

## Supporting Information

### **Odd-even effect in chiral side-chain cyanobiphenyl block copolymer assemblies prepared by polymerization-induced chiral self-assembly**

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## S1 Materials and Characterization

### Materials.

4-Cyanopentanoic acid dithiobenzoate (CPADB, 99%, TCI), 4,4'-azobis(4-cyanovaleric acid) (ACVA, 98%, macklin), methyl (*R*)-(+)-lactate (Adamas,  $\geq 98\%$ ), methyl (*S*)-(-)-lactate (Adamas,  $\geq 98\%$ ), tetrabutylammonium fluoride (aladdin, 1.0 M in THF), Cyanobiphenol (Energy Chemical,  $>98\%$ ), tertbutylchlorodiphenylsilane (amethyst,  $\geq 98\%$ ), 2-chloroethanol, 3-chloro-1-propanol, 4-chloro-1-butanol, 5-chloro-1-pentanol, 6-chloro-1-hexanol (Acros, 95%), methacryloyl chloride (Aladdin, 95%), 1,2-triphenylphosphine (Greagent,  $>99\%$ ), 4-dimethylaminopyridine (Macklin, 99%), *n*-(3-dimethylaminopropyl)-*n*'-ethylcarbodiimide hydrochloride (Accela, 97%), lithium aluminum hydride (Aladdin,  $\geq 97\%$ ) were used without further purification. Methylacrylic acid (MAA, 99%, Aladdin) was purified by passing through a basic alumina oxide column prior to storage at  $-10\text{ }^{\circ}\text{C}$ . The chiral monomers CB-*mL/D* (*m* = 3, 6, 7, 8, 9 and 10) were synthesized according to the previously reported procedures.<sup>1,2</sup>

### Characterization.

- <sup>1</sup>H NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz, Bruker, Kalsruhe, Germany) using CDCl<sub>3</sub> or CDCl<sub>3</sub>/DMSO-*d*<sub>6</sub> (6/4, v/v) as the solvents and tetramethylsilane (TMS) as the internal standard at 25 °C.
- Gel permeation chromatography (GPC) measurements were conducted on the TOSOH HLC-8320 gel permeation chromatography (GPC) (Tokyo, Japan), which was equipped with a refractive index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6 × 150 mm, 3.0 μm beads size) columns (Tokyo, Japan) arranged in a series. It can separate polymers in the molecular weight range of 500-190k Da. THF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. The values of the average molecular weight (*M*<sub>n</sub>) and molecular weight distribution (*Đ*) of the polymer was calculated with PMMA standard.
- CD spectra were recorded on a JASCO J-1500 spectropolarimeter equipped with a Peltier-controlled housing unit using an SQ grade cuvette, a single accumulation, a path length of 10 mm, a bandwidth of 2 nm, a scanning rate of 200 nm/min, and a response time of 1 s. The aggregate solutions were diluted with ethanol at 20 °C to generate 0.01 mg/mL dispersions. The magnitude of the circular polarization at the ground state was defined as  $g_{\text{CD}} = 2 \times (\epsilon_L - \epsilon_R)/(\epsilon_L + \epsilon_R)$ , where  $\epsilon_L$  and  $\epsilon_R$  denoted the extinction coefficients for left and right circularly polarized light, respectively. Experimentally, the  $g_{\text{CD}}$  value was defined as  $\Delta\epsilon/\epsilon = [\text{ellipticity}/32,980]/\text{absorbance}$  at the CD extremum. UV-vis spectra were recorded on a Shimadzu UV-2600 spectrophotometer (Nakagyo-ku, Kyoto, Japan).
- TEM images were taken with a HITACHI HT 7700 operated at an accelerating voltage of 100 kV.
- The thermal behaviors were measured by TA instrument DSC 250 (New Castle, DE, USA). The heating rate and cooling rate were both 10°C/min.

6. POM images were measured by CNOPTec BK-POL microscope fitted with a CNOPTec BK-RDY thermo-control system (Chongqing, China).
7. WAXD data were obtained on an X'Pert-Pro MPD X-ray powder diffractometer (Panalytical, Holland) equipped with a copper target, at a scan speed of  $0.375151^\circ \text{ s}^{-1}$  and at a scattering angle range of  $2\theta = 10\text{-}50^\circ$ . Experimentally, a small aliquot mixture after PICSA was filtered directly at room temperature to remove ethanol, and then the LC property of the sample was measured.
8. The monomers were also purified by chiral high performance liquid chromatography (HPLC). Chiral HPLC was performed on an Agilent 1200 Series chromatographs using a Daicel Chiralpak AD-H column (0.46 cm  $\times$  25 cm).
9. SAXS data were measured by Anton Paar SAXSess MC2 diffractometer with  $\text{CuK}_\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ).

