

Supporting Information

Self-evolving materials based on metastable-to-stable crystal transition of polymorphic polyolefin

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1. Experimental Section

1.1 Materials

Isotactic polybutylene-1 (PB, trade name: PB0110) was purchased from Lyondell Basell Industries, which has the M_w of 711 kg/mol, M_w/M_n of 3.5, and melt flow rate (190 °C/2.16 kg) of 0.4 g/10 min. Dicumyl peroxide (DP, >98%, Aladdin), *N,N'*-1,3-phenylene bismaleimide (PM, >97%, J&K scientific corporation) and other chemicals were used as received.

1.2 Characterization

Measurement of Gel fraction. The gel fraction of crosslinked sample was measured by solvent extraction method. The sample was cut into small pieces and then extracted by hot p-xylene (140 °C) for 12 h to dissolve the uncrosslinked portion. Then, the insoluble part (crosslinked part) was dried and weighed. Gel fraction was determined by: Gel fraction = (final weight/initial weight) × 100%.

Differential scanning calorimetry (DSC). Crystallization and melting behaviors were measured on a NETZSCH 214 Polyma DSC instrument (NETZSCH, Germany) equipped with an IC70 intracooler under a nitrogen atmosphere. The samples were heated up from 20 to 160 °C at a heating rate of 10 °C/min to investigate the melting behavior. According to the distinct melting temperatures (T_m 's) of stable (S, form-I) and metastable (M, form-II) crystal phases, the fraction of S crystal phase in PB crystalline domain was evaluated by the following equation:

$$X_S = \frac{\Delta H_{m,S} / \Delta H_{m,S}^0}{\Delta H_{m,S} / \Delta H_{m,S}^0 + \Delta H_{m,M} / \Delta H_{m,M}^0} \quad (S1)$$

where $\Delta H_{m,S}$ and $\Delta H_{m,M}$ are the measured melting enthalpies of S and M crystal phases, respectively. $\Delta H_{m,S}^0$ (141 J/g) and $\Delta H_{m,M}^0$ (62 J/g) are the melting enthalpies of S and M crystal phases of 100% crystallinity, respectively.^[1]

Wide-angle X-ray scattering (WAXS). WAXS analysis was performed on a Nano-inXider vertical SAXS/WAXS system (Xenocs, Sassenage, France) equipped with a semiconductor pixel detector (Pilatus 200 K, Dectris, Swiss). WAXS profiles were attained by plotting the scattering intensity with the scattering vector q [$q = (4\pi\sin\theta)/\lambda$], where θ is half of the scattering angle and λ is the X-ray wavelength ($\lambda = 0.154$ nm).

Measurement of shape memory behavior. For visual demonstration, the rectangular samples (10 mm \times 5 mm) were melted at 140 °C for 5 min, and then stretched at 100% strain instantaneously. The sample was then cooled down to 20 °C and held at 20 °C for different annealing time (t_a) under the fixed strain (100%). For each applied t_a , different temporary shape was obtained after stress release. Then the samples were heated to 120 °C under a stress-free condition to observe the shape recovery ability.

In addition to visual demonstration, the shape memory performances of samples were also quantitatively evaluated on a Q850 dynamic mechanical analyzer (DMA, TA Instruments). The rectangular specimens (20 mm \times 2 mm) were cut from the partially-crosslinked PB films and used for the quantitative shape memory tests. In a typical dual shape memory cycle, the sample was initially melted at 140 °C for 3 min in a zero-stress mode to erase the thermal history. It was stretched to a strain $\varepsilon_{\text{load}}$ instantaneously, then cooled down to 20 °C, and held at 20 °C for different t_a 's under the same strain for crystal phase transition. Subsequently, the external force was released and the sample was able to relax to a temporary strain (ε). Finally, the sample was heated to 120 °C in a zero-stress mode to measure the recovered strain (ε_{rec}).

