Supplementary Material (ESI) for Journal of Materials Chemistry

Supplementary information for

Can sunlight drive the photoinduced bending of polymer films?

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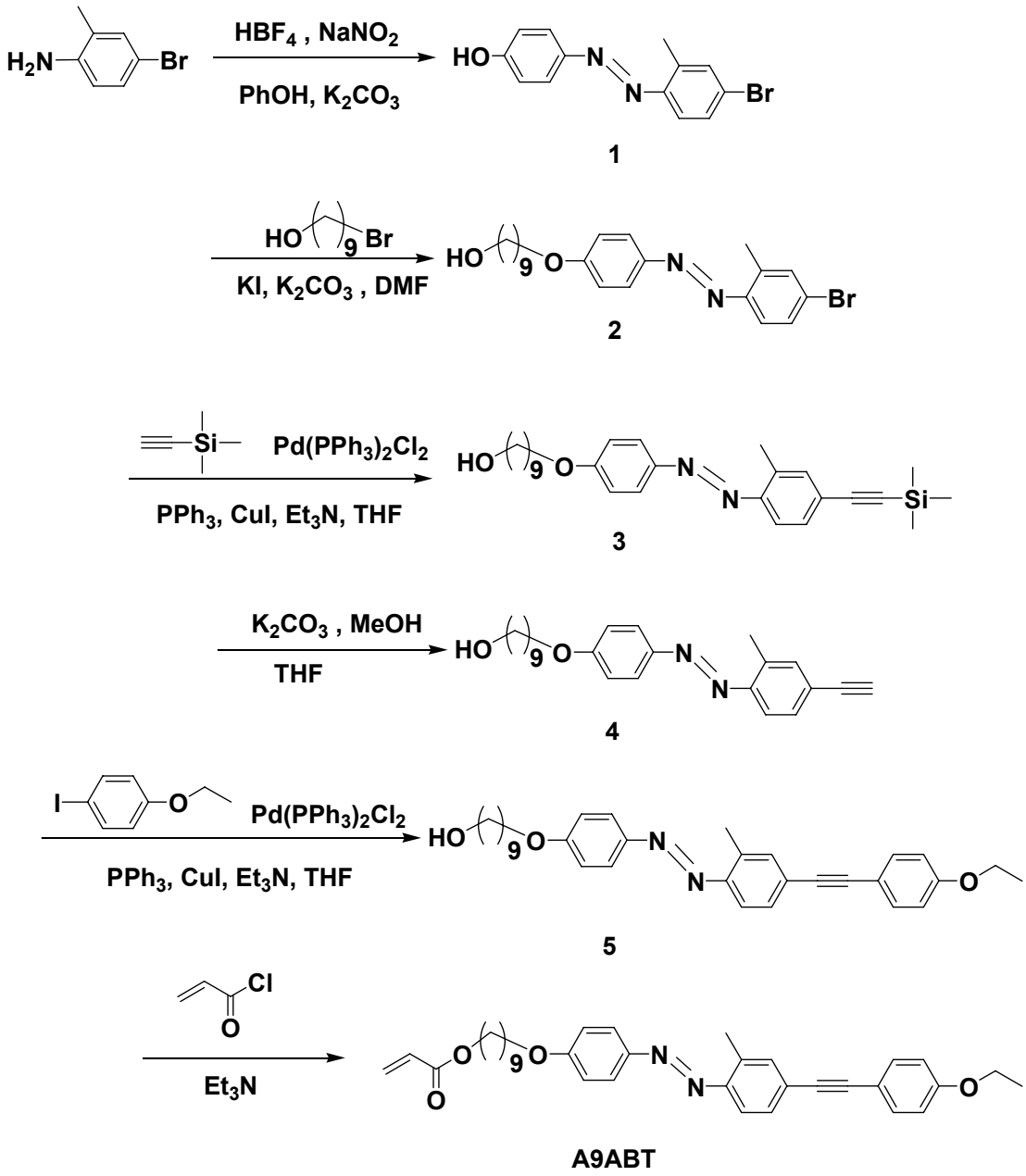
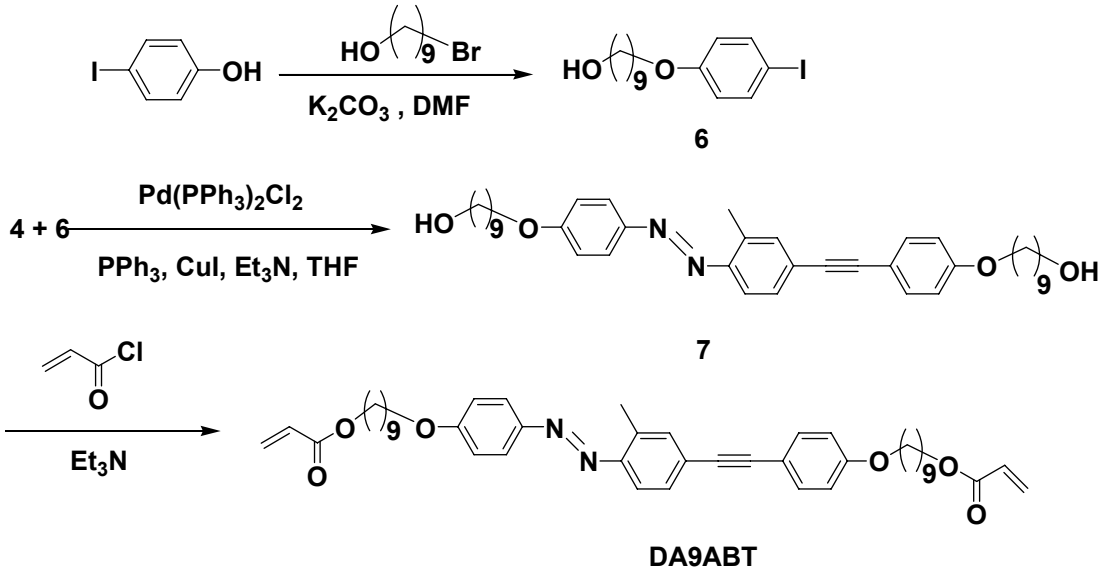
1. Synthesis of Compounds

