

Electronic Supplementary Information

Self-Healing Photoinduced-Deformable Material Fabricated by Liquid Crystalline Elastomers Using Multivalent Hydrogen Bonds as Cross-Linkers

Bin Ni^a, He-Lou Xie^{a*}, Jun Tang^a, Hai-Liang Zhang^{a*} and Er-Qiang Chen^b

^a *Key Laboratory of Polymeric Materials and Application Technology of Hunan Province, Key Laboratory of Advanced Functional Polymer Materials of Colleges and Universities of Hunan Province, College of Chemistry, Xiangtan University, Xiangtan 411105, Hunan Province, China*

^b *Beijing National Laboratory for Molecular Sciences, Department of Polymer Science and Engineering and Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China*

Experimental section

Materials

2-amino-4-hydroxy-6-methylpyrimidine(98%), hexamethylenediisocyanate(98%),2-hydroxyethyl acrylate(98%), 4-butylaniline(97%) and 1,6-dibromo-hexane(98%)were all obtained from Energy Chemical. Tetrahydrofuran (THF, 99%) was dried by refluxing with Na for 8 h. Chloroform was dried by MgSO₄, then refluxed with sodium and distilled. *N,N*-dimethylformamide (DMF, 99.8%) was dried with

anhydrous magnesium sulfate and distilled under reduced pressure. Acetone (AR; Beijing Chemical Co.) was refluxed over potassium permanganate and distilled before used. And others solutions and reagents were used analytical pure or above.

Instruments and Measurements

^1H NMR and ^{13}C NMR spectra were obtained on a BRUKER ARX400 MHz spectrometer with tetramethylsilane (TMS) as the internal standard in chloroform-*d* (CDCl_3). Gel permeation chromatography (GPC, PL-120) were carried out to investigate the apparent number average MW (M_n) and MW distribution (M_w/M_n) at 70 °C using DMF as the eluent and PS as the standards at a flow rate of 1.0 mL/min. Variable temperature infrared was obtained on Perkin-Elmer Spectrum one, and the heating accessories was also the company's products.

Differential scanning calorimetry (DSC, TA-Q10) was used to track the thermal transitions of the samples with a programmed heating and cooling procedure rates of 10 °C/min in nitrogen. Using benzoic acid and indium as standard sample calibrated the temperature and heat flow. The sample with 3-8 mg was encapsulated in sealed aluminum pans. LC texture of the samples was characterized under polarized optical microscopy (POM, Leica DM-LM-P) coupled with a Leica hot stage (FP82HT) under different temperatures. The films with thickness of $\sim 10 \mu\text{m}$ were casted from THF solution and dried at room temperature slowly.

One-dimensional wide-angle X-ray diffractive powder experiments (1D-WAXD) were carried out on a Bruker D8 advance diffraction with a 3 kW ceramic tube as the

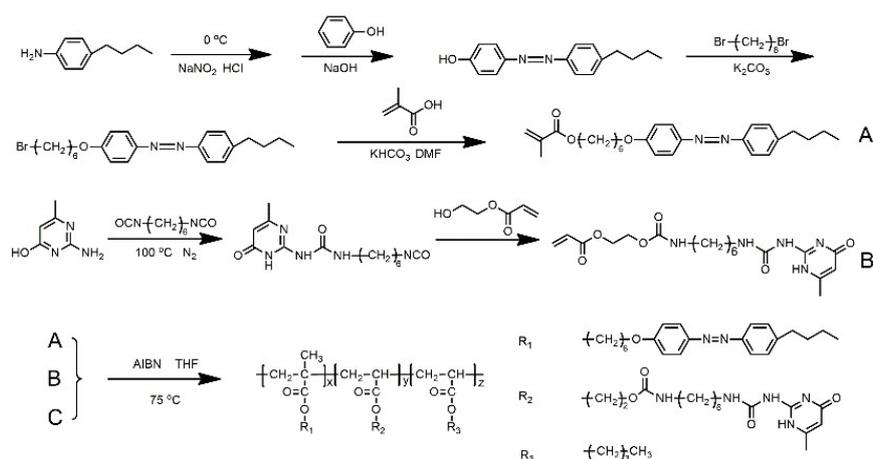
X-ray source (Cu K α) and an X'celerator detector. First, the sample set horizontally in the stage and the reflection peak positions were calibrated silver behenate ($2\theta < 10^\circ$). Background scattering was recorded and deducted from the sample patterns. Two-dimensional wide-angle X-ray diffractive experiments (2D-WAXD) of the shearing samples were carried out to obtain the shearing patterns using a Bruker D8Discover diffraction with a Vantec-500 detector calibrated with silicon powder and silver behenate. Samples were mounted on the sample stage, and the point-focused X-ray beam was aligned both perpendicular and parallel to the mechanical shearing or fiber direction. The background scattering was recorded and subtracted from the sample patterns.

