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Supporting Information

for

Single-Layer Dual-Phase Nematic Elastomer Films with Bending, Accordion-Folding, Curling and Buckling Motions

Li Liu,^a Bin Geng,^a Sayed Mir Sayed,^a Bao-Ping Lin,^a Patrick Keller,^{b,c} Xue-Qin Zhang,^a Ying Sun,^a Hong Yang^{*a}

 ^aSchool of Chemistry and Chemical Engineering, Jiangsu Province Hi-Tech Key Laboratory for Bio-medical Research, Jiangsu Key Laboratory for Science and Application of Molecular Ferroelectrics, Jiangsu Optoelectronic Functional Materials and Engineering Laboratory, Southeast University, Nanjing, 211189, China
^bInstitut Curie, PSL Research University, CNRS, UMR 168, F-75005 Paris, France.
^cSoft Materials Research Center and Department of Chemistry and Biochemistry, University of Colorado, Boulder CO 80309, USA.

General Considerations.

4-Butyloxybenzoic acid was purchased from TCI Inc. 2,5-Dihydroxybenzoic acid, benzyl bromide, dicyclohexylcarbodiimide (DCC), dimethylaminopyridine (DMAP), and dimethylolpropionic acid (DMPA) were purchased from Aladdin Inc. Other chemical reagents were used directly without further purification. All non-aqueous reactions were executed in oven-dried glasswares, under a dry nitrogen atmosphere. All flash chromatography were completed using Macherey-Nagel MN Kieselgel 60 (0.063-1.2 mm).

All ¹H spectras were obtained using either a Bruker HW500 MHz spectrometer (AVANCE AV-500) or a Bruker HW300 MHz spectrometer (AVANCE AV-300), using tetramethylsilane as the interior reference and CDCl₃ as the solvent.

Liquid crystal cells were purchased from Instec Inc. Photomasks were purchased from the 55th Research Institute of China Electronics Technology Group Corporation. Photopolymerization of the liquid crystal mixtures was carried out using an UV plate exposure machine with 365 nm wavelength (ca. 12 mW·cm⁻², Zhengcheng Mechanical and Electrical Technology Co., Ltd.).

Polarized optical microscopy (POM) observations of the liquid crystalline textures of the elastomers were performed on an Olympus BX53P microscope with a Mettler PF82HT hot stage. A Microvision MV-DC200 digital camera with Phenix Phmias2008 Cs Ver2.2 software was used to capture the images.

Synthesis of Liquid Crystalline Monomer.



Benzyl 2,5-Dihydroxybenzoate (1). A solution of 2,5-Dihydroxybenzoic acid (9.24 g,

60.0 mmol) and NaHCO₃ (14.85 g, 176.7 mmol) in dry DMF (90 mL) was stirred at 70 °C for 1 hr. Benzyl bromide (10.26 g, 60.0 mmol) were then added slowly and the mixture was stirred at 70 °C for additional 7 hrs. After cooling to room temperature, the reaction mixture was diluted with 300 mL water and extracted twice with 150 mL 50:50 n-hexane/ethyl acetate mixture. The organic layer was washed twice with water, followed by drying over MgSO₄. Then, the solvents were evaporated under reduced pressure to give crude products. The crude products were subjected to column chromatography to give the product **1** (11.4 g, Yield: 77.7 %) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 7.47 - 7.34 (m, 5H), 7.31 (d, 1H, J = 3.05 Hz), 7.04 - 6.81 (m, 2H), 5.36 (s, 2H), 4.52 (s, 2H).



Benzyl 2,5-Di(4'-butyloxybenzoyloxy)benzoate (3). A solution of compound 1 (9.0 g,

36.9 mmol), 4-Butyloxybenzoic acid (2) (15.75 g, 81.0 mmol), DMAP (1.2 g, 8.1 mmol) and DCC (16.65 g, 81.0 mmol) in 200 mL of dry CH_2Cl_2 was stirred overnight at room temperature. After filtering off the N,N-dicyclohexyl urea, the reaction solution was then concentrated by rotary evaporation. The resulting crude solid was recrystallized in methanol to give the desired product **3** (18.45 g, Yield: 84%) as a white solid. ¹H NMR (500 MHz, CDCl₃): δ 8.25 - 8.01 (m, 4H), 7.9 (d, 1H, J = 2.85 Hz), 7.26 - 7.24 (m, 7H), 7.04 - 6.86 (m, 4H), 5.19 (s, 2H), 4.06 (t, 4H, J = 6.45 Hz), 1.8 (m, 4H), 1.5 (m, 4H), 1.0 (t, 6H, J = 7.25 Hz).



2,5-Di(4'-butyloxybenzoyloxy)benzoic Acid (4). Hydrogen was allowed to bubble through a stirred suspension of 10 % palladium on carbon (4.5 g) in 200 mL of

dichloromethane for 15 minutes. Benzyl ether **3** (18.45 g, 30.9 mmol) was added, and the reaction mixture was stirred at r.t. for 12 hrs. After filtering through a celite pad, the product (14.4 g, 92 %) was further dried under vacuum. ¹H NMR (500 MHz, CDCl₃): δ 8.23-8.07 (m, 4H), 7.9 (d, 1H, J = 2.85 Hz), 7.69-7.38 (dd, 2H, J = 8.7, 2.9 Hz), 7.04 - 6.92 (m, 4H), 4.06 (t, 4H, J = 3.5 Hz), 1.83 (m, 4H), 1.52 (m, 4H), 1.00 (m, 6H).



