

Supporting Information

Photo-induced Spatial Gradient Network for Shape Memory Polymer with Pattern-memorizing Surface

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1. Materials and Characterizations

Materials: Poly(styrene-block-butadiene-block-styrene) (SBS) (70 wt% PB block), 2-Methyl-4'-(methylthio)-2-morpholinopropiophenone (I907) were obtained from Sigma-Aldrich; (2-furanyl)methylmercaptan was purchased from Meryer Chemical Technology Co. Ltd (Shanghai, China); Maleic Anhydride, Triethylamine, were obtained from Adamas-Beta Co. Ltd. (Shanghai, China); 3-Bis(3-Aminopropyl)Tetramethyldisiloxane, Methane sulfonic acid were provided by TCI Chemical Co., Ltd.; Other chemicals were purchased from China National Pharmaceutical Group (Shanghai, China).

Characterizations: ¹H NMR spectra were recorded on a Varian Mercury Plus500 MHz instrument with tetramethylsilane (TMS) as the internal standard and chloroform-d (CDCl₃) as the solvents at the room temperature. UV-*vis* absorption spectrum was recorded via using TU-1091 spectrophotometer (Persee, China). FT-IR spectrum was obtained by using a Spectrum 100 Fourier transformation infrared absorption spectrometer (FT-IR, Nicolet IS10). Phase diagrams were tested by bio-fast scan atomic force microscope (AFM, Dimension Icon & FastScan Bio, Bruker, America). Observation of the surface morphology in situ was carried out by laser scanning confocal microscopy (LSCM, OLS5000, Olympus, Japan) and laser profile micrometer

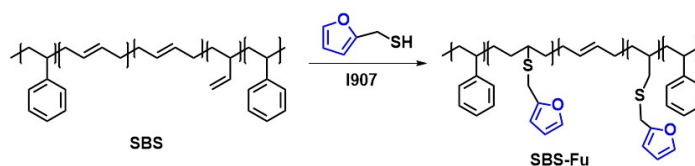
(VF-7510, Keyence, Japan). The tensile tests of the films performed on electronic universal material testing machine (Instron 3365, USA) at room temperature and the crosshead speed in the tensile and rebound experiments were 100 mm/min and 20 mm/min, respectively. Dumbbell specimens were with a width of 4 mm and length of 40 mm. The thickness of the samples was approximately 200 μm .

The UV light source is LED and the intensity of 365 nm UV light is 15 $\text{mW}\cdot\text{cm}^{-2}$. The photo-pictures of the samples were taken by mobile phone (HUAWEI P40, China).

2. Synthesis of Materials

2.1 Synthesis of furan-grafted SBS (SBS-Fu)

The procedure for synthesizing furan-grafted SBS (SBS-Fu) via the thiol-ene click reaction is performed according to the reported literature¹. As shown in **Scheme S1**, 4 g SBS, 0.6 g 2-furfurylthiol and 90 mg photoinitiator I907 were dissolved in 40 mL toluene. After being stirred for 1 h under nitrogen, the solution was irradiated with the 365 nm UV-light for 5 h at room temperature with stirring. After the reaction was complete, the mixture was precipitated in ethanol, filtered and then dried to obtain the furan-containing polymer SBS-Fu. A grafting rate of 12.5% was obtained from ¹H NMR spectrum. The structure of SBS-Fu was verified by ¹H NMR and FT-IR spectra in **Fig. S1 and S2**. ¹H NMR (500 MHz, CDCl₃, ppm): δ =7.36 (furan ring); 7.09-6.55 (benzene ring); 6.32-6.18 (furan ring); 5.62-4.98 (-CH=CH-); 3.72 (-CH₂-S-); 2.13-1.31 (-CH₂-, -CH-). FT-IR (KBr): 3075 cm^{-1} (=C-H, benzene ring); 2924 cm^{-1} , 2847 cm^{-1} (-CH₂-); 1643 cm^{-1} (C=C); 1236 cm^{-1} , 1147 cm^{-1} (C-O-C, furan ring).



Scheme S1 Synthesis route of SBS-Fu.

