

Supporting Information

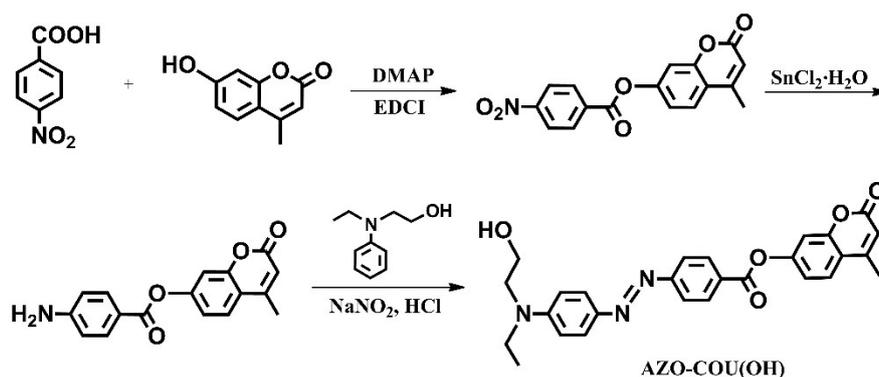
Thermo-Responsive Aluminum-Based Polymer Composite Films with Controllable Deformation

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Synthesis of azobenzene-coumarin (AZO-COU(OH))



Scheme S1 Synthesis of azobenzene-coumarin (AZO-COU(OH))

- (1) A three-necked flask was charged with a mixture of *p*-nitrobenzoic acid (2.00 g, 12 mmol), 4-methyl-7-hydroxycoumarin (1.62 g, 10 mmol) 4-dimethylaminopyridine (DMAP) (0.29 g, 2.4 mmol) and *N,N*-dimethylformamide (DMF) (120 mL). The mixture solution was stirred to dissolve and cooled in an ice bath for 30 minutes under nitrogen. Then the 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCI) (2.75 g, 14.4 mmol) was added and the reaction mixture was cooled in an ice bath for another 30 minutes. Finally, the ice bath was removed and the reaction mixture was stirred at room temperature overnight. The reaction solution was poured into a large amount

of water and the precipitate was collected by filtration. The crude product was washed with a small amount of water and then dried in the vacuum oven to give a white solid intermediates 1, 2.94 g, 95 % yield. $^1\text{H NMR}$ (500MHz, $\text{DMSO-}d_6$, δ , ppm): 1.606 (s, CCH_3 , 3H), 6.345 (s, C=CHCO , 1H), 7.283 (m, Ar-**H**, 2H), 7.709 (d, Ar-**H**, 1H), 8.434 (m, Ar-**H**, 4H).

(2) A three-necked flask was charged with a mixture of intermediates 1 (0.62 g, 2 mmol) and ethanol (40 mL). The mixture was stirred to dissolve under nitrogen. Then $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (1.80 g, 8 mmol) was added and the reaction mixture was stirred for 10 minutes. The reaction mixture was heated to reflux for 8 h and the precipitate was collected by filtration. The crude product was washed with a small amount of ethanol and then dried in the vacuum oven to give a pale yellow solid intermediates 2, 0.45 g, 80 % yield. $^1\text{H NMR}$ (500MHz, $\text{DMSO-}d_6$, δ , ppm): 2.463 (s, CCH_3 , 3H), 6.247 (s, C=CHCO , 1H), 6.641 (d, Ar-**H**, 2H), 7.264-7.398 (m, Ar-**H**, 2H), 7.811-7.862 (m, Ar-**H**, 3H).

