Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis of POSS-functionalized liquid crystalline block copolymers *via* RAFT polymerization for stabilizing blue phase helical soft superstructure

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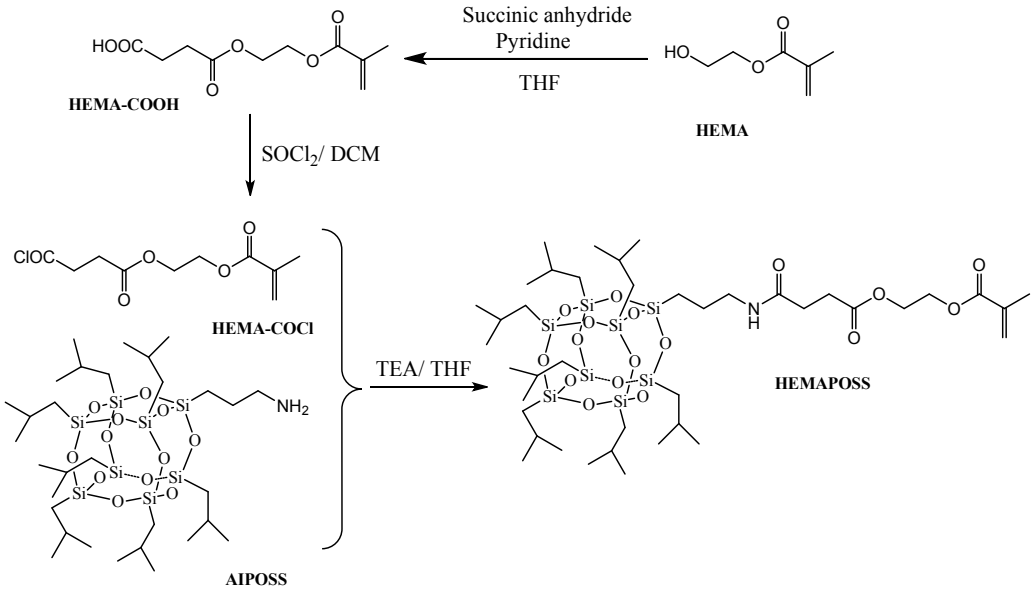
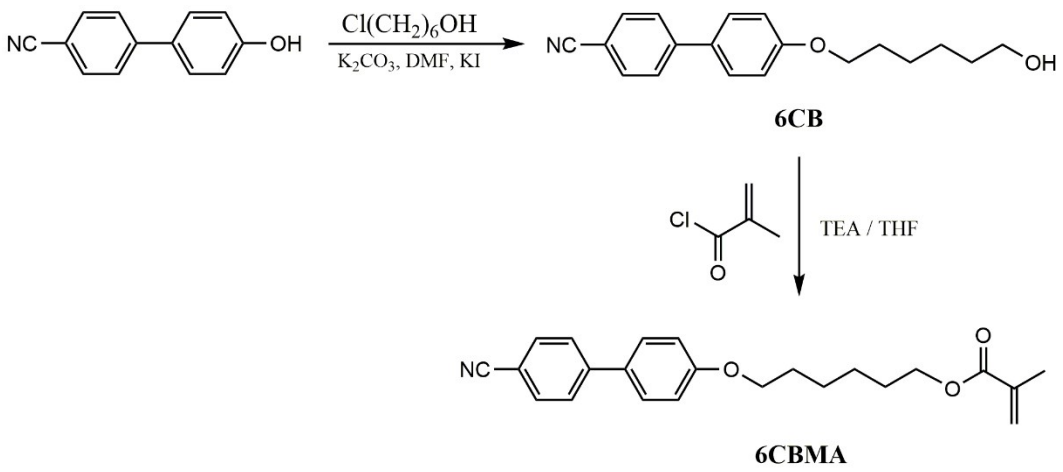


Scheme S1 Synthesis of methacrylate isobutyl POSS monomer (HEMAPOSS).



Scheme S2 Synthesis of 6-(4-cyano-4'-biphenyloxy) hexyl methacrylate (6CBMA).

Synthesis of methacrylate isobutyl POSS monomer (HEMAPOSS)

The synthetic procedure of HEMAPOSS was performed according to our previous work.[1] ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.13 (s, 1H), 5.60 (s, 1H), 4.35 (s, 4H), 3.23 (m, 2H), 2.71 (m, 2H), 2.47 (m, 2H), 1.95 (s, 3H), 1.85 (m, 7H), 1.61 (m, 2H), 0.96 (d, 42H), 0.61 (d, 16H).