Shape fixing ratio (R_f) and recovery ratio (R_r) were evaluated as follow:

$$R_f = \frac{\varepsilon}{\varepsilon_{\text{load}}} \times 100\% \quad (\text{S2})$$

$$R_r = \frac{\varepsilon - \varepsilon_{\text{rec}}}{\varepsilon} \times 100\% \quad (\text{S3})$$

2. Supplementary Text

2.1 Preparation of partially crosslinked PB

To prepare the partially crosslinked polymer, PB was mixed with dicumyl peroxide (DCP, 2 wt% of PB) and *N,N'*-1,3-phenylene bismaleimide (PM, 5 wt% of PB) in a lab line roll mill (15 rpm) at 115 °C for 10 min (Table S1). Afterwards, the polymer was hot-pressed into a sheet at 150 °C for 20 min under a force of 10 MPa (Table S2). The hot-pressed sample was then cooled to 20 °C (Fig. S1), during which process the sample was crystallized into the M (form-II) crystal phase. The film was cut into suitable geometries for various analyses. Gel fraction of the partially crosslinked PB was measured to be ~65%.

Table S1. Per hundred rubber (phr) and gel fraction of each sample in processing PB.

Code	PB (phr)	DCP (phr)	PM (phr)	gel fraction (%)
1	100	2	0	0
2	100	2	3	49
3	100	2	5	65
4	100	0.3	5	34

Table S2. Hot-pressing conditions of each sample in processing PB.

Sample	Temperature (°C)	Time (min)	gel fraction (%)
1	140	20	62
2	150	20	65
3	160	20	36
4	170	20	32
5	150	5	43
6	150	30	64

2.2 Strain-accelerated M-to-S crystal transition

To verify that strain can accelerate the M-to-S crystal transition, the thermal behaviors of stretched PB with different t_a 's were measured by DSC (Fig. S2). Before annealing, the samples were initially melted at 140 °C for 5 min, and then stretched to a strain of 100% or 200% at 140 °C. Here, 140 °C is selected because it is just higher than the T_m of the two phases (M and S phase). The stretching speed is 20 mm/min and does not affect the subsequent crystal transition. As shown in Fig. S2a, when the strain is 100%, the duplet melting endotherms are observed when $t_a = 5\text{--}20$ h, indicating the co-existence of M and S crystal phases. However, only the melting endotherm of S crystal phase is present as t_a approaches to 40 h. The time required for M-to-S crystal transition (*i.e.*, evolution period) is shortened to 40 h at the strain of 100% (Fig. S2a). The evolution period is further shortened to 20 h when the strain increases to 200% (Fig. S2b). The above results can also be repeated with a larger applied strain, but in such case the crosslinked PB film would be too thin for following experiments. These results demonstrate that the M-to-S crystal transition is accelerated with increasing the imposed strain.

2.3 Interrupting M-to-S crystal transition *via* solvent-induced recrystallization

To interrupt the M-to-S crystal transition, the crosslinked PB films with various t_a 's were immersed in 50 °C THF for 5 min. The film samples were then taken out and dried at 80 °C for 24 h to remove the solvent. Such treated samples were then analyzed by WAXS and DSC to investigate the solvent-induced recrystallization (Fig. S3a,b). WAXS results indicate that the M crystal phase was swelled and recrystallized into the M' (form-I'/III) crystal phase with the evaporation of THF. As demonstrated in Fig. S3a, the characteristic peak of form-I' crystals appears at $q = 7.0 \text{ nm}^{-1}$ and that of form-III crystals is at $q = 8.5 \text{ nm}^{-1}$.^[2] DSC results show that the M' crystal phase has the lower T_m (96 °C) than that of S phase (~120 °C) (Fig. S3b). Meanwhile,

M' crystal phase is unstable at high temperature (*e.g.*, $>100\text{ }^{\circ}\text{C}$) and it transforms into the M crystal phase during the heating process (Fig. S3b).

