

Photomechanical Motion of Liquid Crystalline Fibers Bending away from a Light Source

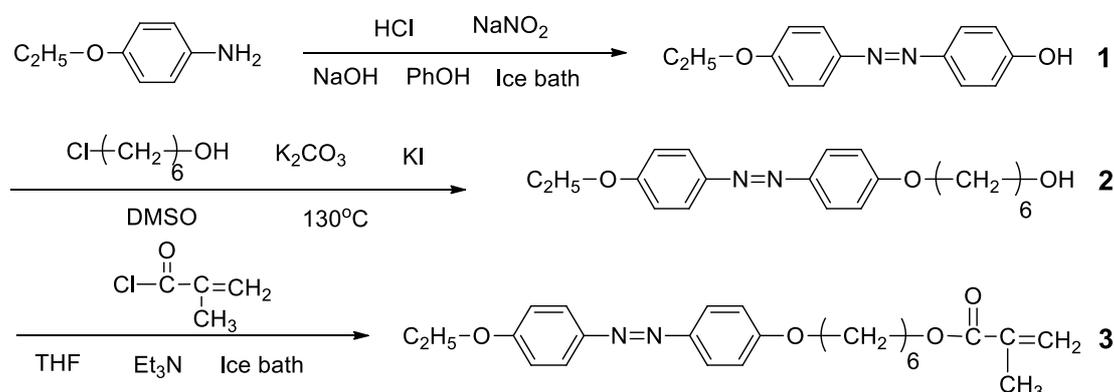
Zhangxiang Cheng,^a Shudeng Ma,^b Yihe Zhang,^{*a} Shuai Huang,^b Yuxuan Chen,^b and Haifeng Yu,^{*b}

^a School of Materials Science and Technology, China University of Geosciences, Beijing 100083, P. R. China.

^b Department of Materials Science and Engineering, and Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Peking University, Beijing 100871, P. R. China.

1. Synthesis and characterization of the monomers

The azobenzene compound M6AB2 was synthesized through three steps of chemical reactions, as shown in Scheme S1. M6BP3OH was gained from the other laboratory.



Scheme S1. Synthesis of the azobenzene compound M6AB2

1.1 Synthesis of 4-ethoxy-4'-hydroxy azobenzene (compound 1)

p-Phenetidine (5.0g, 36.5mmol) was dissolved in aqueous solution with HCl 70mL (12mL 12MHCl and 58mL H₂O) and kept in the ice bath at 0°C. NaNO₂ (2.5g, 36.2mmol) in water (50mL) was added dropwise to former solution and stirred for 30 min. phenol (3.4g, 36.2mmol) and NaOH (4.4g, 110mmol) were dissolved in 65ml H₂O solution. The latter solution was added dropwise to former solution at 0 °C and then stirred for 2h. A yellow precipitate was collected by filtration. The crude product

was washed with water. After drying over a vacuum for 24 hours, yield: 80%.

1.2 Synthesis of 4-ethoxy-4'-(6-hydroxy hexyloxy) azobenzene (compound 2)

Compound 1 (5.0g, 20.7mmol) and K_2CO_3 (3.4g) were dissolved in the DMSO (100mL). 6-chloro-1-hexanol (3.4g, 24.8mmol) and a trace of KI were then added, and the solution was heated at 140°C for 10h. The resulting mixture was poured into water and extracted with chloroform. A rotary evaporator was used to remove the chloroform. The crude product was purified by recrystallization from methanol to obtain the product. Yield: 65%.

1.3 Synthesis of 6-(4-(4-ethoxyphenylazo)phenoxy)-hexyl methacrylate (M6AB2)

M6AB2 was synthesized by an esterification reaction between 4-ethoxy-4'-(6-hydroxy hexyloxy) azobenzene (3g, 8.8mmol) and methacryloyl chloride (2.54ml) in the presence of triethylamine. The resulting mixture was poured into water and extracted with chloroform. A rotary evaporator was used to remove all of the chloroform. The crude product was purified by silica gel column chromatography with dichloromethane as eluent. Yield: 50%. The 1H NMR spectrum of M6AB2 was recorded in $CDCl_3$ solution, as shown in Figure S1. 1H NMR (500MHz, $CDCl_3$, 25°C, TMS): δ 7.88 (4H, m), δ 6.98 (4H, m), δ 6.09 (1H, d), δ 5.54 (1H, d), δ 4.04-4.17 (4H, m), δ 3.72 (2H, m), δ 1.94 (3H, s), δ 1.83 (2H, m), δ 1.73 (2H, m), δ 1.50 (4H, m), δ 1.24 (3H, t).

