Supplementary material (ESI) for Journal of Materials Chemistry

Supplementary information for

Photomobile polymer materials – various three-dimensional movements

Munenori Yamada,[a] Mizuho Kondo,[a] Ryo Miyasato,[a] Yumiko Naka,[a] Jun-ichi Mamiya,[a] Motoi Kinoshita,[a] Atsushi Shishido,[a] Yanlei Yu,[b] Christopher J. Barrett[c] & Tomiki Ikeda[a]

[a] *Chemical Resources Laboratory, Tokyo Institute of Technology, R1-11, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan.*

[b] *Department of Materials Science, Fudan University, 220 Handan Road, Shanghai 200433, China.*

[c] *Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Quebec H3A 2K6, Canada*

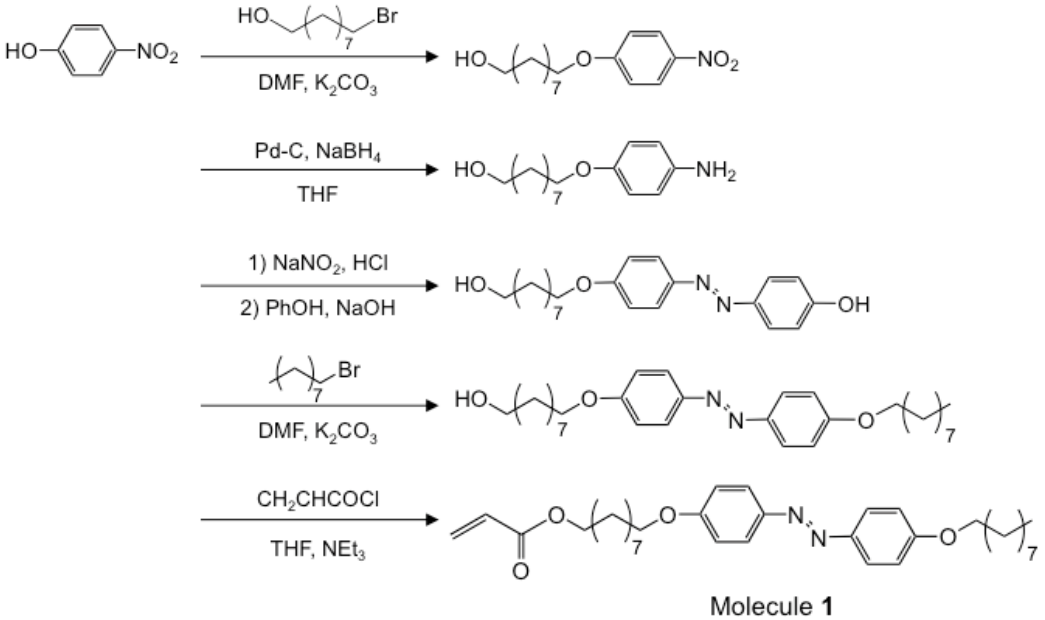
Materials

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

Synthesis of monomers

The LC monomers, 9-[4-(4-nonyloxyphenylazo)phenoxynonyl] acrylate (molecule **1**) and 4,4'-bis[9-(acryloyloxy)nonyloxy]azobenzene (molecule **2**) were synthesized according to a procedure similar to the literature.[1]