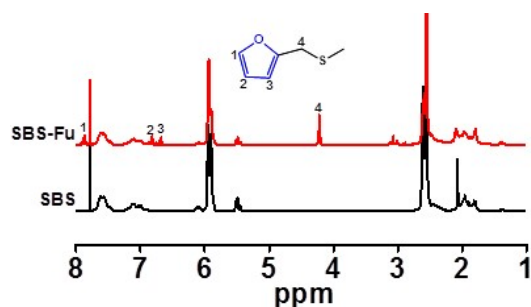


Fig. S1 ^1H NMR spectra of SBS-Fu and SBS in CDCl_3 .

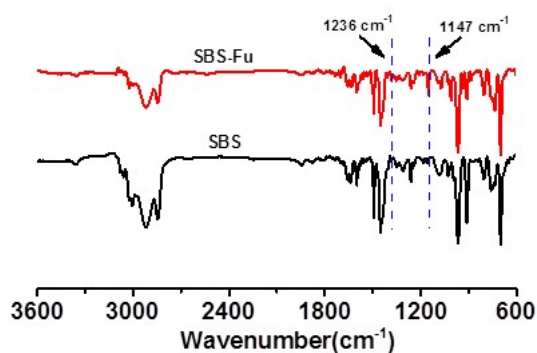
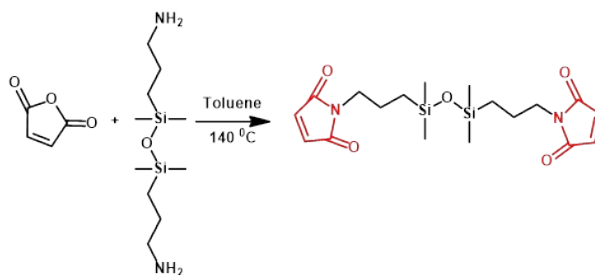


Fig. S2 FT-IR spectra of copolymer SBS-Fu and the raw material SBS.

2.2 Synthesis of silicone-based bismaleimide (DSi-BMI)

The procedure for synthesizing silicone-based bismaleimide (DSi-BMI) is performed according to the reported literature². As shown in **Scheme S2**, Triethylamine (10.58 g, 0.1 mol), methane sulfonic acid (10.1 g, 0.1 mol), maleic anhydride (10.26 g, 0.1 mol) and 3-Bis(3-Aminopropyl)Tetramethyldisiloxane (10 g, 0.04 mol) were mixed in toluene solution of 200 mL. After stirring for 3 h, a trace amount of p-tert-butylphenol was added into mixture. Then, the mixture was heated at 140 °C for 10 h with the azeotropic removal of water by a Dean-Stark trap. After the reaction was complete, the mixture was washed with 5 wt% sodium hydroxide solution and deionized water twice and then dried with anhydrous magnesium sulfate. Subsequently, the toluene solution was removed by evaporation to obtain the products DSi-BMI. ^1H NMR (500 MHz, CDCl_3): δ = 6.67(4H, -CH=CH-); 3.45 (4H, -CH₂-); 2.33(4H, -CH₂-); 1.56(4H, -CH₂-); 0.45(12H, -CH₃).



Scheme S2 Synthesis route of silicone-based bismaleimide (DSi-BMI)

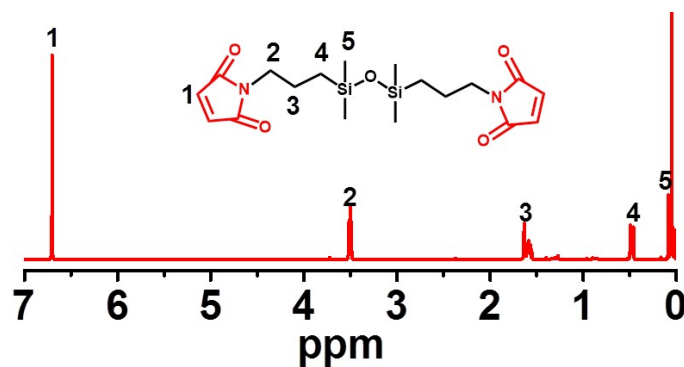


Fig.S3 ^1H NMR spectrum of silicone-based bismaleimide (DSi-BMI) in CDCl_3 .