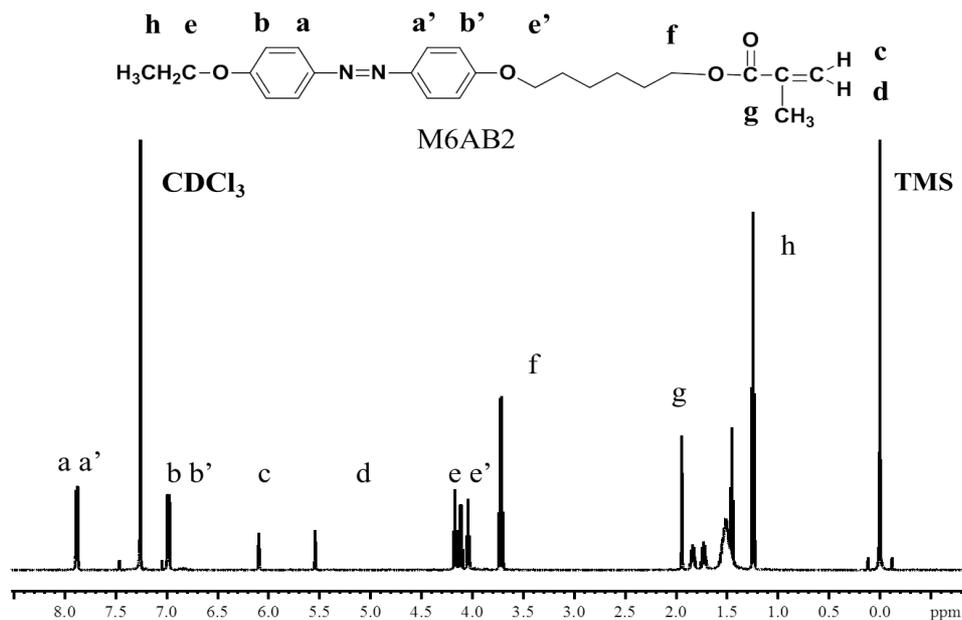


Figure S1. ^1H NMR spectrum of the monomer M6AB2

1.4 Synthesis of the monomer M6BP3OH

Liquid crystal monomer M6BP3OH was gained from the other laboratory, the synthetic route is not clear to us. The ^1H NMR spectrum of M6BP3OH was recorded in CDCl_3 solution, as shown in Figure S2. ^1H NMR (500MHz, CDCl_3 , 25°C , TMS): δ 7.45 (4H, m), δ 6.95 (4H, m), δ 6.09 (1H, d), δ 5.54 (1H, d), δ 4.16 (4H, t), δ 3.99 (2H, t), δ 3.88 (2H, t), δ 2.06 (2H, m), δ 1.94 (3H, s), δ 1.81 (2H, m), δ 1.72 (2H, m), δ 1.50 (4H, m).

