Supporting Materials for:

Environmentally Stable Chiral-Nematic Liquid Crystal Elastomers Exhibiting Mechano-Optical Response

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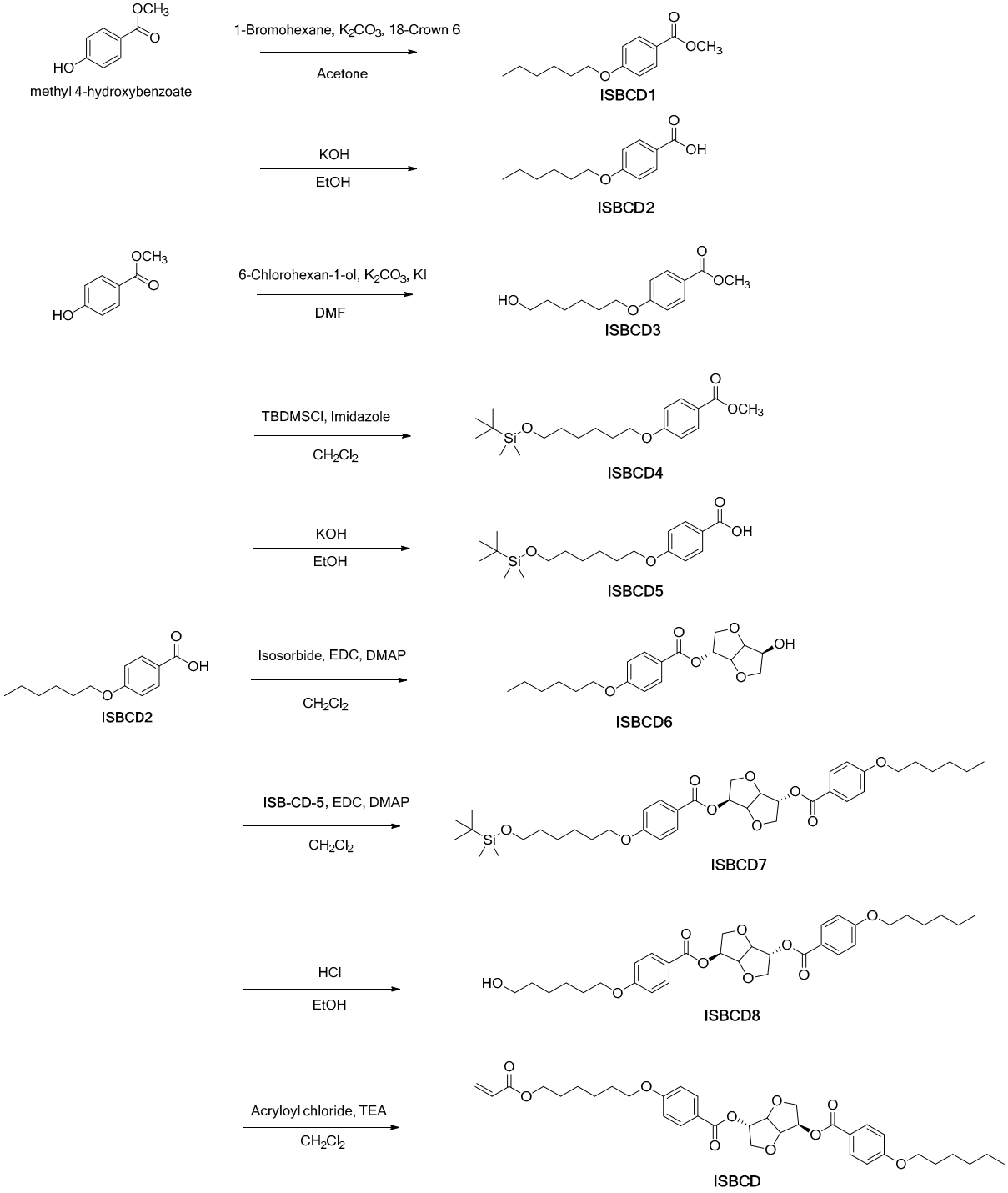
1. Supplementary Texts

Text S1. Synthesis of the chiral dopant monomer



Scheme S1. Synthetic route for **ISBCD**

ISBCD1. Methyl *p*-hydroxybenzoate (1.0 g, 6.6 mmol), 1-bromohexane (0.84 mL, 6.0 mmol), K_2CO_3 (1.6 g, 12 mmol), and 18-crown-6 (0.11 g, 0.42 mmol) were added to acetone (20 mL) in a 50 mL reaction flask and stirred under reflux (60 °C) for 16 h. The reaction mixture was filtered to remove K_2CO_3, and the filtrate was concentrated by evaporation. Ethyl acetate was added to the crude product, which was then washed with saturated Na_2CO_3 aqueous solution, saturated NH_4Cl aqueous solution, saturated NaCl aqueous solution, and H_2O. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain **ISBCD1** as a pale yellow solid in 83% yield (1.2 g, 5.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97 (d, J = 6.8 Hz; 2H; 2,6-*H* in phenyl), 6.88 (d, J = 6.8 Hz; 2H; 3,5-*H* in phenyl), 3.98 (t, J = 6.5 Hz; 2H; OCH_2), 3.86 (s, 3H; OCH_3), 1.81–1.74 (m, 2H; OCH_2CH_2), 1.46–1.41 (m, 2H; $OCH_2CH_2CH_2$), 1.34–1.30 (m, 4H; $O(CH_2)_3(CH_2)_2$), 0.89 (t, J = 7.0 Hz; 3H; $O(CH_2)_5CH_3$).

