}$) temperatures measured by TGA.

Table S2. Dual shape memory cycle for polyimides

	$\epsilon_{\max}(\%)$	$R_f(\%)$	$R_r(\%)$
PI-0	432	99.6	64.5
PI-0.5	460	99.4	93.5
PI-1	394	99.7	97.2
PI-2	111	99.0	92.7
PI-5	35	97.6	95.5

Table S3. Measured SME parameters of the PI-0.5 and PI-5 for four cycles

	Cycle	$\epsilon_{\max}(\%)$	$R_f(\%)$	$R_r(\%)$
PI-0.5	1st	69	98.7	85.5
	2nd	84	98.7	87.0
	3rd	95	98.8	94.3
	4th	105	98.8	94.9
PI-5	1st	61	98.5	87.1
	2nd	67	98.4	94.7
	3rd	70	98.4	97.2
	4th	72	98.3	99.6

Table S4. The R_f and R_r data in a series of triple shape memory cycles for PI-0.5 with different second transition temperature

	$\epsilon_{(S0 \rightarrow S1)}$	$\epsilon_{(S1 \rightarrow S2)}$	$R_{f(S0 \rightarrow S1)}$	$R_{f(S1 \rightarrow S2)}$	$R_{r(S2, re \rightarrow S1, re)}$	$R_{r(S1, re \rightarrow S0, re)}$
260 °C +220 °C	116	422	70.1	99.4	91.5	81.2
260 °C +230 °C	97	398	60.3	99.5	89.4	71.5
260 °C +240 °C	91	439	43.2	99.5	90.7	48.6

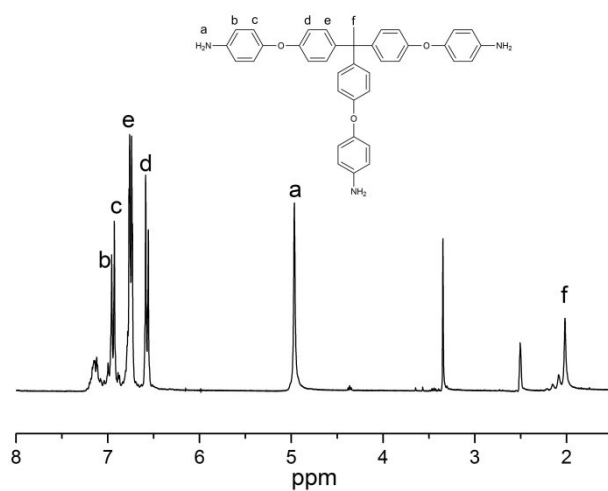


Fig. S1 ^1H NMR spectra of TAPE in DMSO.

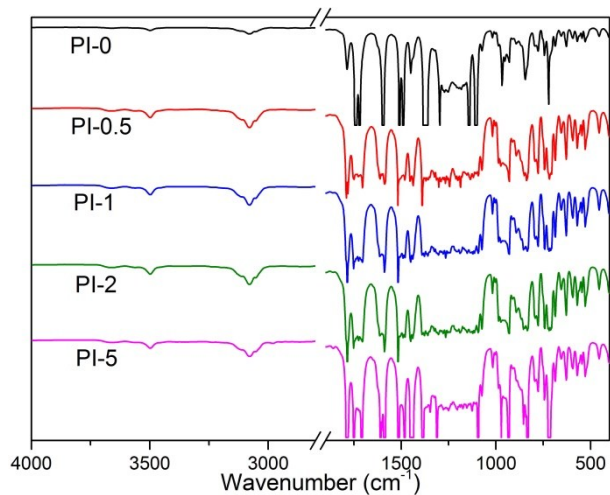


Fig. S2 FT-IR spectra of polyimides. The absorptions of the imide ring appeared at $1770\text{-}1785\text{ cm}^{-1}$ (asymmetrical C=O stretching), $1720\text{-}1735\text{ cm}^{-1}$ (symmetrical C=O stretching), and $1380\text{-}1400\text{ cm}^{-1}$ (C-N stretching).