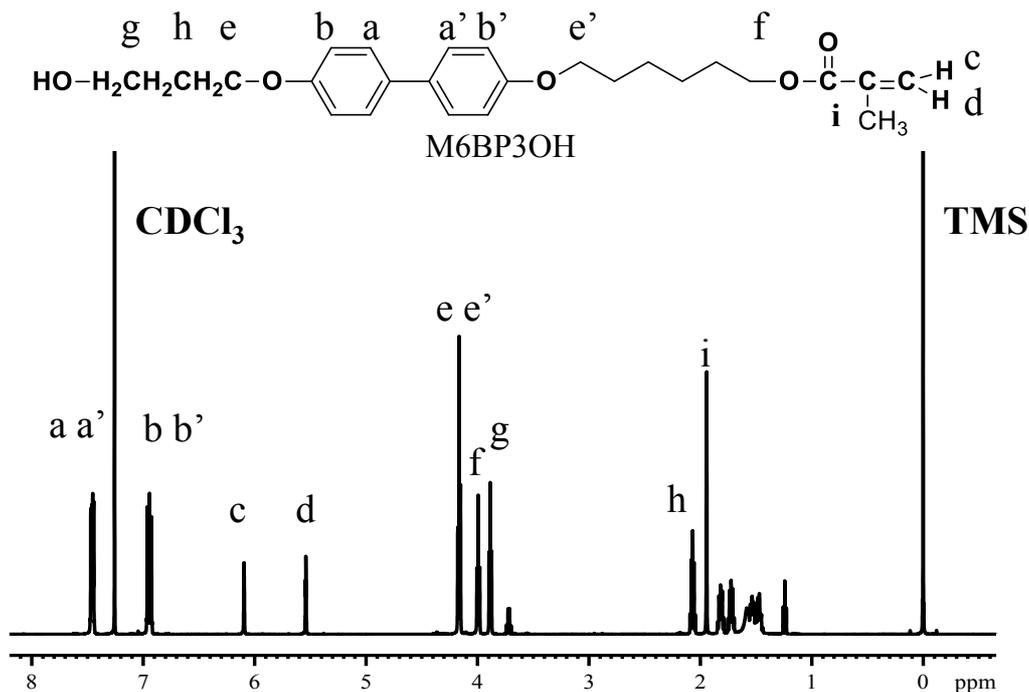


Figure S2. ¹H NMR spectrum of the monomer M6BP3OH

1.5 Differential scanning calorimetry of the monomers

Figure S3 gives the DSC curves of monomer M6AB2 and M6BP3OH. (a) Melting point of M6AB2 is 106 °C at heating process. (b) The peak at 55 °C results from the crystallization of M6BP3OH, the LC-to-isotropic transition temperature is 101 °C.

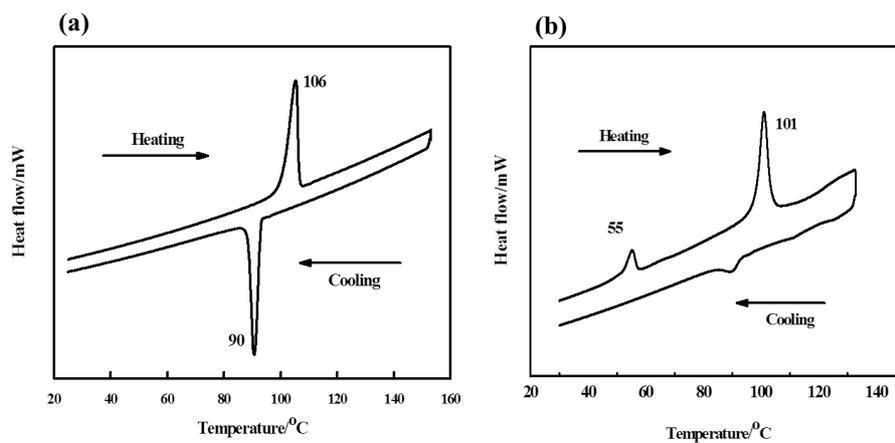
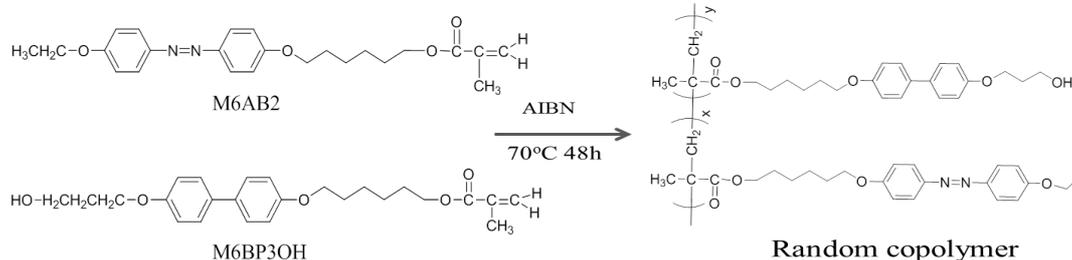


Figure S3. DSC curves of monomer M6AB2 and M6BP3OH.

2. Preparation and characterization of the random copolymers



Scheme S2. Synthetic route for the random copolymer

As shown in Scheme S2, a series of random copolymer was obtained through radical polymerization. The monomers M6AB2 and M6BP3OH were mixed with initiator (AIBN) at 70 °C according to the ratios shown in Table 1.

2.1 Preparation of the random copolymer

Taking sample 3 as an example, the monomers M6AB2 (451mg, 1.1mmol) and M6BP3OH (188mg, 0.47mmol) and AIBN (1wt%, 6.39mg) were dissolved in freshly distilled anisole (10mL). After several freeze-pump-thaw cycles, the mixture was then placed in an oil bath preheated to 70 °C and stirred for over 48 h. The resulting solution was poured into 1000mL of cooled methanol to obtain a crude copolymer. The copolymer was purified by reprecipitation in hexane. A yellow powder was obtained after the precipitate was dried in a vacuum oven for 24 h. Yield: 67%.

2.2 Characterization of the random copolymers

2.2.1 ¹HNMR

¹HNMR spectra were recorded using TMS as the internal standard for deuterated chloroform solution. A small amount of random copolymer solution was measured and molar ratio of the two components was calculated by value of integral of polymer.

