

Supplementary Information

Sulfur-rich Polymers with Heating/UV Light-responsive Shape Memory and Temperature-modulated Self-healing

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Contents

Fig S1. Silver nitrate test paper before and after reaction.

Fig S2. ^1H NMR spectrum for the sample poly (S-St-DCPD)2 at different reaction time

Fig S3. ^1H NMR for samples of poly(S-St-DCPD)1-5

Fig S4. ^1H NMR of poly(S-DCPD) at different time

Fig S5. DSC for Poly (S-St) and Poly (S-DCPD)

Fig S6. Representative characterizations of Poly(S-St-DCPD)1-5.

Fig S7. poly (S-St-DCPD)5 shape memory behavior at 60°C.

Fig S8. Shape memory behavior of poly (S-St-DCPD)2 under shaded ultraviolet light irradiation.

Fig S9. a) shows the light transmission of poly (S-St-DCPD) 2. b) is poly (S-St-DCPD) 5 opaque.

Fig S10. Response temperature under different ratios.

Figure S11. a) The strain–stress curves of polymers. b) Stress-strain curve of polymer after self-healing.

Scheme S1 Structure deformation of polymer affected by heat/UV light.

Scheme S2. Sulfur, α -pinene dicyclopentadiene undergoes Inverse Vulcanization.

Fig S12. ^1H NMR spectrum of Poly (S- α -pinene - Dicyclopentadiene).

Fig S13. FTIR spectrum of Poly (S- α -pinene - Dicyclopentadiene).

Fig S14. Poly (S- α -pinene - Dicyclopentadiene) shape memory behavior at 20°C.

Fig S15. Shape memory behavior of Poly (S- α -pinene - Dicyclopentadiene) under ultraviolet light irradiation.

Scheme S3. Sulfur, 1,3-divinylbenzene, styrene Inverse Vulcanization.

Fig S16. ^1H NMR spectrum of Poly (S- Styrene -1,3-Divinylbenzene).

Fig S17. FTIR spectrum of Poly (S- Styrene -1,3-Divinylbenzene).

Fig S18. Poly (S- Styrene -1,3-Divinylbenzene) shape memory behavior at 40°C.

Fig S19. Shape memory behavior of Poly (S- Styrene -1,3-Divinylbenzene) under ultraviolet light irradiation.

Scheme S4. Sulfur, hexadecene, dicyclopentadiene Inverse Vulcanization.

Fig S20. ¹H NMR spectrum of Poly (S- Hexadecene- Dicyclopentadiene).

Fig S21. FTIR spectrum of Poly (S- Hexadecene- Dicyclopentadiene).

Fig S22. Poly (S- Hexadecene- Dicyclopentadiene) shape memory behavior at 30°C.

Chemicals and materials

Dicyclopentadiene,99.0%; Zinc diethyldithiocarbamate 99.0%; α -pinene, AR; Hexadecene, AR; 1,3-Divinylbenzene, 99.0%; Xylene,90.0%, purchased from Energy chemical, used directly without any further purification. Sulfur ,99%; Styrene , AR,

purchased from Beijing Chemical Plant, used directly without any further purification as well.

Materials and methods

Poly (S-St-DCPD)1: Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (1.35 g) and DCPD (0.15 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis (%): C: 28.93,H: 2.40,S: 67.34. yield: 3.93g (98%).

Poly (S-St-DCPD)2: Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (1.2 g) and DCPD (0.3 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis (%): C: 30.71,H: 2.54,S: 65.72. yield: 3.95g (99%).

Poly (S-St-DCPD)3: Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (1.0 g) and DCPD (0.5 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis (%): C: 31.95,H: 2.67,S: 64.13. yield: 3.95g (99%).

Poly (S-St-DCPD)4: Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (0.8 g) and DCPD (0.7 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis(%): C: 33.38,H: 2.67,S: 62.56. yield: 3.97g (99%).

Poly (S-St-DCPD)5: Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg,

1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (0.6 g) and DCPD (0.9 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis(%): C: 33.66,H: 3.12,S: 62.27. yield: 3.98 g (> 99%).

Poly (S-St): Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (1.5 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis(%): C: 18.86,H: 1.76,S: 78.24. yield: 3.88 g (97%).

Poly (S-DCPD): Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then DCPD (1.5 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product. Elemental analysis(%): C: 34.72,H: 3.20,S: 61.65. yield: 3.96 g (99%).

Poly (S-alpha-pinene-DCPD): Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then alpha-pinene (0.9 g) and DCPD (0.6 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product.

Poly (S-Styrene-1, 3-Divinylbenzene): Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (1.2 g) and 1,3-Divinylbenzene (0.3 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room

temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product.

Poly(S-Hexadecene-DCPD): Elemental sulfur (2.5 g) and dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then Hexadecene (0.6 g) and DCPD (0.9 g) were added and the mixture was stirred at the same temperature for 30 min. The resulted polymer poured into silicone mould while it was still hot and cured in an preheated oven at 130 °C for 12 h. After cooling down to room temperature, the resulted polymer was taken out the oven, washed with distilled water, and dried in the air as the final product.

Characterization methods

¹H NMR analysis: use Bruker AM 600 M nuclear magnetic resonance instrument, produced by Bruker Company in the United States, use DMSO and DCl₃ as solvent, and the sample concentration is 1 g·L⁻¹. FTIR analysis: Use Digilab Merlin FTS 3000 FTIR from the United States. XRD analysis: Rigaku D/Max-2400 XRD ray scanner, scanning angle: 5°-90°. CHNS elemental analysis: it was determined by Elementar UNICUBE organic element Analyzer (EA) in Germany, DSC analysis: use NETZSCH TA differential scanning calorimeter, nitrogen atmosphere, heating rate 10°C/min, test temperature -50°C-150°C, sample weight 0.05 g. TGA analysis: use Seiko EXSTAR 7200 TGA/DTA instrument. Thermal scans were conducted on 3-5 mg samples under nitrogen atmosphere. All samples were heated from 25 °C to 800 °C at a standard rate of 10 °C min⁻¹. Mechanical test : Suzhou Shimadzu AGS-X mechanical tester was used to test the tensile property and Young's modulus, according to the national standard GB228-76, the standard sample is made, and the sample is tested between the testing machine.