(3) A three-necked flask was charged with a mixture of intermediates 2 (2.81 g, 10 mmol) and 18% HCl (12 mL). The mixture was refluxed at 40 °C for 30 minutes and cooled to 0 °C in an ice bath. Then the saturated solution sodium nitrite (0.71 g, 10 mmol) was added. The mixture was stirred at 0 °C for 30 minutes to get the diazo salt. Another three-necked flask was charged with *N*-ethyl-*N*-hydroxyethylaniline (1.65 g, 10 mmol) and methanol/water(1:1, V/V) (36 mL), It was stirred to dissolve in ice bath. The prepared diazo salt was added to the solution dropwisely at 0-5 °C and stirred overnight. The pH of the reaction solution was adjusted to 5-6 by a saturated anhydrous sodium acetate solution and the precipitate was collected by filtration. The crude product was further purified by column chromatography with petroleum ether and ethyl acetate (2/1, v/v) to afford orange solid azobenzene-coumarin (AZO-COU(OH)), 3.67 g, 80 % yield. $^1\text{H NMR}$ (500MHz, $\text{DMSO-}d_6$, δ , ppm): 1.167 (t, CH_2CH_3 , 3H), 2.479 (s, CH=CCH_3 , 3H), 3.535 (m, $\text{CH}_2\text{NCH}_2\text{CH}_3$, 4H), 3.623 (q, HOCH_2 -, 2H), 4.857 (t, CH_2OH , 1H), 6.431 (s, C=CHCO , 1H), 6.878 (d, Ar-**H**, 2H), 7.398 (s, Ar-**H**, 1H), 7.502 (d, Ar-**H**, 1H), 7.838 (d, Ar-**H**, 2H), 7.893 (d, Ar-**H**, 1H), 7.931 (d, Ar-**H**, 2H), 8.281 (d, Ar-

H, 2H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, δ , ppm): 12.495, 18.683, 45.699, 52.708, 58.738, 110.782, 113.258, 114.312, 118.924, 122.431, 126.290, 126.944, 128.581, 131.755, 132.631, 142.675, 146.075, 151.953, 153.461, 154.034, 156.394, 160.122, 164.283. HRMS (ESI, m/z): Calcd for $\text{C}_{27}\text{H}_{23}\text{N}_3\text{O}_5$ $[\text{M}+\text{H}]^+$ 472.1794; Found, 472.1867.