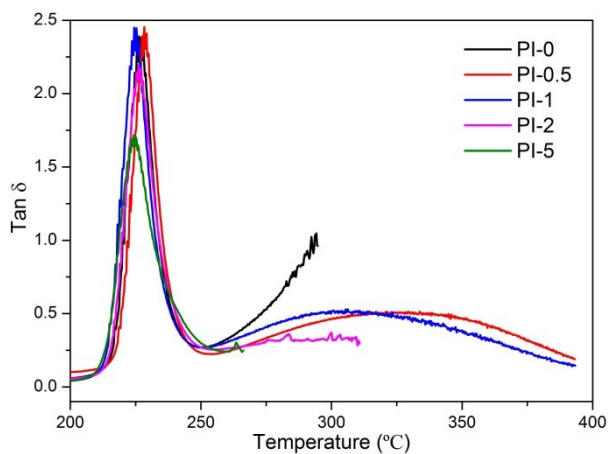


Fig. S3 $\text{Tan } \delta$ curves of polyimides.

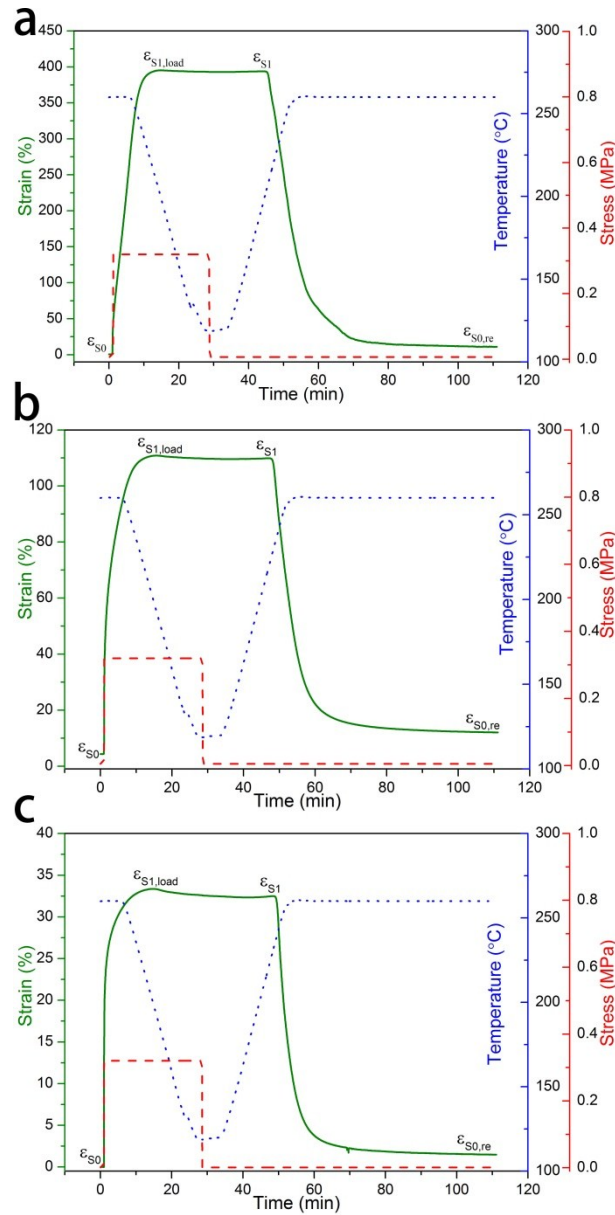


Fig. S4 a) Dual shape memory cycle for PI-1 at $T_d=T_r=260$ °C, $T_f=120$ °C. $R_f=99.6\%$, $R_r=97.2\%$. b) Dual shape memory cycle for PI-2 at $T_d=T_r=260$ °C, $T_f=120$ °C. $R_f=99.0\%$, $R_r=92.3\%$. c) Dual shape memory cycle for PI-5 at $T_d=T_r=260$ °C, $T_f=120$ °C. $R_f=97.6\%$, $R_r=95.5\%$. Solid line: strain; dotted line: temperature; dashed line: stress.