The synthesis of monomer **A9ABT** and crosslinker **DA9ABT** is outlined in Scheme S1 and S2. The compounds were prepared using a procedure similar to the literature.[1, 2]



Scheme S1. Synthetic route for monomer **A9ABT**.



Scheme S2. Synthetic route for crosslinker **DA9ABT**.

^{1}H NMR spectra of the monomer and crosslinker were recorded in $CDCl_3$ with a Lambda-300 spectrometer. Chemical shifts of ^{1}H signals were quoted to internal standard $CDCl_3$ (δ = 7.24), and listed as chemical shifts in ppm (δ) as follows:

9-[4-[2-Methyl-4-(4-ethoxyphenylethynyl)phenylazo]phenoxy]nonylacrylate (A9ABT)

^{1}H NMR ($CDCl_3$, δ, ppm): 1.24-1.84 (m, 17H), 2.34 (s, 3H), 3.96 (t, 2H), 4.01-4.11 (m, 4H), 5.59 (s, 1H), 6.06(s, 1H), 6.27 (s, 1H), 6.86 (d, 2H), 6.97 (d, 2H), 7.37 (d, 1H), 7.46-7.48 (m, 3H), 7.59 (d, 1H), 7.89 (d, 2H). Anal. Calcd for $C_{35}H_{40}N_2O_4$: C, 76.06; H, 7.29; N, 5.07. Found: C, 76.21; H, 7.34; N, 5.10.