2.4 Fabrication of crosslinked PB film of specified crystal patterns

The ink printing patterns (grayscale value of 1.0) were designed with Microsoft PowerPoint and were printed onto the crosslinked PB films with S crystal phase using a laser printer (Canon imageCLASS MF233d). Herein, the grayscale value of 1.0 means “black” and the value of 0 denotes “white”. The films with ink patterns were then exposed to near-infrared light emitted by a xenon lamp (PSU-H-LED, 808 nm, $500\text{ mW}\cdot\text{cm}^{-2}$) for 20 s to melt the patterned parts (Fig. S4a). The thermal images and photothermal temperatures were attained with a HIKVISION H36 thermal imager during photothermal treatment. The temperature of patterned area reaches $150\text{ }^{\circ}\text{C}$, which is sufficient to melt the S crystal phase. The rest area without photothermal effect is only $30\text{ }^{\circ}\text{C}$, thus no phase change occurs. Accordingly, after cooling to $20\text{ }^{\circ}\text{C}$, the patterned area crystallizes into M crystal phase, while the rest area remains as S crystal phase (Fig. S4c). Finally, the printed ink on the film was gently removed by wiping with ethyl acetate (Fig. S4a).

2.5 Swelling behavior of crosslinked PB films with different crystal phases in solvent

We examined the swelling behavior of crosslinked PB films during M-to-S phase transition. Before immersing in the solvent, the film was initially melted at $140\text{ }^{\circ}\text{C}$ for 5 min, and then cooled to $20\text{ }^{\circ}\text{C}$ and annealed for various t_a 's for M-to-S crystal transition. Subsequently, this film was immersed in $50\text{ }^{\circ}\text{C}$ tetrahydrofuran (THF) for 5 min and the area change was evaluated. The area change with t_a was normalized by the area of the film with $t_a = 72\text{ h}$. Fig. S5 shows that the area change reduces with t_a , due to the increase of S phase. The area of the film with M crystal phase ($t_a = 0\text{ h}$) expands to ~ 3.4 times larger than that of the film with S crystal phase ($t_a = 72\text{ h}$). These

results demonstrate that the swelling behaviors of M and S crystal phases are much different in THF.

2.6 Shape morphing enabled by crystal heterogeneity

To evaluate the shape morphing ability of crosslinked PB film enabled by crystal heterogeneity (Fig. 4a), the samples were initially placed at 140 °C for 5 min to eliminate the thermal history, and then stretched to a strain of 200% at 140 °C. The stretched films were cooled to 20 °C and annealed for 40 h, allowing for a complete M-to-S crystal transition. Afterwards, the films were treated by ink pattern printing and photothermal effect to encode M crystal patterns under the fixed strain. Finally, the films with specific crystal patterns were cut into arm-like specimens and annealed at 20 °C for different t_a 's. They were then heated to 120 °C to examine the shape morphing behavior under the stress-free condition. Fig. S6 demonstrates that the arm-shaped film with a $t_a = 0$ h joint has a maximum bending angle of $\sim 90^\circ$ upon heating to 120 °C, which angle reduced to 0° when $t_a = 10$ h. This result indicates that the shape morphing ability of arm-like film is obviously weakened with prolonging t_a .

2.7 Recyclable 3D shapes obtained by reprogramming the crystal patterns

As shown in Fig. S7, the crystal heterogeneity of deformed PB can be erased by melting at 140 °C. The molten film recrystallizes into the M crystal phase upon cooling to 20 °C and further transforms into the S crystal phase after annealing at 20 °C for more than 168 h. A new crystal pattern can be encoded into the recycled film by ink printing technique, and then be reformed into another configuration (Fig. S7).