(4"-Acryloyloxybutyl) 2,5-Di(4'-butyloxybenzoyloxy)benzoate (6). 4hydroxybutyl acrylate (8.8 g, 61 mmol), compound 4 (25.8 g, 50.8 mmol), DMAP (0.244 g, 2.60 mmol) and dry CH₂Cl₂ (100 mL) were added into a 250 mL Schlenk-

type flask. Under a nitrogen atmosphere, DCC (10.53 g, 50.8 mmol) was added into the above flask in one portion at 0 °C, the reaction mixture was stirred at room temperature overnight. After filtering off the solids, the solvents were concentrated by rotary evaporation and the crude solids was purified by chromatography (petroleum ether: ethyl acetate=15:1) to give the product **6** (19.2 g, yield 60 %) as a white solid. ¹H NMR (300 MHz, CDCl₃) δ 8.15 (dd, 4H, J = 8.8, 3.3 Hz), 7.89 (d, 1H, J = 2.7 Hz), 7.46 (dd, 1H, J = 8.7, 2.8 Hz), 7.32 – 7.24 (m, 1H), 6.98 (d, 4H, J = 8.5 Hz), 6.36 (d, 1H, J = 17.3 Hz), 6.08 (dd, 1H, J = 17.3, 10.4 Hz), 5.79 (d, 1H, J = 10.4 Hz), 4.21 (t, 2H, J = 6.0 Hz), 4.05 (dd, 6H, J = 15.1, 6.4 Hz), 1.91 – 1.74 (m, 4H), 1.71 – 1.49 (m, 8H), 1.00 (t, 6H, J = 7.4 Hz).



Typical Preparation Protocol of Dual-Phase LCE.

The LC mixture was prepared by mixing 90 mol% LC monomer A444 ((4"acryloyloxybutyl)-2,5-di(4'-butyloxybenzoyloxy) benzoate), 9 mol% cross-linker (hexanediol and 1 mol% photo-initiator diacrylate) (2,2-dimethoxy-2phenylacetophenone). The LC mixture was added into a 5 mL screw-capped vial and fully dissolved in 1 mL of dry CH₂Cl₂. The organic solvent was then removed in vacuum to prepare a homogeneous LC mixture. The LC mixture was first heated up to above the isotropic phase (100 °C) and then filled into an anti-parallel surface-rubbed LC cell (20 µm gap) by capillary suction. The cell was filled up by the LC mixture completely in approximately 10 minutes. The filled cell was slowly cooled down at -1 °C/min to the nematic phase of the mixture (60 °C) to achieve a good planar alignment. The photomask was placed on the upper surface of the LC cell. The first photopolymerization was carried out by using an UV plate exposure machine under a light intensity of ca. 12 mW·cm⁻² for 15 seconds. After the first UV irradiation, the photomask was removed from the LC cell and the sample was then heated to 100 °C, which was just above the unreacted mesogen's clearing temperature (85 °C) meanwhile below the crosslinked LCEs' clearing point (123 °C), preserving the exposed LCEs' anisotropic order. The second photopolymerization was carried out by irradiation with the UV light for another 30 seconds. After cooled to room temperature, LCE film was obtained by dissolving the LC cell in a 40% aqueous hydrofluoric acid solution.



Fig. S1 The thermal-responsive motion images of LCE films (A) $\alpha = 0^{0}$ (Movie *S1*), (B) $\alpha = 45^{0}$ (Movie *S2*), and (C) $\alpha = 90^{0}$ (Movie *S3*) on heating.



Fig. S2 Schematic illustration of LCE ribbons' three representative transformation modes (bending, accordion-like folding/shrinkage and culing).



Fig. S3 Photo images of 1X1 array (A) and 2X2 array (B) umbrella patterned photomasks. The thermal-responsive motion images of the 1X1 array (C) and 2X2 array (D) umbrella patterned dual-phase LCE films. (Movies *S10,11* show the motions respectively.)

Our original goal was to use the umbrella pattern to stimulate White's voxelated LCE films with +1 topological defect.¹ However, as shown in Fig. S3C,D and Movie S10,11, the tip regions of the umbrella patterned dual-phase LCE film could not buckle out the plane to form cones as achieved in the reference,¹ but wrinkle instead. The reason behind these two different thermal responsibilities is the divergence in orientational distributions of molecular directors. In voxelated LCE systems,¹ the mesogenic directors varied azimuthally by 360° around the tip (defect) points so that the anisotropic-to-isotropic transition would cause radial expansions around each tip region and macroscopically lead to the emergence of cones. Contrarily, in our case, since the molecular directors of the four monodomain nematic brushes were aligned along one single direction, the four intervalic brushes would shrink in one uniform orientation and expand in the orthogonal direction. Overall, the whole film did planarly wrinkle.

Reference

1 T. H. Ware, M. E. McConney, J. J. Wie, V. P. Tondiglia and T. J. White, *Science*, 2015, **347**, 982–984.