Experimental for the H₂S gas determination Hot press

Experimental process: Elemental sulfur (2.5 g) either with or without dihexyl zinc dithioformate (25 mg, 1 wt%) were added into a round bottom flask, the mixture was then stirred at 140 °C until a homogeneous solution formed. Then styrene (0.6 g) and DCPD (0.9 g) were added and the mixture, before sealing the flask with a rubber septum connected to an outlet tube. The outlet of the tube was placed to flow over silver nitrate paper, and the reaction continued at the same temperature for 30 min. The generation of H₂S gas is determined by observing the discoloration of the test paper. The experimental results are shown in Figure 1 below.

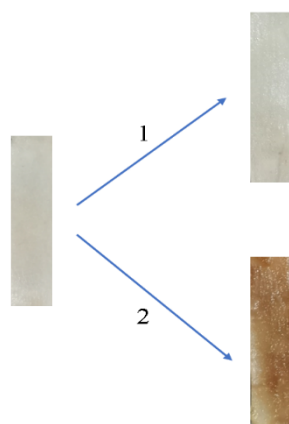


Figure S1 Silver nitrate test paper before and after reaction (1. 1 wt. % $\text{Zn}(\text{DTC})_2$ catalyst, 2. Without catalyst)

Figure S1 photos of the silver nitrate test paper before and after the reaction. 1 is the color of the test paper after the catalyst is added, and it can be seen that only less H_2S gas is produced by the color of the test paper; 2 is the color of the test paper after the reaction without catalyst.

The detection of CPD during the polymerization with DCPD

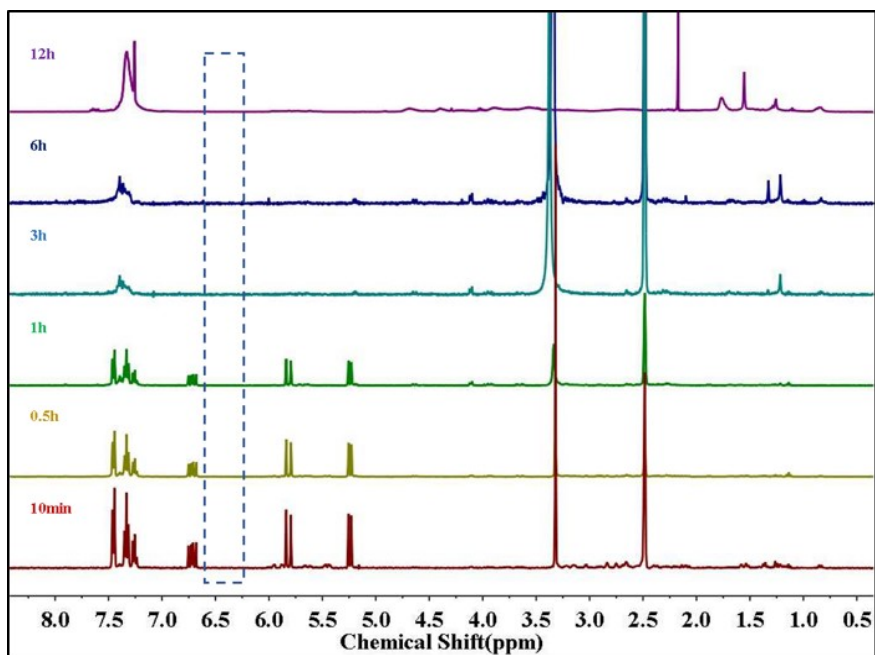


Figure S2. ^1H NMR of poly(S-St-DCPD)₂ at different reaction time

The reaction was carried out under the standard conditions in current research. As shown in Figure S2, both Styrene and DCPD were fully converted into the polymer in 3 h reaction time. However, there is no identical peaks, normally should be at 6.25-6.60 ppm, for CPD observed during the entire reaction time from 10 min to 3 h, and even in a prolonged reaction time of 6 and 12 h. This observation indicated that there was little decomposition of DCPD into CPD under the current reaction conditions.

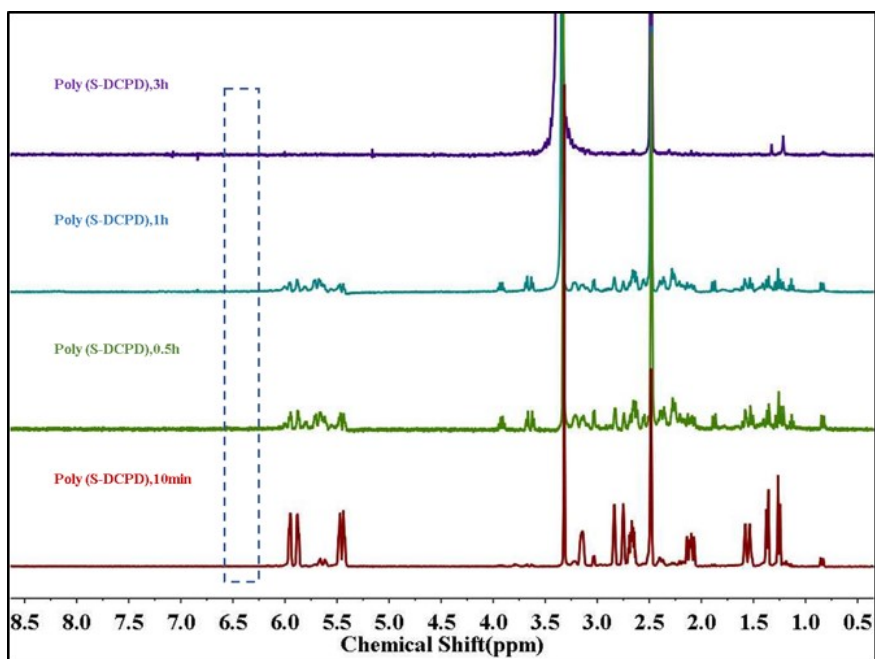


Figure S3. ¹H NMR of poly(S-DCPD) at different reaction time

The ¹H NMR of poly(S-DCPD) at the different time under the same reaction conditions in this work. No CPD peaks were observed during the polymerization.