9-(4-((4-((4-(9-(Acryloyloxy)nonyloxy)phenyl)diazenyl)-3-methylphenyl)ethynyl)phenoxy) nonylacrylate (DA9ABT)

^{1}H NMR ($CDCl_3$, δ, ppm): 1.24-1.84 (m, 28H), 2.34 (s, 3H), 3.68 (t, 4H), 4.05 (t, 4H), 5.61 (d, 2H), 6.06 (d, 2H), 6.27 (d, 2H), 6.86 (d, 2H), 6.97 (d, 2H), 7.37 (d, 1H), 7.46-7.48 (m, 3H), 7.59 (d, 1H), 7.89 (d, 2H). Anal. Calcd for $C_{45}H_{56}N_2O_6$: C, 74.97; H, 7.83; N, 3.89. Found: C, 75.10; H, 7.55; N, 3.71.

2. Characterization of Monomer and Crosslinker

The thermodynamic properties of the monomer and crosslinker were determined by a differential scanning calorimeter (DSC; Seiko I&E, SSC-5200 and DSC220C) at a scanning rate of 3 °C/min. At least

three scans were performed for each sample to check the reproducibility. Liquid-crystalline (LC) behavior and phase transition behavior were examined with a polarizing optical microscope (POM; Olympus, Model BH-2) equipped with a hot-stage (Mettler, FP-90 and FP-82). The results are shown in Figure S1 and S2. It was found that both **A9ABT** and **DA9ABT** exhibited a nematic phase over a wide temperature range more than 50 °C upon heating and cooling. For **A9ABT**, a typical schlieren texture was observed from 88 °C to 174 °C upon heating. When cooled down from the isotropic phase, **A9ABT** entered the nematic phase at 171 °C, followed by a crystallization at 62 °C. **DA9ABT** showed the nematic phase from 84 °C to 136 °C upon heating, and from 131 °C to 24 °C upon cooling, respectively.