The UV and Vis light source of the photo-induced deformable experiment are 365 nm UV LED (FUWO, FUV-6BK160mW/cm²) and a 470 nm LED(FUWO, F7B-B20160mW/cm²), respectively. And all photographs of bending and unbending were recorded via digital camera (Canon Ixus 125). UV-vis absorption spectra was carried out via Cary 100 with the Flashing xenon lamp as the light source and the scanning range was 200 nm-800 nm. The irritation light source was same as the experiment of photoinduced bending and unbending behavior experiment. The strain and stress experiment was carried out on INSTRON 5567, the speed of stretching was 10 mm/min, and the experiment temperature was 25 °C.

Synthesize of monomers and polymers

Synthesis

The synthetic route of monomers and the polymer were outlined in S-schemes 1.



S-scheme 1. Synthetic route of the monomers and LCEs.

Synthesis of 2-(6'-isocyanato) hexylaminocarbonylamino -6-methyl-4-[1H] pyrimidinone

A mixture solution combined 2-amino-4-hydroxy-6-methylpyrimidine (5.82 g, 46.5 mmol) with hexamethylenediisocyanate (54.4 g, 0.32 mol) was heated under an N_2 atmosphere at 100°C for 12 h. After reaction, precipitated it in the petroleum and the precipitate was filtered, washed with petroleum for several times and dried at 40°C in vacuum, the white powder was obtained. Yield, 90%. $^1\text{H-NMR}$ (400 MHz, CDCl_3): $\delta = 1.41$ (m, 4H, $-\text{CH}_2-$), 1.61 (m, 4H, $-\text{CH}_2-$), 2.21 (s 3H, $-\text{CH}_3$), 3.27 (m, 4H, $-\text{CH}_2\text{-NH-}$), 5.79 (s, 1H, $=\text{CH-}$), 10.10 (s, 1H, $-\text{NH-}$), 11.82 (s, 1H, $-\text{NH-}$), 13.07 (s, 1H, $-\text{NH-}$) ppm.

Synthesis of 2 – (6 - (6 - methyl - 4-[1H] pyrimidine) - urea - hexamethylene carbamate)- ethyl acrylate

2-Hydroxyethyl acrylate (4g, 34 mmol), 2-(6'-isocyanato) hexylaminocarbonylamino-

-6-methyl-4-[1H] pyrimidinone (2 g, 6.8 mmol), dibutyltindilaurate (0.06g, 0.095mmol) and 100 mL chloroform were added into a 250 ml round-bottom flask. Heating to reflux for 12h, filter, then, the crude product was purified by column chromatography, the white power was obtained. Yield.75%

¹H-NMR (400 MHz, CDCl₃) δ = 1.41 (m, 4H, -CH₂-), 1.61 (m, 4H, -CH₂-), 2.21 (s, 3H, -CH₃), 3.27 (m, 4H, -CH₂-NH-), 4.31 (s, 2H, -CH₂-O-), 4.38 (s, 2H, -CH₂-O-), 5.58 (m, 2H, =CH₂), 5.79 (s, 1H, =CH-), 6.1(s, 1H, =CH-) 10.10 (s, 1H, -NH-), 11.82 (s, 1H, -NH-), 13.07 (s, 1H, -NH-) ppm.

¹³ C-NMR(CDCl₃) δ (ppm): 18.34 (-CH₃), 25.75-29.10 (-CH₂-), 33.47-35.56(-CH₂-NH-), 64.64-68.14(-CH₂-O-), 114.70(=CH-CO-), 129.06(CH₂=CH-), 136.52(CH₂=CH-), 145.85(-NH-C=N), 146.89(-O-CO-NH-), 150.89(-NH-CO-NH-), 161.49(-CO-NH-), 167.54(-COO-), 171.12(=N-CO-), 185.38(-NH-C=).

FTIR-KBr: ν -NH (3310), =CH (3049), -CH₃(2944), -CH₂- (2944, 2874, 1431), -CO- (1704), -NH-CO-(1588,1541), -C-O-C-(1256, 1192), -CH=C(977)

Synthesis of 4-((4-butylphenyl)diazenyl)phenol

4-butylaniline (7.45 g, 50mmol) and NaNO₂ (3.6 g, 52mmol) were dissolved in a mixture of water (25mL) and HCl (11.9 mol/L, 5 mL), then the mixture solution was added dropwise into an aqueous solution of phenol (5g, 55mmol) and NaOH (5g, 130mmol) under magnetic stirring at 0 °C. After that, the reaction solution was filtered under reduced pressure. The crude product 4-((4-butylphenyl)diazenyl)phenol was purified and collected by flash chromatography.

^1H NMR (CDCl_3), δ (ppm): 7.88 -7.92 (s, 4H, Ar-H), 7.3(m, 2H, Ar-H), 7.0(m, 2H, Ar-H), 2.6 (m, 2H,- CH_2 -) 1.4-1.9(m, 4H, - CH_2 -), 0.96 (m 3H, - CH_3).

