

Fast Photoinduced Deformation of Hydrogen-Bonded Supramolecular Polymers Containing α -Cyanostilbene Derivative

Experimental Section

Materials

Z-TCS was synthesized according to the synthetic route as shown in below (Scheme S1) and purified through column chromatography. Poly(4-vinylpyridine) (P4VP, weight-average molecular weight, $M_w = 1.70 \times 10^5$, PDI = 1.63) was synthesized by bulk polymerization. 4-vinyl pyridine (98%, Alfa Aesar) was purchased from Shanghai jingchun biochemical technology co., Ltd. and purified via vacuum distillation. 2,2'-Azobis(isobutyronitrile) (AIBN, 95%, Alfa Aesar) was purchased from Shanghai jingchun biochemical technology co., Ltd. and purified by recrystallization from ethanol. 3,4,5-trihydroxybenzaldehyde monohydrate (98%, Alfa Aesar), 4-Hydroxybenzyl cyanide (98%, Alfa Aesar), 1-Bromododecane (99%, Alfa Aesar), potassium t-butoxide (98%, Alfa Aesar) were purchased from Shanghai jingchun biochemical technology co., Ltd. and used without further purification. Anhydrous potassium carbonate (K_2CO_3 , 99%), potassium iodide (KI, 99%), anhydrous magnesium sulfate, (99%) N,N-dimethylformamide (DMF, 99.5%), dichloromethane (99.5%), chloroform (99.5%) n-hexane (99.5%), anhydrous ethanol (99.5%), anhydrous ether (99.5%) and hydrochloric acid (36%~38%), were obtained from Xilong Scientific Co., Ltd. (Guangdong, China).

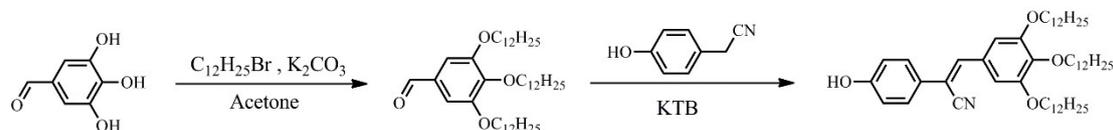
Synthesis of 3,4,5-Tris(dodecyloxy)benzaldehyde. 3,4,5-trihydroxybenzaldehyde monohydrate (5g, 29.05 mmol), K_2CO_3 (24.08 g, 174.53 mmol), KI (catalytic amount) and 150 mL dry DMF were added into a 250 mL three-necked flask and the mixture was stirred at 80 °C for 30 min. And then 1-Bromododecane (28.1 mL, 116.20 mmol) was added into the mixture. The reaction lasted 48 h. After cooling to RT, the mixture was poured into brine and extracted with dichloromethane. The organic layer was dried by anhydrous magnesium sulfate, and the solvent was evaporated by a rotor vapor. The product (15.72 g, 82%) was obtained by column chromatography using dichloromethane and n-hexane (1:1 v/v). 1H NMR (400 MHz, $CDCl_3$) δ [ppm]: 9.83 (s, 1H, -CHO), 7.08 (s, 2H, Ar-H), 4.04 (m, 6H, -OCH₂), 1.79 (m, 6H, -CH₂), 1.48 (m, 6H, -CH₂), 1.26 (m, 48H, -CH₂), 0.88 (t, 9H, -CH₃).

Synthesis of (Z)-2-(4-hydroxyphenyl)-3-(3,4,5-tris(dodecyloxy)phenyl)acrylonitrile (Z-TCS). 4-Hydroxybenzyl cyanide (2 g 15.02 mmol), potassium t-butoxide (2.53 g 22.5 mmol) and 30 mL ethanol were added into a 100 mL three-necked flask and the mixture was stirred under a nitrogen atmosphere at RT for 30 min. 3,4,5-tris(dodecyloxy)benzaldehyde (6.60 g, 10 mmol) was dissolved in 20 mL ethanol and then the solution was slowly dropped into the mixture. The reaction lasted for 24 h at 50 °C under nitrogen atmosphere. After cooling to room temperature, the mixture was neutralized by hydrochloric acid and poured into brine and extracted with dichloromethane. The

organic layer was dried by anhydrous magnesium sulfate, and the solvent was evaporated by a rotor vapor. The yellow product (6.65 g, 86%) was obtained by column chromatography using dichloromethane. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ [ppm]: 7.52 (d, 2H, Ar-**H**), 7.29 (s, 1H, -**CH=C**-), 7.11 (s, 2H, Ar-**H**), 6.89 (d, 2H, Ar-**H**), 5.41 (s, 1H, -**OH**), 4.03 (t, 6H, -**OCH₂-**), 1.87 – 1.74 (m, 6H, -**CH₂-**), 1.49 (m, 6H, -**CH₂-**), 1.26 (m, 55H, -**CH₂-**), 0.88 (t, 9H, -**CH₃**).