9-[4-(4-Nonyloxyphenylazo)phenoxynonyl] acrylate

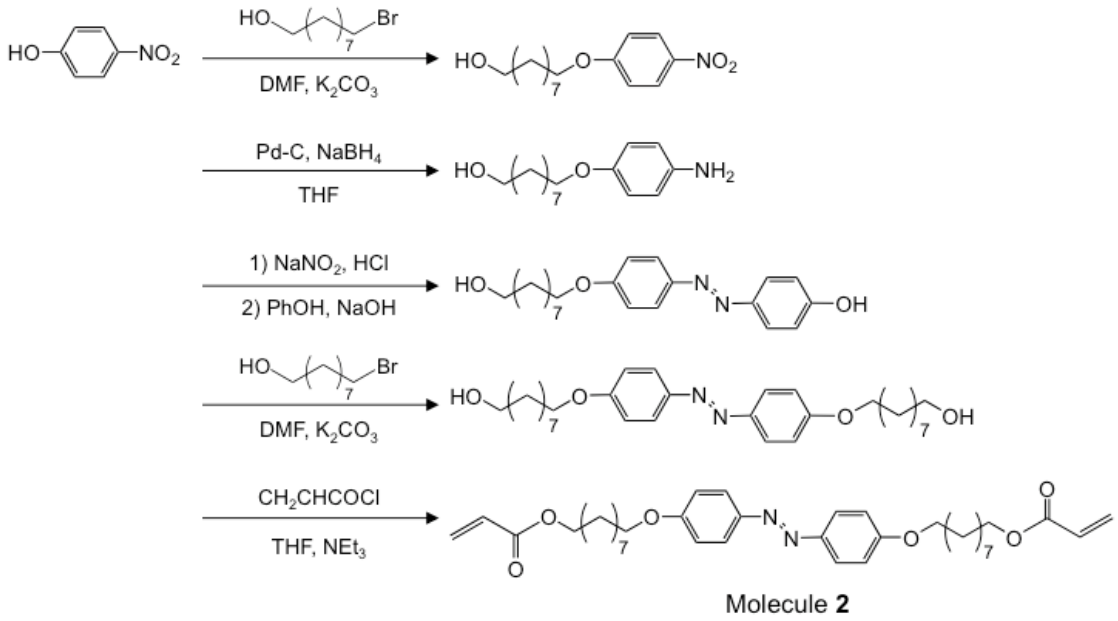


Molecule **1**

Scheme S1. Synthetic route for molecule **1**.

^{1}H NMR ($CDCl_3$, 300 MHz): ḍ = 0.9 (t, J=6.8 Hz, 3H), 1.2-1.8 (m, 34H), 3.9 (t, J=6.5 Hz, 4H), 4.1 (t, J=6.7 Hz, 2H), 5.7 (dd, J=10.4, 1.6 Hz, 1H), 6.1 (dd, J=17.3, 10.4 Hz, 1H), 6.4 (dd, J=17.3, 1.6 Hz, 1H), 6.9 (m, 4H), 7.8 (m, 4H). Elemental analysis: Calcd. for $C_{33}H_{48}N_2O_4$: C, 73.84; H, 9.01; N, 5.22 %. Found: C, 73.68; H, 8.91; N, 5.12 %. MS (FAB) found: m/z 537 $[M+1]^+$ (537 cacld. for $C_{33}H_{48}N_2O_4$).

4,4'-Bis[9-(acryloyloxy)nonyloxy]azobenzene



Molecule **2**

Scheme S2. Synthetic route for molecule **2**.

^{1}H NMR ($CDCl_3$, 300 MHz): ḍ = 1.2-1.8 (m, 28H), 4.0 (t, J=6.5 Hz, 4H), 4.1 (t, J=6.8 Hz, 4H), 5.7 (dd, J=10.4, 1.6 Hz, 2H), 6.0 (dd, J=17.3, 10.4 Hz, 2H), 6.3 (dd, J=17.3, 1.6 Hz, 2H), 6.9 (m, 4H), 7.8 (m, 4H). Elemental analysis: Calcd. for $C_{36}H_{50}N_2O_6$: C, 71.26; H, 8.31; N, 4.62 %. Found: C, 71.08; H, 8.30; N, 4.62 %. MS (FAB) found: m/z 607 $[M+1]^+$ (607 cacld. for $C_{36}H_{50}N_2O_6$).

Preparation of CLCP films and their composites

The CLCP films were prepared by in-situ photopolymerization of a mixture of molecule **1** and **2** (20/80 mol/mol) containing 2 mol% of a photoinitiator (Ciba Specialty, Irgacure 784). First, the melt of the mixture was injected into a glass cell coated with rubbed polyimide alignment layers at 110 °C. After the

sample was cooled down slowly (0.1 °C/min) to a polymerization temperature at 89 °C where it showed a smectic phase, photopolymerization was carried out at > 540 nm (2.8 mW cm^{-2} at 545 nm) with a 500 W high-pressure mercury lamp through glass filters (AGC Techno Glass, Y-52 and IRA-25) for 2.5 h. The CLCP films were taken off from the cells after polymerization.