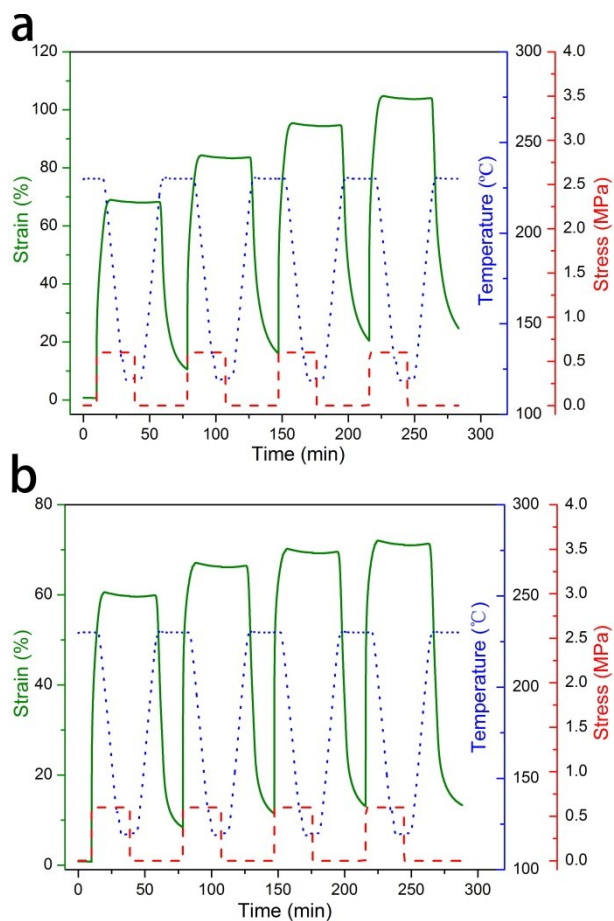


Fig. S5 a) Consecutive dual-shape memory cycles of PI-0.5 with $T_d=T_r=230$ °C, $T_f=120$ °C. b) Consecutive dual-shape memory cycles of PI-5 with $T_d=T_r=230$ °C, $T_f=120$ °C.

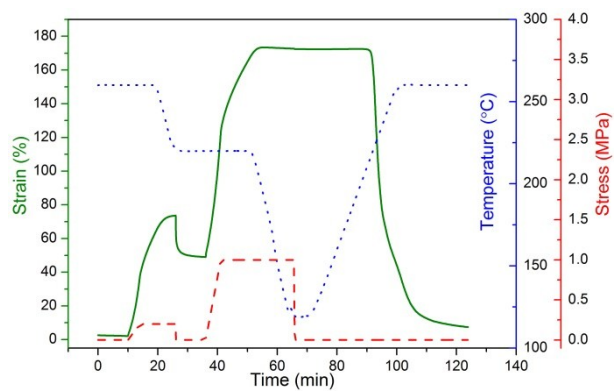


Fig. S6 Triple-shape memory cycle of PI-0.5 with consecutively recovery temperature

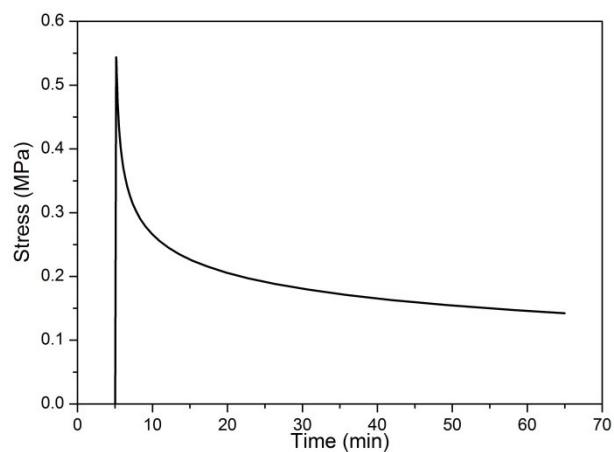


Fig. S7 Stress relaxation experiment performed on PI-0.5 at 260 °C with strain of 200%.

Supporting References

1. L. S. Tan and D. H. Wang, *Journal*, 2013.
2. R. Zhao, T. Zhao, X. Jiang, X. Liu, D. Shi, C. Liu, S. Yang and E. Q. Chen, *Adv Mater*, 2017, **29**.
3. T. Raidt, R. Hoeher, M. Meuris, F. Katzenberg and J. C. Tiller, *Macromolecules*, 2016, **49**, 6918-6927.
4. B. Heuwers, A. Beckel, A. Krieger, F. Katzenberg and J. C. Tiller, *Macromolecular Chemistry and Physics*, 2013, **214**, 912-923.
5. R. Hoeher, T. Raidt, M. Rose, F. Katzenberg and J. C. Tiller, *Journal of Polymer Science Part B: Polymer Physics*, 2013, **51**, 1033-1040.