Synthesis of poly(4-vinyl pyridine) (P4VP). A dry polymerization tube was charged with 5.00 g (47.62 mmol) of 4-vinyl pyridine, 15.62 mg (95.24 μmol) AIBN and a magnetic stir bar, the tube was degassed by three freeze-pump-thaw cycles and sealed under vacuum. Polymerization was carried out at 70 °C for 3 h. The polymerization was terminated by putting the tube into an ice-water mixture, and then the tube was opened. The product was diluted with CHCl_3 and precipitated into ether to obtain P4VP. To eliminate the unreacted 4-vinyl pyridine completely, the precipitated was repeated, until no peak was observed at the elution time of monomer in gel permeation chromatography (GPC) measurement. The M_n and PDI of P4VP were 170000 g/mol and 1.63, respectively.

Polymer Complex Preparation. The supramolecular complexes were prepared as the following procedure. P4VP and Z-TCS were separately dissolved into chloroform to get 5 wt % solutions. In order to obtain the $\text{P4VP}(\text{Z-TCS})_x$ complex, P4VP and Z-TCS solutions were mixed together with calculated proportion related to x . A homogeneous solution was obtained. After mechanical stirring for 24 h at room temperature, the solvent was slowly evaporated. The product was then placed in a vacuum oven at 35 °C to remove residual solvent. The supramolecular complex was thus obtained.



Scheme S1. Synthesis of Z-TCS.

Instruments and measurements

Nuclear magnetic resonance (NMR). $^1\text{H NMR}$ spectroscopy was performed on a Bruker ARX400 MHz spectrometer using tetramethylsilane (TMS) as the internal standard at ambient temperature. The chemical shifts are reported on the ppm scale.

Gel permeation chromatography (GPC). The apparent number average molecular weight (M_n) and polydispersity index ($\text{PDI} = M_w/M_n$) were measured on a GPC (WATERS 1515) instrument with a set of HT3, HT4 and HT5 columns. The μ -styragel columns used THF as an eluent and the flow rate was 1.0 mL min^{-1} at 38 °C. All the GPC data were calibrated with polystyrene standards.

Fourier Transform infrared spectroscopy (FT-IR). FTIR spectra in KBr pellets were recorded on a PE Spectrum One FTIR spectrophotometer.

Differential scanning calorimetry (DSC). DSC traces of the polymer were obtained using a TA Q10 DSC instrument. The temperature and heat flow were calibrated using standard materials

(indium and zinc) at cooling and heating rates of $10\text{ }^{\circ}\text{C min}^{-1}$. The sample, with a typical mass of about 5 mg, was encapsulated in sealed aluminum pans.

Polarizing optical microscope (POM). LC texture of the polymers was examined under POM (Leica DM-LM-P) equipped with a Mettler Toledo hot stage (FP82HT).

One-dimensional wide-angle X-ray diffraction (1D WAXD). 1D WAXD experiments were performed on a BRUKER AXS D8 Advance diffractometer with a 40 kV FL tubes as the X-ray source (Cu $K\alpha$) and the LYNXEYE_XE detector. Background scattering was recorded and subtracted from the sample patterns.

Ultraviolet-visible spectra (UV-Vis). UV-Vis absorption spectra were recorded on an Agilent Cary600 spectrometer.

The thermal effect of 365 nm UV light in the $\text{P4VP}(\text{Z-TCS})_x$ fibers were measured with thermal imagers (FLIR, E40)

The photodeformation of the supramolecular polymers was studied by using a 365 nm UV LED (FUWO, FUV-6BK, 80 mW/cm^2)