Synthesis of 6-(4-cyano-4'-biphenyloxy) hexyl methacrylate (6CBMA)

A mixture of 4-cyano-4'-hydroxybiphenyl (1.95 g, 10 mmol), K_2CO_3 (4.14 g, 30 mmol), and KI (0.0176 g, 1 mmol) in DMF (50 mL) was heated at 100 ^{o}C for 30 min. 6-Chloro-1-hexanol (1.64 g, 12 mmol) was added into the suspension and subjected to reflux for 24 h. After removal of solvent under reduced pressure, the residual solid was washed with water for five times. The crude product was purified by flash column chromatography on silica gel using ethyl acetate/dichloromethane (1:4 v/v) as the eluent. The product, 6-(4-cyano-4'-biphenyloxy)-1-hexanol (6CB), was dried under vacuum at 45 ^{o}C for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.32 (m, 4H), 1.54 (m, 2H), 1.77 (m, 2H), 3.61 (t, 2H), 4.00 (t, 2H), 6.95, 7.51 (d, 4H), 7.60, 7.65 (d, 4H).

6CB (1 g, 3.4 mmol) and triethylamine (0.7 mL, 5 mmol) were dissolved in 20 mL anhydrous THF. Then, methacryloyl chloride (0.53 g, 5 mmol) in 10 mL anhydrous THF was added dropwise to the mixed solution at 0 °C. The mixture was stirred

overnight at room temperature. 200 mL deionized water was added, and the product was extracted with chloroform. After washed with deionized water three times, the product was dried with anhydrous magnesium sulfate and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (1:1 v/v) as the eluent. The product, 6CBMA, was dried under vacuum at room temperature for 24 h. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.20-1.45 (m, 4H); 1.54 (m, 2H); 1.77 (m, 2H), 1.93 (s,3H), 3.98 (t, 2H), 4.15 (t, 2H), 5.52, 6.07 (d, 2H), 6.95,7.51 (d, 4H), 7.60, 7.65 (d, 4H).

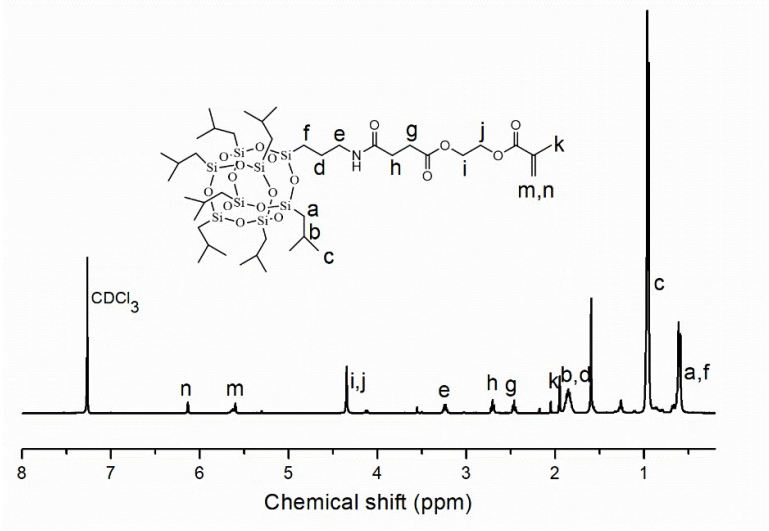


Fig. S1 ^{1}H NMR spectrum of HEMAPOSS in $CDCl_3$.

