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Electronic Supplementary Information

Thermomechanical Liquid Crystalline Elastomer Capillary with Biomimetic Peristaltic Crawling Function

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Syntheses and Characterization of LC Monomer

The LC monomer, 4"-Acryloyloxybutyl 2,5-di(4'-butyloxybenzoyloxy)benzoate (4-ADBB), was synthesized according to the method reported in our previous article.[1] The synthesis and characterization are describe below.

4′-Bromobutyl 2,5-Dihydroxybenzoate (A): $KHCO_3$ (10.7 g, 107 mmol) was added into a stirred mixture of 2,5-dihydroxybenzoic acid (6.3 g, 40 mmol) and 1,4-dibromobutane (15 mL, 174 mmol) in dimethylformamide (DMF, 100 mL). The mixture was heated to 70 ºC and the reaction was carried out at the temperature with stirring for 24 h. After that, the reaction system was cooled down to room temperature, diluted with water (200 mL), and extracted three times with dichloromethane (DCM, 3×300 mL). The organic phases were washed with water (500 mL) and dried over $MgSO_4$. After evaporation of the solvents, the residue was subjected to column chromatography on silica gel with DCM as the eluting solvent to yield white powder (70%).

4′-Acryloyloxybutyl 2,5-Dihydroxybenzoate (B): $KHCO_3$ (3.0 g, 30 mmol) was added to a mixture of **A** (5.2 g, 20 mmol) and acrylic acid (5.2 g, 72 mmol) in DMF (100 mL). The mixture was heated to 50 ºC and the reaction was carried out at the temperature with stirring 24 h. The reaction mixture was cooled down to room temperature, diluted with water (100 mL), and extracted three times with DCM (3×150 mL). The organic phase was washed three times with water (3×300 mL) and dried over $MgSO_4$. After evaporation of the solvents, the residue was subjected to column chromatography on silica gel with DCM as the eluting solvent to yield white powder (90%).

LC Monomer (4-ADBB): A solution of **B** (2.5 g, 10 mmol), 4-n-butyloxybenzoic acid (4.1 g, 21 mmol), *N,N*-dicyclohexylcarbodiimide (6.2 g, 30 mmol), and 4-pyrrolidinopyridine (0.48 g, 3 mmol) in dichloromethane (100 mL) was stirred at room temperature for 24 h. The *N,N*-dicyclohexyl urea was filtered and the filtrate was sequentially washed with water (200 mL), acetic acid solution (5%, 200 mL), and water (200 mL), and dried over $MgSO_4$. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with DCM as the eluting solvent to yield white powder (70%). ^{1}H NMR (300 MHz, d_6-DMSO) δ (ppm): 8.09 (m, 4H, ArH), 7.84 (d, 1H, ArH), 7.66 (m, 1H, ArH), 7.49 (d, 1H, ArH), 7.12 (m, 4H, ArH), 6.25, 6.13, 5.91 (3m, 3H, CH_2=CH), 4.11 (m, 6H, —CH_2—O), 3.95 (t, 2H, —CH_2—O), 1.72 (m, 4H, CH_2), 1.48 (m, 8H, CH_2), 0.95 (t, 6H, CH_3). ^{13}C NMR (75 MHz, d_6-DMSO) δ (ppm): 15.3, 20.3, 26.2, 32.2, 65.2, 66.5, 69.4, 116.4, 122.3, 126.1, 126.8, 129.5, 130.0, 132.9, 133.9, 148.8, 149.4, 164.9, 165.2, 165.9 and 166.4. IR (KBr, cm^{-1}): 3075 (—C=C—H, s), 2958, 2934, 2872 (C—H, s), 1732 (C=O, s), 1634 (C=C, s), 1608, 1581, 1512 (Benz. ring, s), 1475, 1389 (C—H, d), 1252, 1182, 1166, 1073 (C—O—C, s).

Syntheses and Characterization of Polyimide

A highly transparent polyimide (PIHA), used to prepare the LC cell alignment layers, was prepared in this laboratory by the following procedure.[2]

