

Supporting information for

Is Chemical Crosslinking Necessary for the Photoinduced Bending of Polymer Films?

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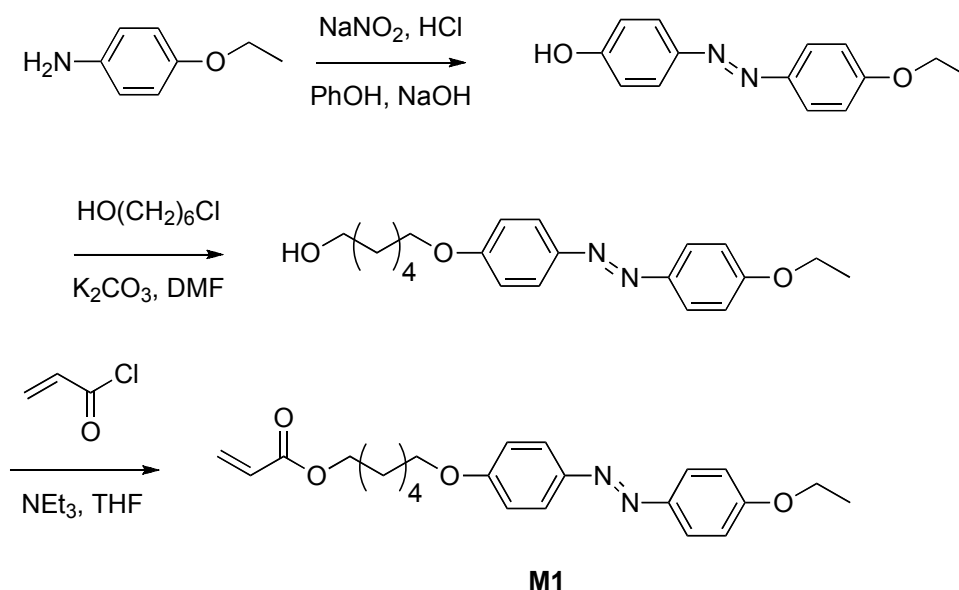
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Materials

All reagents were purchased from Aldrich, Kanto, Tokyo Kasei, or Wako, and were used as received without further purification.

Synthesis of monomers

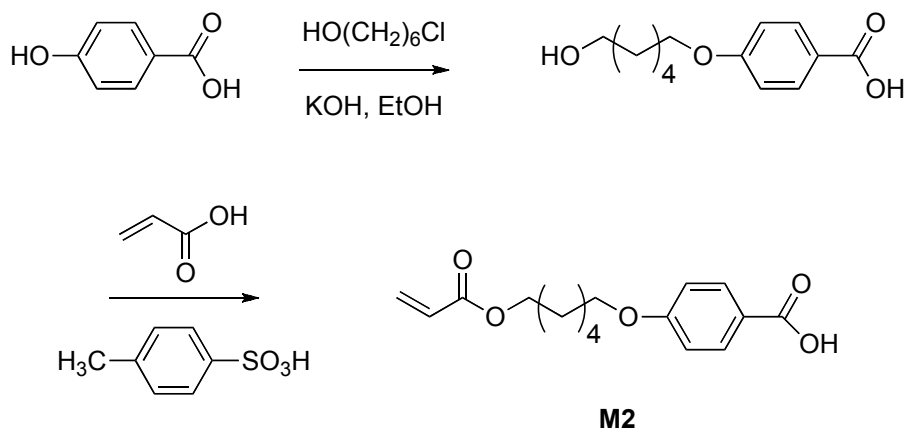
6-[4-(4-Ethoxyphenylazo)phenoxy]hexyl acrylate (M1)



The monomer **M1** was synthesized by a diazo-coupling reaction between 4-ethoxyaniline and phenol in the presence of sodium nitrite and hydrochloric acid and the following reaction with 6-chloro-1-hexanol and acryloyl chloride as previously reported.^{1,2}

¹H NMR (CDCl₃, 300 MHz): δ = 1.43-1.86 (m, 11H), 4.02 (t, J = 6.4 Hz, 2H), 4.08 (q, J = 7.0 Hz, 2H), 4.16 (t, J = 6.6 Hz, 2H), 5.80 (d, J = 10 Hz, 1H), 6.08 (dd, J = 10, 17 Hz, 1H), 6.38 (d, J = 17 Hz, 1H), 6.97 (d, J = 9 Hz, 4H), 7.85 (d, J = 9 Hz, 4H). Elemental analysis: Calcd. for C₂₃H₂₈N₂O₄: C, 69.67; H, 7.12; N, 7.07 %. Found: C, 69.55; H, 7.14; N, 7.10 %. MS (FAB) found: m/z 397 [M+1]⁺ (396.20 caclcd for C₂₃H₂₈N₂O₄).