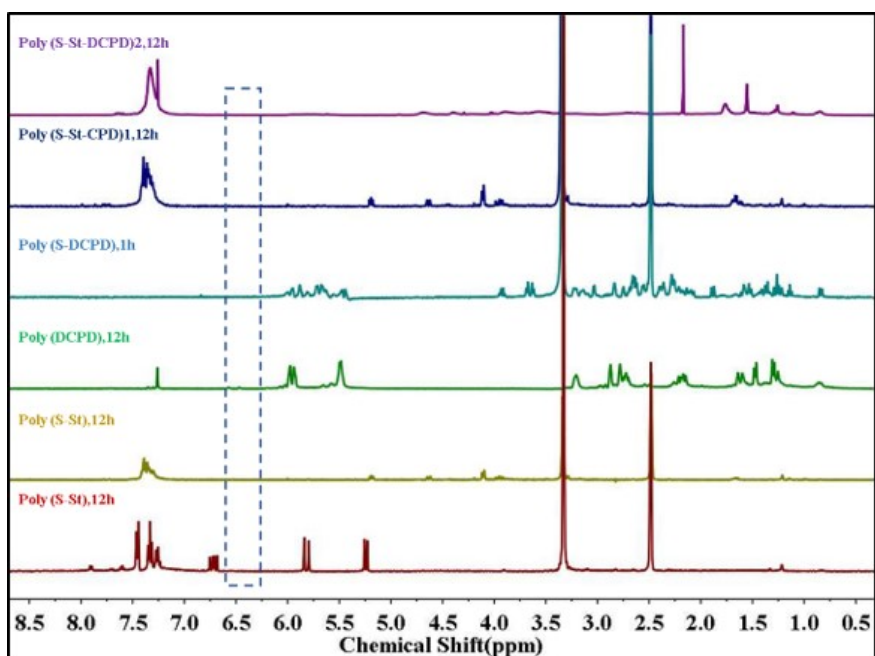


Figure S4. Comparison of ¹H NMR of different polymers at different reaction time.

Compared three different polymers and their reaction at different reaction time, there were no CPD observed for all the polymerization with S8 involved. The decomposition of DCPD into CPD was only observed in the DCPD self-polymerization in 12 h, with around 1.5% CPD peaks in the NMR at 6.25 -6.50 ppm appeared.

Hot press

The obtained polymer at 200 °C, 10 MPa for half an hour, and finally the polymer film.

Shape memory behavior based on thermoelasticity^[1, 2]

The polymer film is cut into strips and folded into a u-shape at 40°C. Then, the u-shaped sample was cooled at -40 °C for 90 minutes to fix its shape. Subsequently, observe whether the u-shaped sample can be restored to its original shape at different temperatures.

Based on light-induced shape memory behavior^[2, 3]

The polymer film is folded into a u-shape, irradiated under ultraviolet rays, and then cooled at -40 °C for 90 minutes to fix the shape. Then put the sample in the oven and record the recovery process.

Gel amount

$$Gelamount (\%) = \left[1 - \frac{q_3 - q_4 - q_0}{q_2 - q_1} \right] \times 100\%$$

q_0 is the quality of the filter paper soxhlet backflow loss, q_1 is the quality of the iron wire. q_2 is the quality of the iron wire and the sample package, q_3 is the quality of the sample package, and q_4 is the mass of the sample package after Soxhlet extraction and drying in an oven at 50 °C.

Sample Preparation

The sample was cut into small slices about 1mm in size within 5mm×5mm. The mass of the sample was between 2.00 g-3.00 g, xylene used as the extractant.

Measurement process

The sample was cut into small pieces, and the filter papers and iron wire were dried in the oven for 6 hours (50°C) prior to use, then cooled down in another drying oven for later use. After accurately weigh out the sample (0.20000 g - 0.30000 g), the sample was wrapped with filter paper, subsequently tightened with iron wire; the mass of the obtained sample package was accurately weighed out. The sample package was then Soxhlet extracted with xylene for 24 hours at 200 °C. After cooled down to room temperature, the sample package was dried in a vacuum oven overnight. The mass of the sample, sample pack, filter paper, and iron wire were measured after Soxhlet extraction, respectively.

Characterization

It can be seen from the above table that as the ratio of diolefin increases, the gel amount of the polymer will also increase; the increase in the degree of crosslinking will result in an increase in the T_g of polymers with a high ratio of diolefins. This is also the reason why reverse vulcanization polymers with different response temperatures can be produced.

Table S1 Gel content in different proportions

Entry	Sample name	Gel amount (%)
1	Poly (S-St-DCPD)1	10.85
2	Poly (S-St-DCPD)2	18.33
3	Poly (S-St-DCPD)3	37.40
4	Poly (S-St-DCPD)4	41.01
5	Poly (S-St-DCPD)5	42.45
6	poly(S-St)	0.00
7	poly(S-DCPD)	75.80