ISBCD2. ISBCD1 (1.0 g, 4.2 mmol) and KOH (1.2 g, 21 mmol) were added to ethanol (30 mL) in a 50 mL reaction flask and stirred under reflux (80 °C) for 5 h. The reaction mixture was acidified to pH 3 using 5% HCl aqueous solution, and the solvent was removed by filtration. Ethyl acetate was added to the crude product, which was then washed with saturated NH_4Cl aqueous solution, saturated NaCl aqueous solution, and H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was recrystallized to obtain **ISBCD2** as white needle-shaped crystals in 94% yield (0.88 g, 4.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03 (d, J = 9.1 Hz; 2H; 2,6-*H* in phenyl), 6.92 (d, J = 9.1 Hz; 2H; 3,5-*H* in phenyl), 4.01 (t, J = 6.6 Hz; 2H; OCH_2), 1.83–1.76 (m, 2H; OCH_2CH_2), 1.49–1.42 (m, 2H; $OCH_2CH_2CH_2$), 1.35–1.31 (m, 4H; $OCH_2CH_2CH_2(CH_2)_2$), 0.92 (t, J = 7.0 Hz; 3H; CH_3).

ISBCD3. 6-chloro-1-hexanol (2.7 g, 20 mmol), methyl *p*-hydroxybenzoate (2.0 g, 13 mmol), K_2CO_3 (2.7 g, 20 mmol), and KI (0.10 g, 0.50 mmol) were added to DMF (50 mL) in a 100 mL reaction flask and stirred at 100 °C for 24 h. Ethyl acetate was added to the crude product, which was then washed with saturated NaCl aqueous solution and H_2O. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by silica gel column chromatography (eluent: 10% ethyl acetate in CH_2Cl_2) to obtain **ISBCD3** as a white solid in 79% yield (2.6 g, 10 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95 (d, J = 8.1 Hz; 2H; 2,6-*H* in phenyl), 6.88 (d, J = 7.7 Hz; 2H; 3,5-*H* in phenyl), 3.99 (t, J = 6.3 Hz; 2H; OCH_2), 3.86 (s, 3H; OCH_3), 3.67 (t, J = 6.5 Hz; 2H; $HOCH_2$), 1.82–1.76 (m, 2H; OCH_2CH_2), 1.63–1.56 (m, 2H; $HOCH_2CH_2$), 1.51–1.42 (m, 2H; $HOCH_2CH_2(CH_2)_2$).

ISBCD4. **ISBCD3** (2.0 g, 7.9 mmol) and imidazole (1.1 g, 16 mmol) were added to CH_2Cl_2 (50 mL) in a 100 mL reaction flask and stirred for 10 min at 0 °C under argon atmosphere. *tert*-Butyldimethylsilyl chloride (1.3 g, 8.7 mmol) was added to the reaction mixture. The temperature was gradually increased to room temperature, and the reaction mixture was stirred at room temperature for 6 h. The crude product was washed with saturated $NaHCO_3$ aqueous solution, NaCl aqueous solution, and H_2O. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain **ISBCD4** as a white solid in 93% yield (2.7 g, 7.4 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.95 (dd, J = 8.8, 2.9 Hz; 2H; 2,6-*H* in phenyl), 6.87 (d, J = 8.6, 3.6 Hz; 2H; 3,5-*H* in phenyl), 3.98 (t, J = 3.2 Hz; 2H; OCH_2), 3.85 (s, 1H; $COOCH_3$), 3.59 (t, J = 6.5 Hz; 2H; $SiOCH_2$), 1.78 (s, 2H; OCH_2CH_2), 1.58–1.34 (m, 6H; $OCH_2CH_2CH_2$), 0.87 (s, 9H; $Si(CH_2)_2C(CH_3)_3$, 0.87 (s, 6H; $Si(CH_2)_2(CH_2)_3$).

ISBCD5. **ISBCD4** (2.0 g, 5.5 mmol) and KOH (1.2 g, 21 mmol) were added to ethanol (50 mL) in a 100 mL reaction flask and stirred under reflux (80 °C) for 1 h. The reaction mixture was acidified to pH 3 using 1 M CH_3COOH aqueous solution, and the solvent was removed by filtration. The reaction mixture was poured into 400 mL H_2O. The precipitate was collected by vacuum filtration and washed with H_2O. The product was then dried under reduced pressure and purified by silica gel column chromatography (CH_2Cl_2) to obtain **ISBCD5** as a white solid in 88% yield (1.7 g, 4.8 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.03 (dd, J = 7.0, 2.0 Hz; 2H; 2,6-*H* in phenyl), 6.91 (dd, J = 7.0, 2.0 Hz; 2H; 3,5-*H* in phenyl), 4.01 (t, J = 6.3 Hz; 2H; OCH_2), 3.61 (t, J = 6.3 Hz; 2H; $SiOCH_2$), 1.84–1.77 (m, 2H; OCH_2CH_2), 1.57–1.39 (m, 6H; $OCH_2(CH_2)_3$, 0.88 (s, 9H; $Si(CH)_2(CH_3)_3$, 0.03 (s, 6H; $Si(CH_3)_2(CH_3)_3$).

ISBCD6. ISBCD2 (0.50 g, 2.2 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (0.43 g, 2.2 mmol), 4-dimethylaminopyridine (0.27 g, 2.2 mmol), and isosorbide (0.39 g, 2.7 mmol) were added to CH_2Cl_2 (20 mL) in a 50 mL reaction flask and stirred for 24 h under argon atmosphere. The crude product was washed with saturated $NaHCO_3$ aqueous solution, NaCl aqueous solution, and H_2O. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product was purified by silica gel column chromatography (10% ethyl acetate, CH_2Cl_2 solution) to obtain **ISBCD6** as a white solid in 52% yield (0.41 g, 1.2 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.98 (d, J = 8.6 Hz; 2H; 2,6-*H* in phenyl), 6.89 (d, J = 8.6 Hz; 2H; 3,5-*H* in phenyl), 5.37-5.33 (m, 1H; OCH_2CHOCH in isosorbide), 4.95 (t, J = 5.2 Hz; 1H; $OCHCHCH_2O$ in isosorbide), 4.43 (d, J = 4.5 Hz; 1H; $OCHHCHOCH$), 4.35 (d, J = 2.2 Hz; 1H; $OCHHCHOCH$), 4.00–3.85 (m, 6H; isosorbide $CH_2OCHCHCH_2OCHCHOH$, $OCH_2(CH_2)_4CH_3$), 1.81–1.74 (m, 2H; $OCH_2CH_2(CH_2)_3CH_3$), 1.48–1.30 (m, 6H; $O(CH_2)_2(CH_2)_3CH_3$), 0.89 (t, J = 4.5 Hz; 3H; $O(CH_2)_2(CH_2)_3CH_3$).