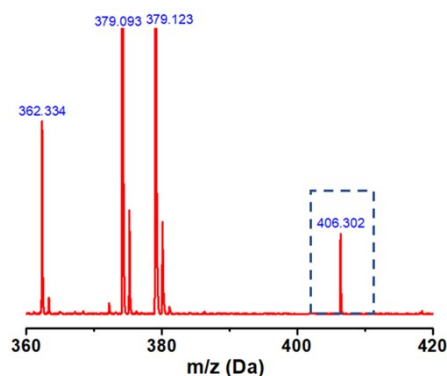


Fig.S4 Mass spectrometry of DSi-BMI in ethanol.

2.3 Preparation of SBS-based SMP with patterned surface

A toluene solution (10 mL) of SBS-Fu (1 g) and DSi-BMI (0.3 g) was poured into a square teflon mold with the size of $5 \times 5 \times 1$ cm. After standing for 12 h at room temperature, the film of SBS-Fu/DSi-BMI with average thickness of 200 μm was obtained, and then we cut it into a certain shape for standby. The prepared film was exposed to 365 nm UV light (15 mW cm^{-2}) using a photomask for a specific time to initiate the photodimerization of maleimide, resulting in the formation of micropattern on SMP surface. Standing for 10 h until the diffusion is completed, and then the exposed

film was heated at 50 °C for 20 min to trigger the D-A crosslinking reaction to form the spatial gradient network.

2.4 Preparation of thermal-induced shape reconfigurations of patterned film

The prepared film of SBS-Fu/DSi-BMI was exposed for a specific time under 365 nm UV-light with 200 μm striped mask of a certain angle during being stretched to 100% strain. Standing for 10 h until the diffusion is completed, and then the exposed and stretching film was heated at 50 °C for 20 min to trigger the D-A crosslinking reaction to form the spatial gradient network. The crosslinked film was heated for 5 min at 85 °C and cooling down to room temperature before releasing tension for fixing temporary shape. After being heated at 85 °C, the film of temporary shape would be curl to form 3D configurations. When the 3D shape film was heated at 125 °C for 20 min, it would recover to 2D pattern film as a new permanent shape due to the occurrence of inverse D-A decrosslinking reaction.

3. Results and discussion

3.1 The fabrication of diffusion micropattern on SMP surface

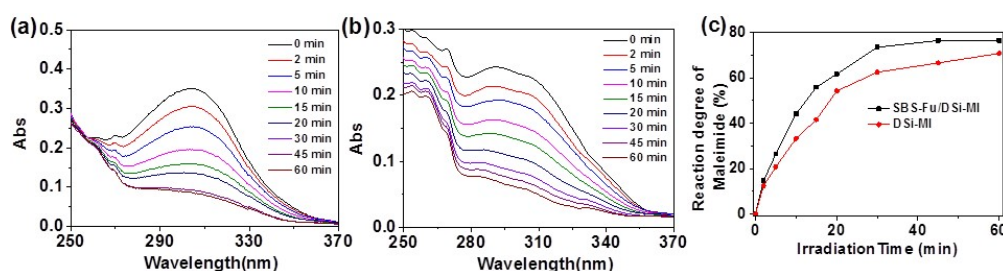


Fig. S5 The investigation of photodimerization of DSi-BMI kinetics by UV-vis spectra. (a) The evolution of UV-vis spectra of SBS-Fu and DSi-BMI system coated on a quartz plate under 365 nm UV-light; (b) The evolution of UV-vis spectra of photodimerization of DSi-BMI. (c) The conversion degree of DSi-BMI or SBS-Fu/DSi-BMI versus irradiation time determined by UV spectroscopy data. The evolution of the characteristic ultraviolet absorption peak at around 296 nm, typical for DSi-BMI, was chosen for conversion calculations of reaction degree of DSi-BMI.