2,2′-Bis(trifluoromethyl)benzidine (**A**, 3.76 g, 11.5 mmol) and 4,4′-bis(3-aminophenoxy) diphenylsulfone (**B**, 3.68 g, 11.5 mmol) as the diamine monomers were dissolved in *N*-methyl -2-pyrrolidinone (NMP) to form a solution with the concentration of 20 wt%, which was then cooled with the ice water bath. After completely dissolved, 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (**C**, 10 g, 23 mmol) as the anhydride monomer was added into the above solution under stirring for 12 h. The molar ratio of **C**: **A**: **B** in above reaction was 5:2.5:2.5. The reaction mixture was stirred at room temperature for 6 h to obtain the pristine polyamic acid (PAA). Then, the polyamic acid solution was casted on the substrate surface and heated at 80 ºC for 2 h. The precursor was then thermally imidized by step-wise heating at 150 ºC (1 h), 200 ºC (1 h), and 300 ºC (1 h) to afford the polyimide films. IR (KBr, cm^{-1}): 1782 (C=O sym. str.); 1720 (C=O asym. str.); 1587 (C=C str. Ar.); 1445 (C=C str. Ar.); 1364 (C—N—C str. imide.); 1302 (C—SO_2—C str. imide.); 1232 (Ar.—O—Ar.); 1125 (—CF_3); 964, 835 (Ar.—H); 778, 745 (subst. Ar.); 1660-1670 (non PAA structure band). The LC cell alignment layers on the glass capillary surfaces were prepared by using above polyamic acid (PAA) through the same imidization procedure.

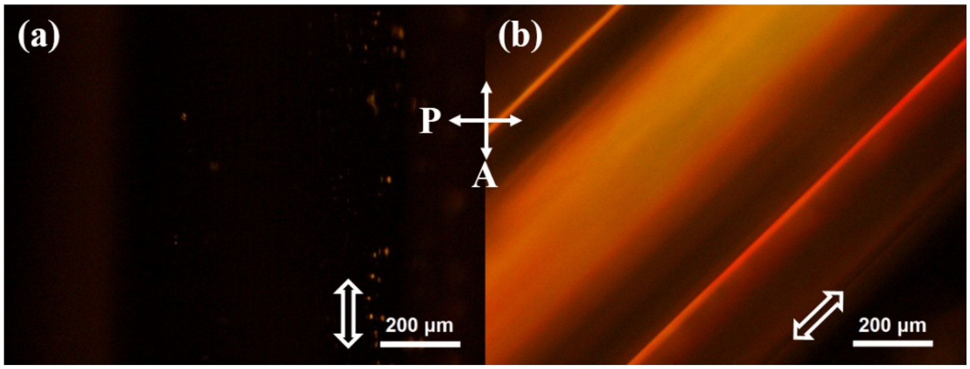

Figure S1. POM images of the tubular liquid crystal cell filled with aligned LCE precursor before photoinduced polymerization/crosslinking. The inserted white double-sided arrows represent the long axis directions (alignment direction) of the LC cells: (a) the alignment direction is parallel to the analyzer; (b) the alignment direction is 45º to the analyzer. P and A represent polarizer and analyzer, respectively.

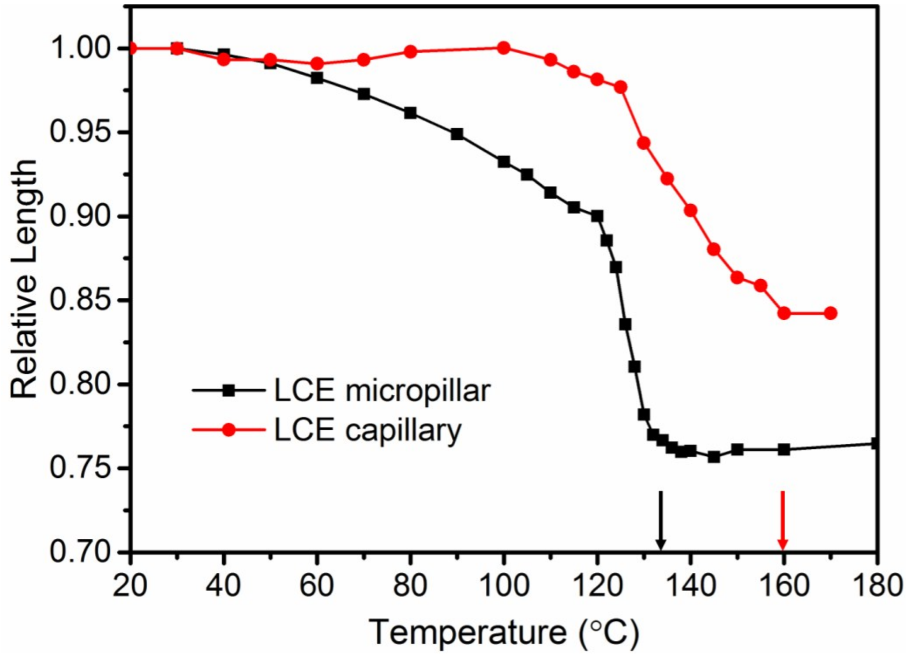

Figure S2. Temperature-dependent deformations of the LCE capillary and LCE micropillar. There is no residual polyimide layer on the micropillar surface, which was prepared by the method reported before.[1]