The CLCP laminated films composed of a CLCP layer and a PE film were prepared by thermal compression bonding. First, an adhesive mixture of polyethylene emulsion (Unitika, ARROWBASE SB-1200) and a solution of waterborne polyurethane (Adeka, BONTIGHTER HUX380) (weight ratio of solid content: 70/30) was coated on an unstretched low-density PE film with 50-μm thickness (Tohcello, TUX-FCS) with a bar coater and dried in an oven at 115 °C for 60 s, forming the adhesion layer on the PE film. Then the CLCP film and the coated PE film were laminated between two glass plates under pressure (approximately 0.5 kgf cm^{-2}) at 105 °C for 60 s. The CLCP laminated film was obtained by separating the film from the glass plates. (Fig. S1)

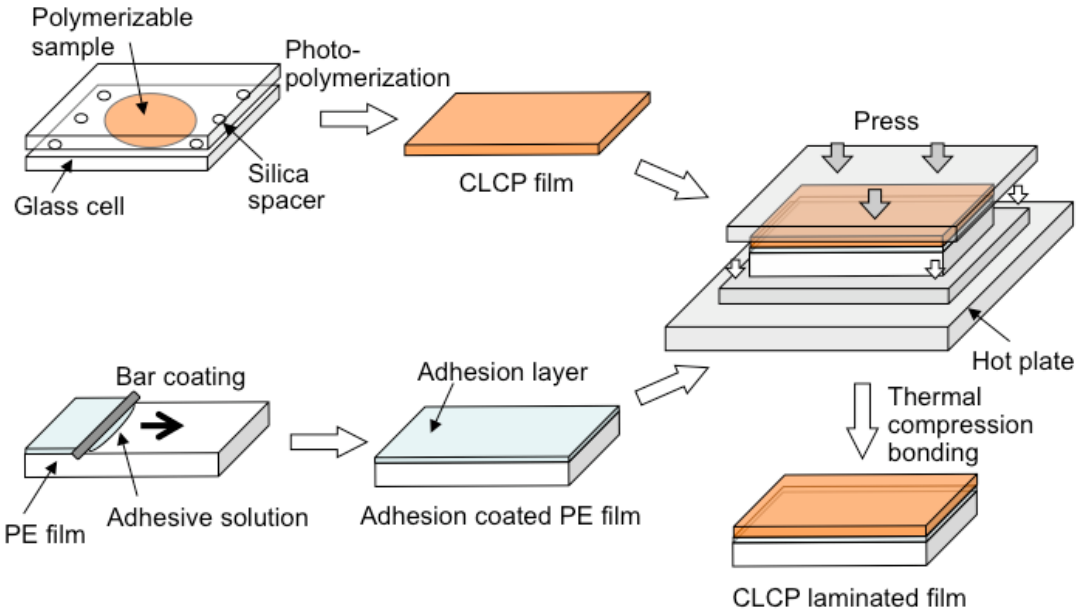


Figure S1. Fabrication of the CLCP monolayer and laminated films.

Characterization

^{1}H NMR spectra were measured using a Lambda-300 spectrometer operating at 300 MHz with tetramethylsilane as an internal reference for chemical shifts. The thermodynamic properties of the LC monomers (molecule **1** and **2**) and CLCPs were determined by DSC (Seiko I&E, SSC-5200 and DSC220C) at heating and cooling rates of 2 °C/min for the monomers and 10 °C/min for the CLCPs. At least three scans

were performed to check the reproducibility. The LC phases were evaluated with a polarizing optical microscope (POM; Olympus BH-2) equipped with a Metter hot stage (FP-90 and FP-82).

A DSC thermogram of the third heating process of the CLCP film is shown in Fig. S2. It was found that the glass-transition temperature (T_g) of the CLCP film appears around room temperature. The LC alignment of the CLCP film was evaluated with a POM (Fig. S3). The regular maximum and minimum values with 90˚ separations show that the azobenzene mesogens are preferentially aligned along the rubbing direction.

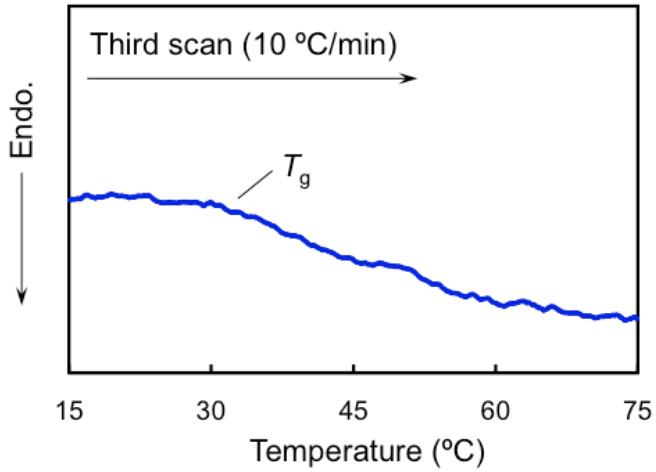


Figure S2. DSC thermogram of the CLCP film.

