

1 **Supporting Information**

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3 **Crosslinking-free preparation of thermoplastic triblock liquid crystal**
4 **elastomer actuators**

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20 1. Experimental section

21 1.1 Materials

22 All reagents were used as received without further purification. Styrene-butadiene-
23 styrene triblock copolymers (SBS) ($M_w \sim 140000$, 30 wt.% styrene) was purchased from
24 Sigma-Aldrich. 2-Methyl-4'-(methylthio)-2-morpholinopropiophenone (I907) and 4-
25 dimethylaminopyridine (DMAP) were acquired from TCI. Diisopropyl azodicarboxylate
26 (DIAD), triphenylphosphine (TPP), and tin (II) chloride were purchased from Macklin.
27 2-Mercaptoethanol, phenol, ethyl 6-bromohexanoate, N-(3-dimethylaminopropyl)-N'-
28 ethylcarbodiimide hydrochloride (EDC) and 2-butanol were acquired from Energy
29 Chemical. 4-Aminoanisole, and p-Nitrophenol were purchased from Aladdin. Other
30 reagents, including N, N-dimethylformamide (DMF), methylbenzene, hydrochloric acid
31 (37 wt.%), methanol (AR), ethanol (AR), sodium hydroxide (NaOH), sodium
32 bicarbonate (NaHCO_3), tetrahydrofuran (THF), potassium carbonate (K_2CO_3),
33 potassium iodide (KI), and potassium hydroxide (KOH) were obtained from Tianjin Bodi
34 Chemical Co., Ltd.

35

36 1.2 Synthesis of AZO monomers

37 M_m and M_b were synthesized by the general methods,^[36] as shown in Scheme S1.
38 Their structures were characterized by $^1\text{H-NMR}$ and FT-IR spectra, and their
39 characteristic temperatures and liquid crystal properties were analyzed by DSC curves
40 and POM images (Figure S2 and S3).

41

42 1.3 Synthesis of hydroxy-functionalized SBS (SBS-OH)

43 SBS-OH was synthesized by thiol-ene "click" reaction, as shown in Scheme S2.
44 Typically, SBS (2 g, $\text{Bd} = 0.026$ mol) was dissolved in anhydrous toluene (50 mL) in a
45 round bottomed flask, after which 2-mercaptoethanol (10.9 mL, 0.15 mol) and a trace
46 quantity of the photo initiator I907 (0.06 mg, 0.00021 mmol) were injected into the flask
47 in a nitrogen atmosphere. The solution was stirred and irradiated with the 320-500 nm
48 light for 12 h at room temperature. The resulting polymer was precipitated in a large
49 volume of cold methanol, filtered, and dried under vacuum at room temperature. Its
50 structure and characteristic temperature were measured by $^1\text{H-NMR}$ and DSC analysis
51 (Figure S4).

52

53 1.4 Synthesis of liquid crystal elastomers (SBS-AZO90-N)

54 The synthetic routes of SBS-AZO90-N are shown in Scheme S2. The synthesis
55 procedures for SBS-AZO90-1 are described in detail below as an example. SBS-
56 AZO90-1 was prepared using a 9:10 molar ratio of AZO monomers and the hydroxyl
57 group in SBS-OH, where the molar ratio of M_b to M_m is 1:5. SBS-OH (0.4 g, -OH=2.56
58 mmol) was completely dissolved in DMF (20 mL) at 60 °C. Then, prescribed quantities
59 of AZO monomers M_b (0.148g, 0.42 mmol) and M_m (0.657g, 2.10 mmol), EDC (0.984
60 g, 6.34 mmol) and DMAP (0.244 g, 2.00 mmol) were added to the solution, and the
61 mixture was refluxed at 60 °C for 12 h. The reactant solution was cooled to room
62 temperature, precipitated into 300mL methanol solution twice, and the resulting
63 precipitate was dried to a constant weight. The synthetic process was monitored by
64 $^1\text{H-NMR}$ spectra (Fig. S3). According to the NMR integration results, the total grafting
65 ratio of the AZO monomer was 70%, with 14% of M_b and 56% of M_m grafting. The
66 control sample SBS-AZO90-0 was prepared using a 9:10 molar ratio of M_m and the
67 hydroxyl group in SBS-OH, and the synthesis method as above.

68

69 1.5 Preparation of the AZO-LCE films

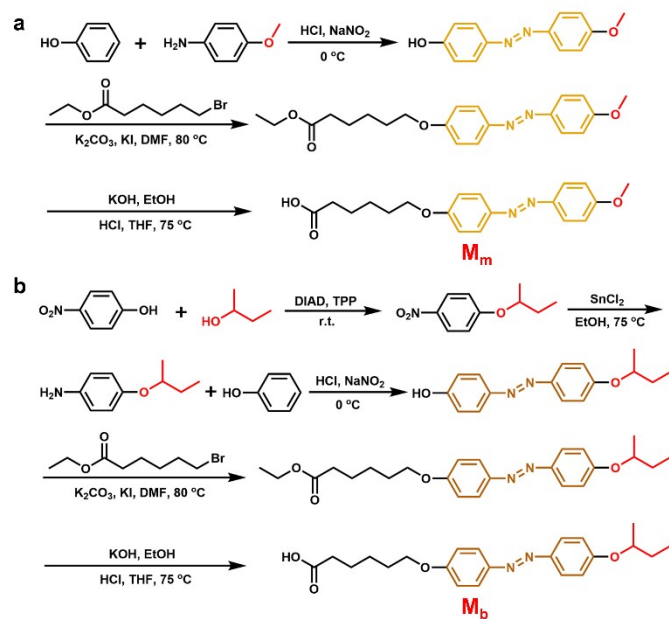
70 SBS-AZO90-N samples have excellent solubility and recyclability. Typically, SBS-
71 AZO90-N (0.09 g) was completely dissolved in chloroform (1.8 ml), and the polymer
72 solution was cast onto a PTFE mold. The films were dried in air for 1 day and kept
73 under vacuum for another 1 day at r. t. to completely remove residual solvent. The
74 thickness of AZO-LCEs films was 60 μm .

75

76 1.6 Preparation of SBS-based LCE actuators

77 SBS-based LCE actuators were prepared by uniaxial stretching above T_g^{PS} . SBS-
78 AZO90-N film (with a length of 20 mm and a width of 10 mm before stretching) was
79 stretched at 120 °C to an elongation of 100~300%. Subsequently, the uniaxially
80 stretched film was slowly cooled to r. t. to gradually generate PS aggregation domains
81 as physical architecture to lock in the orientation, after which the external force was
82 removed.