3. Supplementary Figures

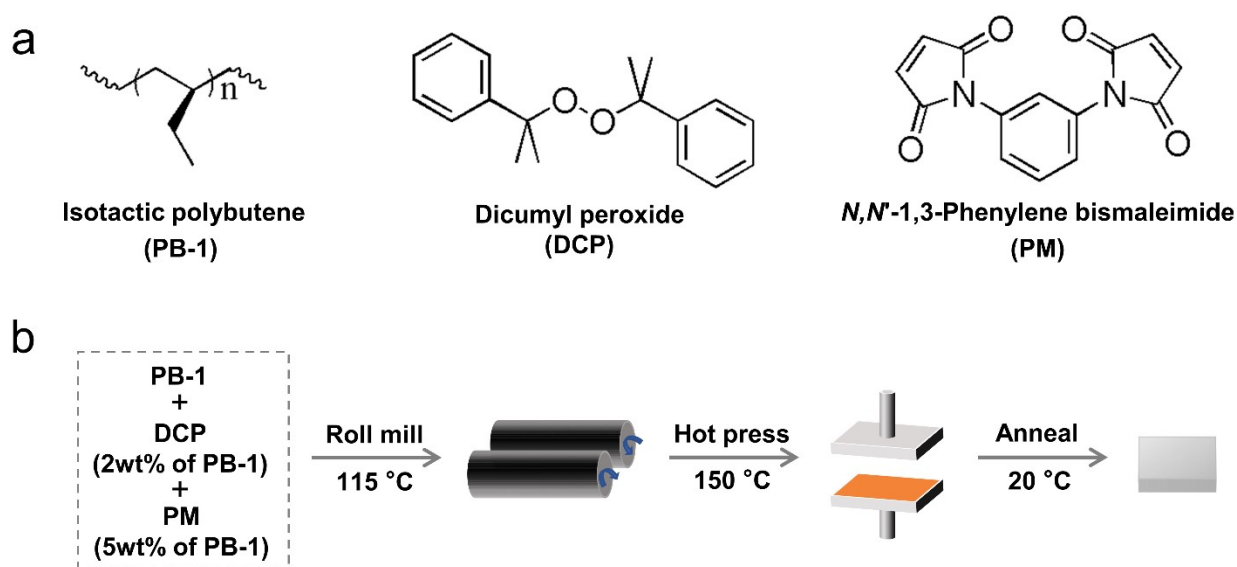


Fig. S1. Preparation of partially-crosslinked PB. (a) Chemical structure formula of PB, peroxide initiator, and rubber vulcanizing agent. (b) Processing procedure of partially-crosslinked PB.

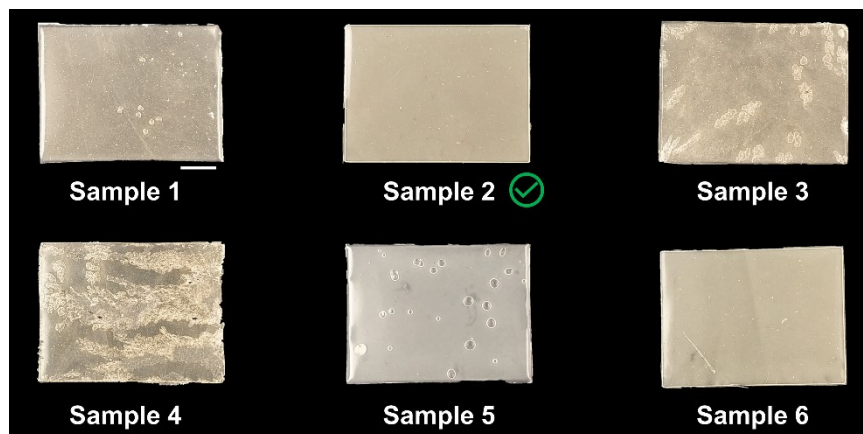


Fig. S2. Various crosslinked PB with different hot-pressing temperature and time. Scale: 10 mm.