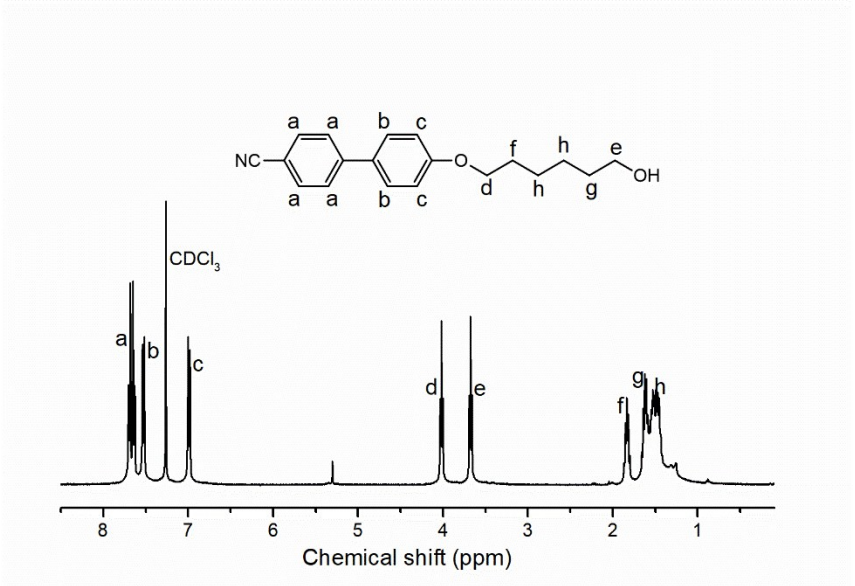


Fig. S2 ^{1}H NMR spectrum of 6CB in $CDCl_3$.

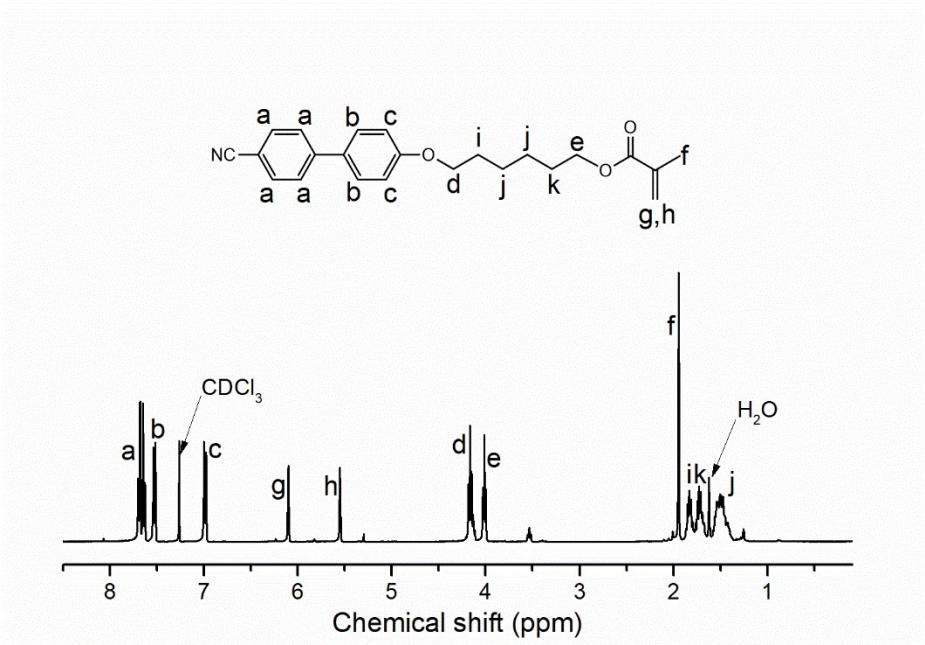


Fig. S3 ^{1}H NMR spectrum of 6CBMA in $CDCl_3$.