Synthesis of 1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-butylphenyl)diazene

The mixture of 4-((4-butylphenyl)diazenyl) phenol (6.35 g, 25mmol), K_2CO_3 (6.6 g, 50mmol), 1,6-dibromo-hexane (12.2 g, 50 mmol) and 200 mL refined acetone were added into a 500mL round-flask, and then, the reaction solution was heated to reflux and react for 24 h with magnetic stirring. After hot filtration, the product was precipitated into cold methanol and then filtered. The precipitation was separated through a silicon column using CH_2Cl_2 as the eluent. The production was obtained.

Yield,70%

^1H NMR (CDCl_3), δ (ppm): 7.88 -7.92 (s, 4H, Ar-H), 7.3(m, 2H, Ar-H),7.0(m, 2H, Ar-H), 4.03(m, 2H, - CH_2 -), 3.43(m, 2H, - CH_2 -), 2.6 (m, 2H,- CH_2 -) 1.4-1.9(m, 12H, - CH_2 -), 0.96 (m 3H, - CH_3).

Synthesis of MAzo, 6-(4-((4-butylphenyl)diazenyl)phenoxy)hexyl methacrylate

In a 500 mL flask with a magnetic stirrer, a mixture of 1-(4-((6-bromohexyl)oxy)phenyl)-2-(4-butylphenyl)diazene (7.5 g, 18mmol), methacrylic acid (2.2 g, 27mmol), K_2CO_3 (3.4 g, 54mmol) and DMF (250mL) was added. The reaction mixture was heated to 100 °C with continuous stirring for 24 h. The reaction mixture was added to ice water (2000 mL) and the crude product precipitate was collected.

Chromatogram column separation, get the target product. ^1H NMR (CDCl_3), δ (ppm):

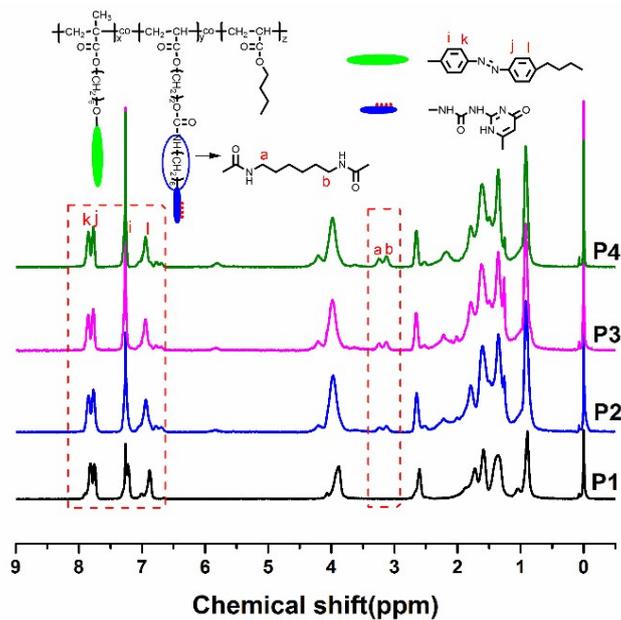
7.88 -7.92 (s, 4H, Ar-H), 7.3(m, 2H, Ar-H),7.0(m, 2H, Ar-H), 5.58-6.1 (m, 2H, =CH₂), 4.1-4.2 (m, 2H, -CH₂-), 2.6 (m, 2H, -CH₂-), 1.9 (m, 3H, -CH₃), 1.4-1.9(m, 10H, -CH₂-), 1.0 (m 3H, -CH₃).

¹³ C-NMR(CDCl₃) δ (ppm): 14.1(=CH-CH₃) 18.95(-CH₃), 22.3-29.65(-CH₂-) 39.63-40.72(-CH₂-)62.41-62.85(-CH₂-O-),128.31 (CH₂=C(CH₃)), 131(CH₂=C) 106.66 (aromatic C ortho to C-O), 124.71(aromatic C ortho to C-N), 128.33(aromatic C ortho to C-C), 154.68-156.09(aromatic C-N), 161.08(aromatic C-O),1165.92(-CO-).

FTIR-KBr: ν =CH (3048), -CH₃(2929), -CH₂- (2929, 2870, 1448), -CO- (1703), C=C(1638), ArC-H (1590,1482,832), -N=N-(1458), -C-O-C-(1312), Ph-O-C-(1259,1170), -CH=C(927).

Synthesis of LCEs

In this work, the LC monomer (MAZo), the cross-linker monomer (HHU), and the monomer (BA) were added into the tube according to the proportion. As the example of P1, MAZo (2 g, 4.8mmol), BA(0.768g, 6 mmol), HHU(0.441g, 1.08 mmol), AIBN(0.008 g, 0.047mmol), and THF(8 mL) were added to a reaction tube. After taking turns of freezing–thaw cycles for three times, the tube was sealed under vacuum and the polymer tube is placed in the constant temperature of 75°C for 12 hours. After the reaction time, open the tube, the reaction solution was diluted with THF and dropwise to a large amount of methanol for precipitating, centrifuge, and then dried in a vacuum oven at room temperature for 24h. Yield, 70%.

