

Supporting Information

Experimental section

Materials.

Poly(styrene-butadiene-styrene) (SBS, YH-792) was purchased from Sinopec Baling Petrochemical Co., Ltd (Hunan, China). Poly(tetramethylene glycol) (PTMG, $M_w = 250, 1000, 2000$) were purchased from Shanghai Macklin Biochemical Co., Ltd. Benzophenone (BP, 99.5%), rhodamine B (98%), NaCl (99%), and acrylylchloride (95%) were purchased from Adamas-Beta Reagent. Triethylamine (TEA), dichloromethane (DCM, 99%), methanol (99%), ethanol (99%), and acetone (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All reagents were used as received.

Synthesis of long-chain crosslinkers (PTMGDA).

To a 100-mL round-bottom flask in an ice-water bath, DCM (40 mL) and TEA (6.4 mL) were added with vigorous stirring by a magnetic stir bar under the protection of N_2 atmosphere. 4.0 g PTMG ($M_w = 2000$) was then dissolved in the solution of DCM. When the temperature inside the flask approached 0 °C, acryloyl chloride (4.2 mL) was slowly injected with a syringe. After adding all acryloyl chloride, the ice-water bath was removed and the mixture was stirred for 24 h at room temperature. The precipitates were washed with saturated NaCl solution and filtered with a Buchner funnel. The mixture solvents were separated by a separatory funnel, and the organic phase was collected. The product was obtained after removal of solvent with a rotary evaporator. The product of PTMGDA-2000 was yellow liquid at room temperature. PTMGDA-1000 and PTMGDA-250 were synthesized with a similar process.

Preparation of neat SBS film.

1.0 g of SBS was dissolved in 10 mL of DCM, and the mixture was vigorously stirred using a magnetic stir bar until the solid material was completely dissolved. A predetermined quantity of the solution was then applied to the surface of a glass template. Following a drying period of one hour at room temperature, the SBS film was formed and subsequently removed from the template for future use.

When preparing films of the same specifications, a fixed amount of solution was used for casting. For example, 3 mL of solution was used when casting films on a mold with dimensions of 7.5 cm × 2.5 cm, and 4 mL of solution was used when casting films on a mold with dimensions of 5 cm × 5 cm. The films had a uniform thickness after drying.

Unless otherwise specified, the standard thickness of SBS films is approximately 200 μm , and the length and width dimensions are cut according to the size required for testing.

Preparation of long-chain crosslinked SBS film.

1.0 g SBS was dissolved in 10 mL DCM. The mixture was stirred vigorously with a magnetic stir bar until the solid was completely dissolved. The solution was homogeneously mixed with initiator of BP (0.06 g, 0.33 mmol) and a long chain crosslinker of PTMGDA-2000 (0.06g, 0.03 mmol). The resulting mixture was cast onto a pre-cleaned glass slide, and dried in air at 60 °C for 60 min to give a long chain crosslinker-hybridized SBS film. The film was exposed to ultraviolet (UV) light ($\lambda = 365 \text{ nm}$) of 200 mW/cm² for 30 min to give a crosslinked SBS film (designated as C-SBS film). Unless otherwise specified, the standard thickness of C-SBS films is approximately 200 μm , and the length and width dimensions are cut according to the size required for testing.

Patterning of SBS film.

1.0 g of SBS was dissolved in 10 mL of DCM, and the mixture was vigorously stirred using a magnetic stir bar until the solid was completely dissolved. The solution was then homogeneously mixed with an initiator of BP (0.05 g, 0.275 mmol) and a long-chain crosslinker of PTMGDA-2000 (0.06g, 0.03 mmol). This mixture was also stirred vigorously until the solid was fully dissolved. Subsequently, the solution was cast onto a pre-prepared glass template and dried at room temperature for one hour to yield a PTMGDA-2000-hybridized SBS film. The film was then covered with a photomask and exposed to UV light ($\lambda=365 \text{ nm}$, and 200 mW/cm²) for 30 minutes under a nitrogen atmosphere to produce a surface-patterned film. Unless otherwise specified, the standard thickness of patterned films is approximately 200 μm , and the length and width dimensions are cut according to the size required for patterning and testing.