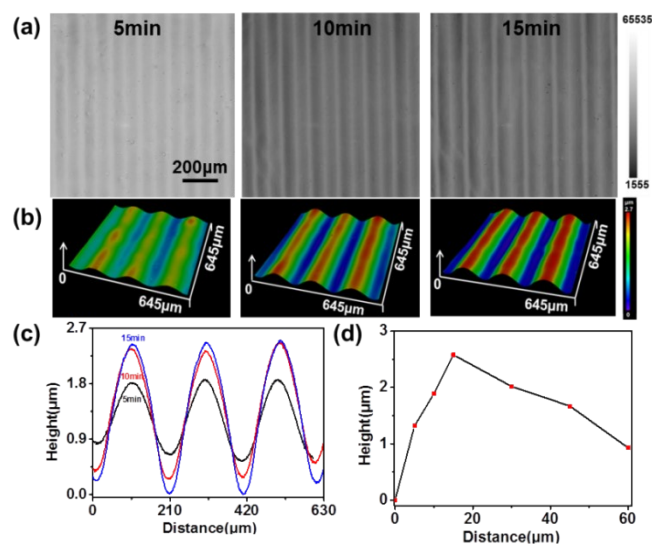


Fig. S6 Photo-induced growth of micropatterns on SMP surface. (a) Time-dependent 2D LSCM strength images of micropattern after UV illumination for 5 min, 10 min and 15 min with stripe mask (size: 100 μm); (b) 3D LSCM images of micropattern according to (a); (c) Typical profiles of grown micropattern under different UV irradiation time according to (b); (e) The average height variation of exposed region versus illumination time.

3.2 Diffusion pattern memory cycle based on spatial gradient crosslinking network

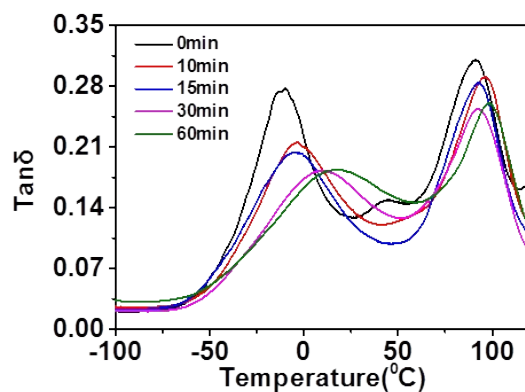


Fig. S7 Tan δ curves of SBS-Fu/DSi-BMI after UV illumination for 0 min, 10 min, 15 min, 30 min and 60 min.

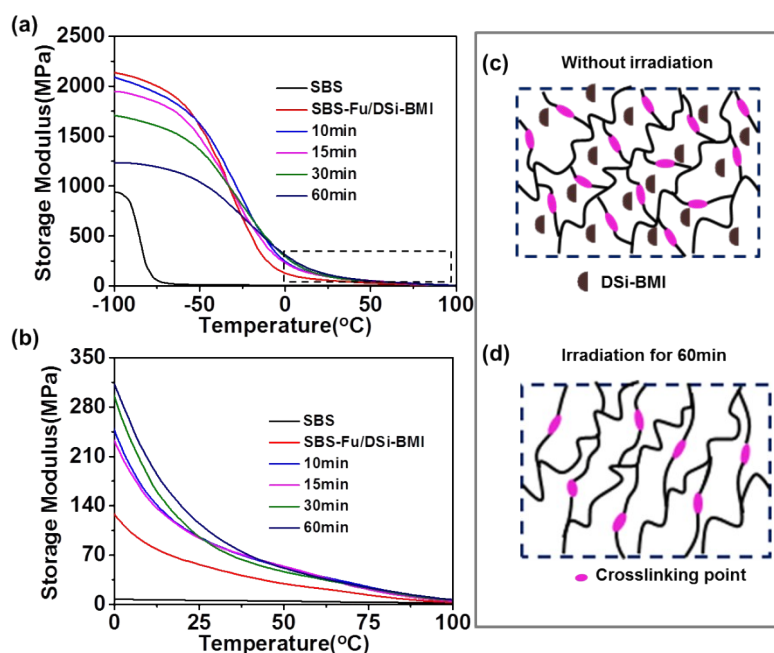


Fig. S8 Storage modulus of film. (a) Storage modulus curve of SBS and SBS-Fu/DSi-BMI after UV illumination for 0 min, 10 min, 15 min, 30 min and 60 min; (b) Storage modulus curve of enlarged view of the box marked in (a); (c, d) The schematic representation of polymer network on the film of SBS-Fu/DSi-BMI under without irradiation and irradiation for 60 min.