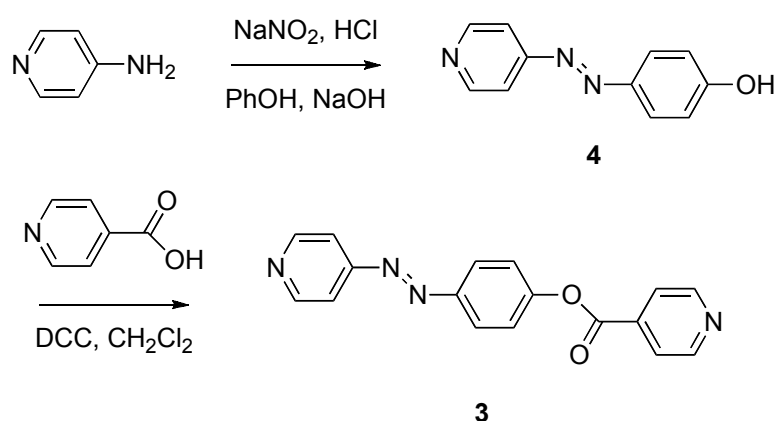
4-Carboxyphenoxyhexyl acrylate (**M2**)



The monomer **M2** was synthesized via etherification between 4-hydroxybenzoic acid and 6-chloro-1-hexanol in the presence of potassium hydroxide and the following reaction with acrylic acid as previously reported.³

¹H NMR (CD₃OD, 300 MHz): δ = 1.42-1.49 (m, 4H), 1.61-1.80 (m, 4H), 3.98 (t, J = 6.6 Hz, 2H), 4.15 (t, J = 6.6 Hz, 2H), 5.80 (d, J = 11 Hz, 1H), 6.06 (dd, J = 10, 17 Hz, 1H), 6.29 (d, J = 17 Hz, 1H), 6.90 (d, J = 9 Hz, 2H), 7.89 (d, J = 9 Hz, 2H). Elemental analysis: Calcd. for C₁₆H₂₀O₅: C, 65.74; H, 6.90; O, 27.37 %. Found: C, 65.55; H, 7.03; O, 27.30 %. MS (FAB) found: m/z 292 [M]⁺ (292.13 cacl'd for C₁₆H₂₀O₅).

Scheme S1. Synthesis of crosslinker **3**.



4-(4-Hydroxyphenylazo)pyridine (**4**)

Crosslinker **3** was prepared according to the procedures shown in Scheme S1. 4-Aminopyridine (6.0 g, 64 mmol) was dissolved in 50 mL of hydrochloric acid (7.3 N) and the resulting solution was cooled to 0 °C. With stirring, a mixture of 4.0 g (58 mmol) of sodium nitrite, 5.0 g (53 mmol) of phenol and sodium hydroxide

(50 mmol) in water (20 mL) was added dropwise into the solution to produce diazonium salt. The reaction mixture was stirred at 0 °C for 2 h. After sodium hydroxide was added to the reaction mixture to give pH 7, the precipitated solid was collected and extracted with ethyl acetate. The extracts were washed with water, dried over MgSO₄, and filtered. After the solvent was removed, **4** (3.8 g, 19 mmol) was obtained in 36 % yield.

¹H NMR (CD₃OD, 300 MHz): δ = 6.91 (d, *J* = 9 Hz, 2H), 7.73 (d, *J* = 6 Hz, 2H), 7.87 (d, *J* = 9 Hz, 2H), 8.66 (d, *J* = 6 Hz, 2H).

4-(4-Pyridylazo)phenyl 4'-pyridinecarboxylate (**3**)

A mixture of **4** (0.67 g, 3.4 mmol), isonicotinic acid (1.3 g, 10 mmol) and a trace of 4-dimethylaminopyridine was prepared in dry dichloromethane (150 mL) under nitrogen atmosphere, and the resulting solution was cooled to 0 °C. With stirring, 0.67 g (4.3 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) in dry dichloromethane (50 mL) was added dropwise to the solution at 0 °C, and the reaction mixture was stirred at room temperature for 24 h. The precipitate was removed, and the solution was extracted with ethyl acetate. The extracts were washed with water, dried over MgSO₄, and filtered. After the solvent was removed, the crude product was purified by column chromatography on silica gel (ethyl acetate) to give **3** (0.65 g, 2.1 mmol) in 63 % yield.