ISBCD7. ISBCD5 (1.5 g, 4.3 mmol), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (0.81 g, 4.3 mmol), and 4-dimethylaminopyridine (0.52 g, 4.3 mmol) were added to CH_2Cl_2 (50 mL) in a 100 mL reaction flask and stirred for 10 min at 0 °C under argon atmosphere. **ISBCD6** (1.8 g, 5.1 mmol) was added to the reaction mixture. The temperature was gradually increased to room temperature, and the reaction mixture was stirred at room temperature for 24 h. The crude product was washed with saturated $NaHCO_3$ aqueous solution, NaCl aqueous solution, and H_2O. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2) to obtain **ISBCD7** as a white solid in 61% yield (1.8 g, 2.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97 (dd, J = 26.3, 9.1 Hz; 4H; 2,6-*H* in phenyl), 6.89 (dd, J = 10.7, 8.8 Hz; 4H; 3,5-*H* in phenyl), 5.44 (d, J = 2.7 Hz; 1H; $OCHHCHOCH$ in isosorbide), 5.40–5.35 (m, 1H; $OCH_2CHOCHO$ in isosorbide), 5.02 (t, J = 5.0 Hz; 1H; OCH_2CHCHO in isosorbide), 4.65 (d, J = 4.5 Hz; 1H; $OCHHCHOCH$ in isosorbide), 3.97–4.12 (m, 8H; phenyl$(OCH_2)_2$, $OCH_2CHOCHO$ in isosorbide), 3.60 (t, J = 6.6 Hz; 2H; $HOCH_2(CH_2)_5$), 1.82–1.75 (m, 4H; $OCH_2CH_2(CH_2)_3CH_2OH$, $OCH_2CH_2(CH_2)_3CH_3$), 1.57–1.29 (m, 12H; $O(CH_2)_2(CH_2)_3CH_2OH$, $OCH_2CH_2(CH_2)_3CH_3$), 0.92–0.85 (m, 12H; $O(CH_2)_5CH_3$, $Si(CH_3)_2(CH_3)_3$), 0.03 (s, 6H; $Si(CH_3)_2(CH_3)_3$).

ISBCD8. **ISBCD7** (1.5 g, 2.2 mmol) was added to ethanol (25 mL) in a 50 mL reaction flask and stirred for 10 min at 0 °C under argon atmosphere. The reaction mixture was acidified to pH 3 using 1M HCl aqueous solution. The temperature was gradually increased to room temperature, and the reaction mixture was stirred at room temperature for 5 h. Ethyl acetate was added to the crude product, which was then washed with saturated $NaHCO_3$ aqueous solution, saturated NH_4Cl aqueous solution, saturated NaCl aqueous solution, and H_2O. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain **ISBCD8** as a white solid in 93% yield (1.2 g, 2.0 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97 (dd, J = 25.8, 9.1 Hz; 4H; 2,6-*H* in phenyl), 6.88 (dd, J = 10.0, 9.1 Hz; 4H; 3,5-*H* in phenyl), 5.41 (d, J = 2.7 Hz; 1H; $OCHHCHOCH$ in isosorbide), 5.39–5.35 (m, 1H; $OCH_2CHOCHO$ in isosorbide), 5.02 (t, J = 5.0 Hz; 1H; OCH_2CHCHO in isosorbide), 4.65 (d, J = 4.5 Hz; 1H; $OCHHCHOCH$ in isosorbide), 3.96–4.13 (m, 8H; phenyl$(OCH_2)_2$, $OCH_2CHOCHO$ in isosorbide), 3.61 (t, J = 6.3 Hz; 2H; $HOCH_2(CH_2)_5$), 1.83–1.74 (m, 4H; $OCH_2CH_2(CH_2)_3CH_2OH$, $OCH_2CH_2(CH_2)_3CH_3$), 1.61–1.55 (m, 2H; $HOCH_2CH_2$), 1.53–1.39 (m, 6H; $HOCH_2CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2$), 1.35–1.30 (m, 4H; $CH_3CH_2CH_2$) 0.89 (t, J = 7.3 Hz; 3H; $O(CH_2)_5CH_3$).

ISBCD. ISBCD8 (1.3 g, 2.3 mmol) and triethylamine (0.46 g, 5.4 mmol) were added to CH_2Cl_2 (30 mL) in a reaction flask and stirred for 10 min at 0 °C under argon atmosphere. Acryloyl chloride (0.20 g, 2.7 mmol) was added dropwise to the reaction mixture. The temperature was gradually increased to room temperature, and the reaction mixture was stirred at room temperature for 5 h. The crude product was washed with saturated $NaHCO_3$ aqueous solution, NaCl aqueous solution, and H_2O. The organic layer was then dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2) to obtain **ISBCD** as a white solid in 71% yield (1.0 g, 1.6 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.97 (dd, J = 25.4, 9.1 Hz; 4H; 2,6-*H* in phenyl), 6.88 (dd, J = 10.3, 9.1 Hz; 4H; 3,5-*H* in phenyl), 6.38 (dd, J =