In order to deeply explore the mechanical properties of patterned films, the stress-strain curves of SBS-Fu/DSi-BMI under different exposure time were measured by universal tensile machine. As shown in **Fig. S9**, with the increase of illumination time, the breaking strength of the films increase gradually, as long with the decrease of elongation at break. Upon being exposed to UV-light for 15 min, the breaking strength of the film was 5.9 MPa with the elongation at break of 390.7%. This is because that, the rigidity of PB phase region increases gradually due to D-A crosslinking reaction with the increase of illumination time, resulting in the increase of breaking strength and the decrease of breaking elongation.

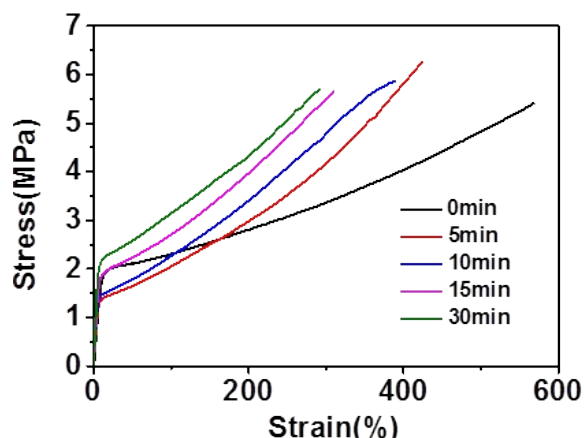


Fig. S9 Stress-strain curves of the patterned film obtained by the film composed of SBS-Fu/DSi-BMI being exposed for 0 min, 5 min, 10 min, 15 min and 30 min.

In order to explore the influence of DSi-BMI addition and patterned process on SBS phase structure, the micro-phase separation behavior was observed by AFM. **Fig.S10** shows the phase diagram of pure SBS, SBS-Fu, SBS-Fu/DSi-BMI and irradiated SBS-Fu/DSi-BMI films. The bright and dark area represents PS and PB phase, respectively. Compared with the bicontinuous phase of pure SBS, furan-grafted on PB phase can destroy the original interaction and form a new bicontinuous phase structure. After the addition of DSi-BMI, the D-A crosslinking reaction occurred in PB phase region, which limited the movement of molecular chain, resulting in the phase transition from bicontinuous to dispersed phase. When the film of SBS-Fu/DSi-BMI was exposed under 365 nm UV-light, some dots disperse in PB continuous phase. With the increase of irradiation time, the migration of a large number of molecules and D-A reaction make the dots dispersed in PB phase become a columnar structure in exposed region, but there is little change in the unexposed region (**Fig. S11**). Thus, different degree of D-A reaction between exposed and unexposed region due to photodimerization-induced diffusion, affect the size of phase region, resulting in the different shape memory effect.

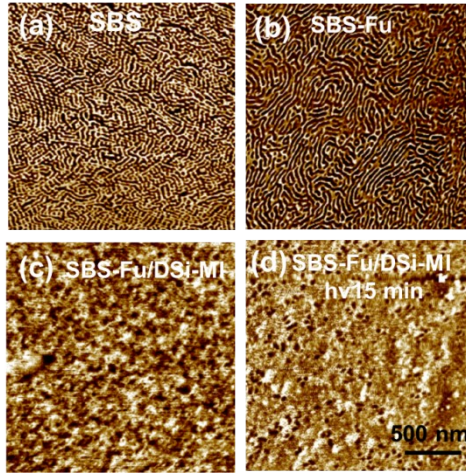


Fig. S10 AFM phase diagram of SBS, SBS-Fu, SBS-Fu/DSi-BMI and SBS-Fu/DSi-BMI irradiated for 15 min.