¹H NMR (CDCl₃, 300 MHz): δ = 7.41 (d, *J* = 9 Hz, 2H), 7.71 (d, *J* = 6 Hz, 2H), 8.00 (d, *J* = 6 Hz, 2H), 8.05 (d, *J* = 9 Hz, 2H), 8.80 (d, *J* = 6 Hz, 2H), 8.87 (d, *J* = 6 Hz, 2H). Elemental analysis: Calcd. for C₁₇H₁₂N₄O₂: C, 67.10; H, 3.97; N, 18.41 %. Found: C, 67.07; H, 3.78; N, 18.38 %. MS (FAB) found: *m/z* 305 [M+1]⁺ (304.10 caclcd for C₁₇H₁₂N₄O₂).

Polymerization

A solution of monomers **M1** (400 mg, 1 mmol) and **M2** (300 mg, 1 mmol) containing 2 mol% of an initiator (azobis(isobutyronitrile)) in dry DMF (8 ml) was degassed by three freeze-pump-thaw cycles and then sealed off. The mixture was stirred and heated at 66 °C in a sealed tube for 24 h. The cooled solution was poured into 500 mL of methanol with stirring to precipitate the copolymer. The copolymer obtained was purified by reprecipitation from dichloromethane into methanol three times and dried under vacuum for 24 h. The content of the azobenzene units, which was estimated from elemental analysis of the copolymer, was 40 mol%.

Preparation of complex

After the addition of a solution of the copolymer in THF (1 mL) to the crosslinker (copolymer/crosslinker, 1/1, mol/mol), the solvent was evaporated slowly under vacuum to give a complex.

Characterization of LC properties

The thermodynamic properties of the copolymer and the complexes of the copolymer and each crosslinker were determined by DSC (Seiko I&E, SSC-5200 and DSC220C) at a heating and cooling rate of 10 °C/min. At least three scans were performed to check the reproducibility. The LC alignment in hydrogen-bonded CLCP films was evaluated with a polarizing optical microscope (POM, Olympus, BX50) (Figure S1). The regular maximum and minimum values with 90° separations show that the azobenzene mesogens are preferentially aligned along the rubbing direction of the NaCl substrates.

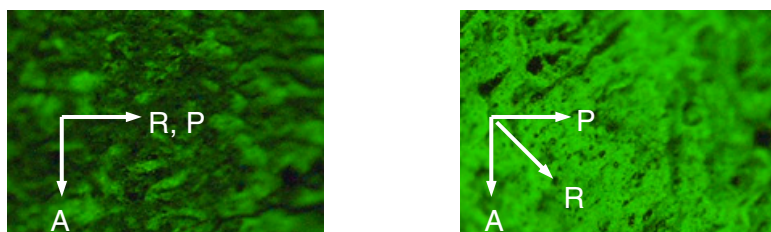


Figure S1. Polarizing optical microscopic images of the hydrogen-bonded CLCP films. A, analyzer; P, polarizer; R, rubbing direction.

IR measurements

As shown in Figure S2, the complexes of **1+2** and **1+3** showed IR bands corresponding to the hydrogen-bonded O-H stretch of the carbonyl groups at 1930 and 2500 cm^{-1} , which indicates the formation of hydrogen bonding between the benzoic acid group of **1** and the pyridyl group of **2** or **3**.^{4,5}