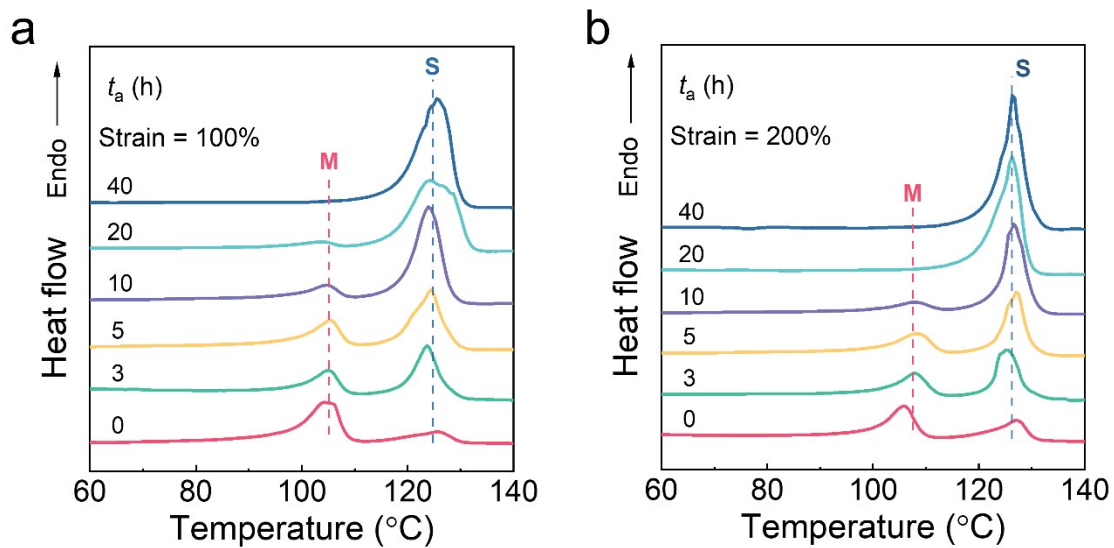


Fig. S3. Thermal behavior of stretched PB after annealing at 20 °C for various periods. DSC heating curves of the sample strained at (a) 100% and (b) 200%. The heating rates are 10 °C/min. Before annealing, the samples were initially melted at 140 °C for 5 min, and then stretched to a strain of 100% or 200% at 140 °C.

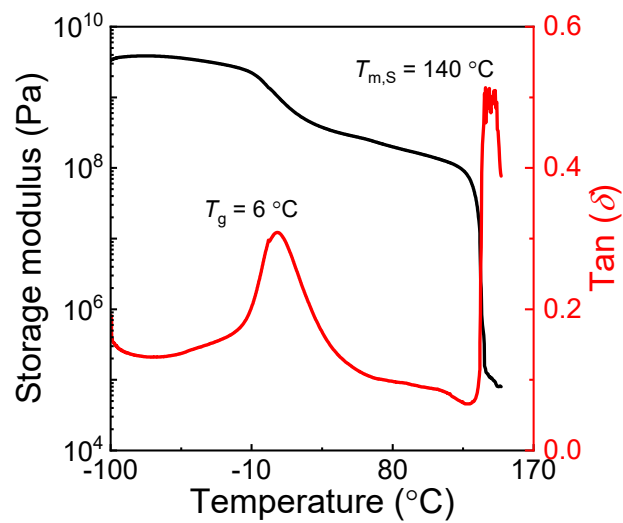


Fig. S4. DMA curve of the crosslinked PB that exclusively contains the S phase.