17.3, 1.6 Hz; 1H; C*H*H=CH), 6.14–6.06 (m, 1H; CH_2=C*H*), 5.80 (dd, *J* = 10.5, 1.5 Hz; 1H; CH*H*=CH), 5.44 (d, *J* = 2.9 Hz; 1H; OC*H*HCHOCH in isosorbide), 5.39–5.35 (m, 1H; OCH_2C*H*OCHO in isosorbide), 5.02 (t, *J* = 5.0 Hz; 1H; OCH_2CHCHO in isosorbide), 4.65 (d, *J* = 4.7 Hz; 1H; OCH*H*CHOCH in isosorbide), 4.15 (t, *J* = 6.6 Hz; 2H; $CH_3(CH_2)_4CH_2O$), 4.12–3.97 (m, 8H; OCH*H*C*H*OC*H*OC*H*HCHOCHO in isosorbide, CH_2=CHCOO$CH_2(CH_2)_4CH_2O$, 1.84–1.74 (m, 4H; (phenyl-OCH_2CH_2)$_2$), 1.84–1.65 (m, 2H; $COOCH_2CH_2$), 1.53–1.39 (m, 6H; $HOCH_2CH_2CH_2CH_2$, $CH_3CH_2CH_2CH_2$), 1.39–1.28 (m, 4H; $CH_3CH_2CH_2$) 0.89 (t, *J* = 7.0 Hz; 3H; $O(CH_2)_5CH_3$). ^{13}C-NMR (100 MHz, $CDCl_3$, δ): 166.42, 165.84, 165.44, 163.36, 163.31, 131.91, 130.71, 128.63, 121.67, 121.60, 114,24, 114,20, 86.27, 81.29,78.27,77.32, 74.30, 73.69, 70.81, 68.33, 68.09, 64.56, 31.64, 29.14, 29.06, 28.62, 25.80, 25.77, 25.74, 22.68, 14.13 ppm. MS (ESI+) m/z: $[M + Na]^+$ calcd. for $C_{35}H_{44}NaO_{10}$: 647.28; found 647.18. Anal. calcd. for $C_{35}H_{44}O_{10}$: C, 67.29; H, 7.10; O, 25.61; found: C, 67.05; H, 7.09; N, 0.14.

Text S2. Preparation of polydimethylsiloxane (PDMS) film Glass plates (7.0 × 5.0 cm^2) were cleaned ultrasonically in three consecutive steps with 1.0 wt% neutral detergent (WAKO, Contaminon N) in water, distilled water, and 2-propanol. The glass plates were dried under ambient conditions for 24 h and then treated using a UV-ozone cleaner (SEN LIGHTS CORP., PL17-110) for 10 min. Subsequently, the glass plates were dip-coated and thermally annealed at 60 °C in a bath of ethanol solution with 2.0 g L^{-1} silane coupling agent (octadecyltriethoxysilane) for 30 min. The coated plates were heated to 120 °C for 2 h to complete the silane coupling treatment. The polymerization cells for the PDMS film were assembled using pairs of the resultant glass plates, and the gap between the glass plates was adjusted to 110 μm. The PDMS film precursor (Dow Corning Toray, Sylgard 184) with a PDMS to curing agent ratio of 10/1 (w/w) was then injected into the cell at room temperature. Finally, the cell was heated to 75 °C for 3 h, and the glass plates were removed to yield a PDMS film with a thickness of 110 μm.

Text S3. Cell preparation with rubbing treatment

Glass plates (2.5 × 2.5 cm^2), cleaned via the procedure explained above, were spin-coated (3000 rpm, 1 min) with a polyimide precursor solution to induce in-plane mesogenic orientation. The surface-coated glass plates were baked at 120 °C for 2 h followed by 250 °C for 2 h. The surface of the plate was rubbed by using a cylinder covered with rubbing felt. A pair of the rubbed glass plates (anti-parallel rubbing direction) was then assembled to construct a rubbed cell with a cell gap of 10 μm.

Text S4. Preparation of N* LC (*x*) elastomers

A PDMS film was attached to a glass plate (2.5 × 2.5 cm^2) cleaned via the procedure described above. A pair of PDMS-attached glass plates was then assembled into a polymerization cell, and the gap between the PDMS films, which acted as remover layers, was adjusted to 55 μm. The N* LC mixture was injected into the cell by capillary force in the dark at 80 °C (the isotropic temperature of the mixture). The cell was then cooled to 25 °C. Shear stress was applied to the cell in the direction parallel to the direction of LC injection to induce homogeneous alignment in the N* LC phase. The mixture was photopolymerized by irradiation with 365 nm UV LED light (Iwasaki Electric Co., LHPUV365; 5.0 mW cm^{-2}) for 5 min at 25 °C. After polymerization, the glass plates and PDMS layers were removed to obtain an N* LC elastomer with a size of 2.5 × 2.5 cm^2 and thickness of 55 μm.