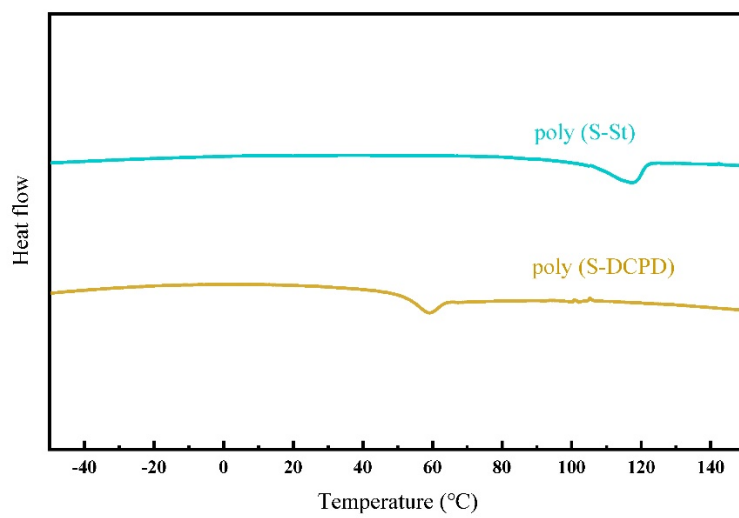


Figure S5. DSC for Poly (S-St and Poly (S-DCPD).

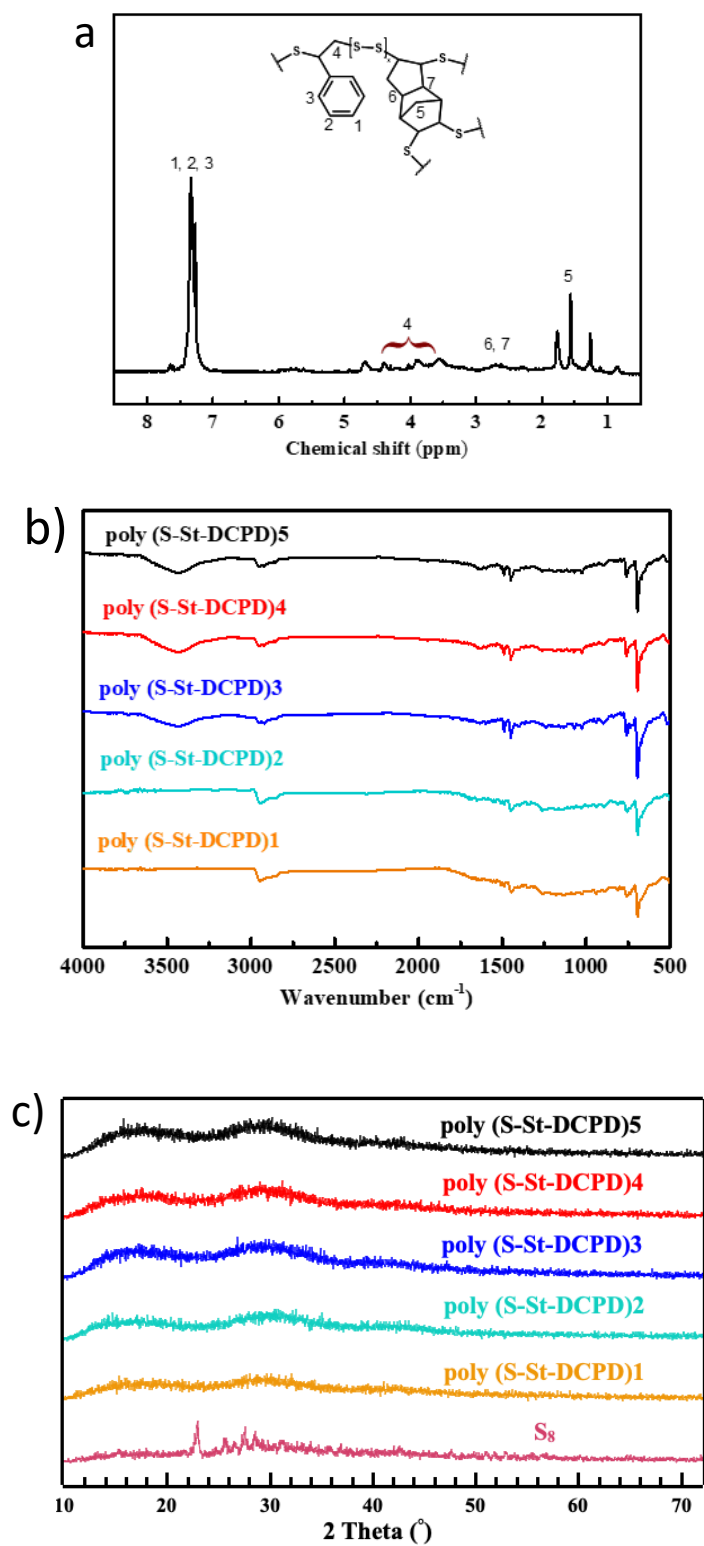


Figure S6. Representative spectra for the characterizations of resultant Poly(S-St-DCPD)1-5. ^1H NMR (a), FTIR (b), and PXRD (c).