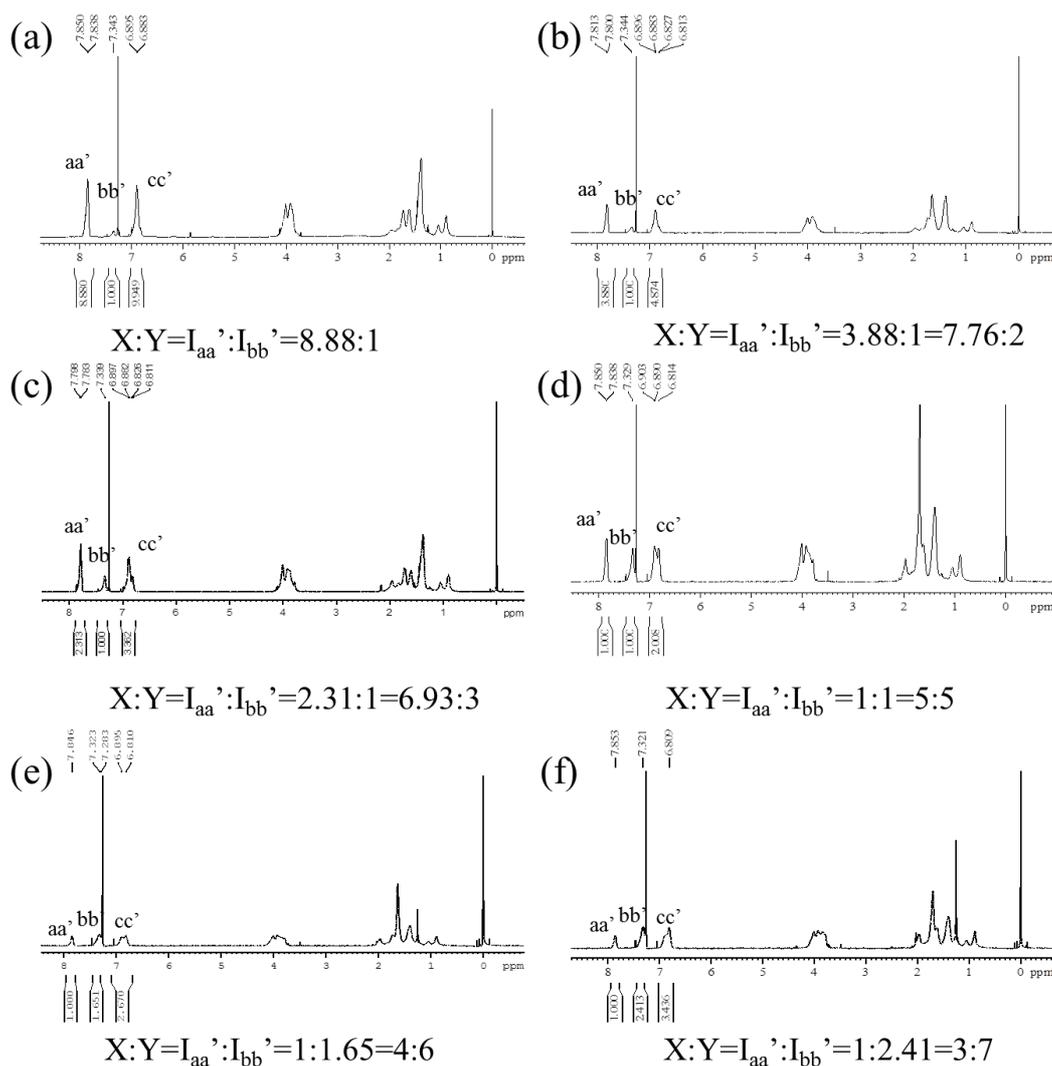


Figure S4. ^1H NMR spectra of (a) sample P91 (feed ratio=9:1), (b) sample P82 (feed ratio=8:2), (c) sample P73 (feed ratio=7:3), (d) sample P55 (feed ratio=5:5), (e) sample P46 (feed ratio=4:6), and (f) sample P37 (feed ratio=3:7)

2.2.2 Gel-permeation chromatography

Gel-permeation chromatography (GPC) has been used a measuring of size-exclusion chromatography (Waters 2489 (UV Detector)/Waters 2414 (RI Detector)) and GPC two columns. THF was used as an eluent at a flow rate 1mL/min. The calibration of molecular weight was calculated by using PS standards. A series of polymers were used by GPC to calculate distribution of molecular weight.