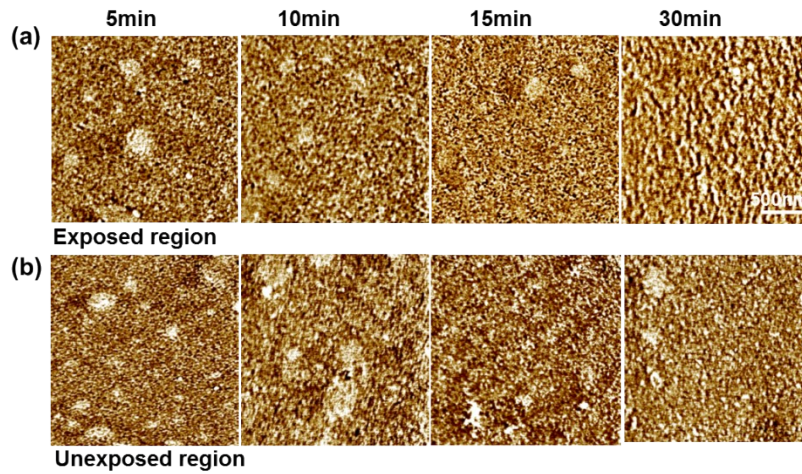


Fig. S11 The phase diagram of the exposed and unexposed region of the film under (a) 5 min, (b) 10 min, (c) 15 min and (d) 30 min illumination.

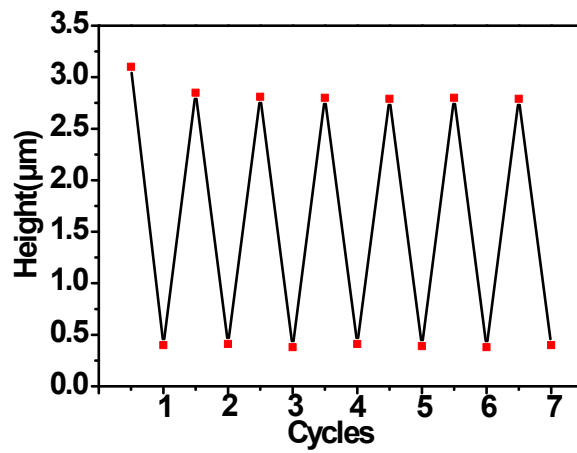


Fig.S12 The memory cycles of patterned height, showing that the recovery of structure after sequential hot-pressing and recovery at 85 °C.

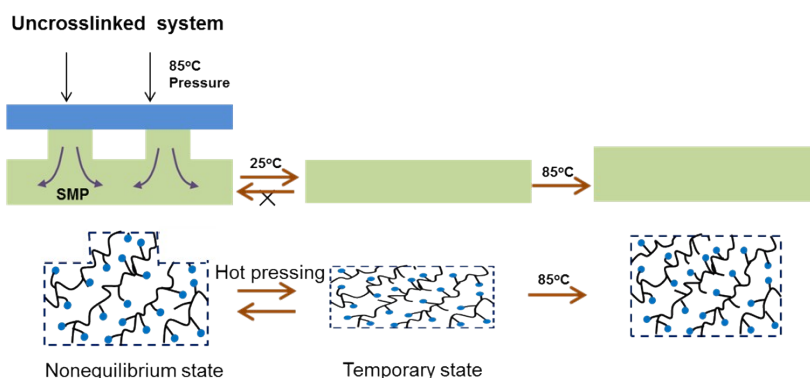


Fig. S13 Schematic illustration of the programming and recovery process of uncrosslinked patterned SMP and their network under mechanical loading traditionally.