## S2 Experimental Procedures

### 1. Synthesis of PMAA<sub>63</sub> macro-CTA via RAFT solution polymerization.

For a typical polymerization system, MAA (11.85 g, 137.8 mmol), CPADB (0.56 g, 2.0 mmol), Ethanol (20.6 g) and ACVA (112.2 mg, 0.4 mmol) with the molar ratio of  $[\text{MAA}]_0/[\text{CPADB}]_0/[\text{ACVA}]_0 = 69/1/0.2$  were added into a 50 mL round bottomed flask equipped with a magnetic bar. The reaction medium was purged with argon for 30 min at 0 °C to remove oxygen. After three freeze-thaw-pump cycles, the flask was sealed and placed in an oil bath at 70 °C. After 5 h, the flask was cooled to room temperature with ice-water. The mixture was diluted with EtOH, precipitated in *n*-hexane 3 times. PMAA macro-CTA was purified via dialysis (MWCO 3000 g/mol) in ethanol for 3 days. Then dry under vacuum at 35 °C. The product obtained was a pink solid (10.3 g, monomer conversion: 87%). The DP was 63 measured by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. The  $M_n$  (10600 g/mol) and  $\bar{D}$  (1.1) were measured by GPC after chemical modification of the carboxylic acid groups by benzyl chloride.<sup>3</sup>

### 2. Synthesis of mL/D-x BCP assemblies via polymerization-induced chiral self-assembly.

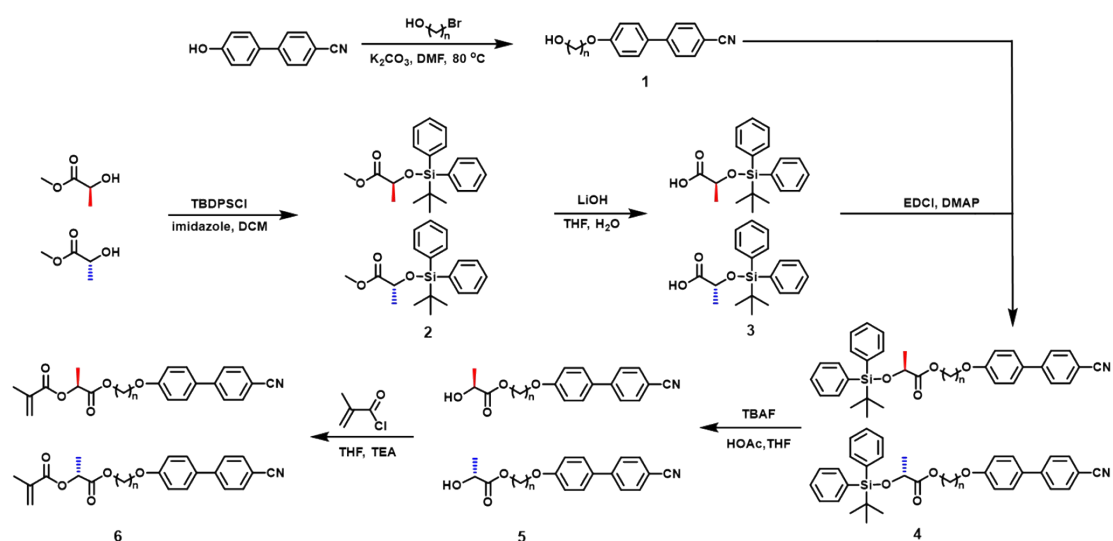
A typical polymerization-induced chiral self-assembly for the synthesis of the mL/D-x BCP assembly at 10 wt% total solid content was carried out as follows. Taking the preparation of 3L/D-60 as an example. PMAA<sub>63</sub> macro-CTA (113.8 mg, 0.02 mmol), ACVA (1.86 mg, 0.0067 mmol), CB-3L/D monomer (471.5 mg, 1.2 mmol) and EtOH (6.2 mL) were added to a reaction tube. Then the reaction tube was flame-sealed under argon atmosphere after being deoxygenated with three standard freeze-pump-thaw cycles. The polymerization was carried out at 70 °C for 9 h. Then the polymerization was quenched by cooling the tube in an ice-water bath and exposing the solution to air. The resulting CB-BCP was diluted and further characterized by using <sup>1</sup>H NMR, TEM, AFM and CD instruments. The  $M_n$  and  $\bar{D}$  were measured by GPC after chemical modification of the carboxylic acid groups by benzyl chloride.<sup>3</sup>