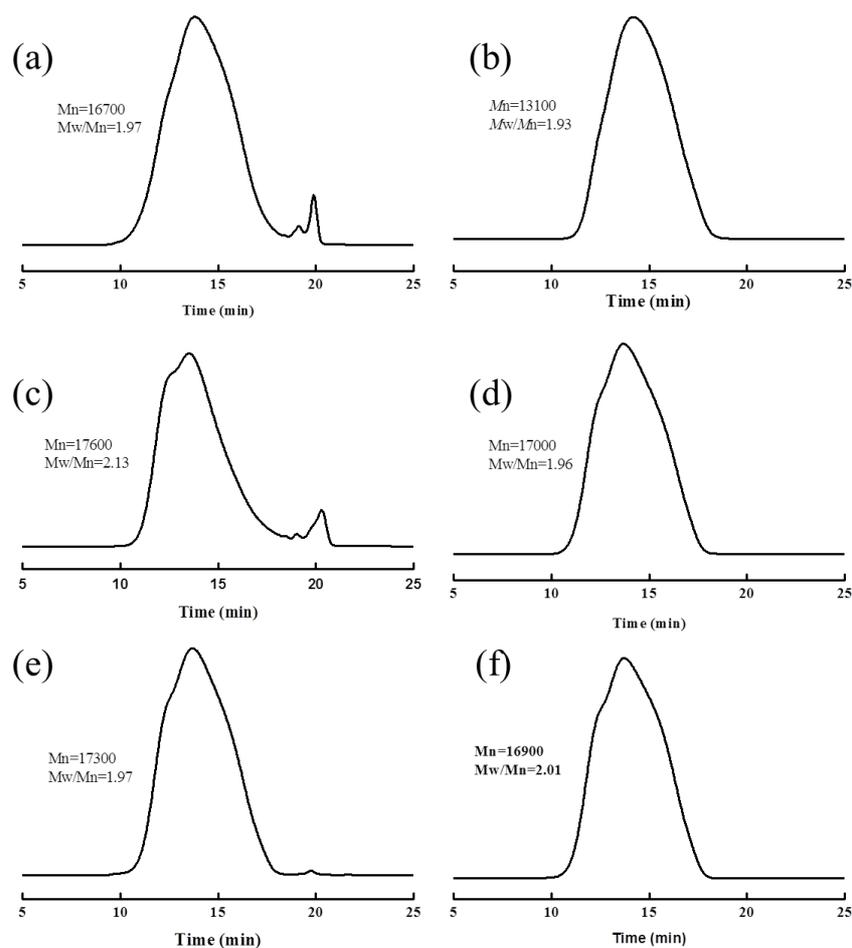


Figure S5. GPC curves for (a) sample P91 (feed ratio=9:1), (b) sample P82 (feed ratio=8:2), (c) sample P73 (feed ratio=7:3), (d) sample P55 (feed ratio=5:5), (e) sample P46 (feed ratio=4:6), and (f) sample P37 (feed ratio=3:7)

2.2.3 Differential scanning calorimetry

The thermal properties of the random copolymer were investigated by differential scanning calorimetry (DSC) (PE DSC8000). DSC scans were performed within the temperature range 20-160 °C at a heating rate of 10°C/min under nitrogen. The glass transition (T_g) and between the liquid crystal phase and the isotropic phase transition temperature was determined by DSC scans. Figure S6 shows the DSC scan profile for a series of random copolymer.