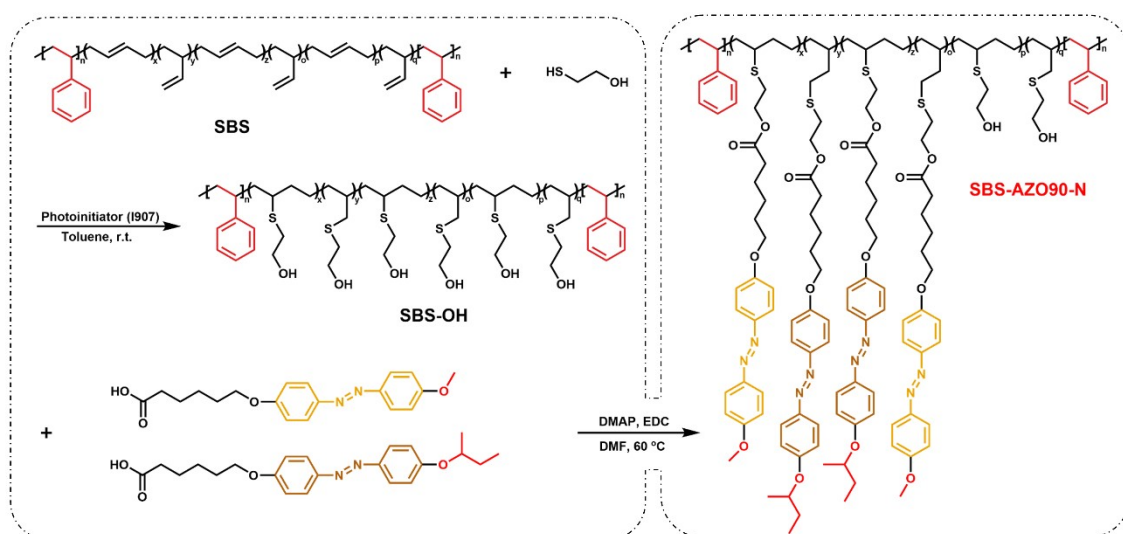
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85 **Scheme S1.** Synthesis routes of AZO mesogen monomers: a) M_m , b) M_b .

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88 **Scheme S2.** Synthesis routes of SBS-based AZO-LCEs (SBS-AZO90-N).

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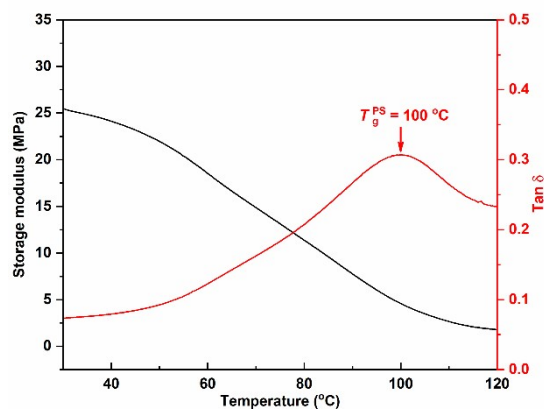
91 **2. General Characterization**

92 Proton nuclear magnetic resonance spectra ($^1\text{H-NMR}$) were obtained using a
93 Bruker Avance II 400 MHz spectrometer (Bruker Co., Ltd., Karlsruhe, Germany) to
94 determine the molecular structures of all the synthesized monomers and polymers.
95 Fourier transform infrared spectroscopy (FT-IR) was carried out using a Bruker
96 Equinox55 (Bruker Co., Ltd., Karlsruhe, Germany) with an infrared polarizer, and
97 transmission FT-IR spectra were recorded at a rate of $5\text{ }^\circ\text{C min}^{-1}$ between $30\text{ }^\circ\text{C}$ and
98 $120\text{ }^\circ\text{C}$ to characterize the dynamics of hydrogen bonding and orientation of AZO
99 mesogens in the AZO-LCEs during a temperature change. The thermal transition
100 temperatures of all the samples were measured by differential scanning calorimetry
101 (DSC TAQ2000) using approximately 8 mg of a sample under a nitrogen atmosphere
102 (nitrogen flow rate = 50 mL min^{-1}) and a heating and cooling rate of $10\text{ }^\circ\text{C min}^{-1}$. The
103 shape memory properties were quantitatively characterized by DMA (TAQ800) under
104 controlled force mode. Ultraviolet-visible spectrophotometer (UV-Vis): UV-2600
105 (SHIMADZU, Kyoto Japan), used to measure the radiation absorption of AZO
106 monomers in the ultraviolet and visible spectral regions and to analyze the optical
107 response properties of substances. 1D/2D-WAXD were performed using a Bruker D8
108 Advance X-ray diffractometer with a CuK α radiation source (wherein wavelength
109 $\lambda=1.54\text{ \AA}$). An optical microscope (Leica DMLP) equipped with a hot stage was used
110 to observe the liquid crystalline textures. The strips were tested by an Instron 5567A
111 machine for the stress-strain experiments at a rate of 10 mm/min at room temperature.
112 The photoreaction was carried out using an OmniCure@Series 1000 UV-vis lamp with
113 365/400-500 nm filters.