performance

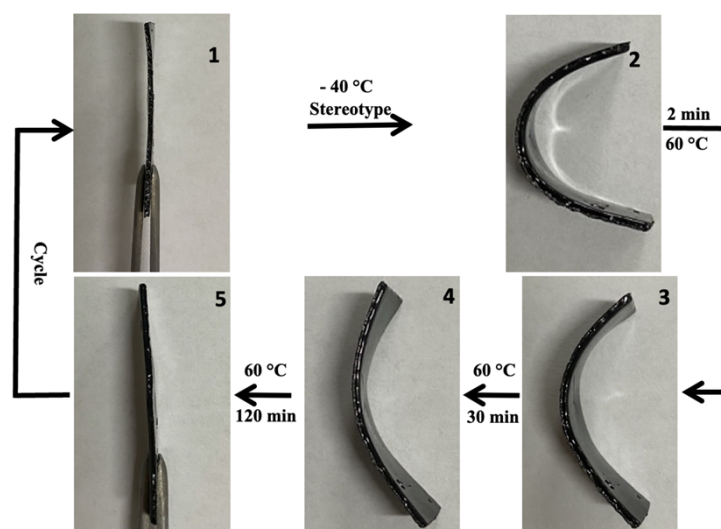


Figure S7. poly (S-St-DCPD)5 shape memory behavior at 60°C

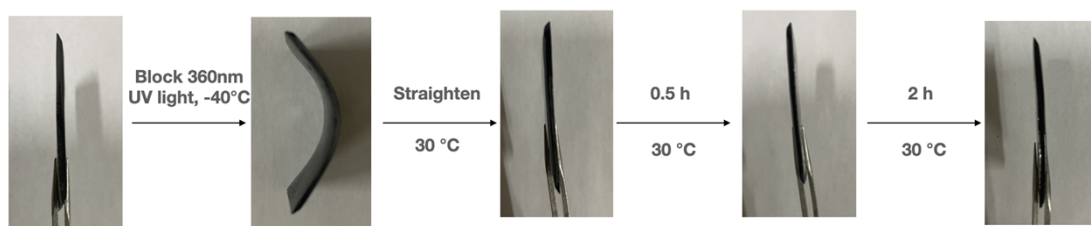


Figure S8. Shape memory behavior of poly (S-St-DCPD)2 under shaded ultraviolet light irradiation

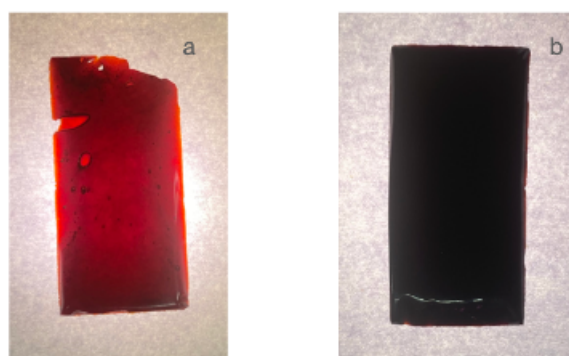


Figure S9 a) shows the light transmission of poly (S-St-DCPD) 2. b) is poly (S-St-DCPD) 5 opaque.

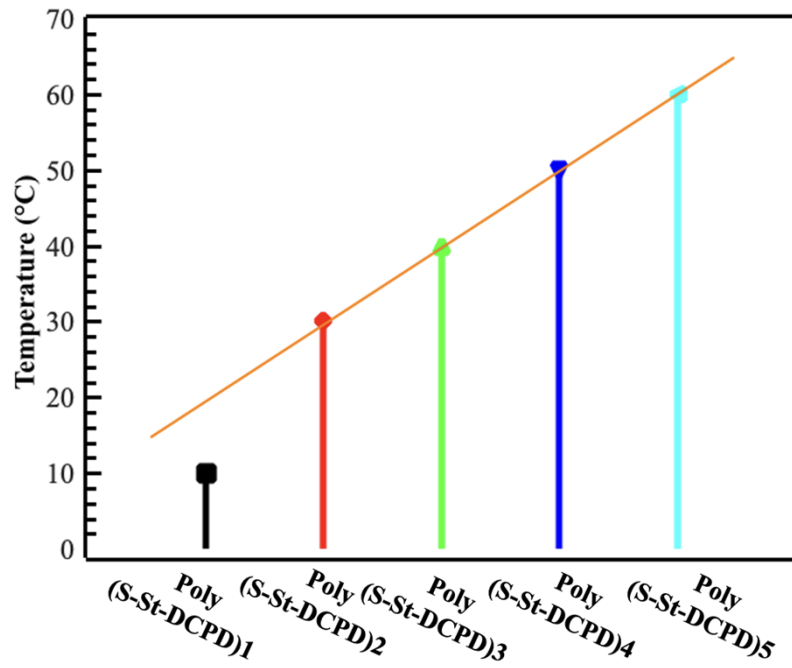


Figure S10. Response temperature under different ratios. The response temperature was defined as the lowest temperature at which the material starts showing shape memory. The speed to the shape memory effect was set to 30 min recovery of the original shape with heating.

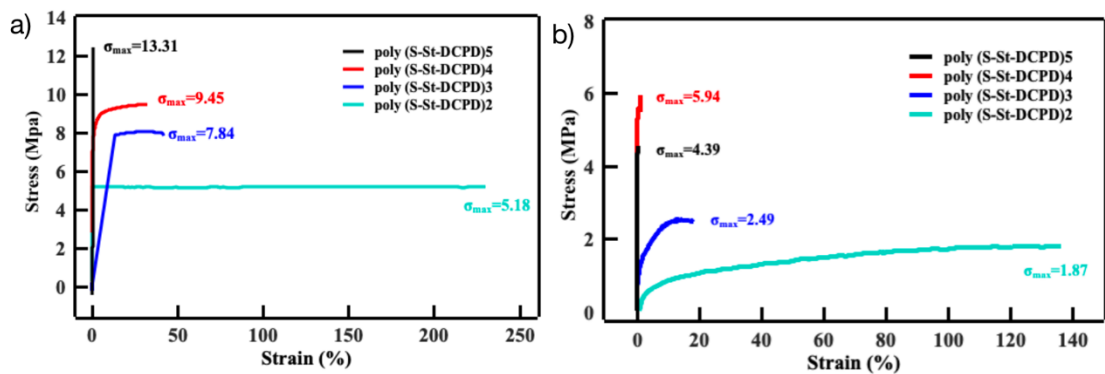
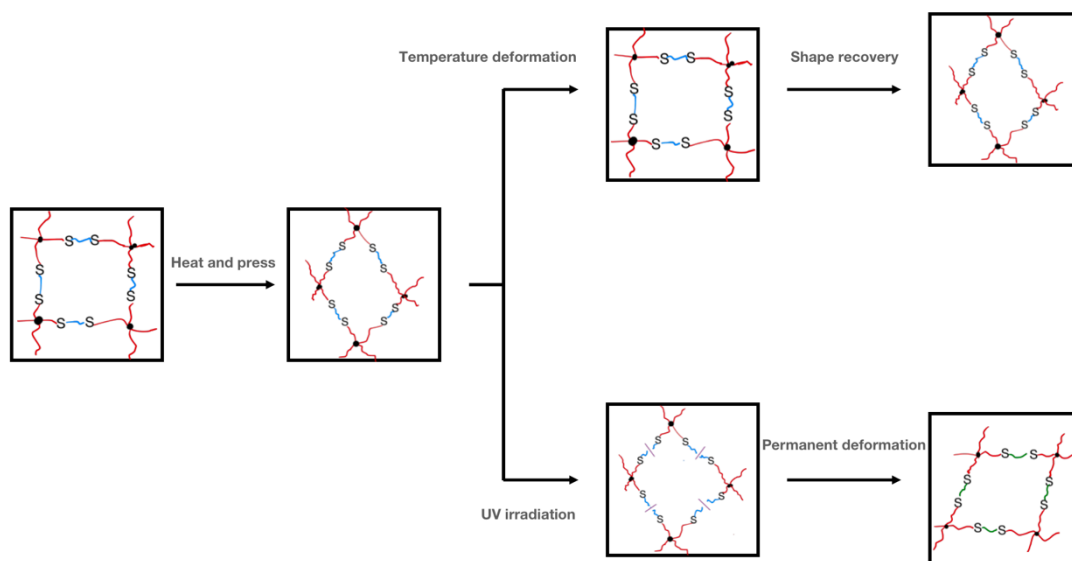