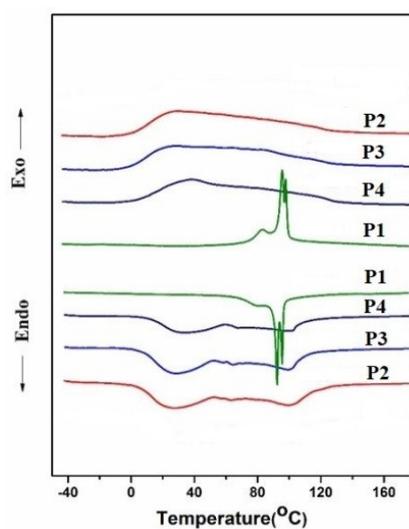


S-figure 1. ^1H NMR spectra of *Pns*.

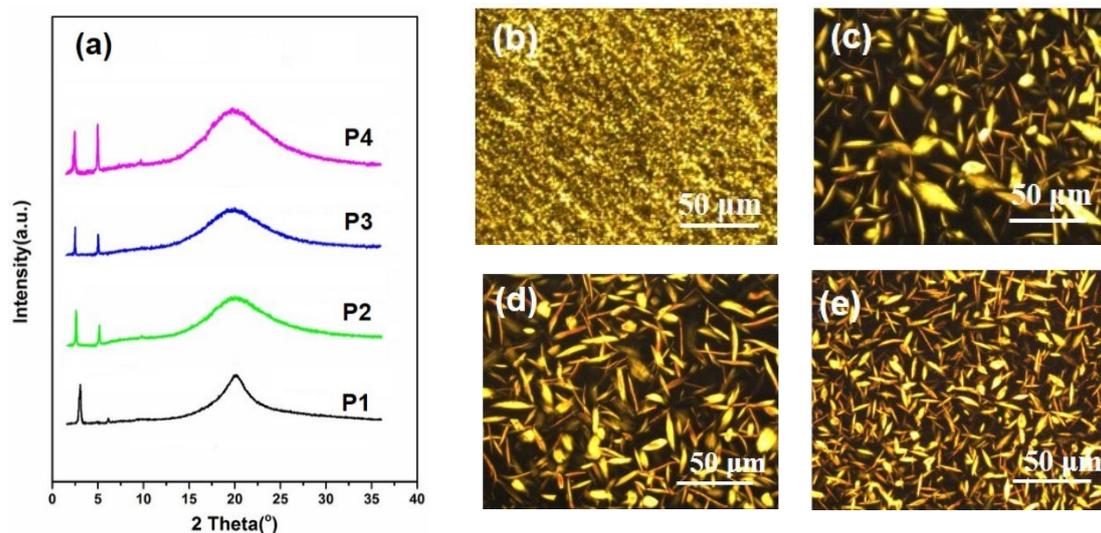
S-Table 1 Molecular Characteristics Result of the series copolymer

| Sample | Content of LC ^a | Butyl Acrylate ^a | Content of Cross-linker ^a | Mn ($10^4 \times \text{g/mol}$) ^b | PDI ^b |
|--------|----------------------------|-----------------------------|--------------------------------------|--|------------------|
| P1 | 100% | 0 | 0 | 1.83 | 1.64 |
| P2 | 57.7% | 32.6% | 9.7% | 1.57 | 1.65 |
| P3 | 55.8% | 30.1% | 14.1% | 1.48 | 1.66 |
| P4 | 51.5% | 28.2% | 20.3% | 1.47 | 1.70 |

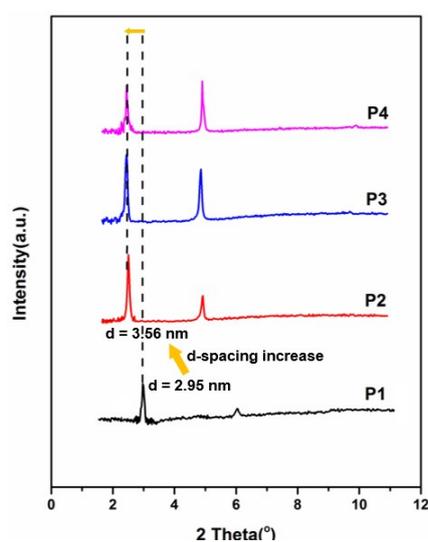
^aActual mole fraction was calculated via ^1H NMR; ^b Obtained from GPC-1515 instrument, linear PS as standards; all these content percentage was mass fraction.