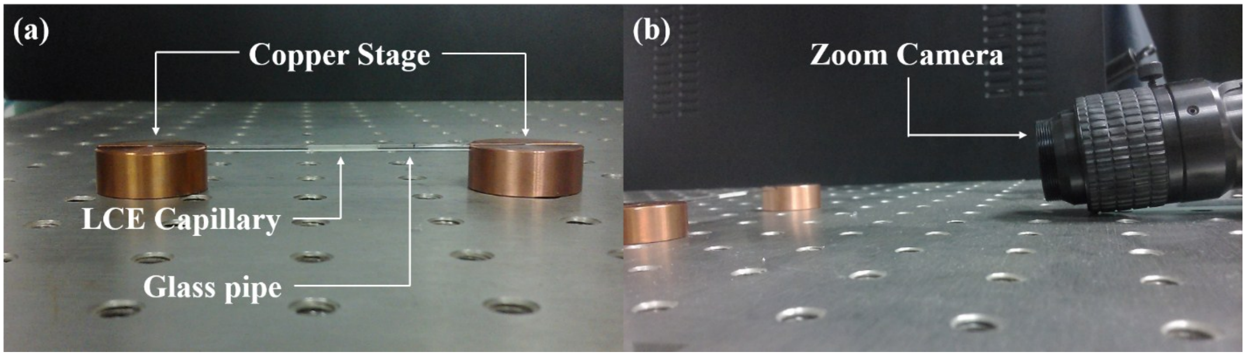

Figure S3. Experimental setup for investigating the LCE capillary peristaltic crawling locomotion. (a) Both ends of a glass tube with ~ 1 mm inner diameter were immobilized on two copper stages, and the LCE capillary was placed in the glass tube. (b) Photographs and videos of the peristaltic crawling locomotion were recorded by a zoom CCD camera.

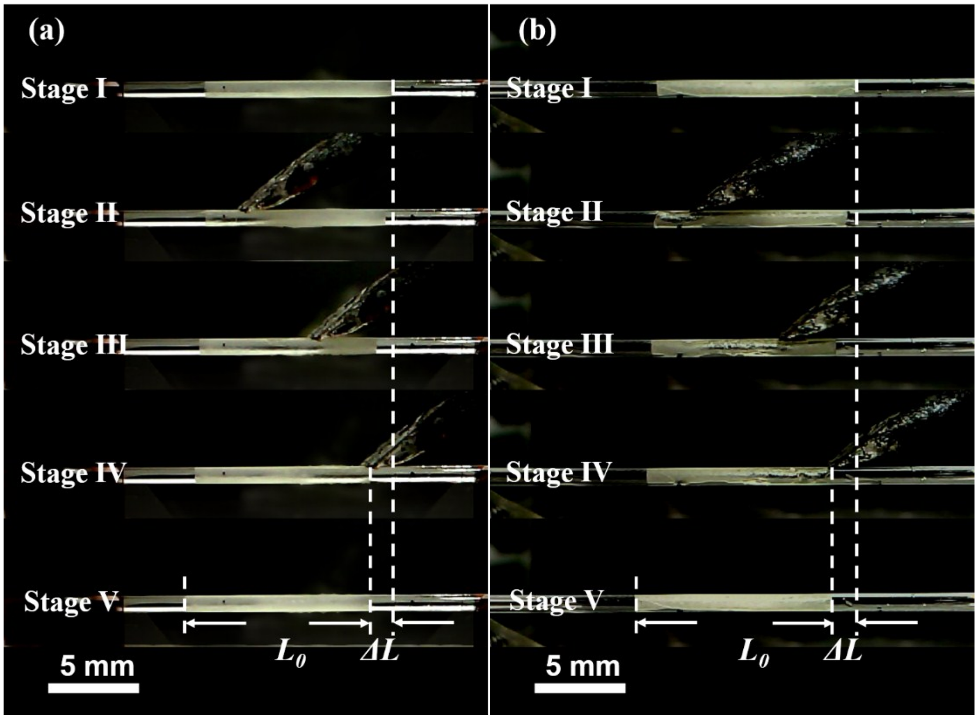

Figure S4. Peristaltic crawling for cases with or without the silicone oil: (a) the glass tube was fully filled with silicone oil; (b) no silicone oil was filled in the glass tube. The locomotion was observed for both cases with no obvious difference between them.

REFERENCES

(1) R. B. Wei, L. Y. Zhou, Y. N. He, X. G. Wang and P. Keller, *Polymer*, 2013, **54**, 5321-5329.

(2) S. K. Kim, X. Y. Wang, S. Ando and X. G. Wang, *Eur. Polym. J.*, 2015, **64**, 206-214.