114

115 **3. Supplementary Figures and Discussion**

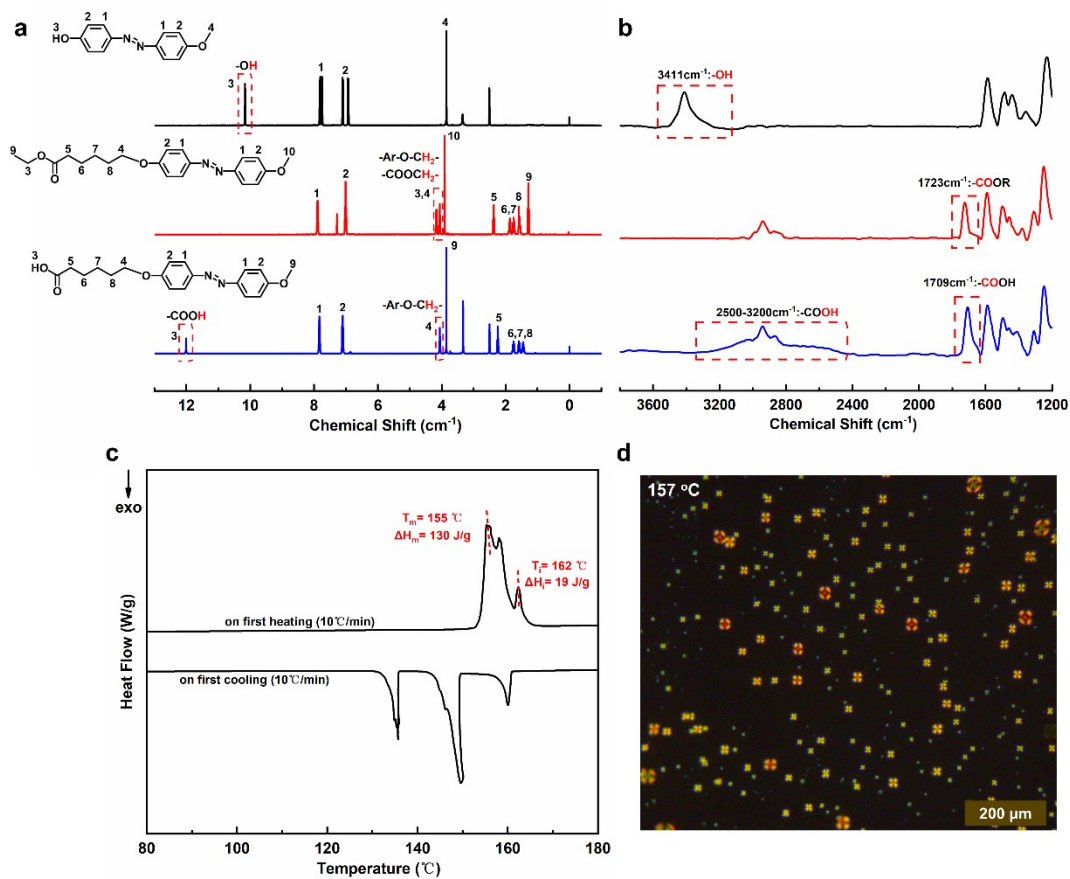
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118 **Figure S1.** Storage modulus and loss factor curves of the starting material SBS

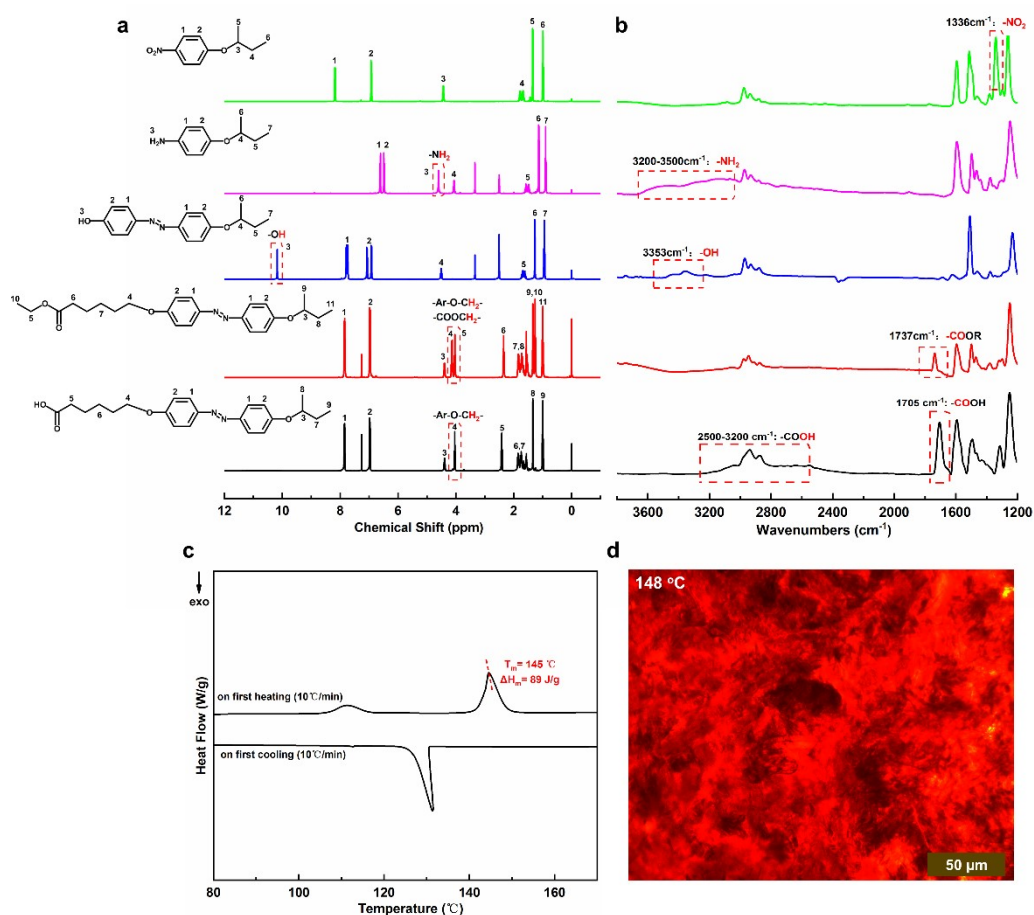
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121 **Figure S2.** a) ¹H NMR spectra of M_m and intermediates. b) FT-IR spectra of M_m and intermediates. c)

122 DSC curves of M_m. d) POM (200 μm) image of M_m in LC phase.

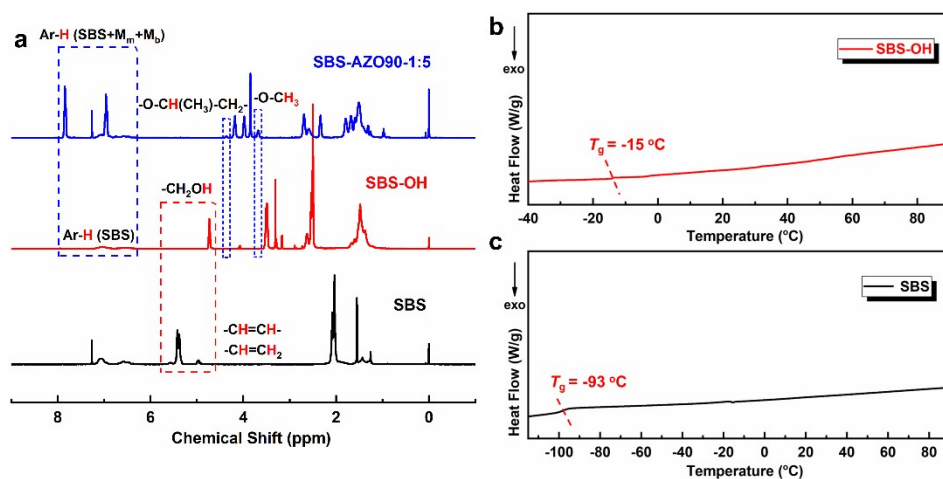


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124 **Figure S3.** a) ¹H NMR spectra of M_b and intermediates. b) FT-IR spectra of M_b and intermediates. c)