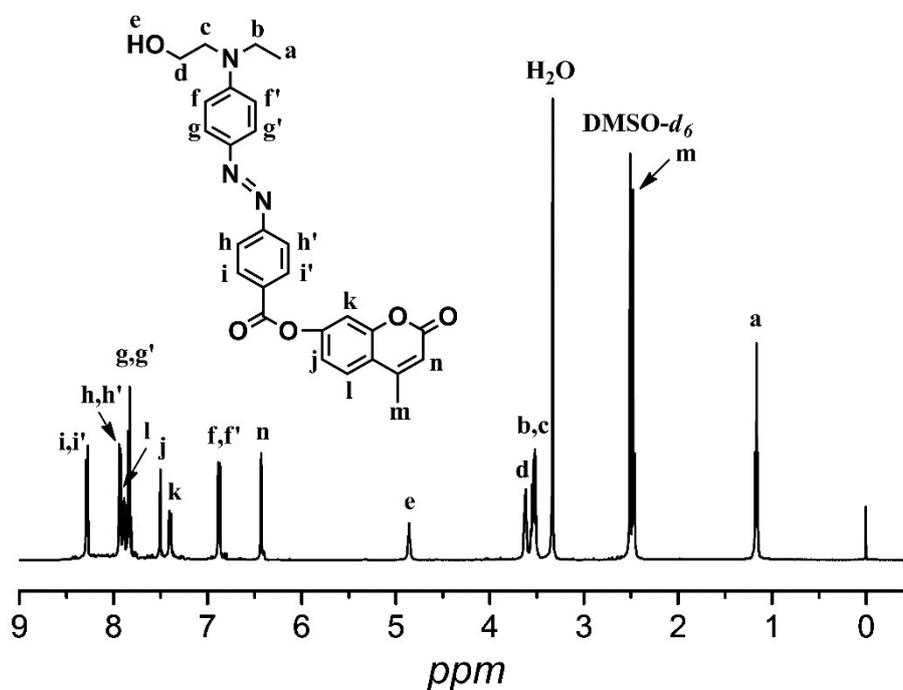
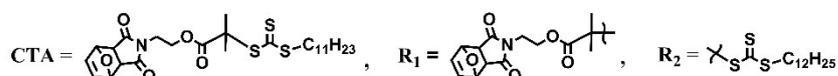
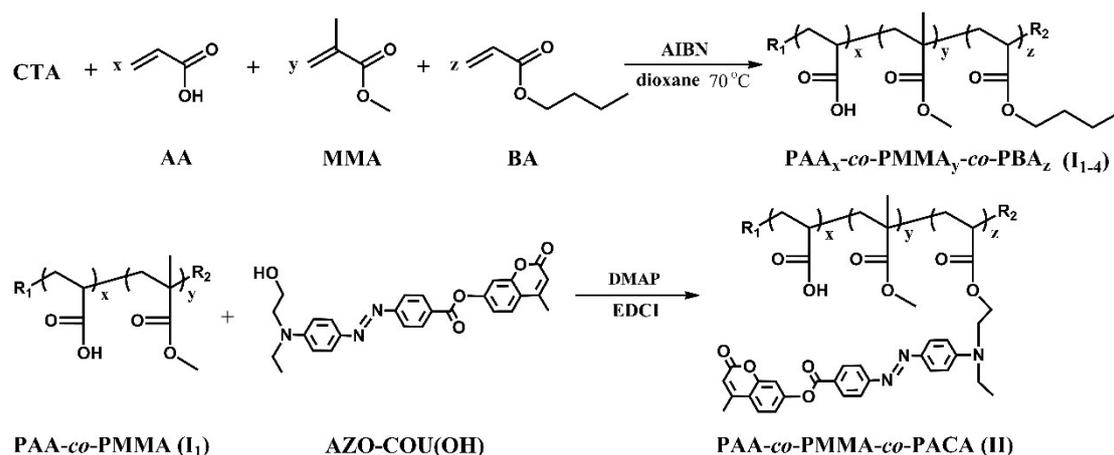


Fig. S1 ^1H NMR spectrum of AZO-COU(OH) in $\text{DMSO-}d_6$

Synthesis of copolymers PAA-*co*-PMMA (I₁), PAA-*co*-PMMA-*co*-PBA (I₂₋₄) and PAA-*co*-PMMA-*co*-PACA (II)



I₁: x=292, y=298, z=0; I₂: x=266, y=258, z=40; I₃: x=253, y=238, z=53; I₄: x=238, y=133, z=109

II: x=241, y=298, z=51

Scheme S2 Synthesis of copolymers PAA-*co*-PMMA (I₁), PAA-*co*-PMMA-*co*-PBA (I₂₋₄) and PAA-*co*-PMMA-*co*-PACA (II).

Synthesis of copolymer (I₁₋₄)

A typical procedure for the synthesis was as follows. Methyl methacrylate (3.3 g, 33 mmol), acrylic acid (2.376 g, 33 mmol), dodecyl trithioester (CTA) (40 mg, 0.11 mmol) and AIBN (4 mg, 0.024 mmol) were dissolved in dry dioxane (11 mL) in a Schlenk tube. The solution was degassed by three freeze-pump-thaw cycles and then heated at 70 °C for 8 h. The reaction mixture was diluted with tetrahydrofuran (THF) (10 mL) and poured into a large amount of anhydrous ether. The precipitate was collected by filtration. The crude product was purified by a repeated dissolving/precipitation process (THF/ethyl ether). The copolymer PAA-*co*-PMMA (I₁) was dried in vacuum oven overnight, 5.39 g, 95 % yield. ¹H NMR (500MHz, DMSO-*d*₆, δ, ppm): 0.750-2.184 (m, CH₂, 2366H), 3.558 (m, OCH₃, 894H), 12.233 (br s, COOH, 292H). FT-IR (KBr, cm⁻¹): 3288, 2987, 1736, 1450, 1388, 1242, 1135, 1055, 985, 842, 755, 645. *M*_n,¹H NMR: 50.8 kDa.