Figure S11. a) The strain–stress curves of polymers. b) Stress-strain curve of polymer after self-healing.

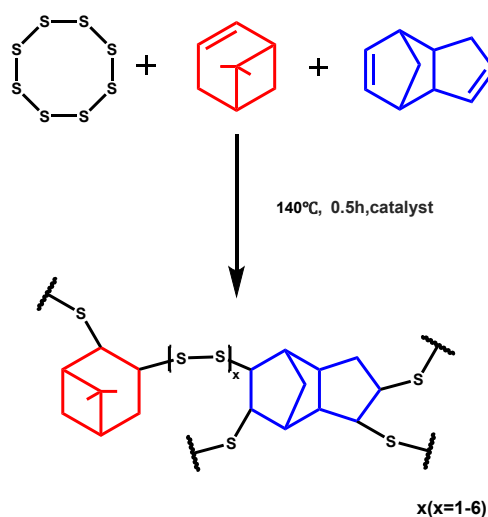


Scheme S1. Structure deformation of polymer affected by heat/UV light

The preparation, characterization and performance of the series S-rich polymers

1. Sulfur, α -pinene, dicyclopentadiene Proportion (2.5/0.9/0.6) :

Using sulfur, α -pinene, and dicyclopentadiene as raw materials for copolymerization, the reverse vulcanization sulfur polymer was synthesized, as shown in the figure:



Scheme S2. Sulfur, α -pinene dicyclopentadiene undergoes Inverse Vulcanization

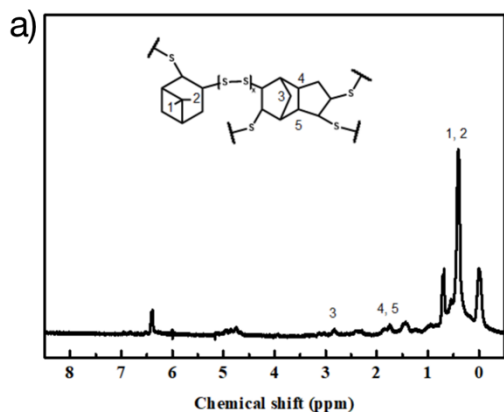


Figure S12. ^1H NMR spectrum of Poly (S- α -pinene - Dicyclopentadiene)

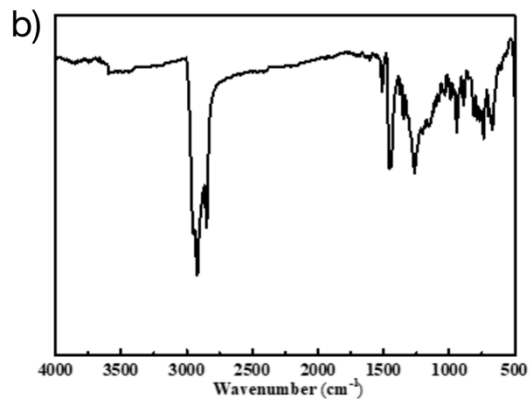


Figure S13. FTIR spectrum of Poly (S- α -pinene - Dicyclopentadiene)

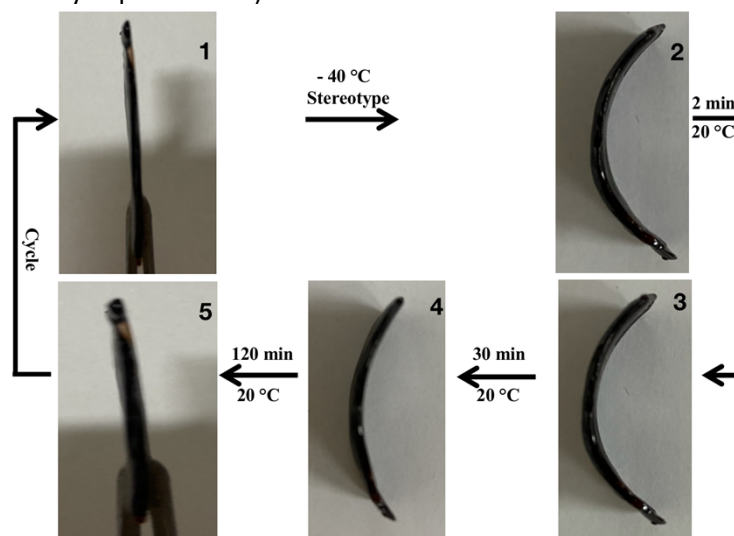


Figure S14. Poly (S- α -pinene - Dicyclopentadiene) shape memory behavior at 20°C.