NMR spectroscopy.

The structural evaluation of the crosslinkers were characterized on AVANCE III 500MHz hydrogen nuclear magnetic resonance (¹H NMR) spectrometer (Bruker, Germany). 5 mg of PTMGDA-250, PTMGDA-1000, and PTMGDA-2000 were respectively dissolved in 0.6 mL deuterated chloroform (CDCl₃) for NMR measurement at 25 °C. To verify the interaction between SBS and acetone, 10 mg of SBS was dissolved in 0.6 mL CDCl₃. Add 50 μL of acetone to the system two times and perform NMR measurement respectively.

ATR-FTIR spectroscopy.

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Thermo Scientific Nicolet IS10 infrared spectrometer. Neat SBS and C-SBS films were directly measured at a range of 4000-550 cm^{-1} . All spectra were collected by 32 scans with a resolution of 4 cm^{-1} at room temperature.

UV-vis spectroscopy.

The absorption spectra were conducted on a UV-vis spectrophotometer (UV-2400, SDPTOP) to test the transmittance at a range of 300-700 nm at room temperature. The transparency of SBS and C-SBS films was obtained by subtracting the air background. The transparency of patterned films was obtained by subtracting the background of quartz cuvettes with acetone.

Tensile testing.

The tensile testing was performed using a tensile tester (HY-0580, manufactured by Shanghai Hengyi Test Instrument Co., Ltd.) at a stretching rate of 100 $\text{mm}\cdot\text{min}^{-1}$. For all tests, a 50.0 N load cell was employed. The specimen was securely mounted in the grips of the tensile tester. The test was initiated by gradually applying a tensile force, while the load and displacement were simultaneously recorded. The stress-strain curve was then generated by plotting the load against the extension of the specimen. The determination of toughness was achieved by calculating the area under the stress-strain curve. This area represents the total energy absorbed by the material during the testing process, which is a crucial indicator of the material's resistance to fracture. A larger area signifies greater toughness, indicating that the material can absorb more energy before breaking.

Refractive Index Testing.

The Abbe refractometer was used to test acetone, DCM. The SBS was dissolved in the solvent for testing and calculated through the mixed refractive index formula:

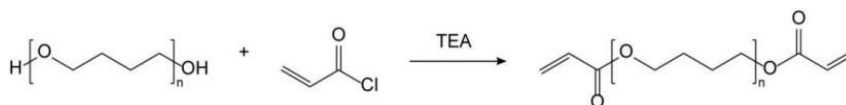
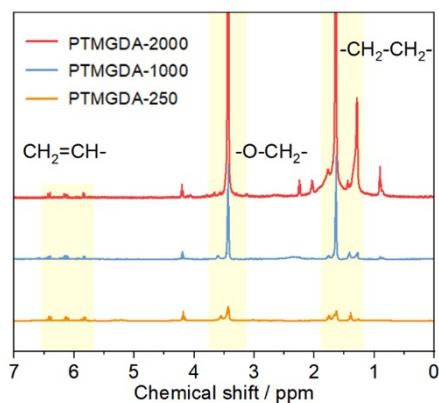
$$n = n_1V_1\% + n_2V_2\%$$

Table S1. Conditions for preparation of various C-SBS films

Sample	SBS (g)	PTMGDA-250 (g)	PTMGDA-1000 (g)	PTMGDA-2000 (g)	BP (g)	DCM (mL)
SBS	1.0	/	/	/	/	10.0
C(250)-SBS	1.0	0.01	/	/	0.06	10.0
C(1000)-SBS	1.0	/	0.03	/	0.06	10.0
C-SBS(2%)	1.0	/	/	0.02	0.02	10.0
C-SBS(4%)	1.0	/	/	0.04	0.04	10.0
C-SBS(6%)	1.0	/	/	0.06	0.06	10.0
C-SBS(10%)	1.0	/	/	0.10	0.10	10.0

Table S2. The refractive indices of DCM, acetone and the DCM solution of SBS.