PAA₂₆₆-*co*-PMMA₂₅₈-*co*-PBA₄₀ (I₂): ¹H NMR (500MHz, DMSO-*d*₆, δ, ppm): 0.751-2.184 (m, CH₂, 2488H), 3.558 (m, OCH₃, 774H), 3.981 (br s, OCH₂, 80H), 12.231 (br s, COOH, 266H). FT-IR (KBr, cm⁻¹): 3284, 2954, 1736, 1450, 1388, 1238, 1139, 1066,

982, 842, 758, 641. $M_n, ^1\text{H NMR}$: 50.1 kDa.

PAA_{253-co}-PMMA_{238-co}-PBA₅₃ (**I**₃): $^1\text{H NMR}$ (500MHz, DMSO-*d*₆, δ , ppm): 0.751-2.192 (m, **CH**₂, 2479H), 3.560 (m, **OCH**₃, 714H), 3.969 (br s, **OCH**₂, 106H), 12.244 (br s, **COOH**, 253H). FT-IR (KBr, cm^{-1}): 3288, 2973, 1736, 1457, 1392, 1220, 1143, 1069, 978, 839, 762, 649. $M_n, ^1\text{H NMR}$: 48.8 kDa.

PAA_{238-co}-PMMA_{133-co}-PBA₁₀₉ (**I**₄): $^1\text{H NMR}$ (500MHz, DMSO-*d*₆, δ , ppm): 0.753-2.302 (m, **CH**₂, 2469H), 3.507 (m, **OCH**₃, 399H), 3.979 (br s, **OCH**₂, 218H), 12.254 (br s, **COOH**, 238H). FT-IR (KBr, cm^{-1}): 3240, 2958, 1728, 1450, 1388, 1246, 1168, 1063, 938, 821, 766, 645. $M_n, ^1\text{H NMR}$: 44.4 kDa.

Table S1. Synthesis of copolymers **I**₁₋₄

Code	Mole ratio (%)	Copolymer composition	Contents (%)	M_n^a (KDa)
	AA: MMA: BA		PAA: PMMA: PBA	
I ₁	50: 50: 0	PAA _{292-co} -PMMA ₂₉₈	49: 51: 0	50.8
I ₂	50: 45: 5	PAA _{266-co} -PMMA _{258-co} -PBA ₄₀	47: 46: 7	50.1
I ₃	50: 40: 10	PAA _{253-co} -PMMA _{238-co} -PBA ₅₃	46: 44: 10	48.8
I ₄	50: 25: 25	PAA _{238-co} -PMMA _{133-co} -PBA ₁₀₉	49: 28: 23	44.4

^a Determined by $^1\text{H NMR}$

Synthesis of copolymer (**II**)

A three-necked flask was charged with a mixture of AZ Under a nitrogen atmosphere, copolymer 1 PAA-*co*-PMMA (**I**₁) (2.56 g, 0.05 mmol), O-COU(OH) (1.41 g, 3 mmol) DMAP (0.09 g, 0.72 mmol) and DMF (36 mL). The mixture solution was stirred to dissolve and cooled in an ice bath for 30 minutes under nitrogen. Then EDCI (0.82 g, 4.32 mmol) was added and the reaction mixture was cooled in an ice bath for another 30 minutes. Finally, the ice bath was removed and the reaction mixture was stirred at room temperature for three days. The reaction solution was poured into a large amount