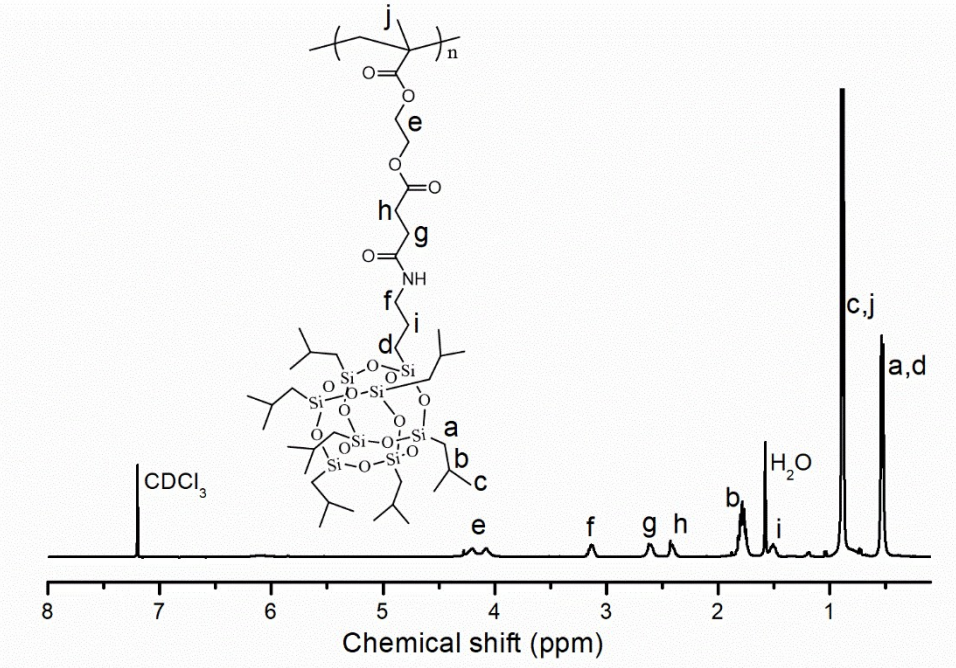
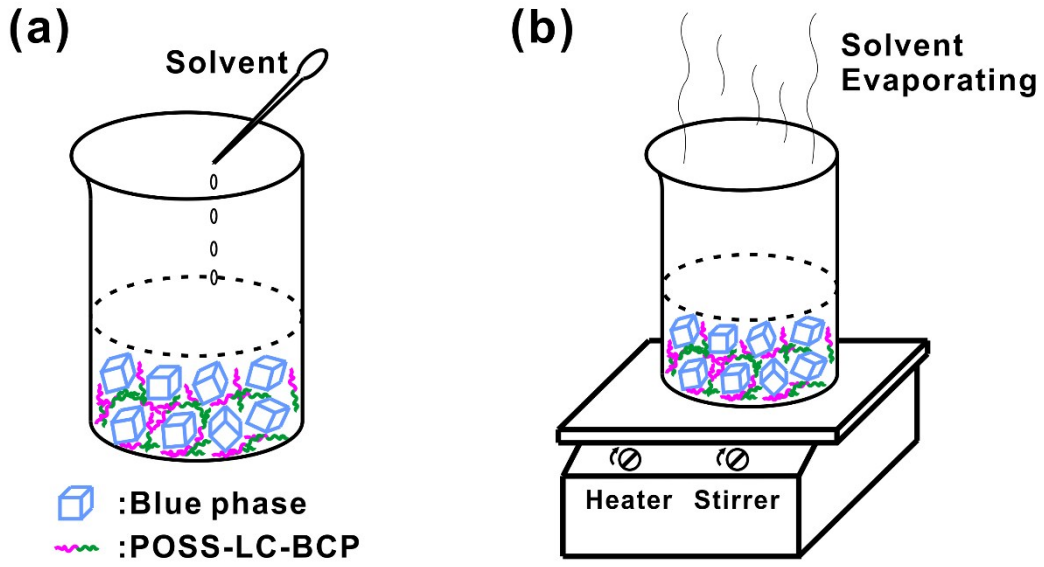


Fig. S4 ^{1}H NMR spectrum of $PHEMAPOSS_{40}$ in $CDCl_3$.



Scheme S3 Preparation of PHEMAPOSS$_{40}$-*b*-P6CBMA$_{167}$ (POSS-LC-BCP) doped BPLC. (a) Mixture of BPLC host and POSS-LC-BCP in dichloromethane. (b) The mixture was stirred at room temperature for at least 1 hour and heated to 50 °C for another 30 min to remove the solvent through evaporation.