2. Supplementary Figures

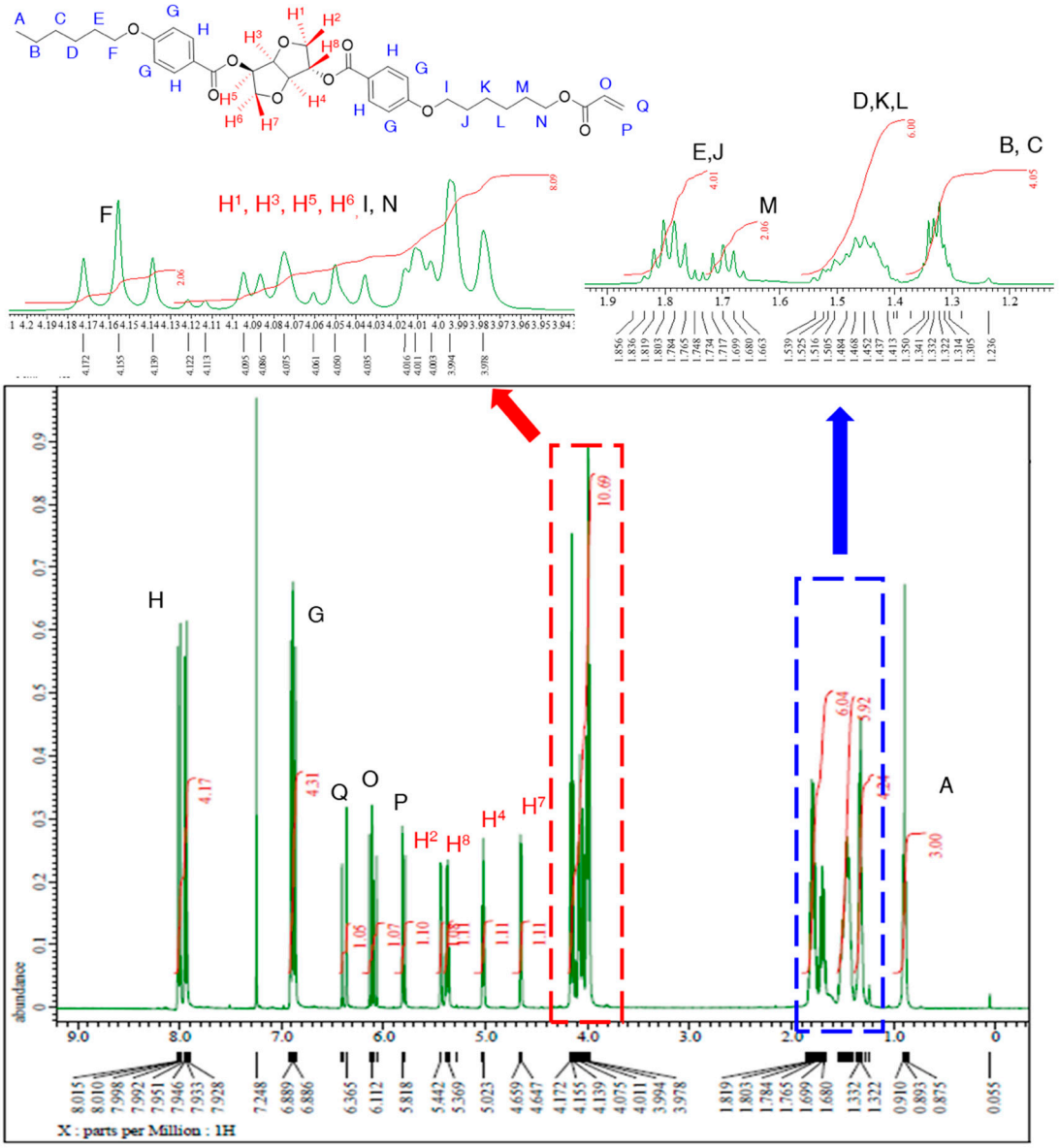


Figure S1. ^{1}H-NMR spectrum of **ISBCD** in $CDCl_3$

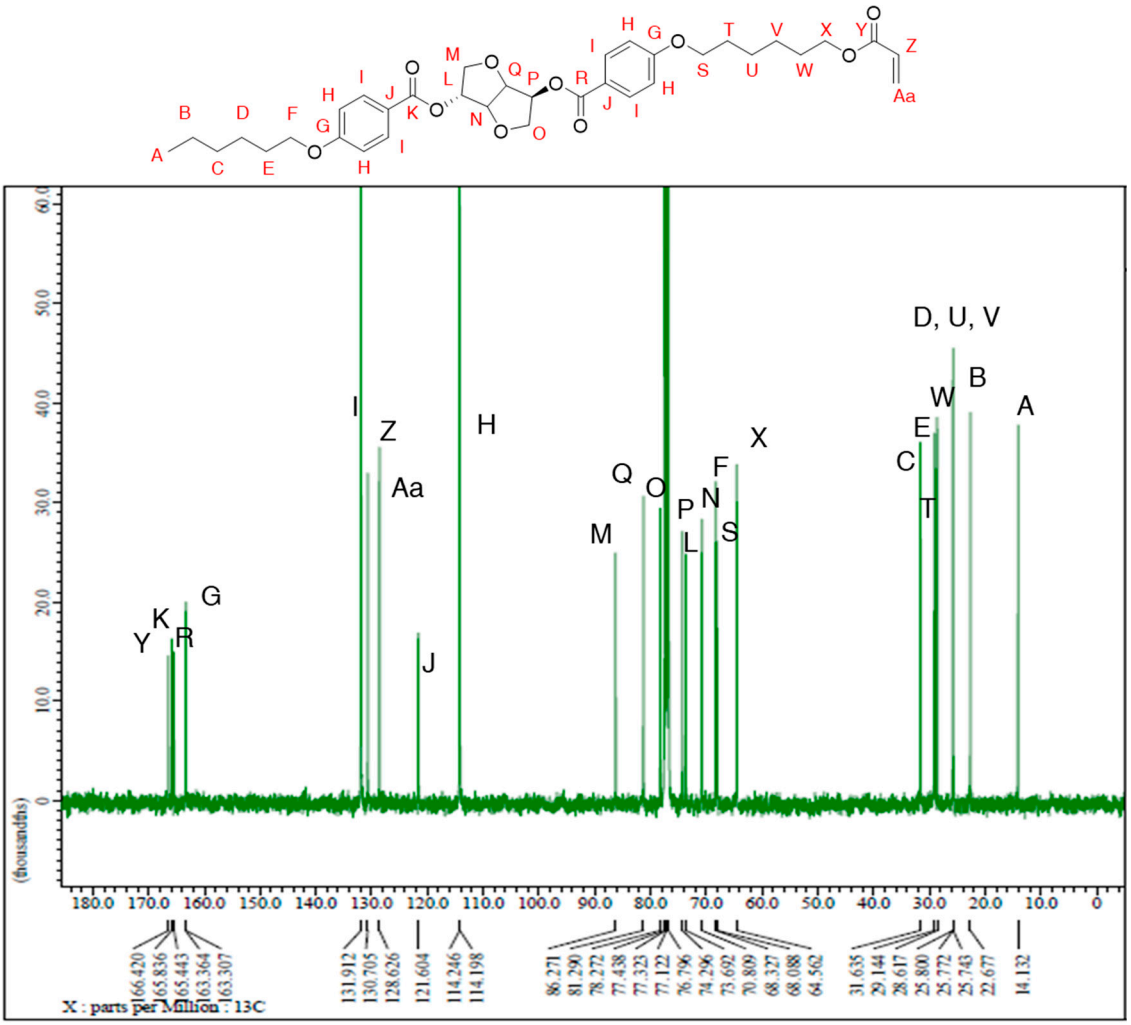


Figure S2. ^{13}C-NMR spectrum of **ISBCD** in $CDCl_3$

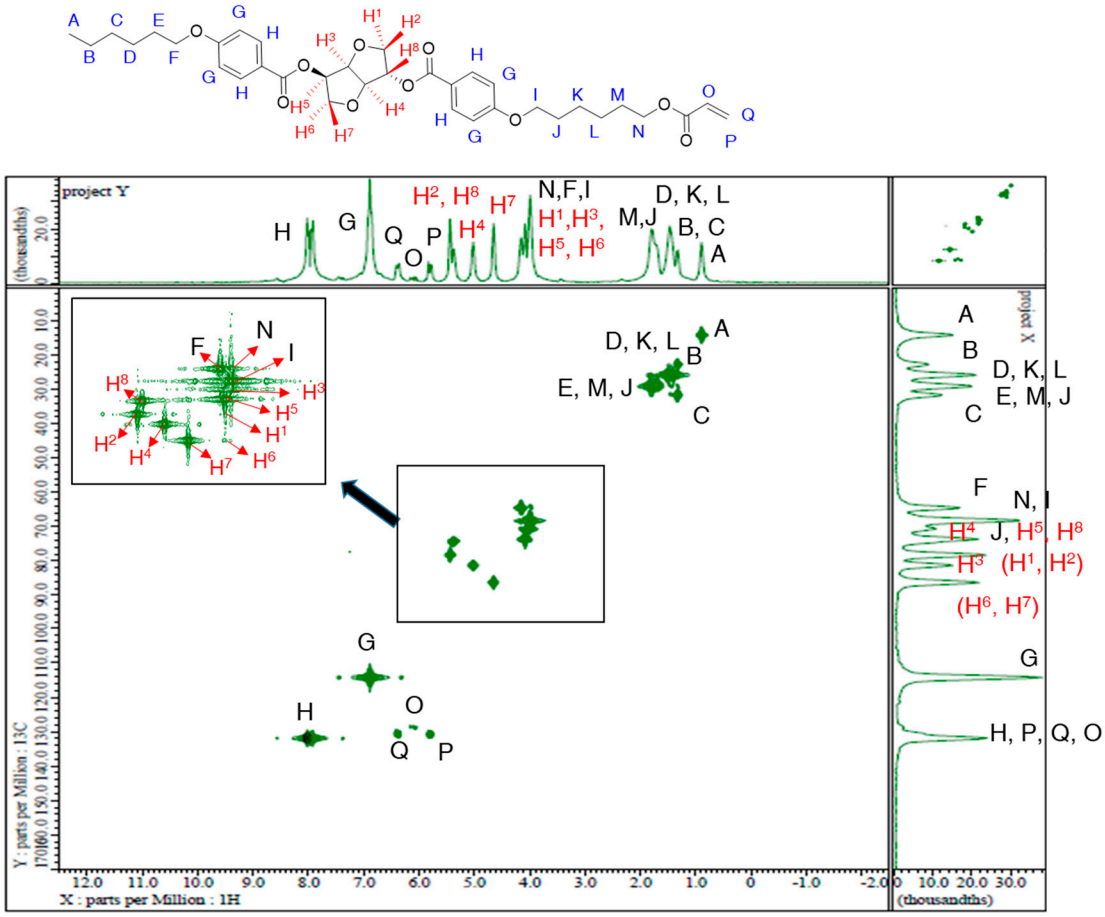


Figure S3. HMQC spectrum of **ISBCD** in $CDCl_3$