Sample	Refractive index
DCM	1.427
Acetone	1.361
The DCM solution of SBS	1.503

**Fig.S1** Reaction route for the synthesis of long-chain crosslinker of PTMGDA.**Fig.S2** ^1H NMR spectra of PTMGDA-250, PTMGDA-1000, and PTMGDA-2000. The samples were tested in CDCl_3 .

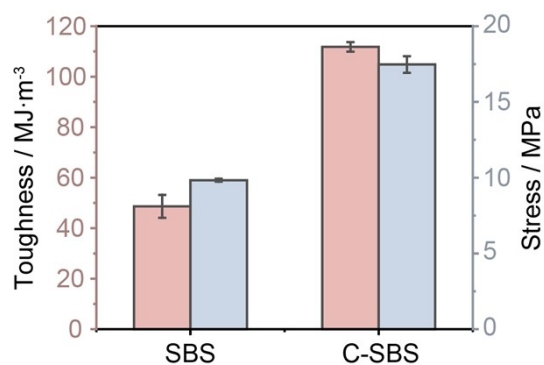


Fig.S3 Toughness and stress of SBS and C-SBS films. The toughness of SBS and C-SBS films was calculated from the area of the stress-strain curves. The toughness and stress of C-SBS are higher than those of neat SBS films.

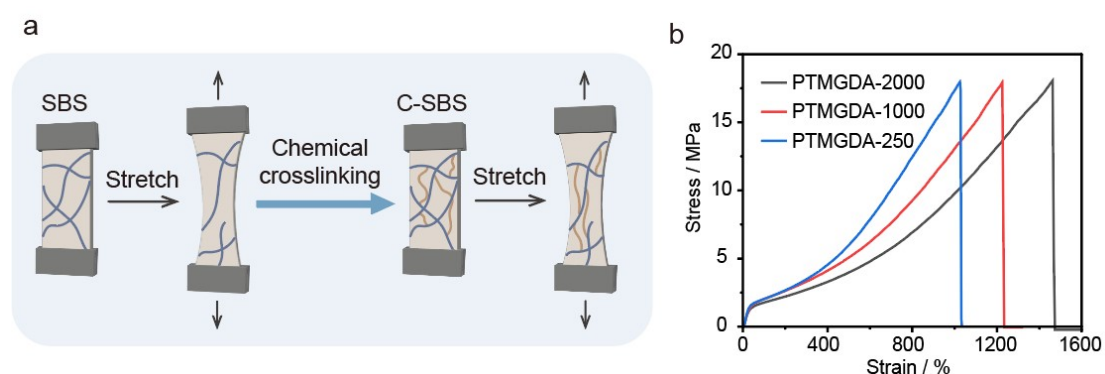


Fig.S4 (a) Schematic illustration of the molecular chain motion of SBS and C-SBS in response to external force. (b) Tensile stress-strain curves C-SBS films. The C-SBS films are prepared using crosslinkers with different chain length. The subscripts of PTMGDA-250, PTMGDA-1000, and PTMGDA-2000 represent the molecular weights of each crosslinker. The short-chain crosslinker of PTMGDA-250 increases the tensile strength, but decreasing the rupture strain in comparison with the neat film of SBS. As the chain length of the crosslinker used increases, the stretchability and toughness of C-SBS film also increase.