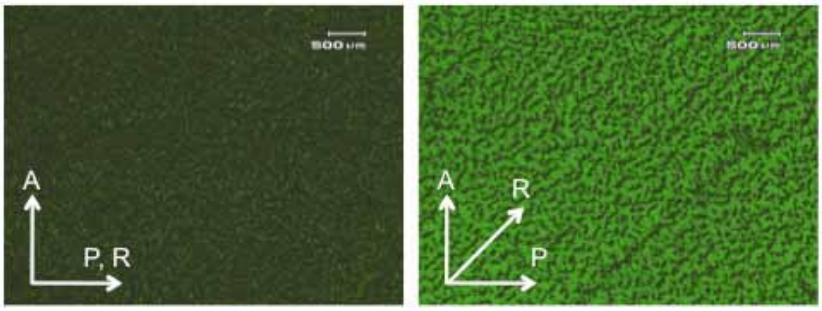


Figure S3. POM images of the CLCP film. A, analyzer; P, polarizer; R, rubbing direction.

Photoirradiation and observation tools

Photoinduced motions of the CLCP laminated films were observed by irradiation with UV light (UV-LED, Keyence, UV-400) and visible light (a halogen lamp through a heat-absorbing filter (Shimadzu, FLH-50)). The photographs and movies of the photoinduced motions were taken with a digital camera (Omron, VC-HRM20Z and VC1000).

Change in length of the CLCP films by photoirradiation was measured with a thermomechanical analyzer (Shimadzu, TMA-60) as follows: A film was fixed by clamping both ends and a force of 10 mN was loaded on the film; then the film was irradiated with UV light (366 nm, 20 mW cm^{-2}) at 30 °C as illustrated in Fig. S4.

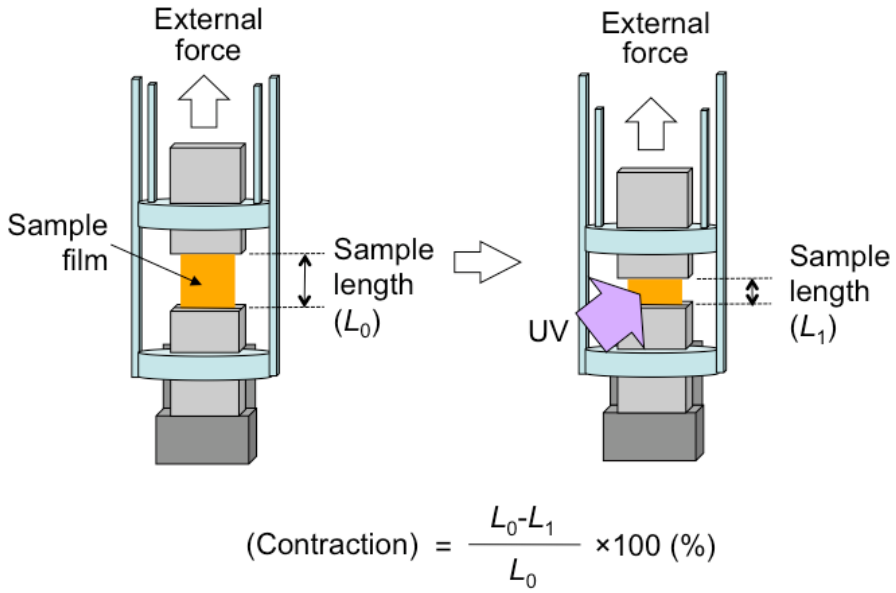


Figure S4. Schematic illustration of the experimental setup to evaluate the change in length of the CLCP films by photoirradiation.

References

1. Yu, Y.; Nakano, M.; Shishido, A.; Shiono, T.; Ikeda, T. *Chem. Mater.* **2004**, *16*, 1637-1643.

Movies

Movie S1. Inchworm walk of the CLCP laminated film induced by alternate irradiation with UV and visible light at room temperature.

Movie S2. Flexible robotic arm motions of the CLCP laminated films induced by irradiation with UV and visible light at room temperature.