### 3. Chemical Modification of carboxylic acid groups on PMAA<sub>63</sub> macro-CTA and mL/D block copolymers.

For GPC studies, the carboxylic acid groups on the PMAA<sub>63</sub> macro-CTA and mL/D-x block

copolymers were fully esterified using benzyl chloride with TMG as a promoter according to Bai and coworkers.<sup>2</sup> Taking the chemical modification of PMAA<sub>63</sub> macro-CTA as an example. PMAA<sub>63</sub> macro-CTA (42.3 mg, 0.5 unit mmol) was dissolved in DMSO (1 mL). Then TMG (115.0 mg, 1 mmol) and benzyl chloride (95.0 mg, 0.75 mmol) were added. After that the mixture was stirred over night at room temperature. The polymer was then precipitated into a large amount of methanol and dried under vacuum at 40 °C to obtain a yellow powder polymer. The chemical modification of *mL/D*-x block copolymers were kept the same as those for PMAA<sub>63</sub> macro-CTA except the 60/40% w/w CHCl<sub>3</sub>/DMSO mixtures as the solvent.<sup>3</sup>

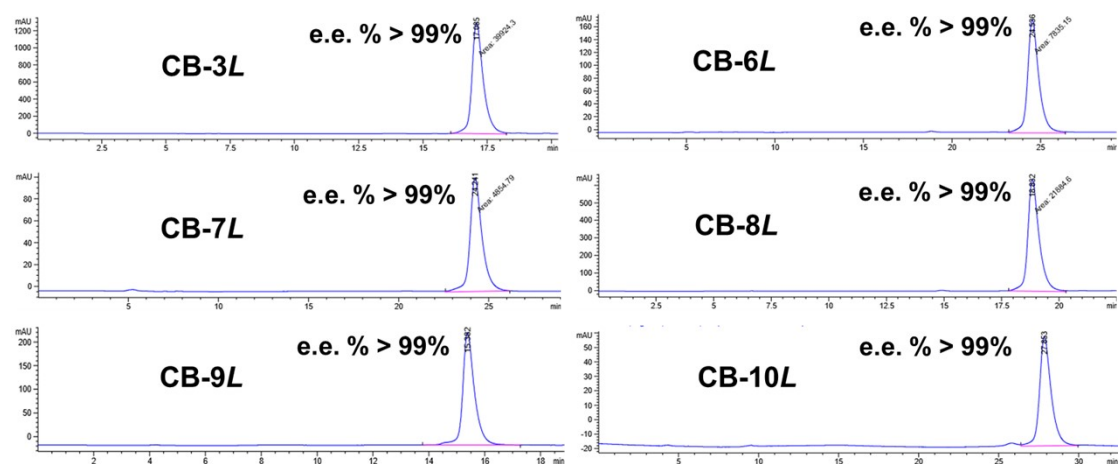
### S3 Supporting Figures



CB-3 ( $n = 0$ ), CB-*mL/D* ( $m = n+4$ )

$n = 0, 2, 3, 4, 5, 6$ . (When  $n = 0$ , there is one oxygen atom in the figure)

**Scheme S1.** Synthetic routes of chiral CB monomers with different spacer units from chiral stereocenter to the CB chromophore.