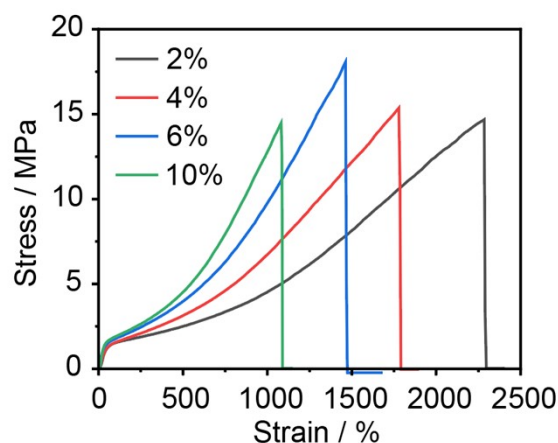


Fig.S5 Tensile stress-strain curves of C-SBS films. The films all use PTMGDA-2000 as crosslinker, and the weight ratio of PTMGDA-2000 to SBS is 2%, 4%, 6%, 10%. The tensile strength and Young's modulus of C-SBS increase with the increase of the amount of crosslinker. At the same time, the elongation at break has a certain decrease. When the ratio exceeds 10%, due to the excessively high crosslinking density, the toughness of the film becomes worse, and both the elongation at break and the strength decrease.

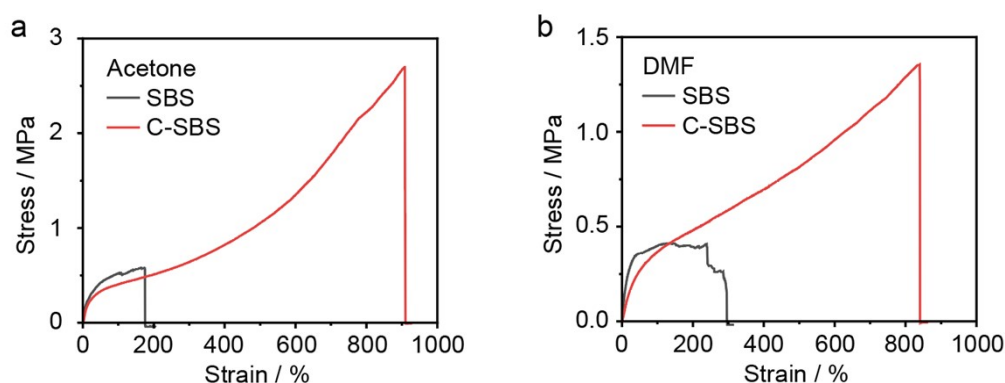


Fig.S6 Stress-strain curves of SBS films and C-SBS films after soaking in (a) acetone and (b) DMF for 20 min. The SBS and C-SBS films were immersed in acetone or DMF for 20 min. The solvent was then rapidly removed from the films. The mechanical properties were evaluated at room temperature on a tensile tester. After immersion in organic solvents, the elongation at break and tensile strength of C-SBS films are significantly higher than those of the SBS films, indicating that the crosslinking structure enhanced the stability and resistance of C-SBS films to organic solvent.

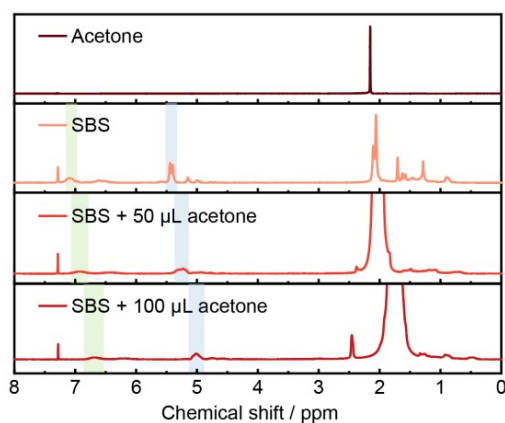


Fig.S7 The ^1H NMR spectra of acetone, SBS, and the mixture of SBS and acetone. The results showed that the peak of H on the benzene ring of SBS, which was originally located at 7.0-7.2 ppm, gradually shifted during the gradual addition of acetone. Meanwhile, the chemical signals of vinyl group of SBS shifted from 5.4 ppm to 5.0 ppm. Moreover, it changed from small and sharp splitting peaks to broad envelope peaks. The above phenomena have confirmed that acetone has a promoting effect on the aggregation of SBS molecules.