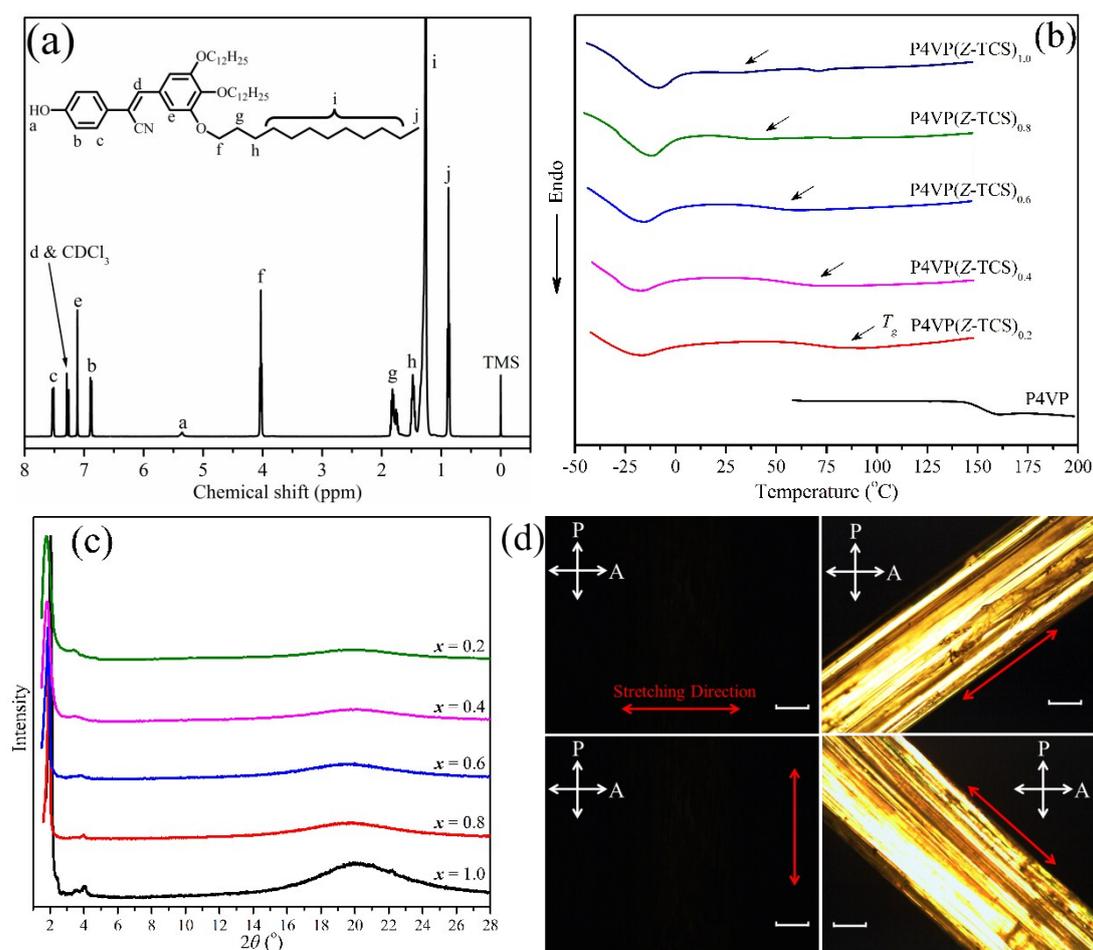


Figure S1. (a) $^1\text{H NMR}$ spectra of Z-TCS. (b) DSC curves of $\text{P4VP}(\text{Z-TCS})_x$ complexes and P4VP during the second heating scan at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$. (c) 1D-WAXD profiles of $\text{P4VP}(\text{Z-TCS})_x$ complexes recorded at $25\text{ }^{\circ}\text{C}$. (d) POM images of $\text{P4VP}(\text{Z-TCS})_{1.0}$ fiber. Red arrows indicate the stretching directions. P: polarizer, A: analyzer. Scale

bars: 300 μm .