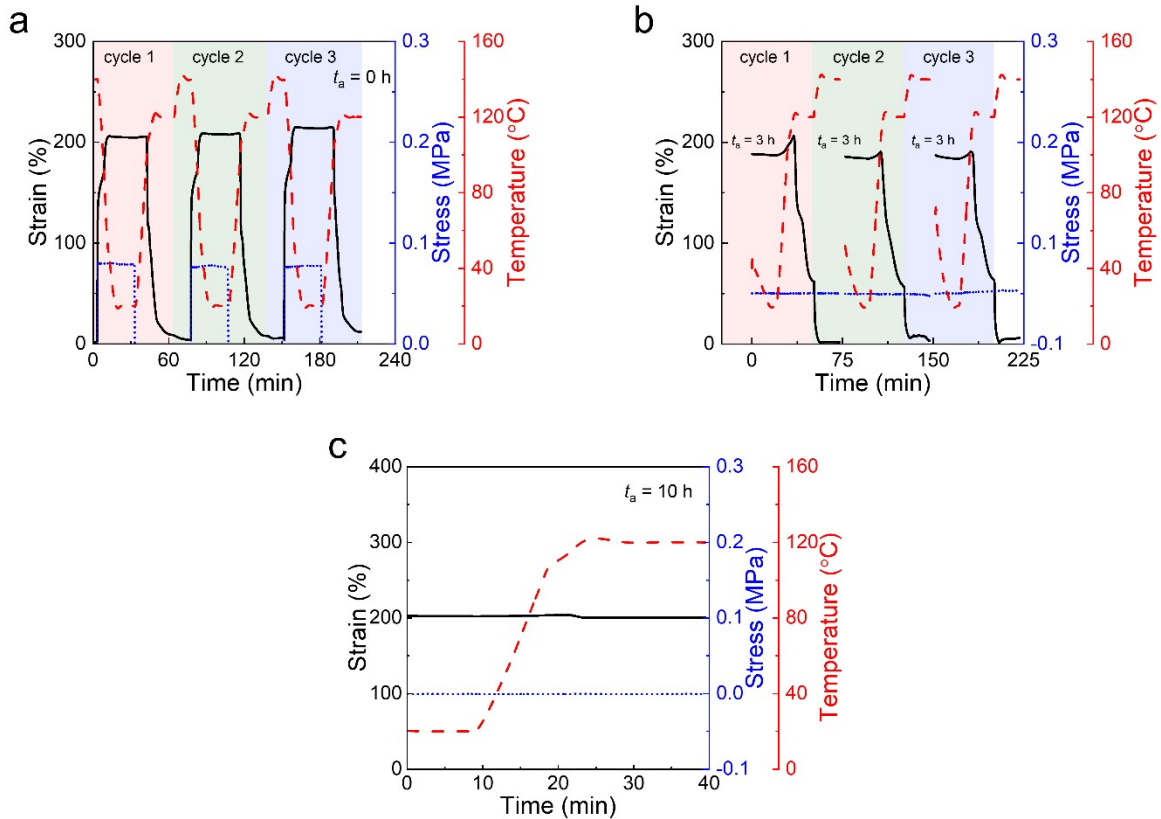


Fig. S5. The consecutive shape memory cycles of crosslinked PB after being annealed for different annealing time (t_a). (a) $t_a = 0$ h. (b) $t_a = 3$ h. (c) $t_a = 10$ h. The whole programming and recovering process of sample with $t_a = 0$ h was conducted by DMA. For samples with $t_a = 3$ h or 10 h, the programming process was carried out through the uniaxial stretching machine, and only the recovering process was tested by DMA considering the ultra-long operating time.

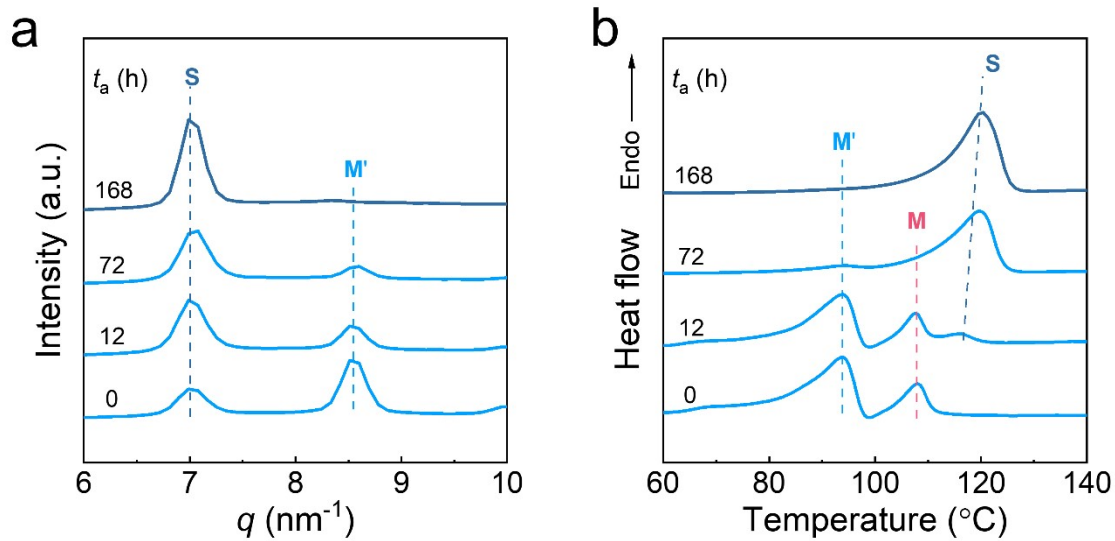


Fig. S6. Crystal phase change of crosslinked PB film with various t_a 's after being immersed in 50 °C THF for 5 min and further dried at 80 °C for 24 h. (a) WAXS profiles. (b) DSC curves recorded upon heating at 10 °C/min.