Fig.S8 Dye-staining experiments. The patterned film was immersed in acetone containing Rhodamine B. The pattern appears after 30 min of sorption of acetone. Upon drying, the non-crosslinking area is stained to become red, while the crosslinking area was not stained by dye.

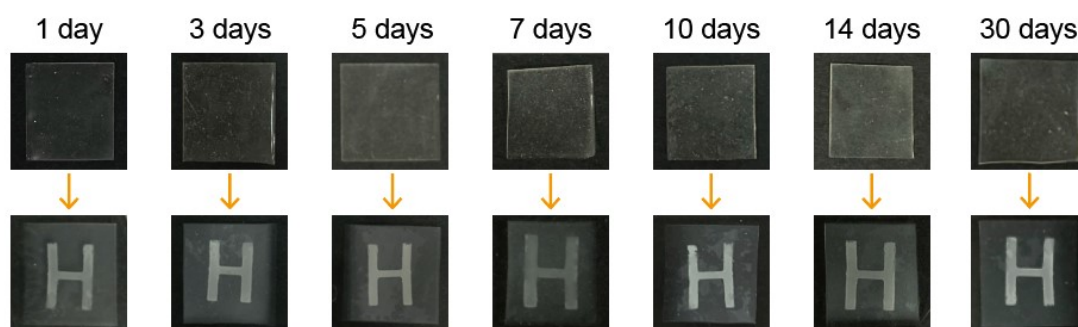


Fig.S9 Digital photos of the patterned films before and after being soaked in acetone. These films were placed under natural conditions for 1 day, 3 days, 5 days, 7 days, 10 days, 14 days and 30 days respectively.



Fig.S10 Digital photograph of cat-shaped patterned film, encrypted in DCM vapor. The sorption of DCM can accelerate the information encryption process to 1 min, which is much more rapid than the drying-induced information encryption.

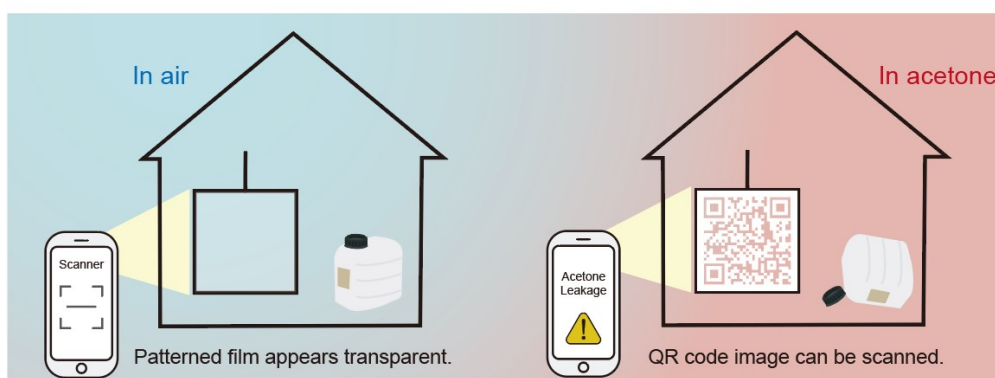


Fig.S11 Schematic diagram of a smart device for the detection of acetone vapor. A film is patterned with a QR code, which is fixed in a closed space. A smart phone is placed with the camera towards the QR code. When the QR code is invisible, indicating that the concentration of acetone vapor is at a normal value. Upon the concentration reaches a value that enables the decryption of the QR code, the camera would scan the QR code to show a text message of acetone leakage. The robust and elastic polymer films with superior patterning performance are expected to have potential application for information encryption and decryption.