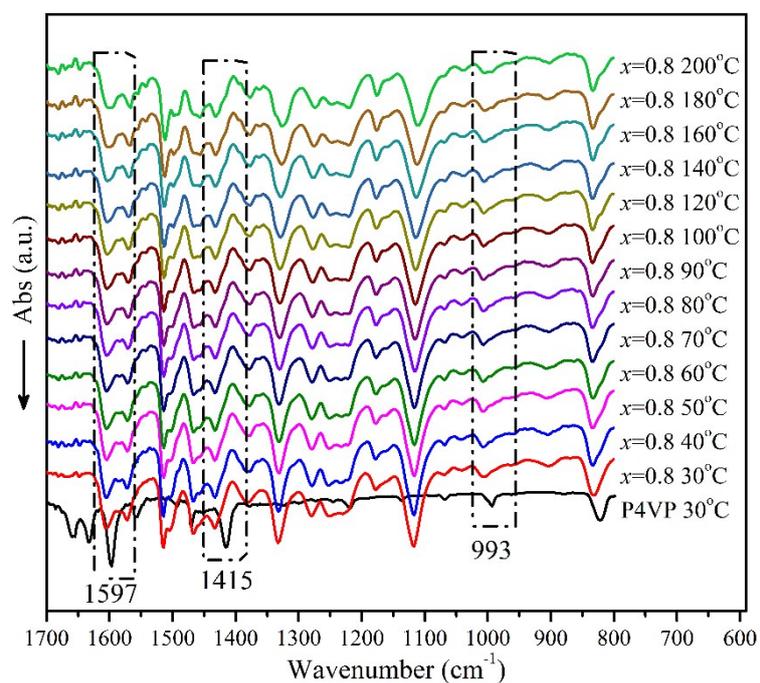


Figure S2. Temperature-variable FTIR spectra of P4VP(Z-TCS)_{0.8}.

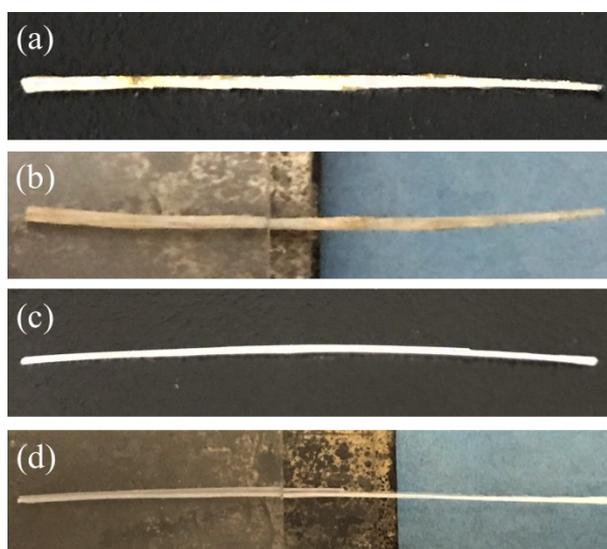


Figure S3. (a) Images of P4VP fiber and (b) after UV irradiation (80 mW cm^{-2}) for 20 min at 150 °C and (c) the P4VP(4-(dodecyloxy)-4'-hydroxyl biphenyl)_{1.0} fiber and (d) after UV irradiation (80 mW cm^{-2}) for 20 min at 75 °C.

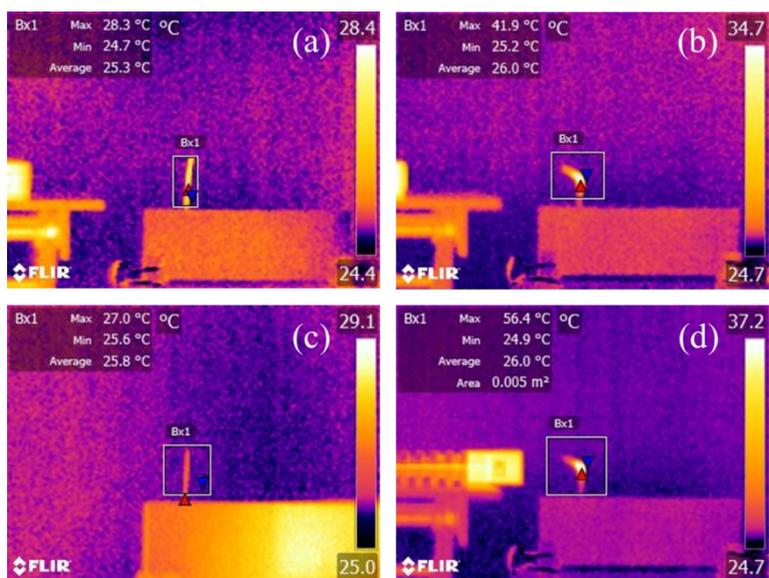


Figure S4. Thermal photographs of the P4VP(Z-TCS)_{0.8} fiber before (a) and after (b) UV irradiation (365 nm, 80 mW cm⁻²) and the P4VP(Z-TCS)_{0.2} fiber before (c) and after (d) UV irradiation. The size of the fibers is about 1 mm × 20 mm.

Movie S1: Bending behavior of P4VP(Z-TCS)_{1.0} fiber.

Movie S2: Heating recovery of P4VP(Z-TCS)_{0.6} fiber.

Movie S3: Reading of the encrypted information “L”.

Movie S4: Reading of the encrypted information “C”.

Movie S5: Reading of the encrypted information “rectangular wave”.