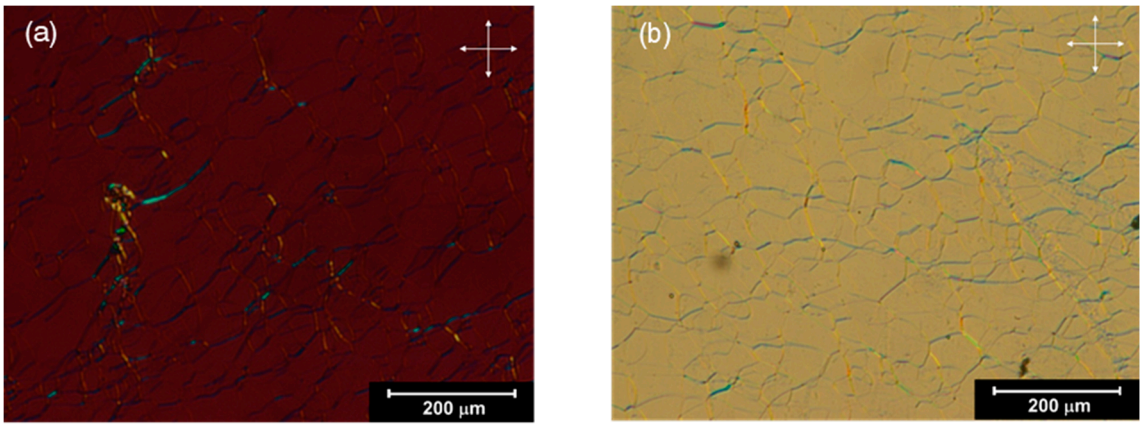


Figure S4. Polarized optical micrographs (POM) of N* LC (2.0) mixtures observed at room temperature (a) before and (b) after polymerization in a rubbing cell

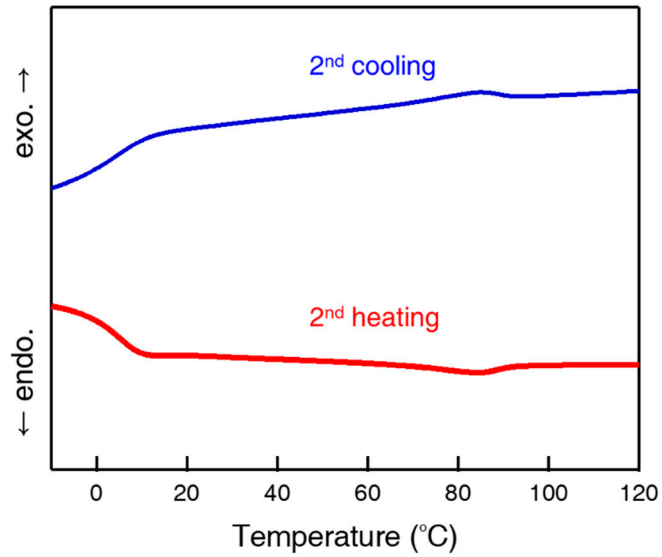


Figure S5. A DSC thermogram of a l-LCP at the 2nd scan process. The scanning rate was 10 °C min^{-1}.