125 DSC curves of M_b. d) POM (50 μm) image of M_b at 148 °C.

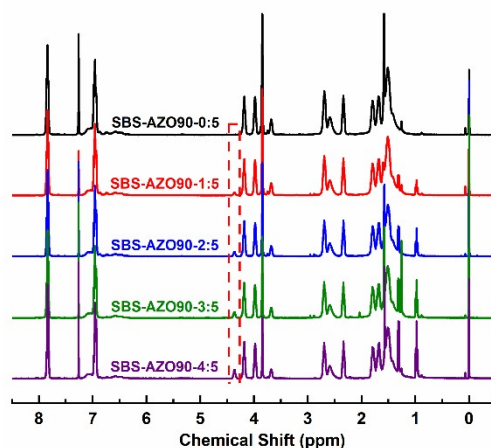
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128 **Figure S4.** a) ¹H-NMR spectra of SBS-AZO90-1:5 and intermediates. b) DSC curves of SBS-OH and c)

129 SBS.



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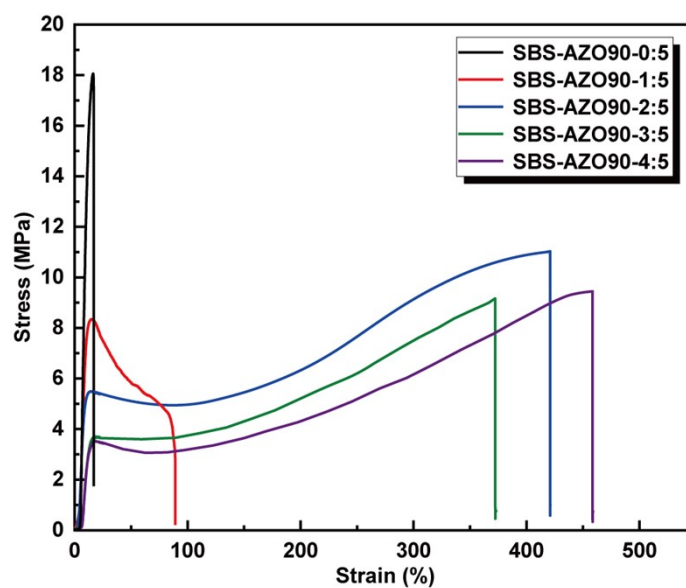
131 **Figure S5.** $^1\text{H-NMR}$ spectra of thermoplastic LCEs SBS-AZO90-N (0~4:5).

132

133 **Table S1.** The calculated grafting degrees based on $^1\text{H-NMR}$ spectra

| Sample | Total grafting degrees | The grafting degrees of M_b | The grafting degrees of M_m |
|---------------|------------------------|-------------------------------|-------------------------------|
| SBS-AZO90-0:5 | 76% | 0% | 76% |
| SBS-AZO90-1:5 | 70% | 17% | 56% |
| SBS-AZO90-2:5 | 71% | 29% | 49% |
| SBS-AZO90-3:5 | 73% | 38% | 45% |
| SBS-AZO90-4:5 | 73% | 45% | 38% |

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136 **Figure S6.** Tensile properties curves of SBS-AZO90 series films.

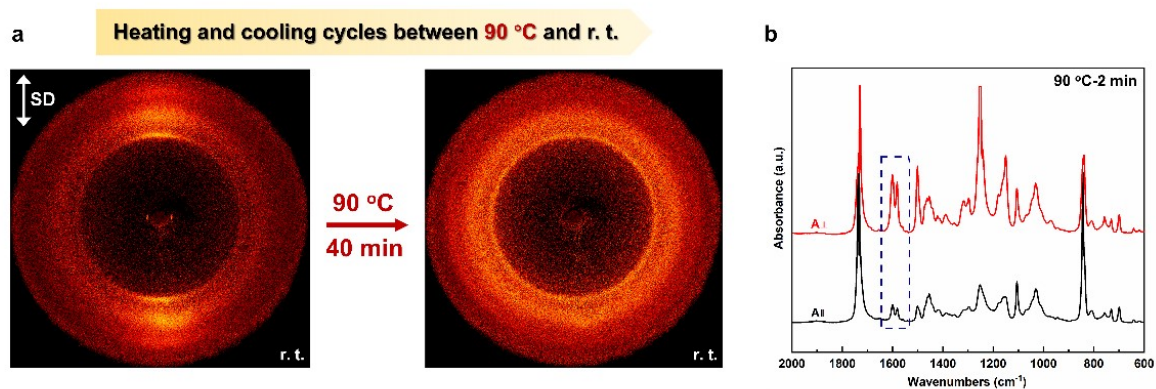
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138 **Table S2.** Tensile properties data of SBS-AZO90 series films

| Sample | Young's modulus (MPa) | Tensile strength at break (MPa) | Elongation at break (%) |
|---------------|-----------------------|---------------------------------|-------------------------|
| SBS-AZO90-0:5 | 296.4 | 18.00 | 6.35 |
| SBS-AZO90-1:5 | 132.8 | 8.46 | 89 |
| SBS-AZO90-2:5 | 111.7 | 11.03 | 420 |
| SBS-AZO90-3:5 | 63.7 | 9.17 | 372 |
| SBS-AZO90-4:5 | 59.0 | 9.43 | 485 |

