# Electronic supplementary information (ESI) for

# Color and Shape Reversible, Recoverable and Repeatable Mechanochromic Shape Memory Polycaprolactone: A Single Material with Dual Functions

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#### 1. Materials

Sodium hydroxide, potassium hydroxide, 3-chloromethyl-5-nitrosalicylaldehyde, 2,3,3trimethylindolenine and ε-caprolactone were purchased from Tokyo Chemical Industry (Japan). 2-iodoethanol, tin (II) 2-ethylhexanoate (Sn(Oct)<sub>2</sub>), pentaerythritol and hexamethylene diisocyanate (HDI) were obtained from Sigma-Aldrich (Singapore). Deuterated chloroform (CDCl<sub>3</sub>), dimethyl sulfoxide-d<sub>6</sub> (DMSO-d<sub>6</sub>) and sodium sulfate anhydrous (Na<sub>2</sub>SO<sub>4</sub>) were received from Merck Millipore (Germany). Acetone, toluene, ethanol, methanol, diethyl ether and acetonitrile were purchased from RCI labscan (Thailand). All chemicals were used without further purification.

#### 2. Synthesis route and NMR

#### Synthesis of spiropyran diol (SP)

2.1 Compound 1 ,1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indol-1-ium iodide

Compound 1 was synthesized as according to Gregory R G. et al<sup>1</sup>.

2.2 Compound 2, 9,9,9a-trimethyl-2,3,9,9a-tetrahydrooxazolo[3,2-a]indole

Compound 2 was synthesized as according to Dingbin, L. *et al*<sup>2</sup>.

2.3 Compound 3, 2-hydroxy-3-(hydroxymethyl)-5-nitrobenzaldehyde

Compound 3 was synthesized as according to O'Bryan, G., *et al*<sup>3</sup>.

2.4 Compound 4, spiropyran diol, (S)-2-(8-(hydroxymethyl)-3',3'-dimethyl-6nitrospiro[chromene-2,2'-indolin]-1'-yl)ethan-1-ol

Compound 4 or spiropyran diol was synthesized as according to Zhang, H.,  $et al^4$ .



Figure S2. <sup>1</sup>H NMR spectrum of spiropyran diol (500 MHz, CDCl<sub>3</sub>)







Figure S4. <sup>1</sup>H NMR spectrum of HO-PCL-OH (500 MHz, CDCl<sub>3</sub>)



Figure S5. <sup>1</sup>H NMR spectrum of 4-armed PCL (500 MHz, CDCl<sub>3</sub>)

#### 3. General analytical method and instrument setup

#### Instrumental methods.

Attenuated total reflectance fourier transform infrared spectra (ATR-FTIR) were recorded by a Bruker ALPHA FTIR spectrophotometer in the range of 4000-650 cm<sup>-1</sup> with 64 scans and a resolution of 4 cm<sup>-1</sup>. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were obtained by a Bruker AVANCE 500 MHz NMR spectrometer using CDCl<sub>3</sub> as the solvent. Number-averaged molecular weight (M<sub>n</sub>), weight-averaged molecular weight (M<sub>w</sub>), and polydispersity index (PDI) of PCL-SP and HO-PCL-OH were evaluated by a Shimadzu LC-20AD and CTO-20A system equipped with four Shodex GPC K-802.5, 803, 804, 805 columns connected in series and with a Shimadzu RID-10A refractive index detector. Chloroform was used as an eluent at a flow rate of 1.0 mL min<sup>-1</sup>. Polystyrene standards were used and the measurements were performed at 40 °C.

# Simultaneous tensile test with UV-Vis spectroscopy

**(a)** 

**(b)** 



(c)







(f)



Figure S6. (a) a JASCO V-670 type UV-Vis spectrophotometer, (b) the light pathway in the reference and sample positions, (c) a Linkam stretching device, (d) the position of Linkam

stretching device in UV-Vis spectrophotometer and (e) scheme of double beam UV-visible spectrometer with a stretching unit.