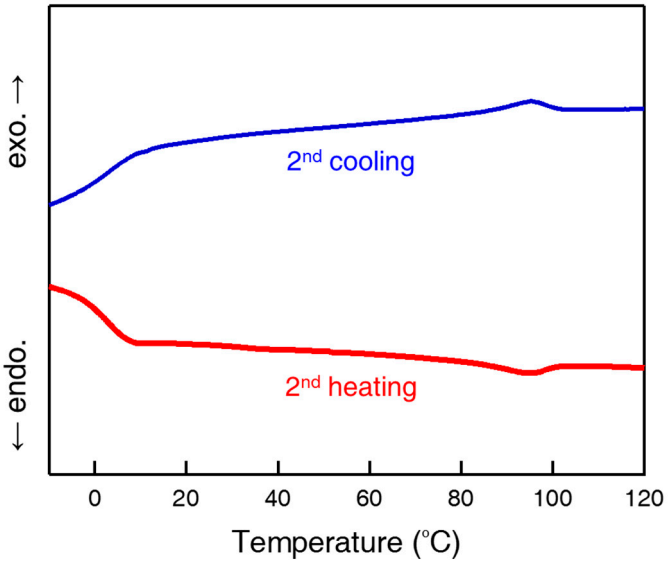


Figure S6. A DSC thermogram of a N* LC (2.0) elastomer at the 2nd scan process. The scanning rate was 10 °C min^{-1}.

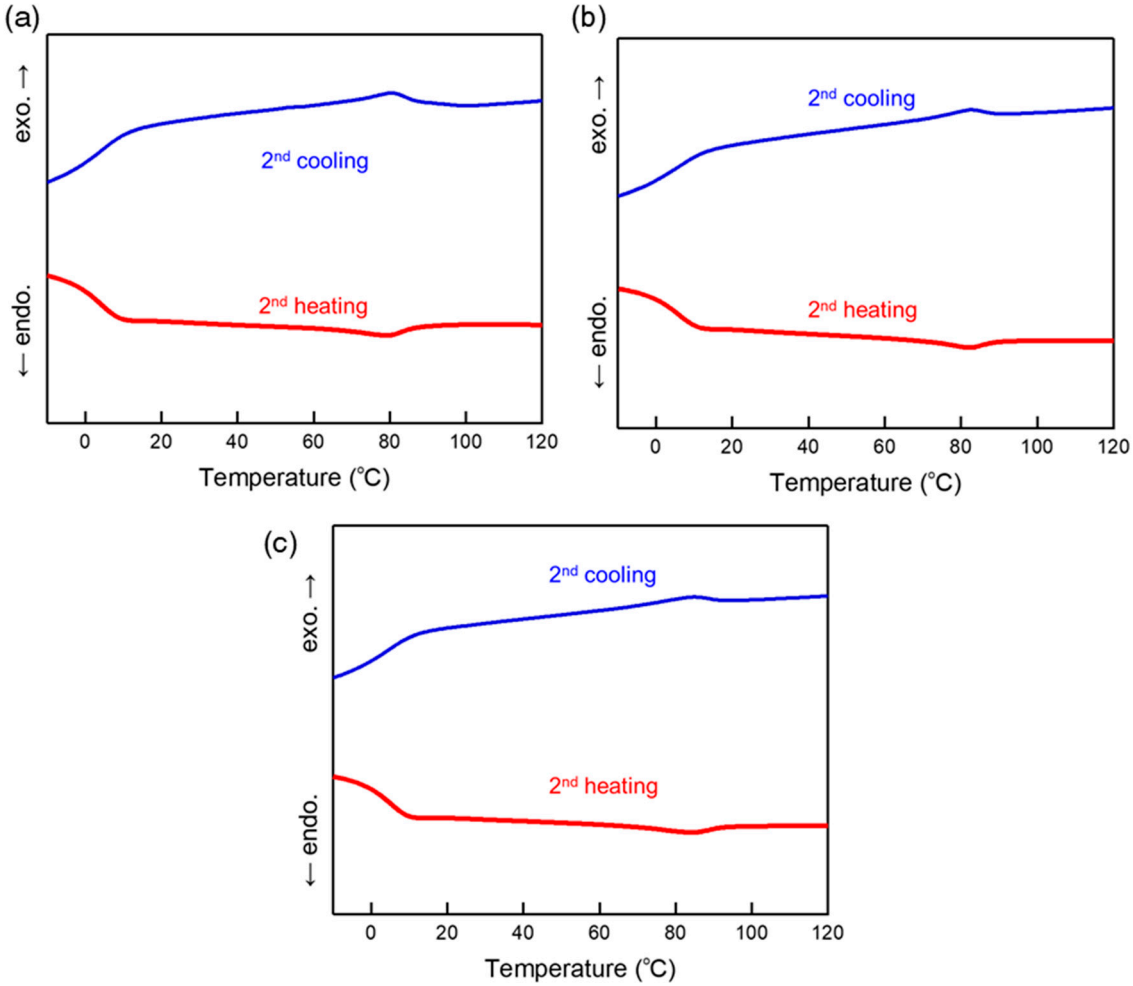


Figure S7. DSC thermograms of N* LC elastomers with different HAB/CN ratios of (a) 70/10, (b) 60/20, and (c) 50/30 at the 2nd scan process. The scanning rate was 10 °C min^{-1}.