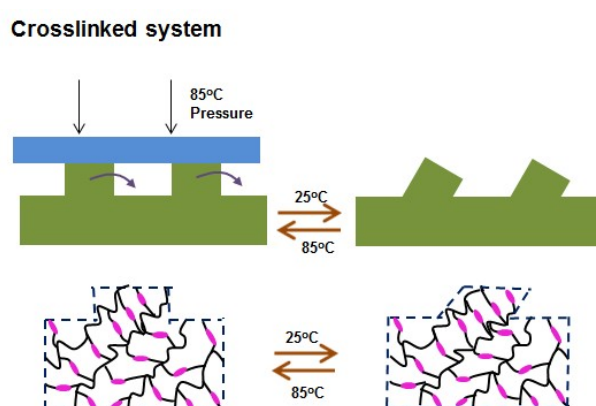


Fig. S14 Schematic illustration of the programming and recovery process of crosslinked SMP with pattern and their network under mechanical loading traditionally

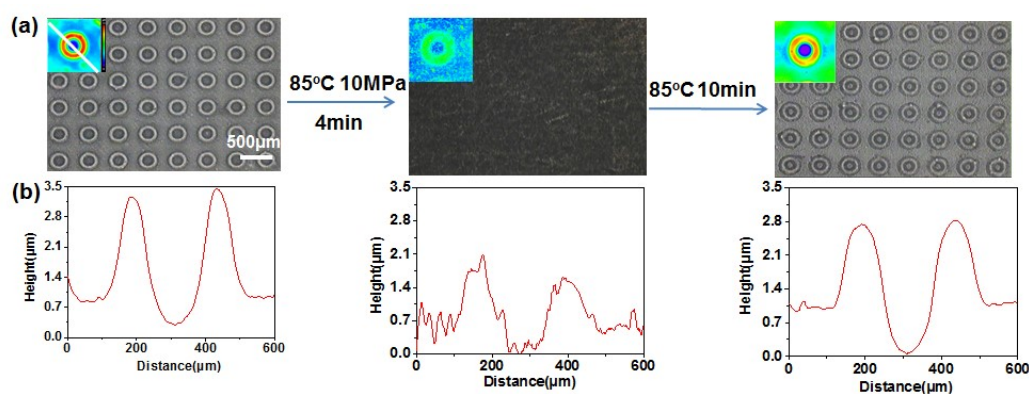


Fig. S15 Shape memory cycle of microstructures on SMP surface. (a,b) The optical and 2D LSCM images and corresponding height profiles of circular ring micropattern on SMP surface under compressing and heating. The initial circular ring micropattern was obtained by the film of SBS-Fu/DSi-BMI being exposed for 15 min under the ring mask of 100 (inner ring diameter of unexposed region)/50(width of the ring of exposed region)/100(spacing of unexposed region) μm .

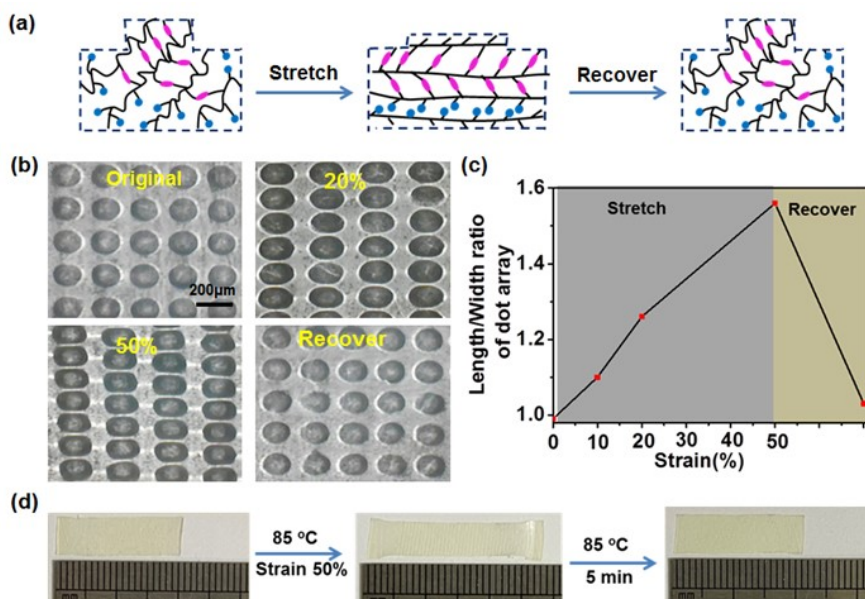


Fig. S16 Shape memory cycle of microstructure on SMP surface during stretching. (a) Schematic illustration of the changed polymer network during stretching and recovery; (b) The optical image of dot array micropattern of 100 μm on film surface under stretching and recovery; (c) variation of length/width ratio of dot array pattern under stretching and recovery; (d) the optical images of patterned film under stretching and heating. The initial micropattern was obtained by the film of SBS-Fu/DSi-BMI being exposed for 15 min under dot array mask of 100 μm.