of water and the precipitate was collected by filtration. Then it was filtered and washed by a small amount of distilled water. The crude product was purified by a repeated dissolving/precipitation process (DMF/anhydrous ether). The copolymer PAA₂₄₁-*co*-PMMA₂₉₈-*co*-PACA₅₁ (**II**) was dried in vacuum oven overnight, 3.77 g, 95 % yield, grafting ratio: 17.4 %. ¹H NMR (500MHz, DMSO-*d*₆, δ, ppm): 0.747-2.180 (m, CH₂, CH₃CH₂N, 2519H), 2.465 (m, C=CHCO, 51H), 3.176-3.554 (m, OCH₃, OCH₂CH₂NCH₂, 1200H), 6.403 (m, CH=CCH₃, 153H), 6.893 (m, Ar-*H*, 102H), 7.390 (m, Ar-*H*, 51H), 7.488 (m, Ar-*H*, 51H), 7.773-7.947 (m, Ar-*H*, 255H), 8.179-8.298 (m, Ar-*H*, 102H), 12.177 (m, COOH, 241H). FT-IR (KBr, cm⁻¹): 3262, 2958, 1732, 1597, 1516, 1447, 1388, 1246, 1128, 1073, 982, 821, 755, 634. *M*_n,¹H NMR: 73.9 kDa.

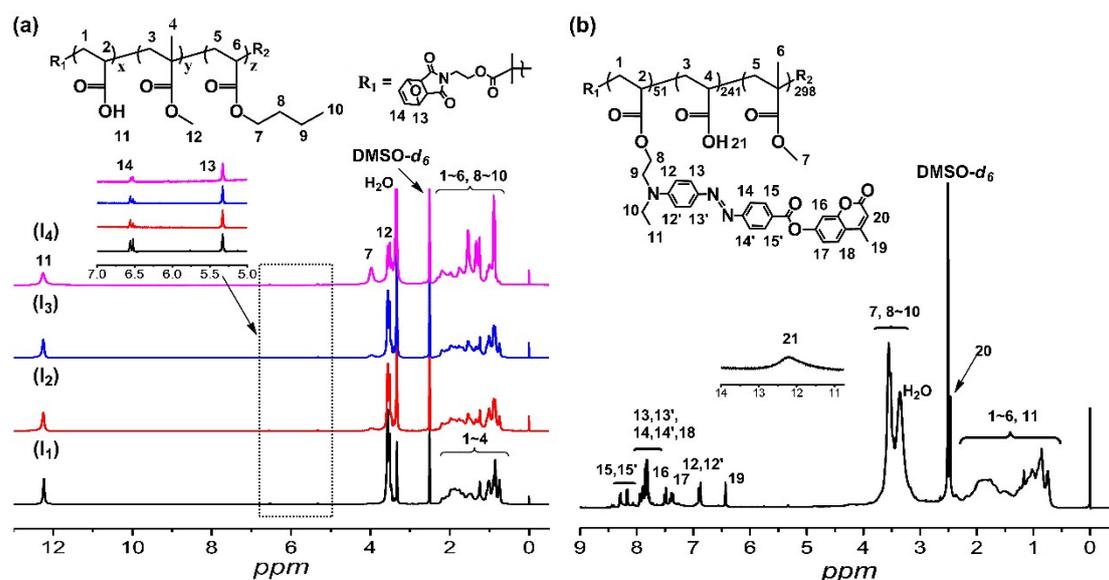


Fig. S2 ¹H NMR spectra of copolymers in DMSO-*d*₆. (a) PAA-*co*-PMMA (**I**₁), PAA-*co*-PMMA-*co*-PBA (**I**₂₋₄). (b) PAA-*co*-PMMA-*co*-PACA (**II**).