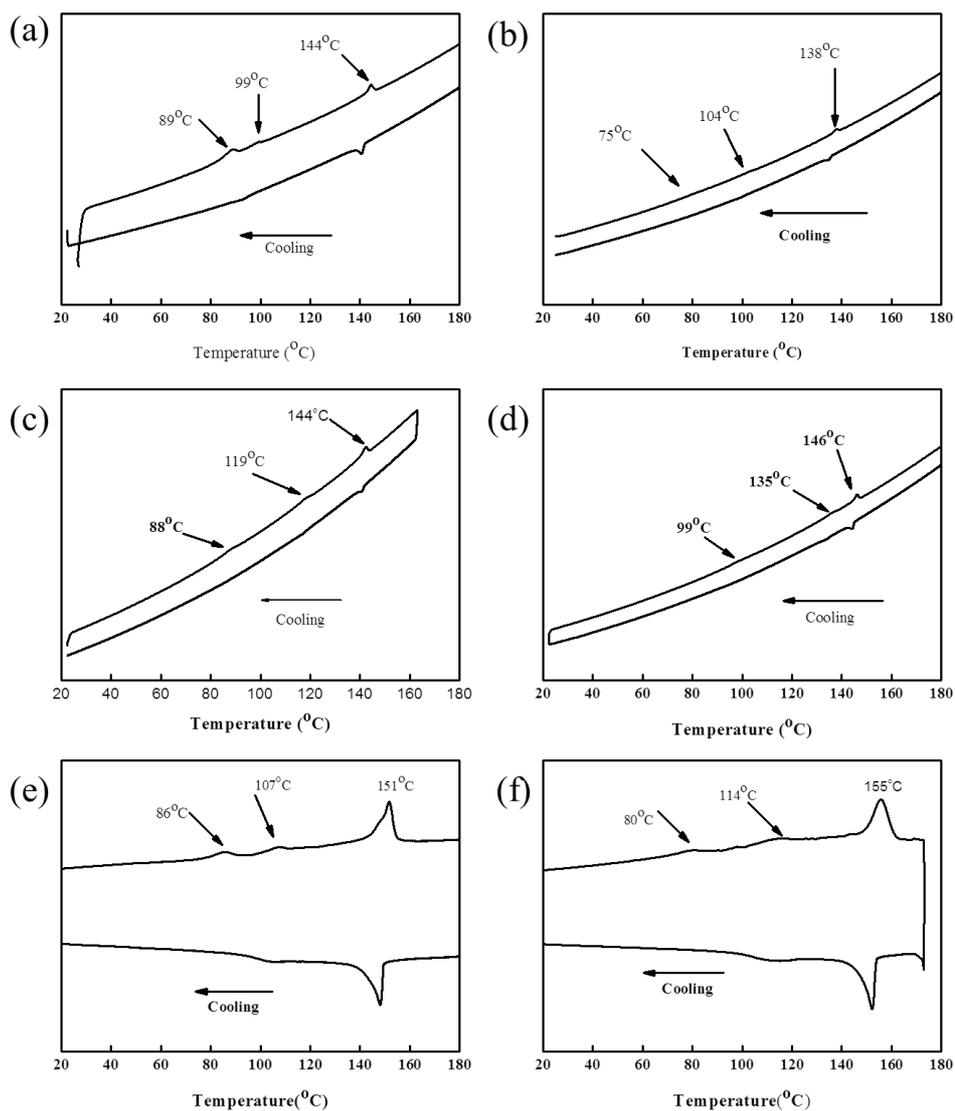


Figure S6. DSC curves of (a) sample P91 (feed ratio=9:1), (b) sample P82 (feed ratio=8:2), (c) sample P73 (feed ratio=7:3), (d) sample P55 (feed ratio=5:5), (e) sample P46 (feed ratio=4:6), and (f) sample P37 (feed ratio=3:7)

2.2.4 Polarizing optical microscopy

The liquid crystal texture of the sample 3 was observed by POM (ZEISS AXIO Scope. A1). Firstly, the copolymer was heated to isotropic state. Then the copolymer was cooled from isotropic phase to liquid crystal phase. The POM texture refers to a polydomain nematic phase.

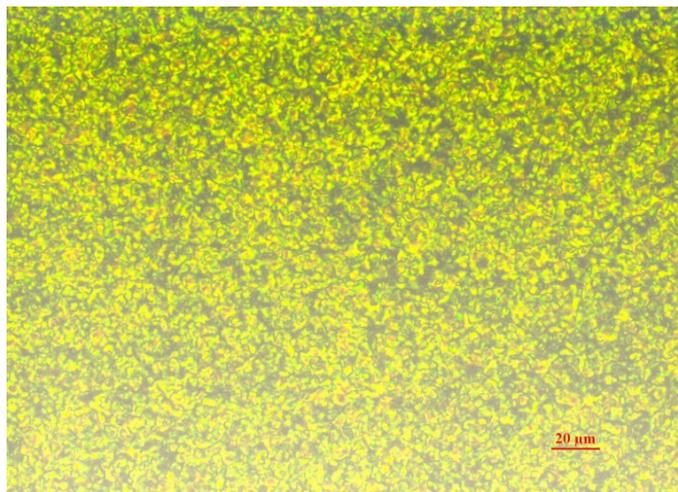


Figure S7. Polarizing optical microscopic picture of the random copolymer (sample 3) at 130 °C. The red bar represents 20 micrometers.

3. Differential scanning calorimetry of the crosslinked LC fibers

The thermal properties of the CLCPs fiber were investigated by DSC at a heating and cooling rate 10°C/min. The glass transition temperature and phase transition temperature of CLCPs fiber were not occurred in DSC curve (Figure S8). At least three scans were examined to guarantee the reproducibility.