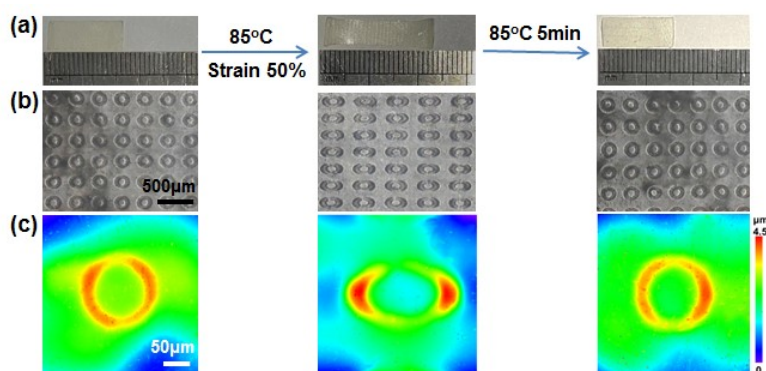


Fig. S17 Shape memory cycle of patterned film during stretching. (a) the optical image of patterned film under stretching and heating; (b) the optical image of the ring micropattern on film(a) surface under stretching and heating; (c) The 2D LSCM image of the ring micropattern on film(a) surface under stretching and heating; The initial circular ring micropattern was obtained by the film of SBS-Fu/DSi-BMI being exposed for 15 min under the ring mask of 100 (inner ring diameter of unexposed region)/50(width of the ring of exposed region)/100(spacing of unexposed region) μm.

3.3 Shape reconfiguration of SMP with patterned surface

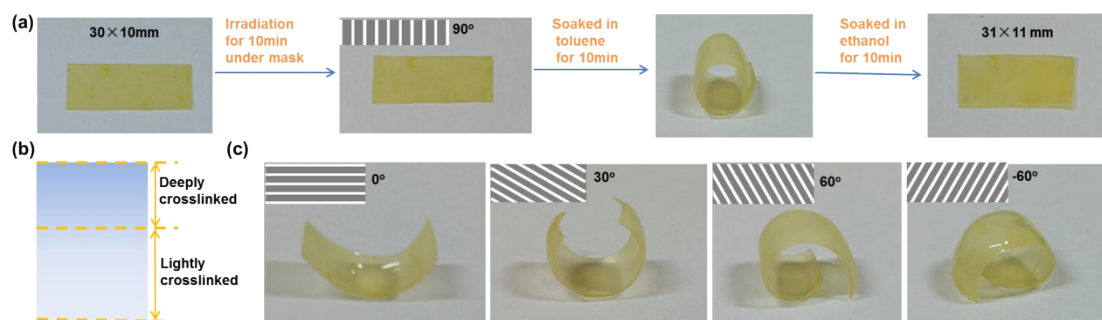


Fig. S18 Solvent-induced shape reconfiguration behavior of patterned film. (a) optical images of solvent-induced film deformation and recovery; (b) schematic illustration of crosslinking degree in exposed region of film; (c) optical images of solvent-induced film deformation. The film was irradiated for 15 min under 200 μm of striped mask having strip angles 90°, 0°, 30°, 60° and -60°, and soaked in toluene for 10 min(a, c), and then soaked in ethanol for 10 min(a). These samples are 10 mm in width and 30 mm in length.

References

1. J. Bai and Z. Shi, *ACS Appl. Mater. Interfaces*, 2017, **9**, 27213-27222.
2. T. Li, T. Ma, J. Li, S. Chen, X. Ma, J. Yin and X. Jiang, *Adv. Mater.*, 2021, **33**, 2007699.