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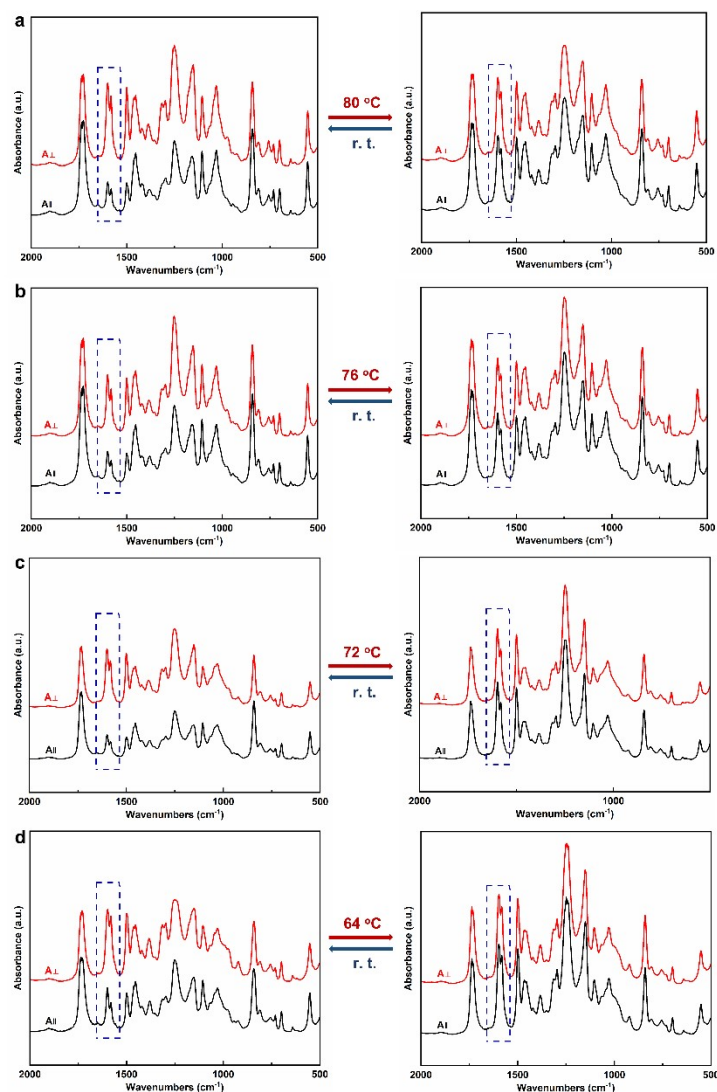
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142 **Figure S7.** a) 2D-WAXD patterns of SBS-AZO90-0:5 during thermal relaxation at 90 °C for 40 min. b)

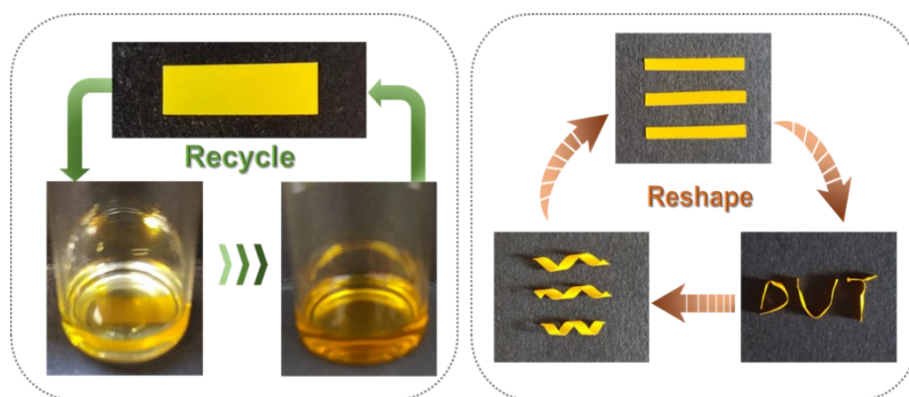
143 Polarized FT-IR spectra of SBS-AZO90-0:5 at 90 °C thermal relaxation for 2 min.



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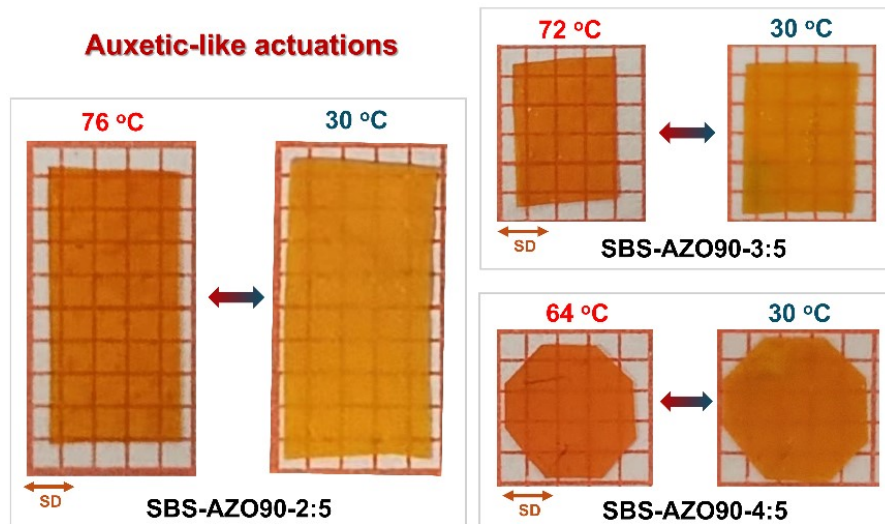
145 **Figure S8.** The *in situ* polarized FT-IR spectra for the infrared dichroism of a monodomain strip: a) SBS-
 146 AZO90-1:5 recorded between 80 °C and r. t.; b) SBS-AZO90-2:5 recorded between 76 °C and r. t.; c)
 147 SBS-AZO90-3:5 recorded between 72 °C and r. t.; d) SBS-AZO90-4:5 recorded between 64 °C and r.
 148 t.