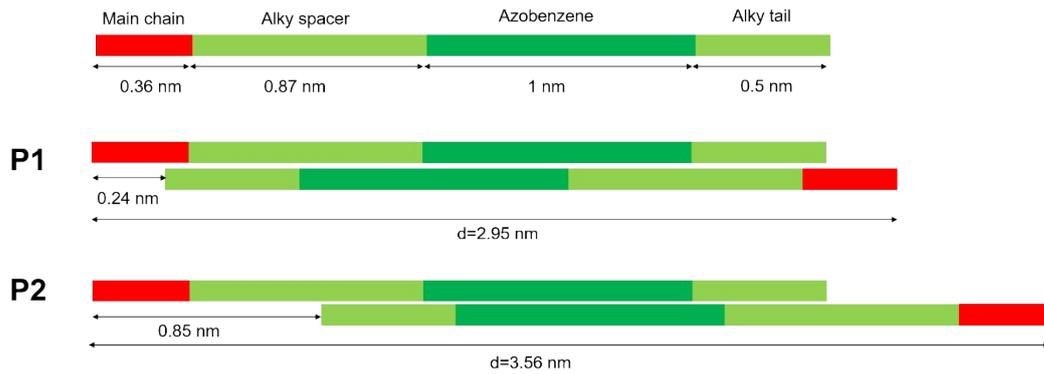
S-figure 2. DSC thermogram of *Pns* at 10 °C/min during the first cooling process and the second heating process.



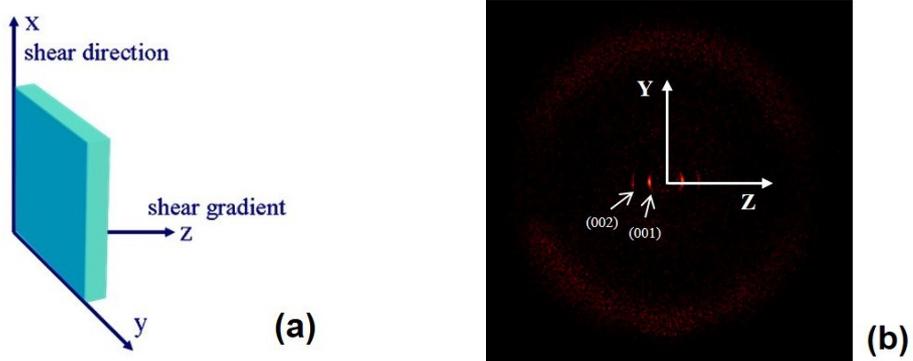
S-figure 3.(a) Set of 1D WAXD powder patterns of *Pns* at room temperature; the Representative textures of P1(b) and P2(c), P3(d), P4(e) at 95°C (200× magnification) respectively.



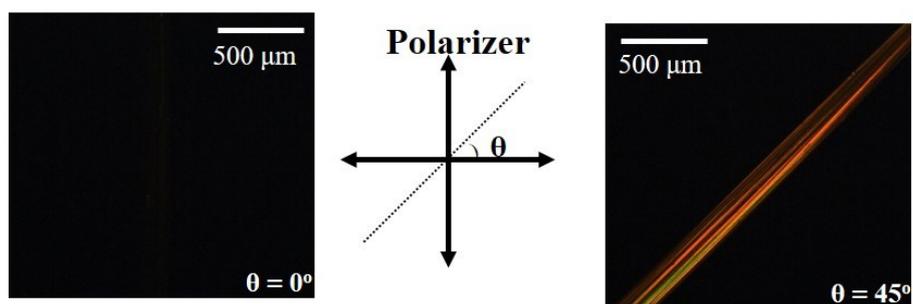
S-figure 4. The magnified image of 1D WAXD powder patterns of low angle area for *Pns* at room temperature.



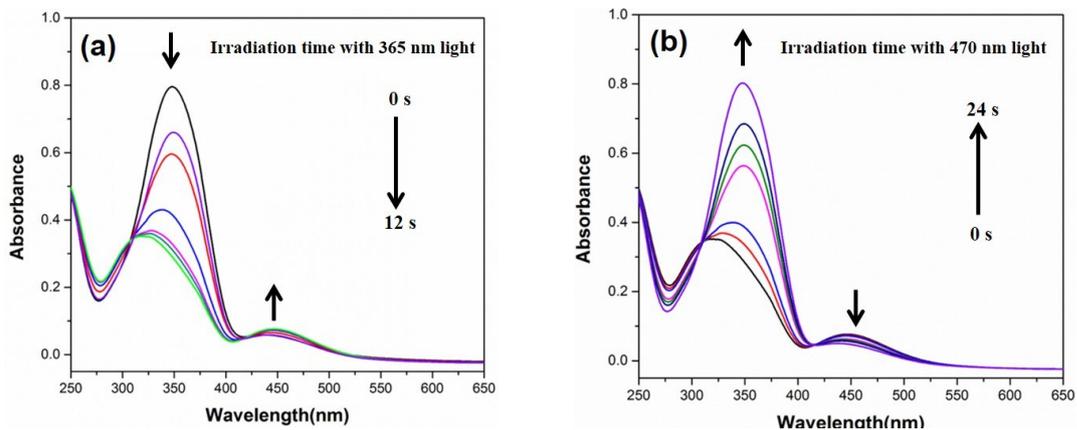
S-figure 5. Schematics of the frustrated molecular packing of P1 and P2.