**Fig. S1.** HPLC spectra and the *e.e.*% values of the chiral CB-containing monomers.

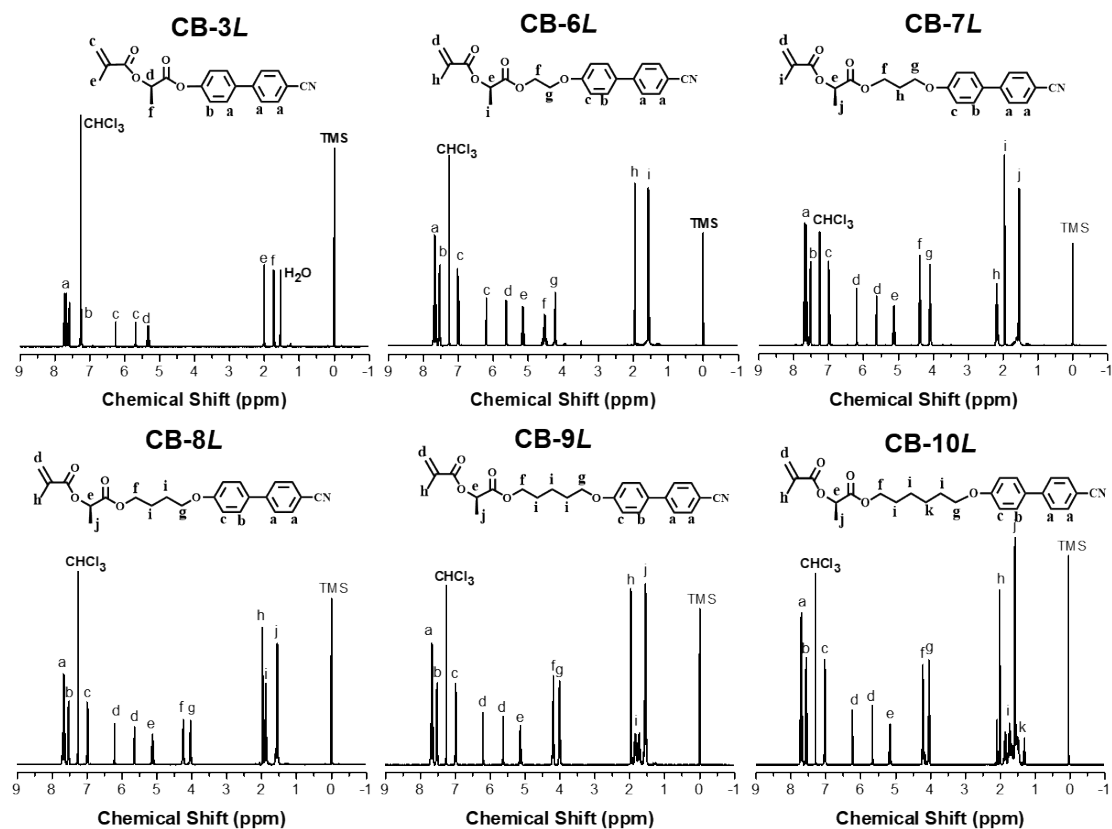


Fig. S2.  $^1\text{H}$  NMR spectra of the L-type chiral CB-containing monomers.