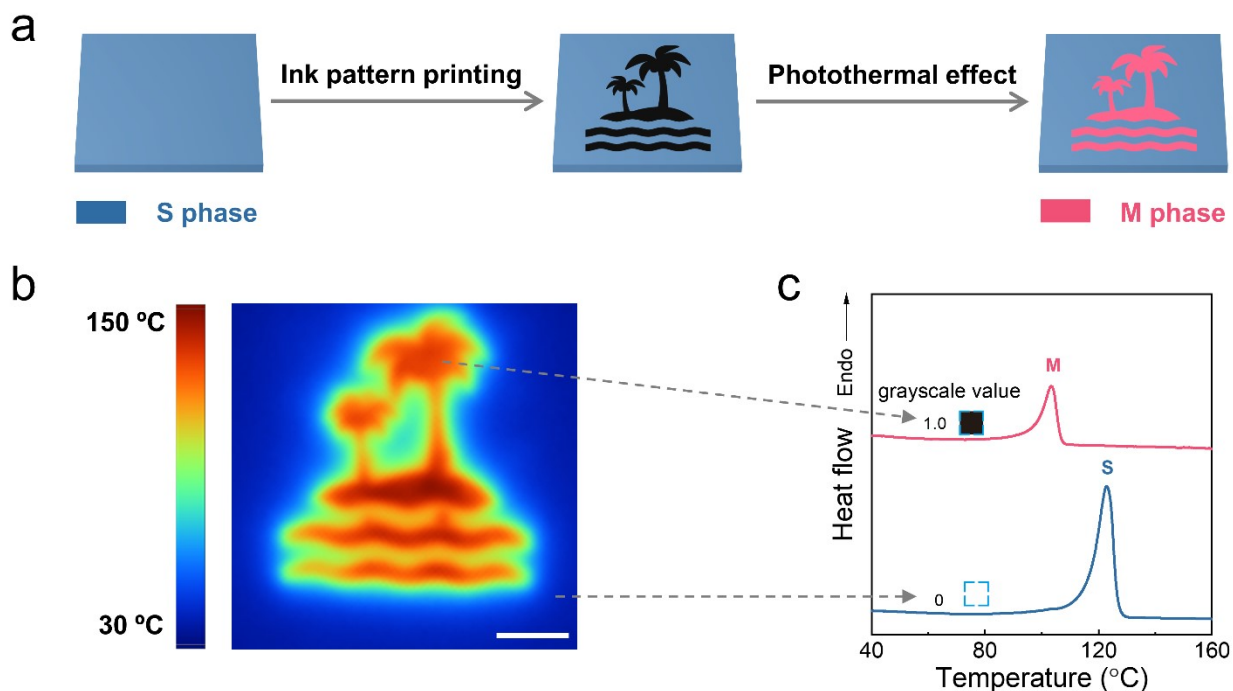


Fig. S7. Fabrication of crosslinked PB film with specific crystal patterns. (a) Crystal patterns written by ink printing and photothermal effect. (b) Infrared thermal images of the printed film after being exposed to infrared light. Scale: 5 mm. (c) DSC heating curves (heating rate: 10 °C/min) of the localized film samples with different ink grayscale values.

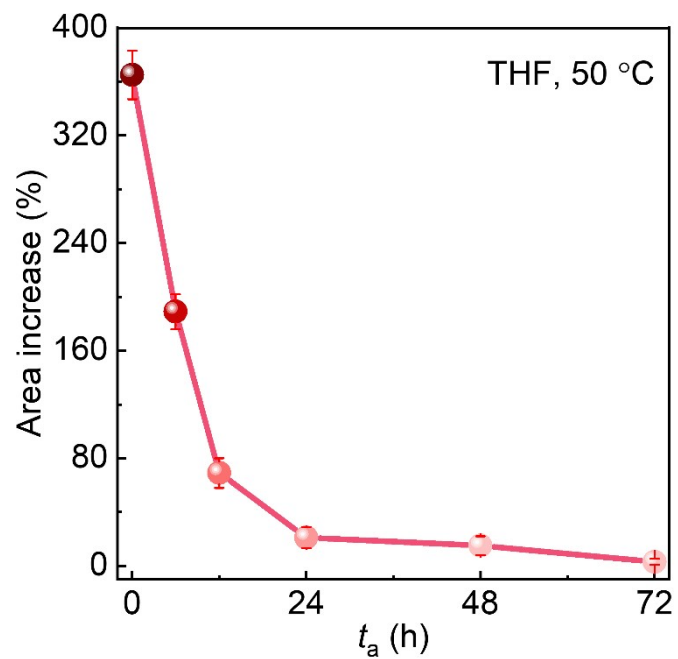


Fig. S8. Changes of film area with various t_a 's after being immersed in 50 °C THF for 5 min. The film area was normalized by that of the film with $t_a = 72$ h.