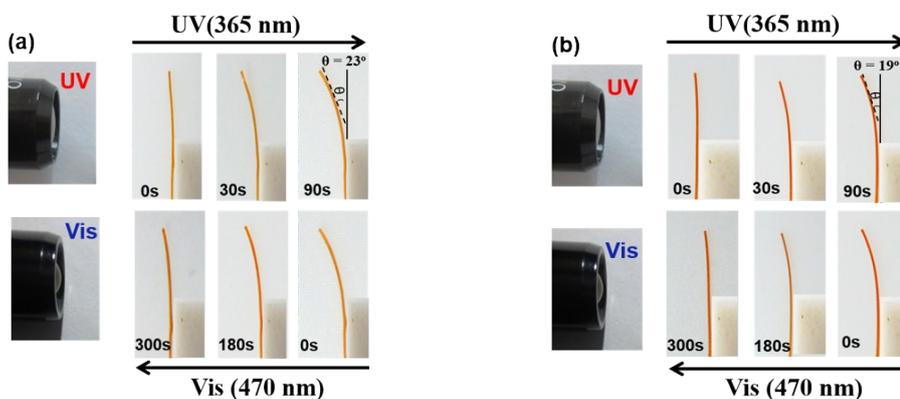
S-figure 6. 2DWAXD film pattern of P2 at room temperature.



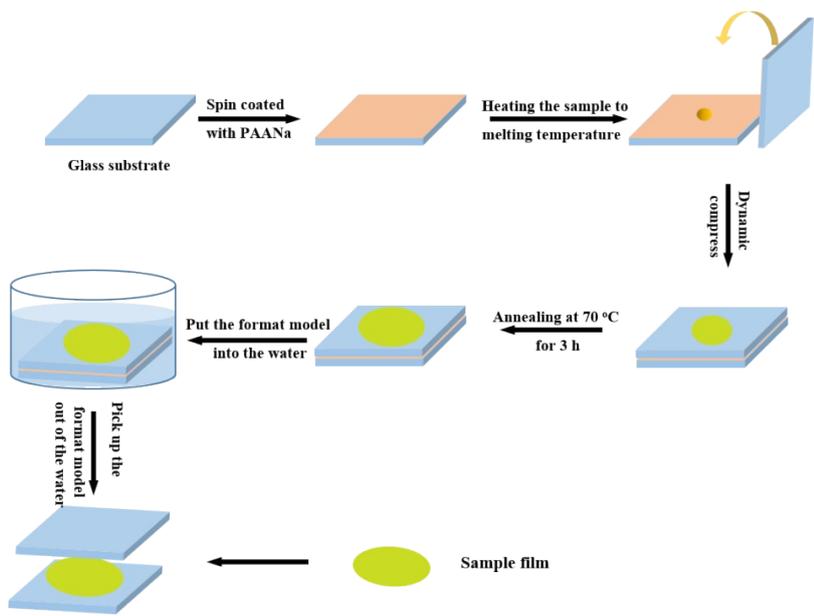
S-figure 7. Polarizing optical micrographs of P2 fiber observed at room temperature, the directions of optical axes of the two polarizers was expressed by the black arrows, and the dashed line shows the drawing direction



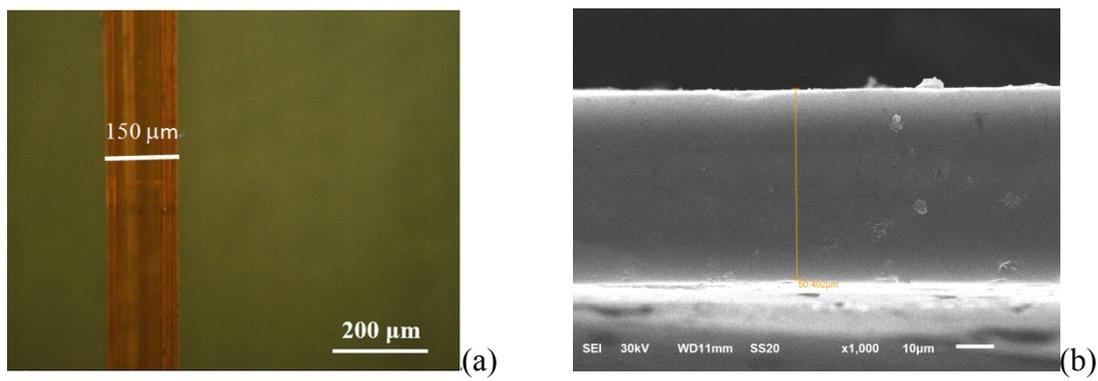
S-figure 8. The change of UV-vis absorption spectra of P2 film at the room temperature with different irradiating time. (a) Exposure the light of 365 nm; (b) Exposure the light of 470 nm at the photostationary state.