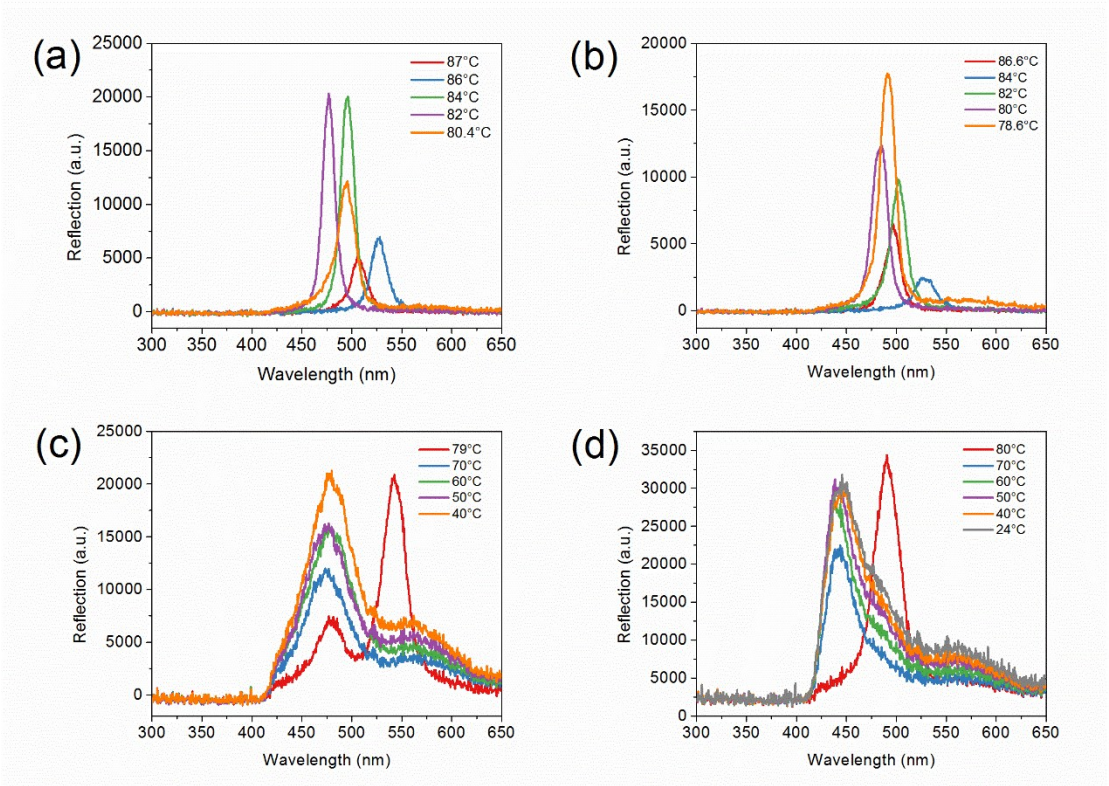


Fig. S5 The reflectance spectra of the samples with (a) 0 wt%, (b) 5 wt%, (c) 15 wt%,

and (d) 20 wt% LCBCPs under different temperatures.

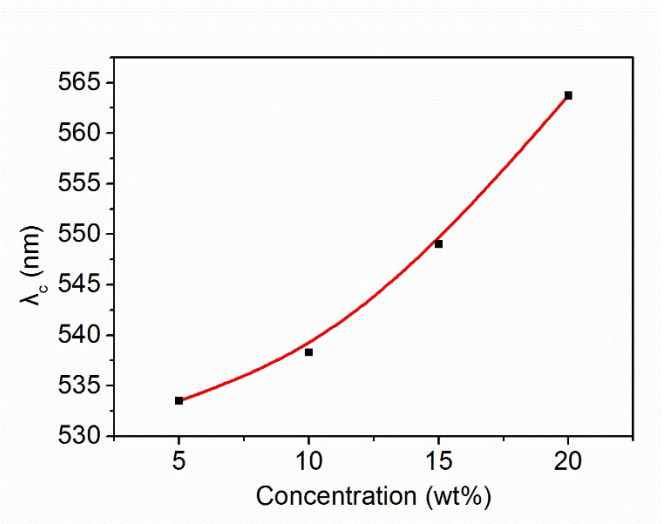


Fig. S6 The λ_c of the samples with different concentration of LC BCPs.

Table S1. Blue phase range of the samples with different concentration of LC BCPs.

Samples(LC BCP Concentration)	T_{Iso-BP}/℃	T_{BP-N*}/℃	BP Range/℃
0 wt%	87	80.4	6.6
5 wt%	86.6	78.2	8.4
15 wt%	79	35	44
20 wt%	80	23	57

Table S2. The E-O properties of PSBP and samples with different concentration of LC BCPs.

Samples	Rise time (μs)	Decay time (μs)	Hysteresis ΔU (V)
20 wt% LC BCP	13 0	30 0	4.9
PSBP	156	20 0	10.2

Reference

1. L. Z. Hong, Z. H. Zhang, Y. Zhang and W. A. Zhang, *Journal of Polymer Science Part a-Polymer Chemistry*, 2014, **52**, 2669-2683.