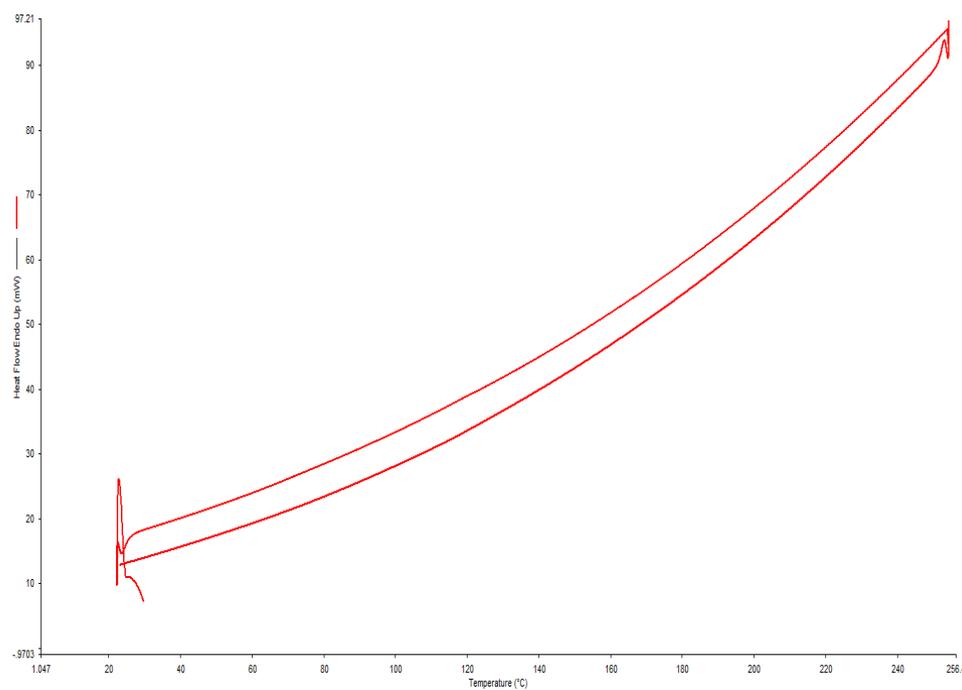


Figure S8. DSC curves of the CLCP (P73) fiber.

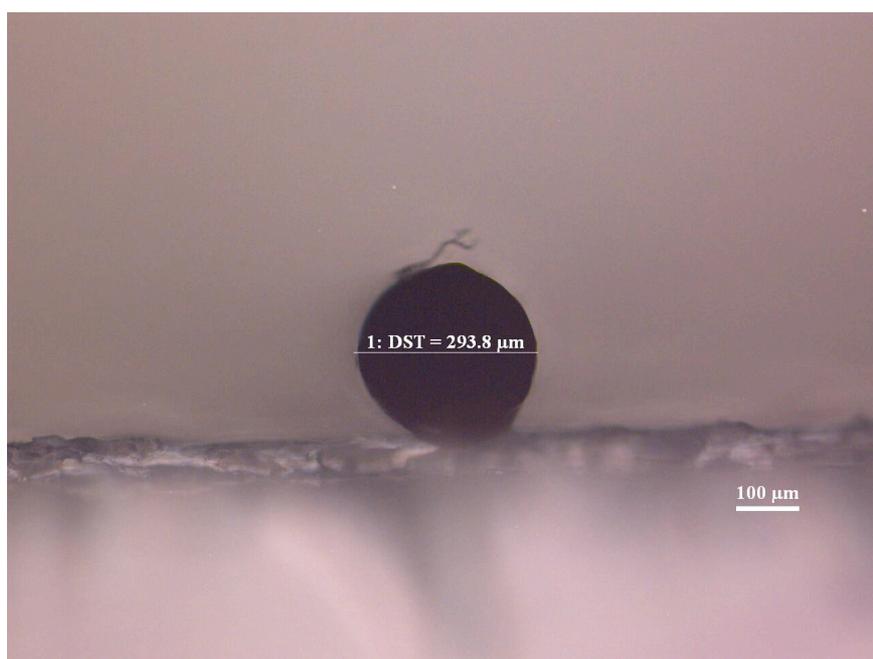


Figure S9. Optical image of the cross-section of the CLCP fiber.