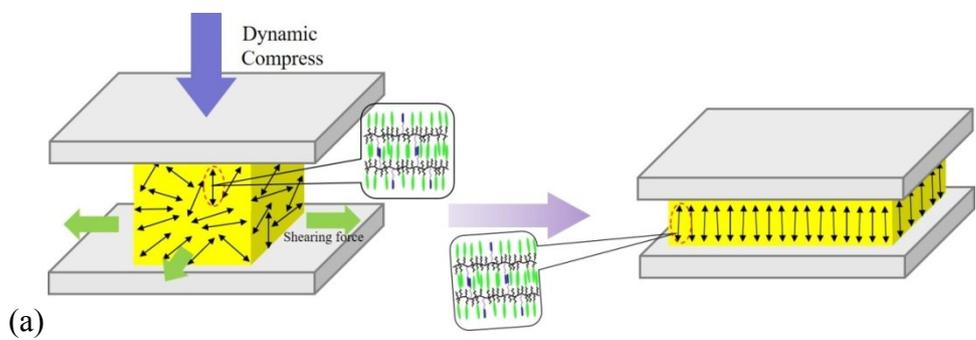
S-figure 9. (a) Photoinduced bending and unbending behavior of the P3(a) and P4(b) fiber upon irradiation with 365 nm UV light (160 mW/cm^2) and 470 nm visible light (160 mW/cm^2).



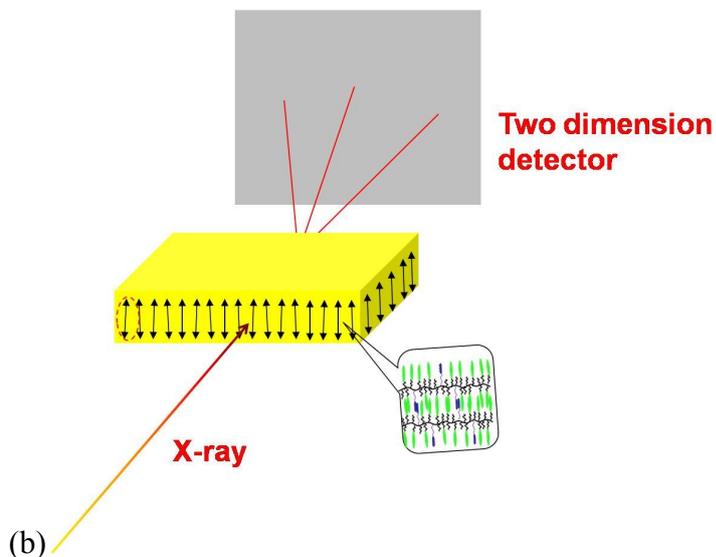
S-figure 10. Preparation process of P2 film.



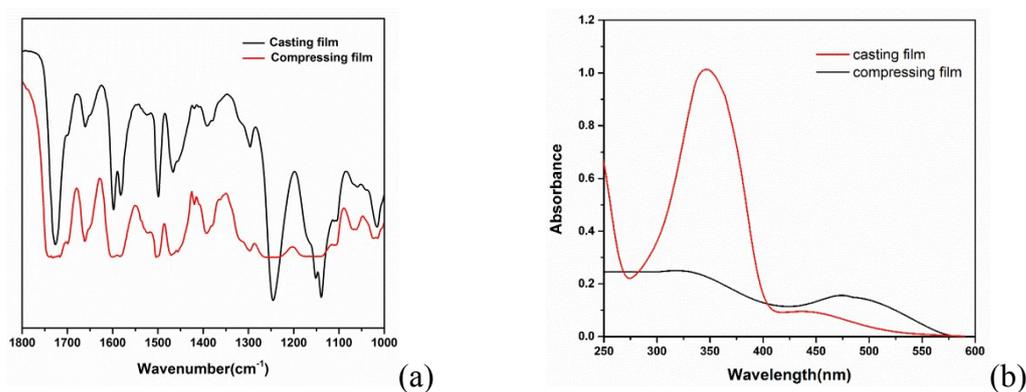
S-figure 11. The diameter of the fiber from the image of the optical micrographs (a), and the thickness of the thin film from the image of the electrical micrographs (b).