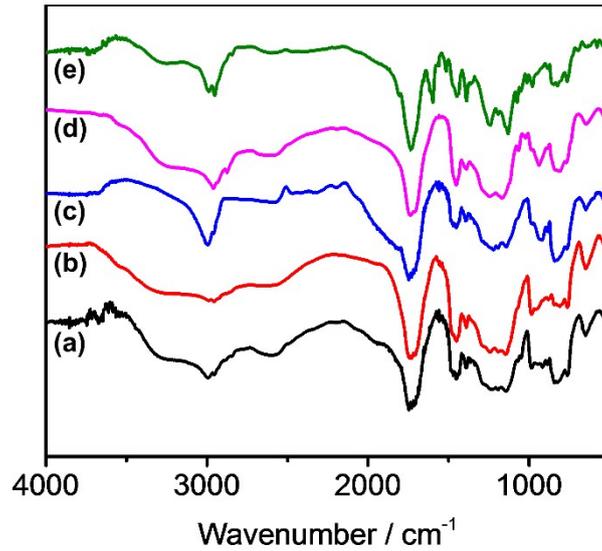


Fig. S3 FT-IR spectra of copolymers (a) PAA-*co*-PMMA (**I**₁), (b-d) PAA-*co*-PMMA-*co*-PBA (**I**₂₋₄). (e) PAA-*co*-PMMA-*co*-PACA (**II**).

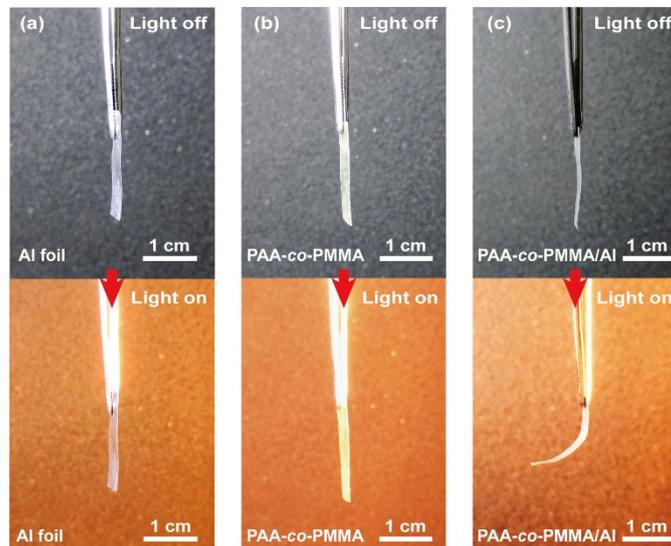


Fig. S4 The thermal responsiveness of Al foil (a), PAA-*co*-PMMA film (b) and PAA-*co*-PMMA/Al composite film (c) under heating (infrared light as the heat source)