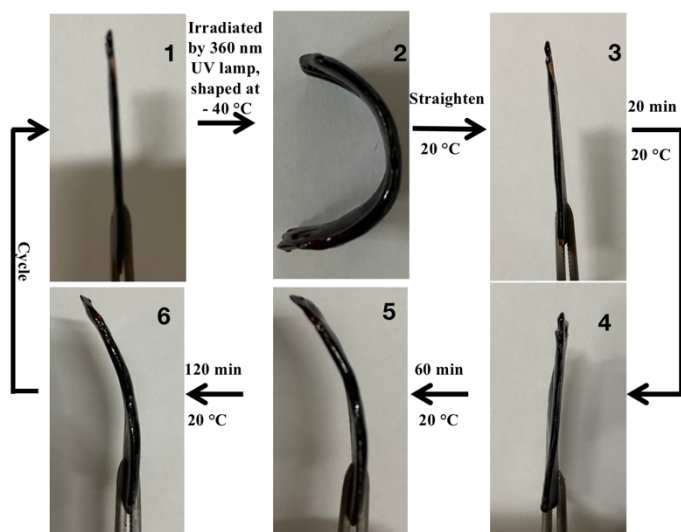
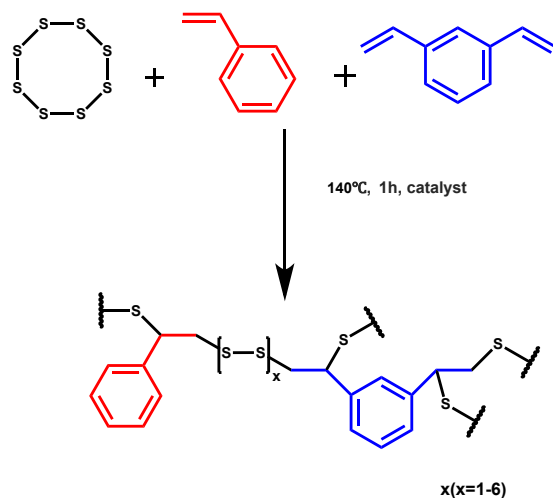


Figure S15. Shape memory behavior of Poly (S- α -pinene- Dicyclopentadiene) under ultraviolet light irradiation.

2. Sulfur, Styrene, 1,3-Divinylbenzene Proportion (2.5/1.2/0.3):

Using sulfur, styrene, and 1,3-divinylbenzene as raw materials for copolymerization, the reverse vulcanization sulfur polymer was synthesized, as shown in the figure.



Scheme S3. Sulfur, 1,3-divinylbenzene, styrene Inverse Vulcanization

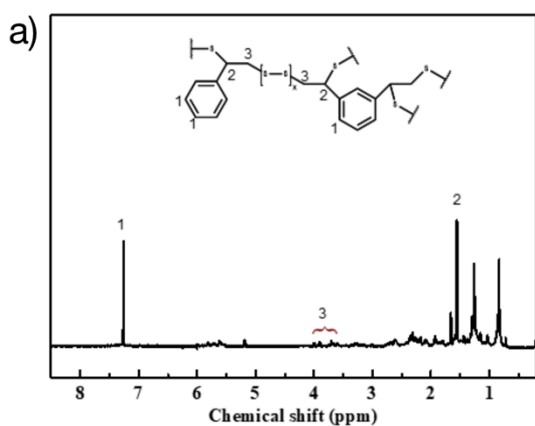


Figure S16. ^1H NMR spectrum of Poly(S-Styrene-1,3-Divinylbenzene)

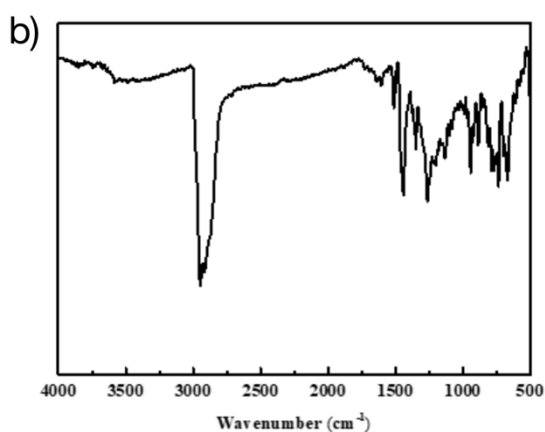


Figure S17. FTIR spectrum of Poly(S-Styrene-1,3-Divinylbenzene)

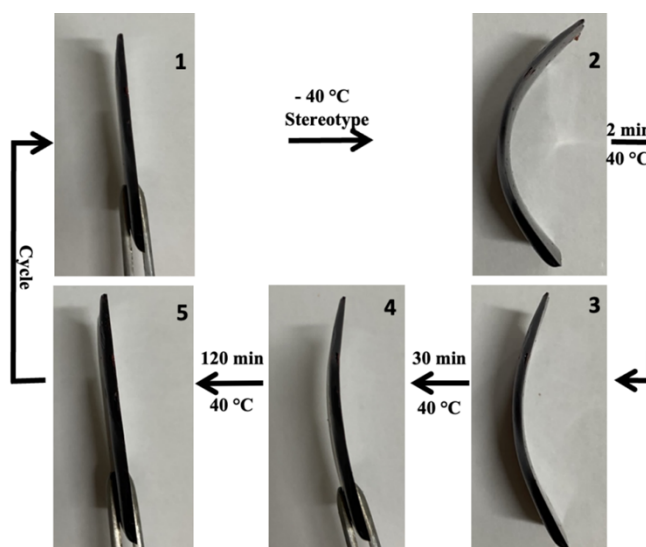


Figure S18. Poly (S- Styrene - 1, 3-Divinylbenzene) shape memory behavior at 40°C