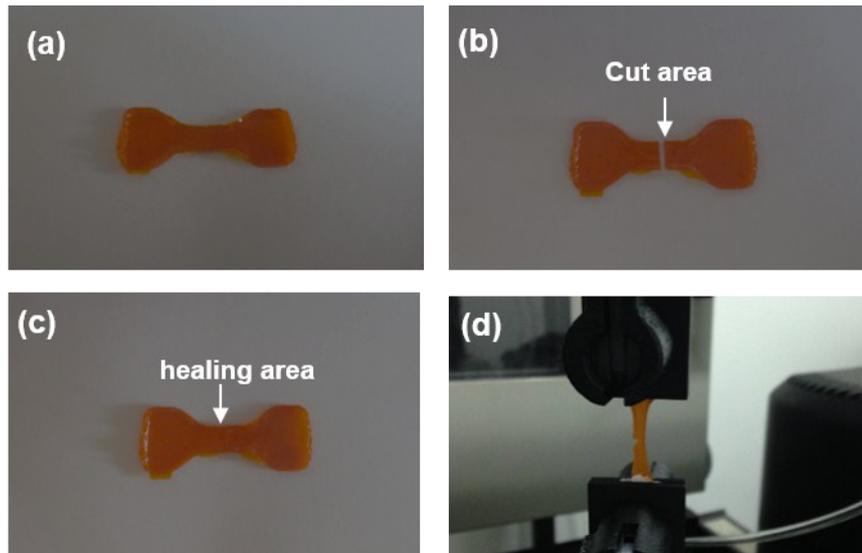
(a)



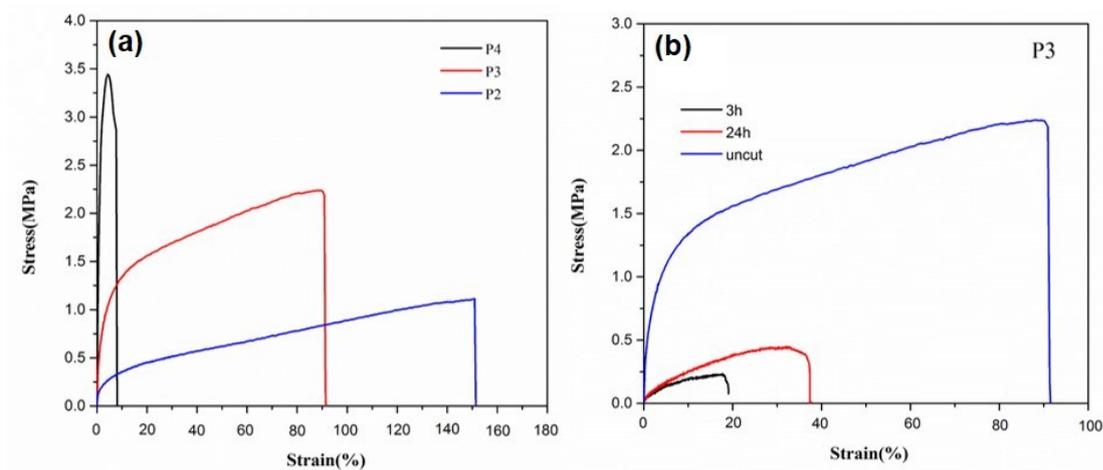
S-figure 12. The process of the dynamic compress for the formation of the orientated structure(a), the relationship between the direction of X-ray and the orientated thin film (b).



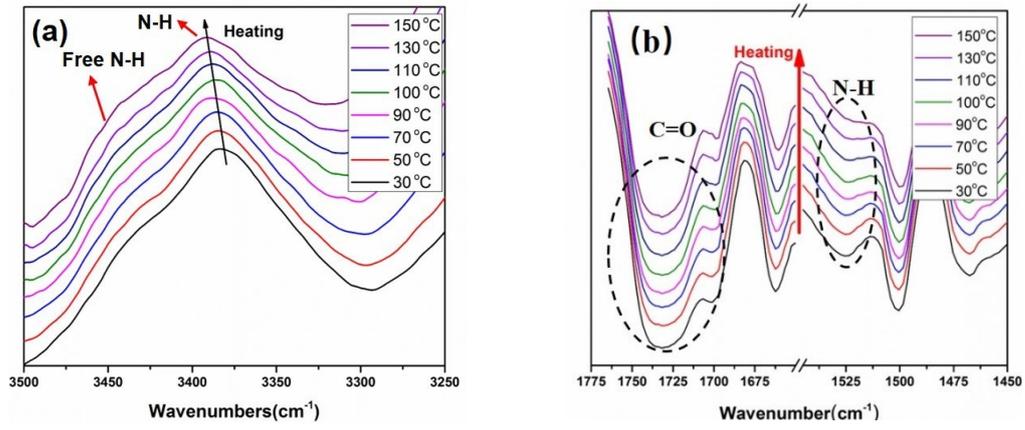
S-figure 13. The FTIR spectra trances (a) and the UV-vis absorption spectra of P2 film(b).



S-figure 14. The healing process of P2 and strain-tress experiment setup, (a) the dumbbell-shaped sample, (b) cutted sample, (c) after seal-healing sample, (d) the process of strain-stress experiment for the healing sample.



S-figure 15. (a)The strain-tress test of P2, P3 and P4; (b) P3 after different time periods of healing at 40 °C



S-figure 16. The FTIR spectra traces of P2 at various temperature upon the heating process.