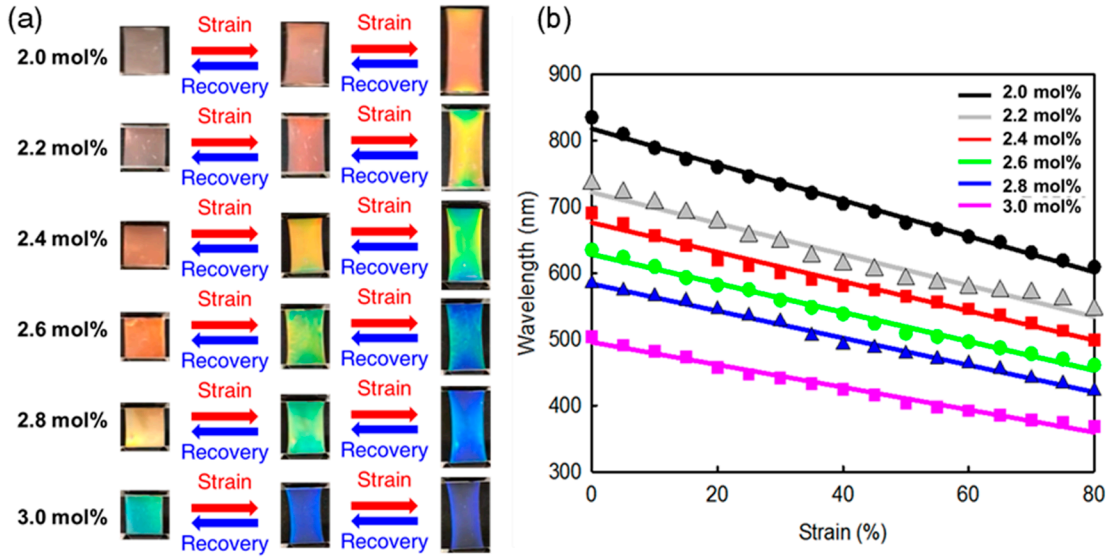


Figure S8. (a) Mechanical responsive color change of N* LC (*x*) elastomer with different chiral dopant concentrations *x* (from 2.0 mol% to 3.0 mol%), under an applied tensile strain of 0% (left), 40% (middle), and 80% (right). (b) A reflection peak wavelength of N* LC (*x*) elastomers as a function of

an applied tensile strain from 0 to 80%.

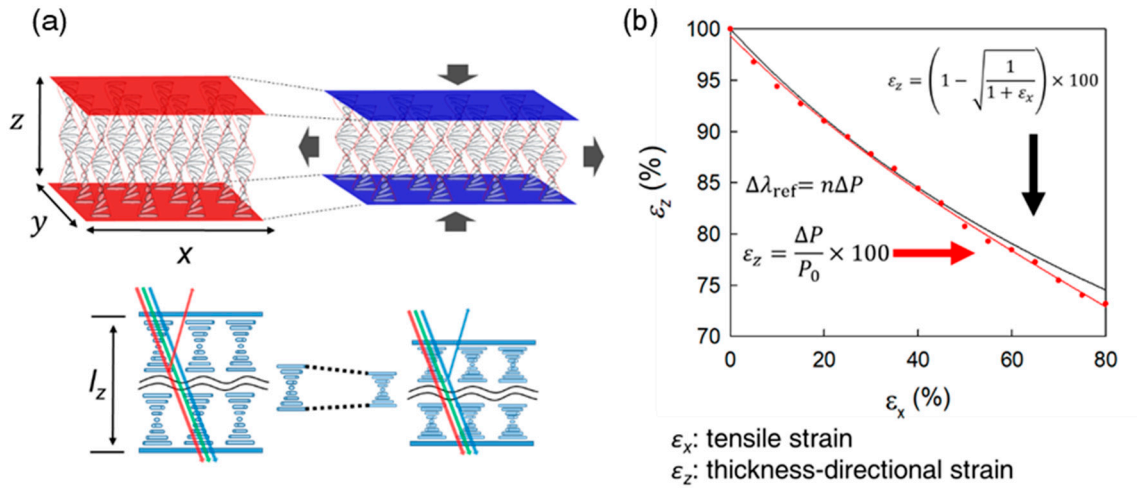


Figure S9. (a) Schematic illustrations of film deformation by elongation along the x-axis. The thickness, helical pitch along the z-axis, and in-plane direction along the y-axis perpendicular to the elongation direction are compressed as the elongation strain increases. (b) The change of helical pitch ε_z (red circles and line) experimentally evaluated by the shift of reflection peak wavelength and the theoretical value of the thickness strain of rubbery elastomers (black line) under the applied tensile strain ε_z calculated using a Poisson ratio of 0.5.

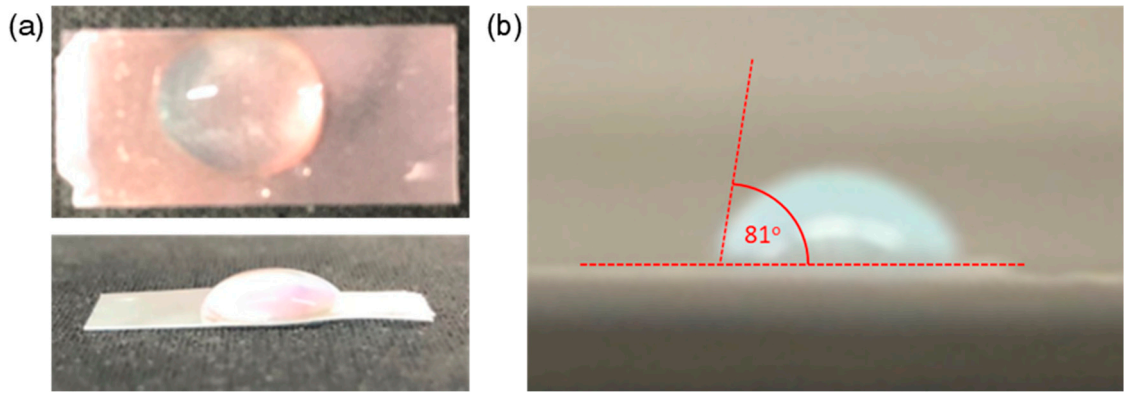


Figure S10. Photographs of N* LC (2.0) elastomer film. (a) Water dropped on the N* LC (2.0) elastomer surface demonstrating hydrophobicity. (b) The contact angle of the droplet over the surface.