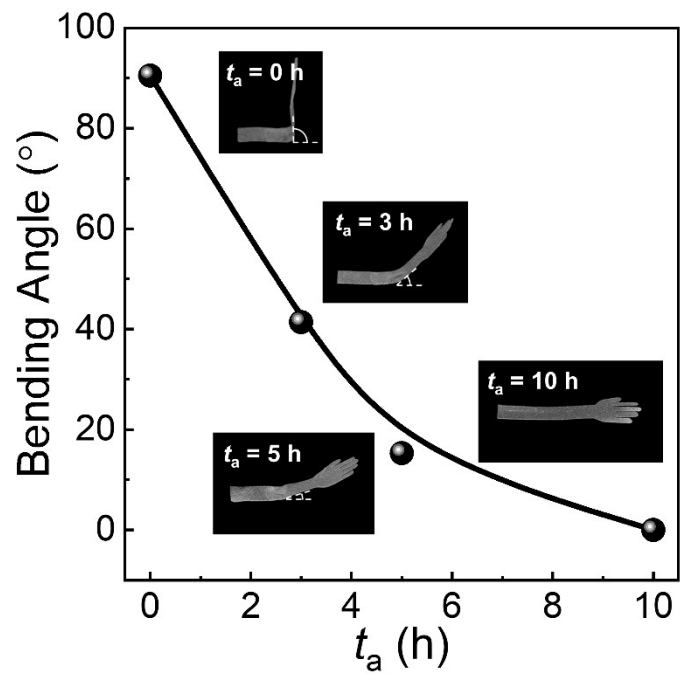


Fig. S9. Bending angles of self-evolving crosslinked PB arms after being annealed for various periods.

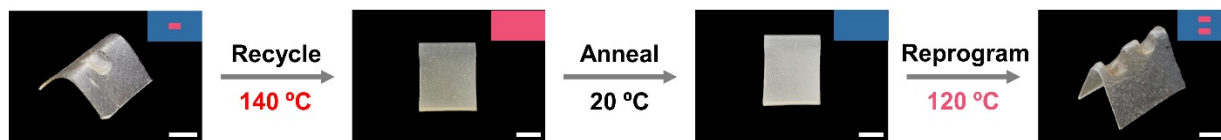


Fig. S10. Recycling and reprogramming of the self-evolving materials. Scale: 5 mm.

4. Supplementary Movies

Movie S1. Morphing of an arm-shaped film

This movie shows a morphing example of the arm-shaped film that was cut from the crosslinked PB film with a strain of 200%. Afterwards, M crystal phase was locally introduced to the selected joints using the ink printing technique. Bending at two joints was observed upon heating to 120 °C.

Movie S2. Morphing of rectangular films with various applied t_a 's

This movie shows four morphing examples of the rectangular films that were cut from the crosslinked PB film with a strain of 200%. M crystal phase was locally introduced to the selected area and the whole sample was then annealed for different t_a 's. The bending angles of rectangular films become smaller with prolonging t_a .

Movie S3. Complex movement of a “hand” enabled by different t_a 's of each finger

This movie shows a morphing example of the hand-like plastic film that was cut from the crosslinked PB film with a strain of 200%. M crystal phase was locally introduced to each finger and the whole sample was then annealed for different t_a 's. Complex movement is achieved when being heated to 120 °C.

5. Supplementary References

[1] Rubin, I. D. *J. Polym. Sci., Part B: Polym. Lett.* **1964**, 2, 747.

[2] Nakamura, K., Aoike, T., Usaka, K., Kanamoto, T. *Macromolecules* **1999**, 32, 4975.