Simultaneous tensile test with WAXD and SAXS approach

(b) Pilatus100k

**(a)** 





**Figure S7.** The WAXD and SAXS simultaneous measurement system under the stretching of a sample by using a Rigaku NanoViewer X-ray diffractometer. (a) rear view, (b) front view and (c) scheme of simultaneous tensile test WAXD and SAXS with approach.



# 4. Physical properties

Figure S8. ATR-FTIR spectra of (a) 75PCL-SP42k, (b) 4-armed PCL, (c) PCL-SP and (d) HDI.



Figure S9. Thermal properties of 75PCL-SP42k (a) 1<sup>st</sup> heating step, (b) 1<sup>st</sup> cooling step and (c)

2<sup>nd</sup> heating step.

# 5. Mechanochromic shape memory behavior



Figure S10. naked eye color change at different strain with region of interest (ROI) (red square).



Figure S11. (a) naked eye color change at different strain, (b) drB of 75PCL-SP41k (•), 65PCL-SP41k (•) and 50PCL-SP41k (•) and (c) crystallinity (•) and gel fraction (•) of films.



Figure S12. (a) rB intensity at the different strain of 75PCL-SP41k (•), 65PCL-SP41k (•) and

50PCL-SP41k (•) and (b) stress strain curve

![](_page_12_Figure_3.jpeg)

Figure S13. Stress-strain curve of 65PCL-SP28k at 1<sup>st</sup> cycle (•), 2<sup>nd</sup> cycle (•), 3<sup>rd</sup> cycle (•) and

 $4^{th}$  cycle (•).

![](_page_13_Figure_0.jpeg)

**Figure S14.** (a) visible spectra of 65PCL-SP54k at the strains from 0 to 26 %, (b) visible spectra of 65PCL-SP54k at the strains from 26 to 360 % and (c) the background-subtracted visible spectra of 65PCL-SP54k.

![](_page_14_Figure_0.jpeg)

**Figure S15.** (a) visible spectra of 50PCL-SP54k at the strains from 0 to 26.87 %, (b) visible spectra of 50PCL-SP54k at the strains from 23.53 to 347.91 % and (c) the background-subtracted visible spectra of 50PCL-SP54k.

![](_page_15_Figure_0.jpeg)

**Figure S16.** (a) Integral area of the peak 592 nm plotted against time for the 75PCL-SP54k (**■**), 65PCL-SP54k (**■**) and 50PCL-SP54k (**■**) (replot from Fig. 6). The comparison of UV-Vis spectral profiles between the stressed (black line) and UV-treatment (color line) states measured for the 75PCL-SP54k (b), 65PCL-SP54k (c) and 50PCL-SP54k (d) films.

![](_page_16_Figure_0.jpeg)

**Figure S17.** Comparison of the stress-strain curves between the WAXD–SAXS experiment and the UV-Vis spectroscopic measurement: (a) 75PCL-SP54k, (b) 65PCL-SP54k and (c) 50PCL-SP54k films.

![](_page_17_Figure_0.jpeg)

**Figure S18.** The stress strain curve of 75PCL-SP54k films obtained during the simultaneous WAXD and SAXS measurements in comparison with the change in the integrated intensity of the visible 592 nm peak (refer to Figure 6). The 2D WAXD and SAXS patterns measured in (a) region I, (b) region II and (c) region III. The pattern figure represents to each strain. The stretching direction was vertical.

![](_page_18_Figure_0.jpeg)

**Figure S19.** The stress strain curve of 75PCL-SP54k film obtained during the simultaneous WAXD and SAXS measurements in comparison with the change in the integrated intensity of the visible 592 nm peak (refer to Figure 6). The 2D WAXD and SAXS patterns measured in the region IV. The pattern figure represents to each strain. The stretching direction was vertical.

Movie S1: 75PCL-SP54k stretched at 28 °C with strain rate 120 µm/s

Movie S2.: 75PCL-SP54k removed force and showing color recovery under ambient light at 28 °C

Movie S3: 75PCL-SP54k induced original shape in hot water at 68 °C (>T<sub>Trans</sub>)

# Reference

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