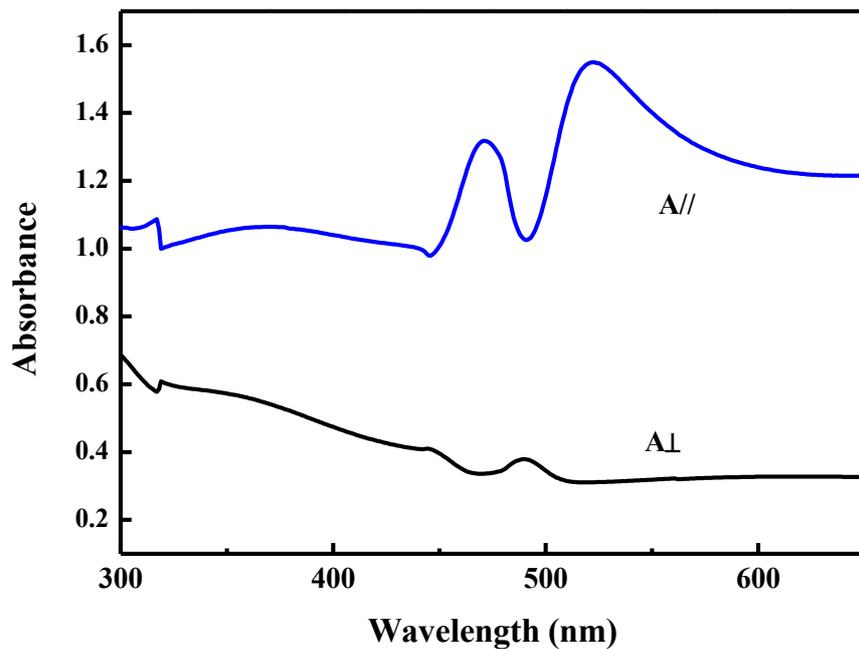


Figure S10 Polarized UV-Vis spectra of crosslinked fiber. The black and blue curves are the absorption perpendicular and parallel to the stretching direction, respectively. The azobenzene mesogens became aligned parallel to the stretching direction.

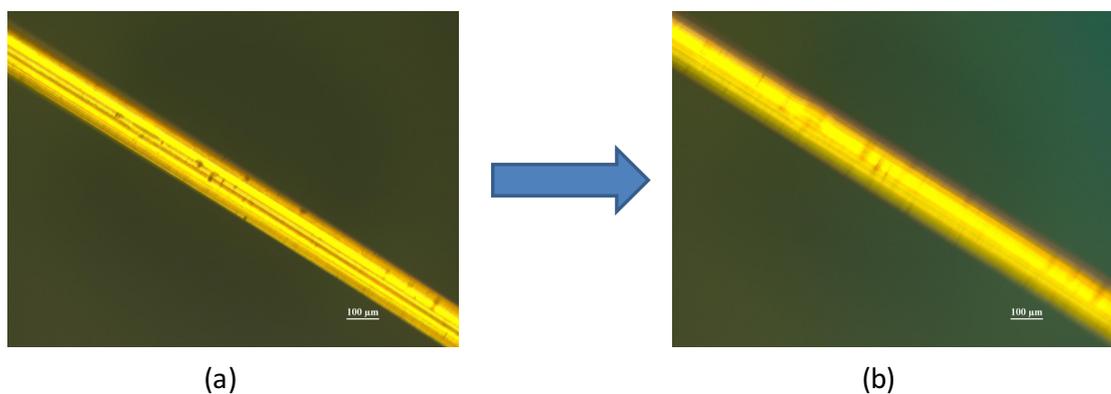


Figure S11. POM pictures of the CLCP (P73) fiber without UV irradiation (a) and under UV irradiation (b). No obvious change in birefringence was observed.



Figure S12. Photoresponsive properties of the AZ-CLCP (P73 upon crosslinking) in a conventional cantilever geometry.

4 Supplementary movie legends

Movie S1. Photoinduced bending behavior of the AZ-CLCP fiber fabricated by random copolymer 3 ($n(\text{M6AB2}):n(\text{M6BP3OH})=7:3$).

Movie S2. Photoinduced bending behavior of the AZ-CLCP fiber fabricated by random copolymer 2 ($n(\text{M6AB2}):n(\text{M6BP3OH})=8:2$).

Movie S3. Photoinduced bending behavior of the AZ-CLCP fiber fabricated by random copolymer 4 ($n(\text{M6AB2}):n(\text{M6BP3OH})=5:5$).

Movie S4. Photoinduced bending behavior of the AZ-CLCP fiber fabricated by random copolymer 5 ($n(\text{M6AB2}):n(\text{M6BP3OH})=4:6$).

Movie S5. Photoinduced bending behavior of the AZ-CLCP fiber fabricated by random copolymer 6 ($n(\text{M6AB2}):n(\text{M6BP3OH})=3:7$).

Movie S6. Upon UV light irradiation, the structural anisotropy of the AZ-CLCP fiber fabricated by random copolymer 3 was not destroyed.

Movie S7. visible light can accelerate recovery process of the AZ-CLCP fiber. The bent AZ-CLCP fiber (fabricated with P55) just needs ca.15s to back to initial state upon 530nm visible light irradiation compared with ca. 60s without visible light irradiation at 100 °C

Movie S8. Photoinduced bending behavior of the AZ-CLCP fiber fabricated by random copolymer 4 ($n(\text{M6AB2}):n(\text{M6BP3OH})=5:5$). Both ends of the fiber were fixed to study the photoinduced expansion behaviors.

Movie S9. Photoinduced bending behavior of the AZ-CLCP in a conventional cantilever geometry fabricated by random copolymer 3 ($n(\text{M6AB2}):n(\text{M6BP3OH})=7:3$).

Movie S10. Recovery behavior of the AZ-CLCP cantilever shown in **Movie S9**.