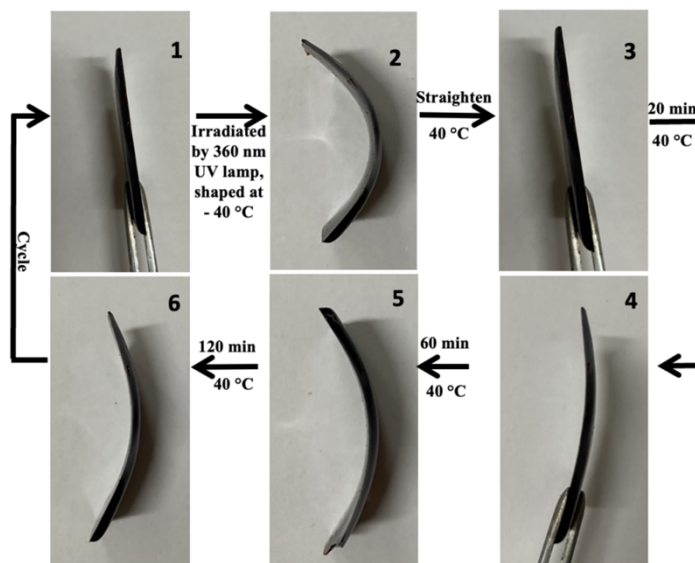
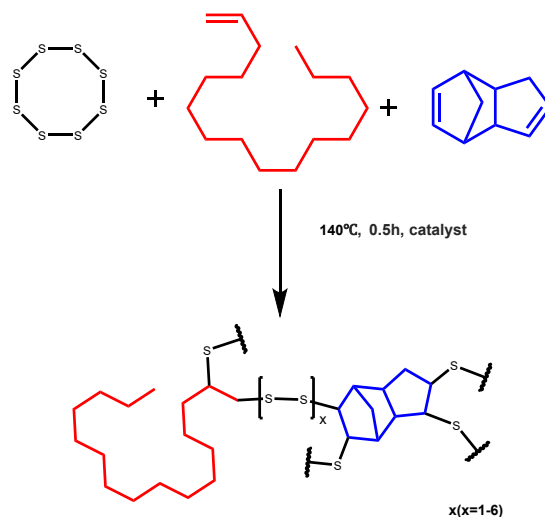


Figure S19. Shape memory behavior of Poly (S- Styrene- 1, 3-Divinylbenzene) under ultraviolet light irradiation

3. Sulfur, Hexadecene, Dicyclopentadiene Proportion (2.5/0.6/0.9)

Using sulfur, hexadecene, and dicyclopentadiene as raw materials for copolymerization, the reverse vulcanization sulfur polymer was synthesized, as shown in the figure.



Scheme S4. Sulfur, hexadecene, dicyclopentadiene

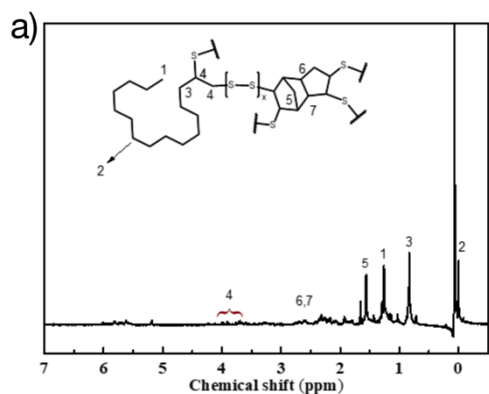


Figure S20. ^1H NMR spectrum of Poly (S- Hexadecene- Dicyclopentadiene)

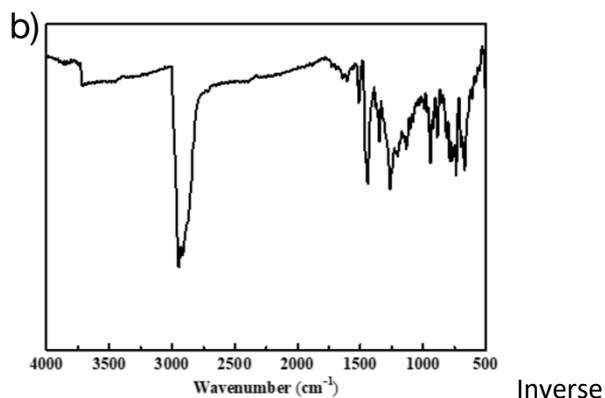


Figure S21. FTIR spectrum of Poly (S- Hexadecene- Dicyclopentadiene)

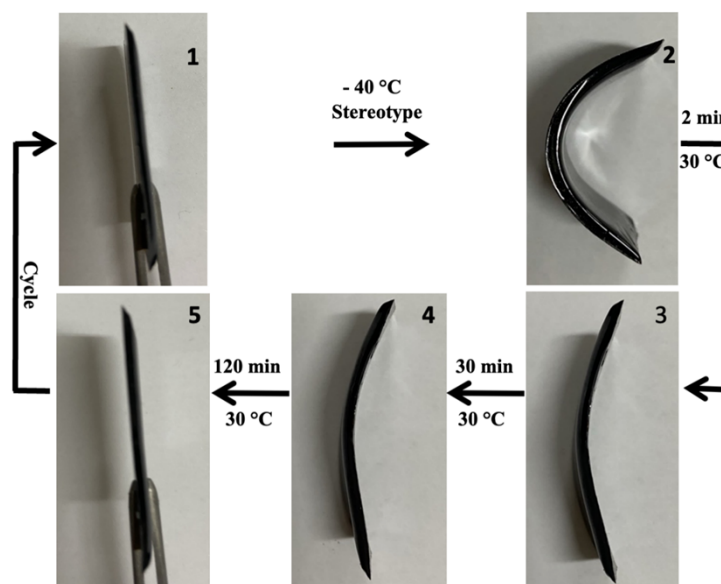


Figure S22. Poly (S- Hexadecene - Dicyclopentadiene) shape memory behavior at 30°C.

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