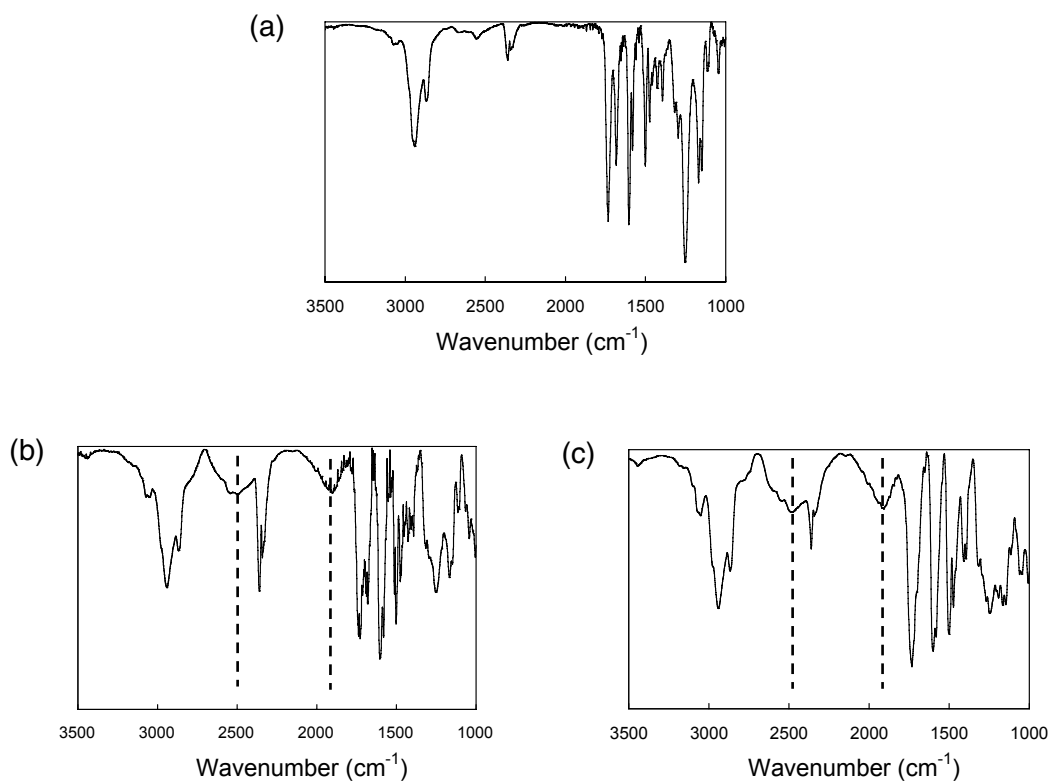


Figure S2. IR spectra of the copolymer **1** (a) and the complexes of **1+2** (b) and **1+3** (c).

Photoinduced bending and unbending

The photoinduced bending and unbending of the hydrogen-bonded CLCP films was studied as follows. A freestanding film on a glass substrate was placed in a Mettler hot stage (FP-90 and FP-82). The bending of the film was observed upon irradiation with UV light at 366 nm from a 500 W high-pressure mercury lamp through glass filters (Asahi Techno Glass, UV-D36, UV-35 and IRA-25S). The bent film was exposed to visible light at >540 nm (Asahi Techno Glass, Y-52 and IRA-25S). The photographs of the bending and unbending were taken by a digital camera (Sony, DSC-F505).

Recyclability of hydrogen-bonded films

We could reconstruct the hydrogen-bonded CLCP films through the recycle process as shown in Figure S3.

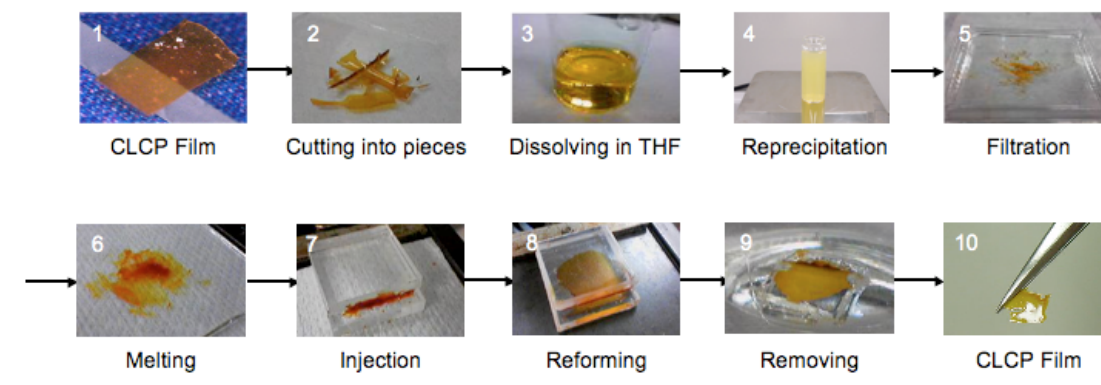


Figure S3. Recycle process of the hydrogen-bonded CLCP films.

References

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