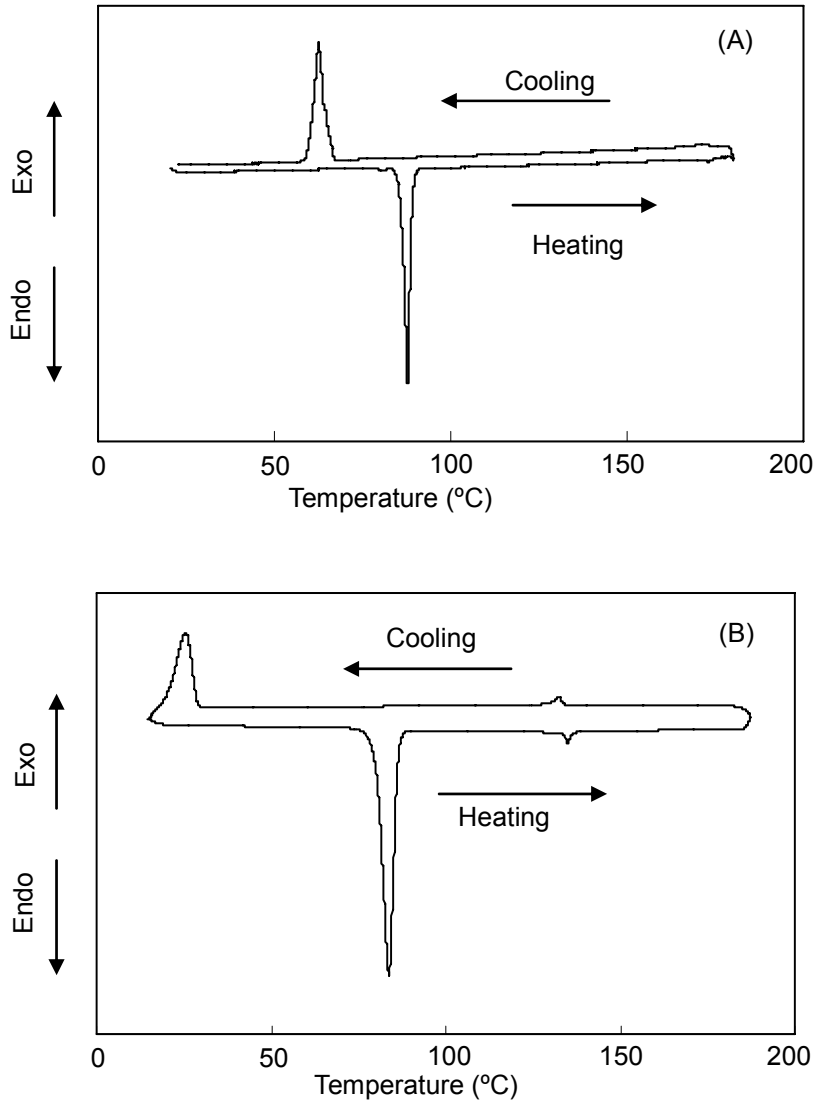


Figure S1. DSC thermograms of **A9ABT** (A) and **DA9ABT** (B) on the third scan at a heating and cooling rate of 3 °C/min.

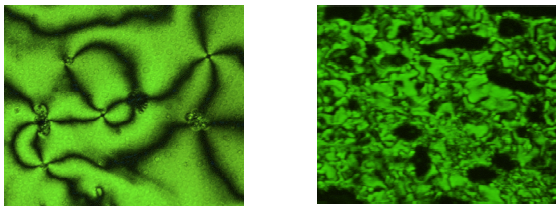


Figure S2. Polarizing optical micrographs of schlieren textures of **A9ABT** (A) and **DA9ABT** (B) at 120 °C when cooled from the isotropic phase.

3. Order Parameter of the Crosslinked Liquid-Crystalline Polymer (CLCP) Film

In order to further evaluate the order parameter of the azotolane CLCP film, the dichroism in the optical absorption spectra of the film was measured with a UV-Vis absorption spectrometer (Jasco V-550). The polarized optical absorption spectra, detected with light polarized parallel and perpendicular to the rubbing direction of the alignment layers, are shown in Figure S3. The dichroic ratio is given by the following equation:

$$R = A_{/\!/}/A_{\perp}$$

where $A_{/\!/}$ and $A_{\perp}$ are the absorbance measured with the light polarized parallel and perpendicular to the rubbing direction of the alignment layers, respectively. The order parameter S is related to the dichroic ratio R by the following equation:

$$S = (R - 1)/(R + 2)$$

From the spectra in Figure S3, we calculated the value of order parameter (S = 0.12) from the polarized absorbance at 420 nm.

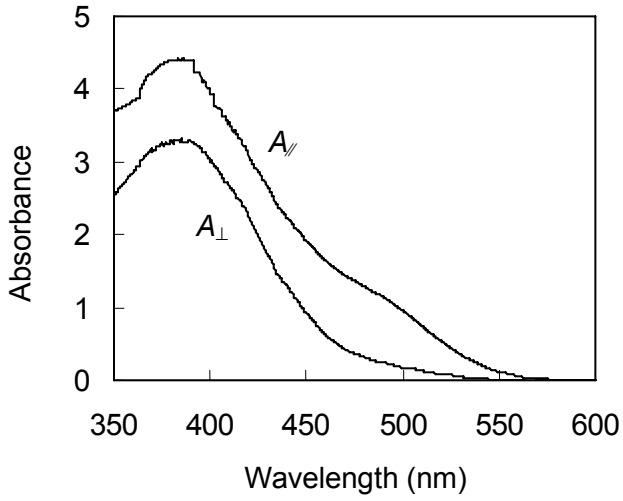


Figure S3. Polarizing absorption spectra of the azotolane CLCP film. $A_{/\!/}$ and $A_{\perp}$ are absorbance measured with light polarized parallel and perpendicular to the rubbing direction of the cell used in the preparation of the CLCP film.

4. References

1. V. Shibaev, S. Kostromin, N. Plate, *Eur. Polym. J.* **1982**, *18*, 651.

2. D. Robello, *J. Polym. Sci. Part A: Polym. Chem.* **1990**, *28*, 1.

5. Movie

Photoinduced bending and unbending behavior of the azotolane CLCP film in sunlight through a lens and different glass filters.