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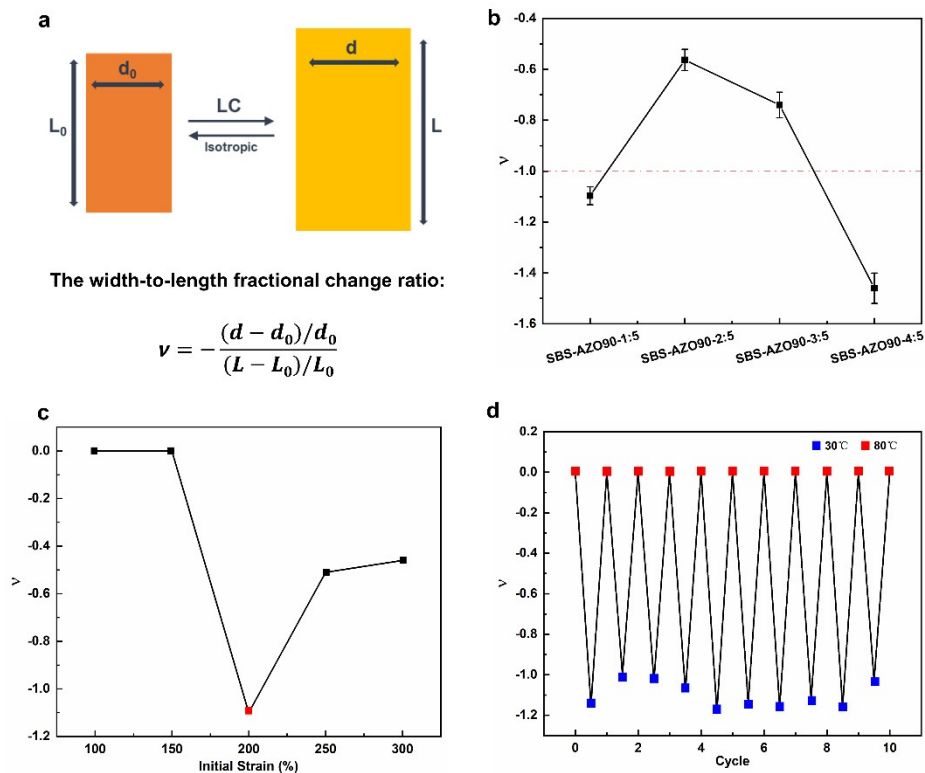
151 **Figure S9.** Photographs showing recycling behaviour and reshaping behaviour.



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153 **Figure S10.** The auxetic-like actuations of the monodomain SBS-AZO90-2:5/3:5/4:5 strips.

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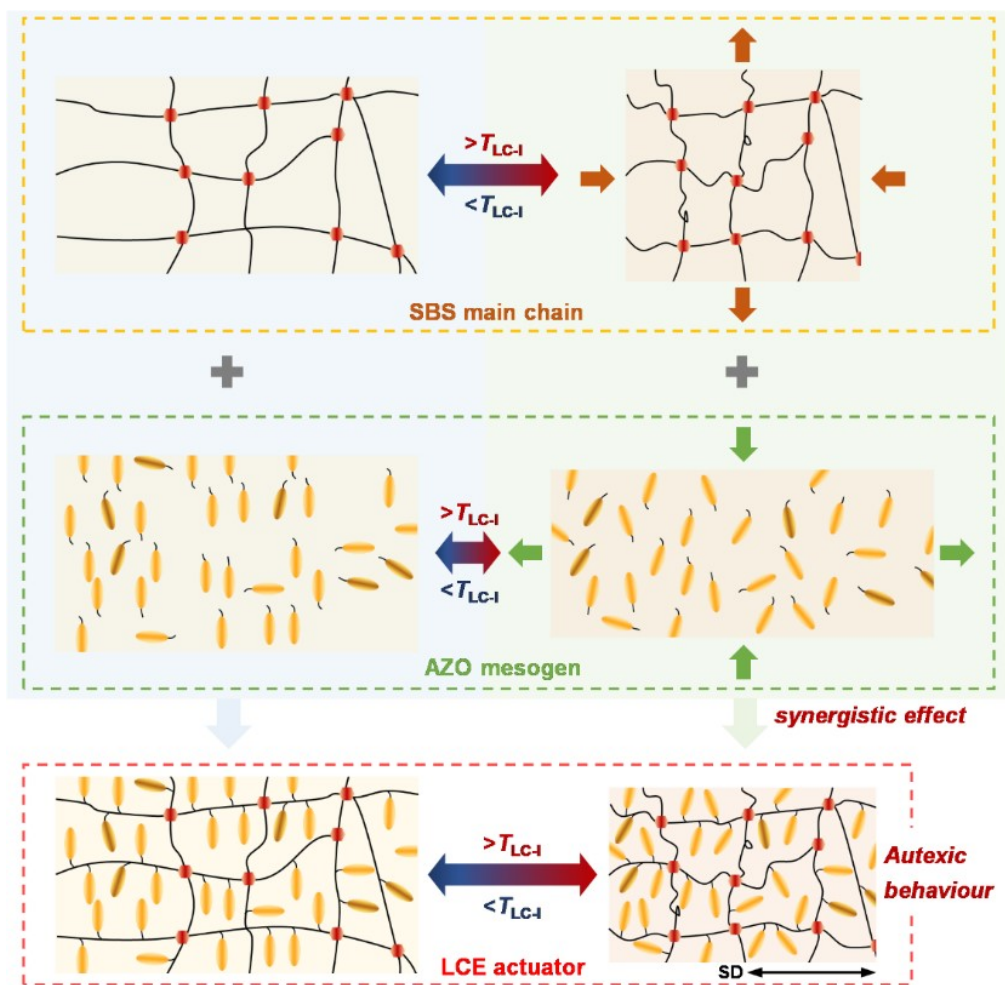
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156 **Figure S11.** a) The definition of width-to-length fractional change ratio, v . b) Change in v as a function

157 of the different initial strains (100%~300%) used in preparing the oriented SBS-AZO90-1:5 strip. c)