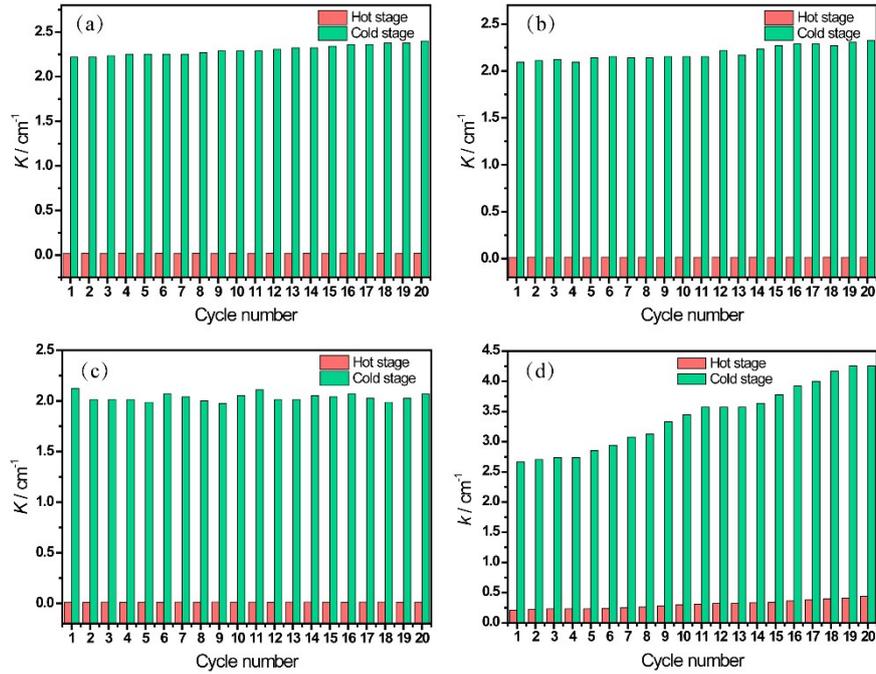


Fig. S5 The dependence of the deformation curvature of PAA-*co*-PMMA-*co*-PBA/Al and PAA-*co*-PMMA-*co*-PACA/Al on cycle number under alternating heating and cooling. (a) I_2 /Al composite film, (b) I_3 /Al composite film, (c) I_4 /Al composite film, (d) II /Al composite film.

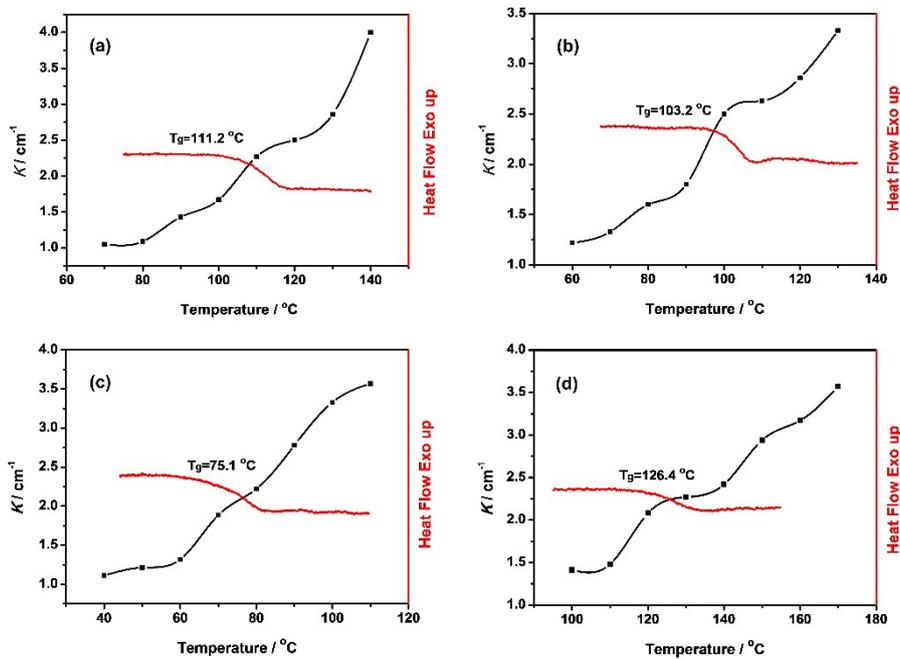


Fig. S6 The dependence of the curvature on heating temperature (black) and DSC curves (red) of composite films. (a) I_2 /Al composite film. (b) I_3 /Al composite film. (c) I_4 /Al composite film. (d) II /Al composite film.

Movie S1. Controlled thermo-responsive deformation of the composite films (PAA-*co*-PMMA-*co*-PACA/Al) by the direction of prestress.

Movie S2. The complex deformation of composite films (PAA-*co*-PMMA-*co*-PACA/Al) mimicking the caterpillar.

Movie S3. The complex deformation of composite films (PAA-*co*-PMMA-*co*-PACA/Al) mimicking the scorpion.

Movie S4. A lotus-like device made of the composite films (PAA-*co*-PMMA-*co*-PACA/Al and PMMA-*co*-PAA-*co*-PBA) mimicking the process from bud to bloom.

Movie S5. The application of the thermo-responsive composite film (PAA-*co*-PMMA-*co*-PACA/Al) in the overheat alarm device.

Movie S6. A soft robot creeper assembled from the composite film (PAA-*co*-PMMA/Al) moving forward in response to alternating heating and cooling.

Movie S7. A soft robot gripper assembled from the composite films (PAA-*co*-PMMA-*co*-PACA/Al) transferring a cotton ball in response to alternating heating and cooling.