158 Change in v as a function of the initial strain (200%) used in preparing the LCE strip actuator. d)

159 Reversible auxetic-like shape change cycles by thermally induced order-disorder phase transition.

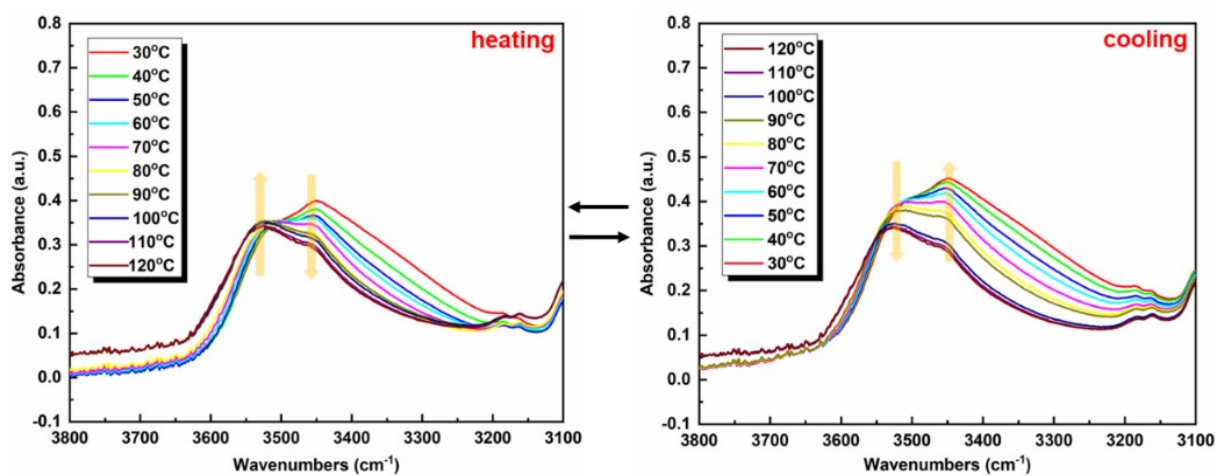


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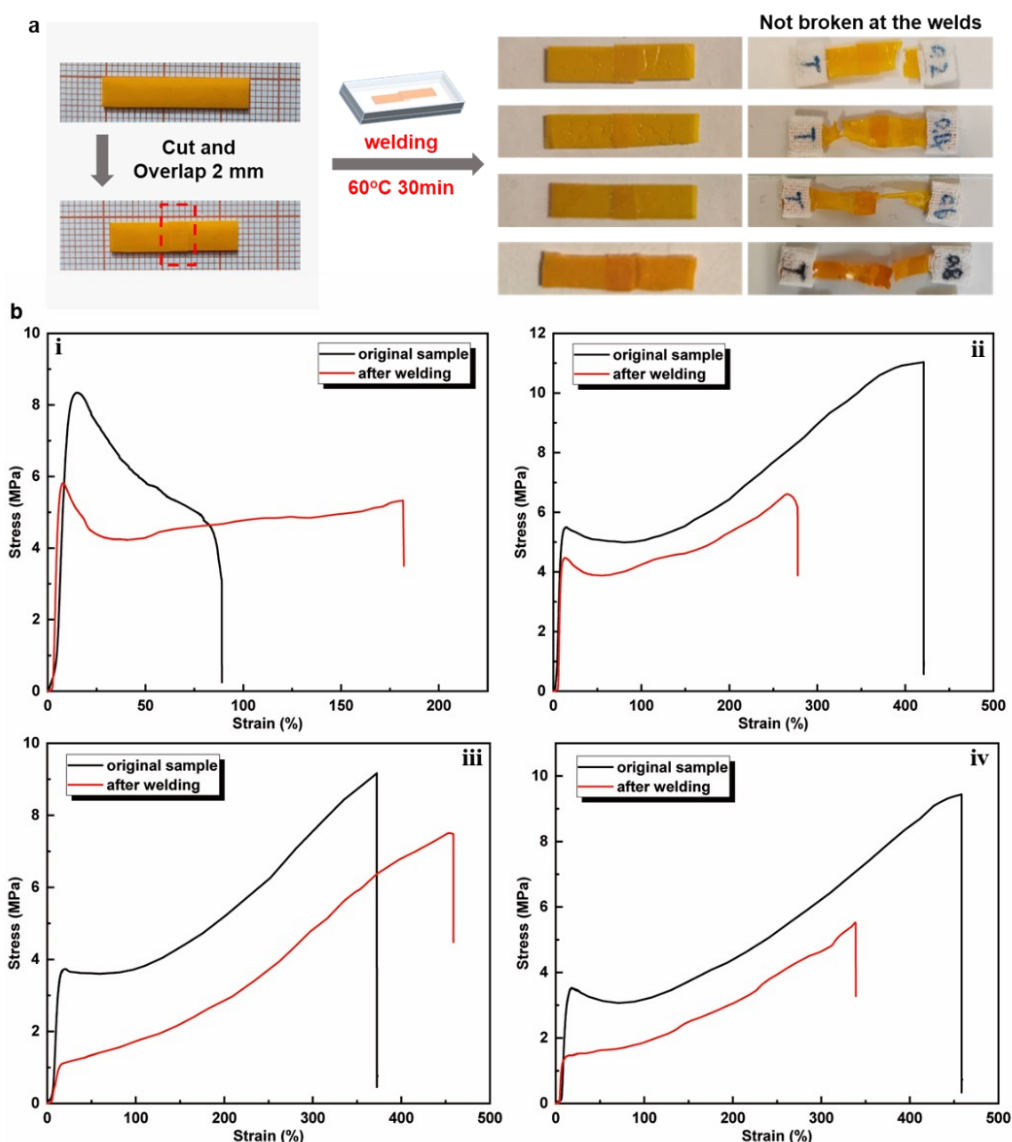
Figure S12. The mechanism of auxetic-like actuations for monodomain SBS-AZO90-N strips.



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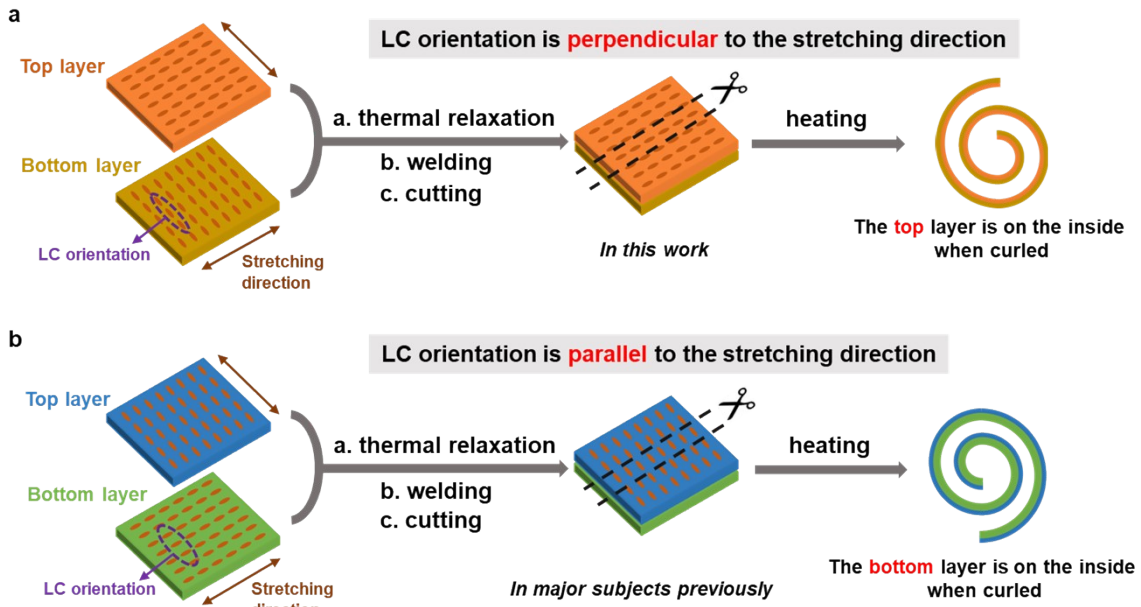
Figure S13. The temperature-dependent *in situ* FT-IR spectra (cyclic temperature change process

165 between 30-120 °C) of SBS-AZO90-1:5.



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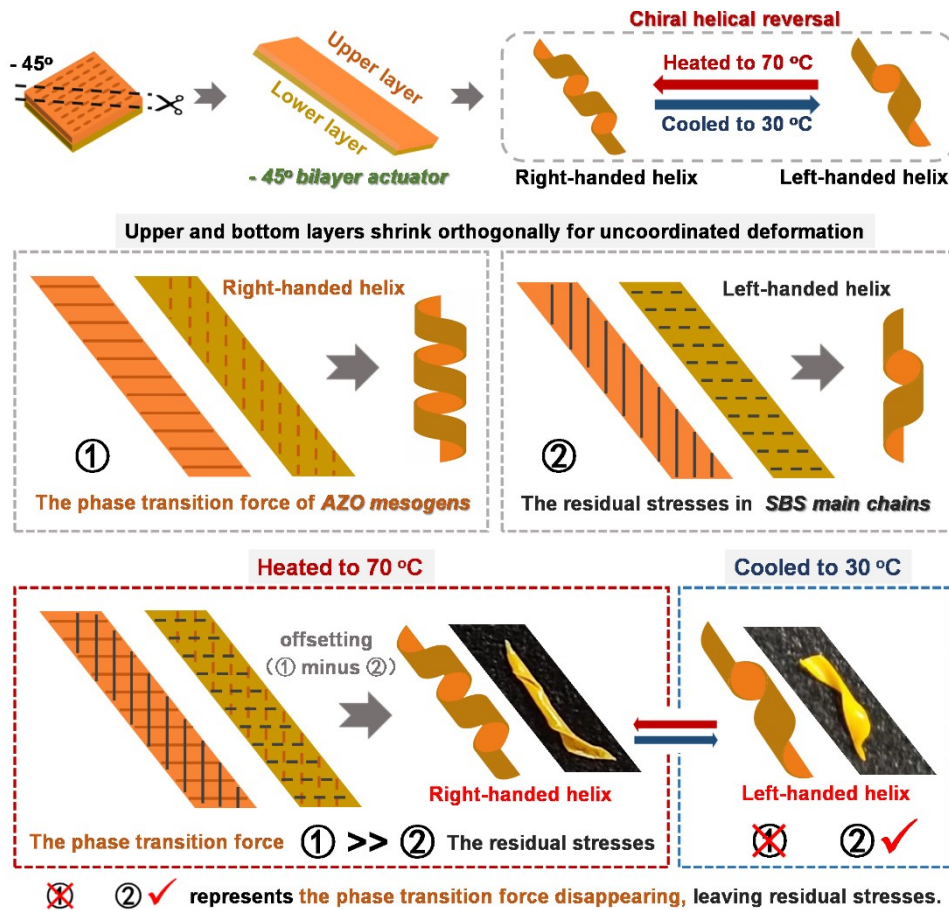
167 **Figure S14.** a) Photographs showing the welding process. The strips (25 mm×5 mm×60 μm) were first
 168 cut into two pieces, of which the edges were immediately overlapped by 2 mm, sandwiched between
 169 two glass slides without external force and heated at 60 °C for 30 min. Then the welding strips were
 170 subjected to stress-strain experiments to obtain the mechanical properties, and they did not break from
 171 the welds during the tensile tests. The breaking stresses were employed to evaluate the welding
 172 efficiency. b) The stress-strain curves (10 mm min⁻¹) of the original films and welded films for i) SBS-
 173 AZO90-1:5; ii) SBS-AZO90-2:5; iii) SBS-AZO90-3:5; iv) SBS-AZO90-4:5.



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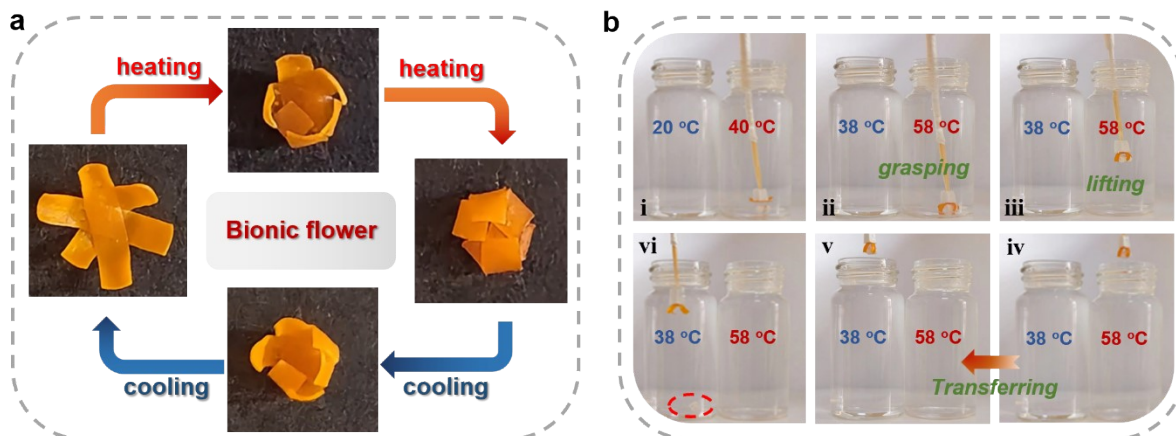
175 **Figure S15.** Photographs showing different curling phenomena for a) vertical and b) parallel systems.

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178 **Figure S16.** The mechanism for reversal behaviours of -45° bilayer actuator.



179

180 **Figure S17.** a) The blooming and closing process of bionic flower actuator. b) An underwater gripper
 181 executing a series of robot-like motion tasks.

182 **4. Movie caption**

183 **Movie S1:** Auxetic-like actuation of SBS-AZO90-1:5 actuator.

184 **Movie S2:** The helical/coiled actuation behaviors of modular-assembled actuators.

185 **Movie S3:** The temporally sequenced asynchronous deformations of the right hand.

186 **Movie S4:** The ambidirectional actuation behaviors of modular-assembled actuators.

187 **Movie S5:** Training movements of two “athletes”.

188 **Movie S6:** The blooming and closing of bionic flower.

189 **Movie S7:** The operational procedure for the underwater gripper.

190