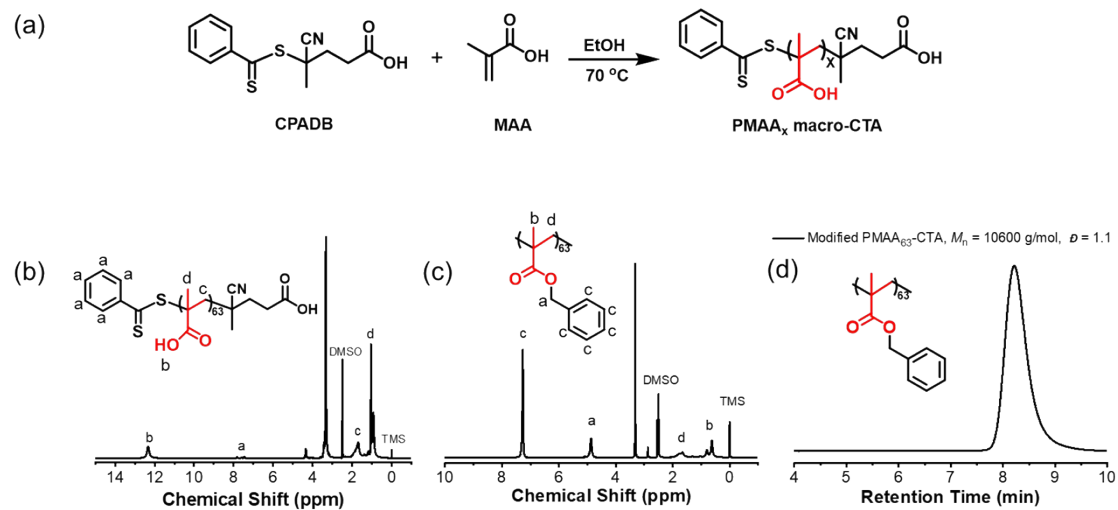
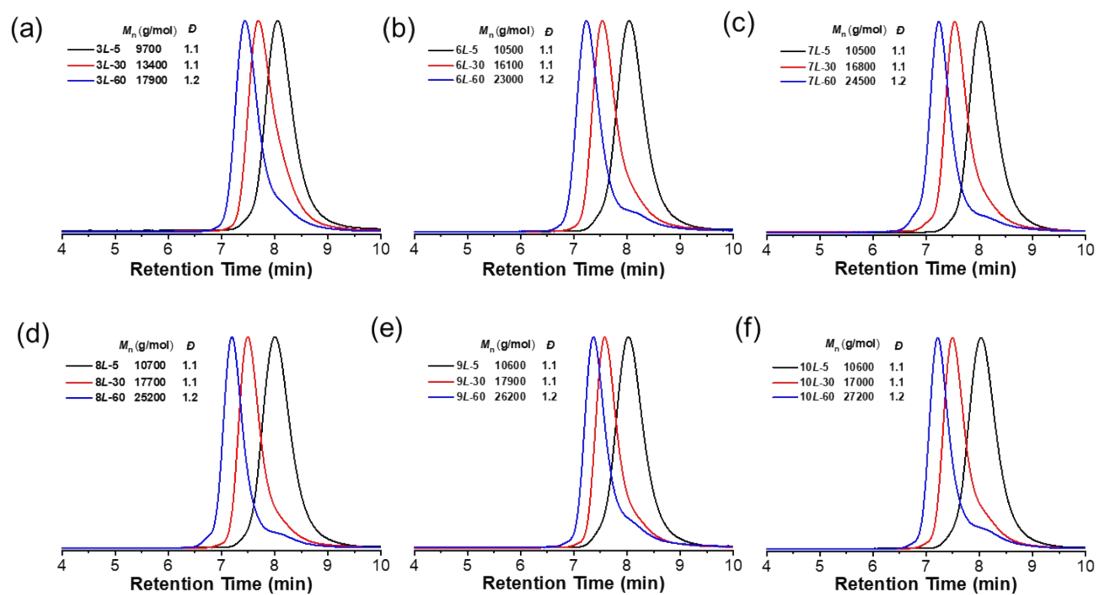
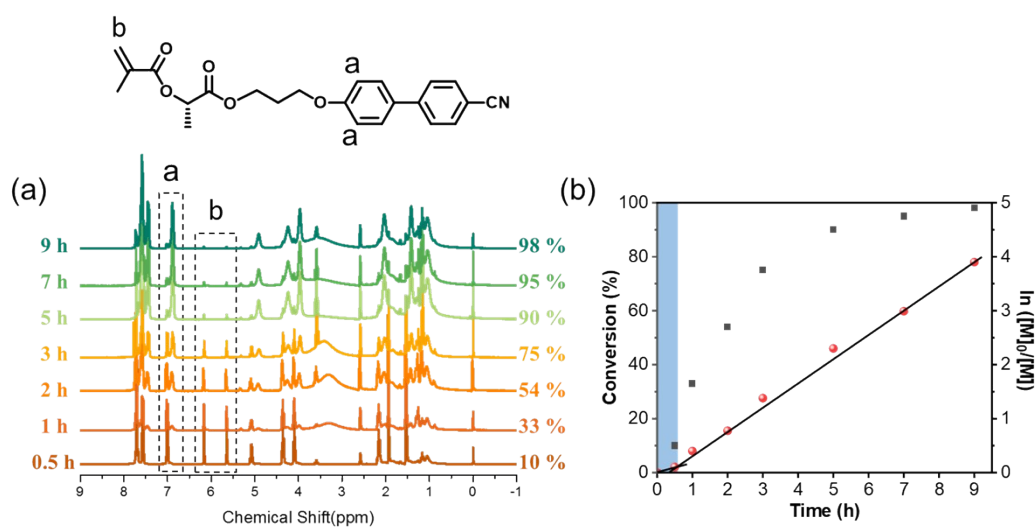


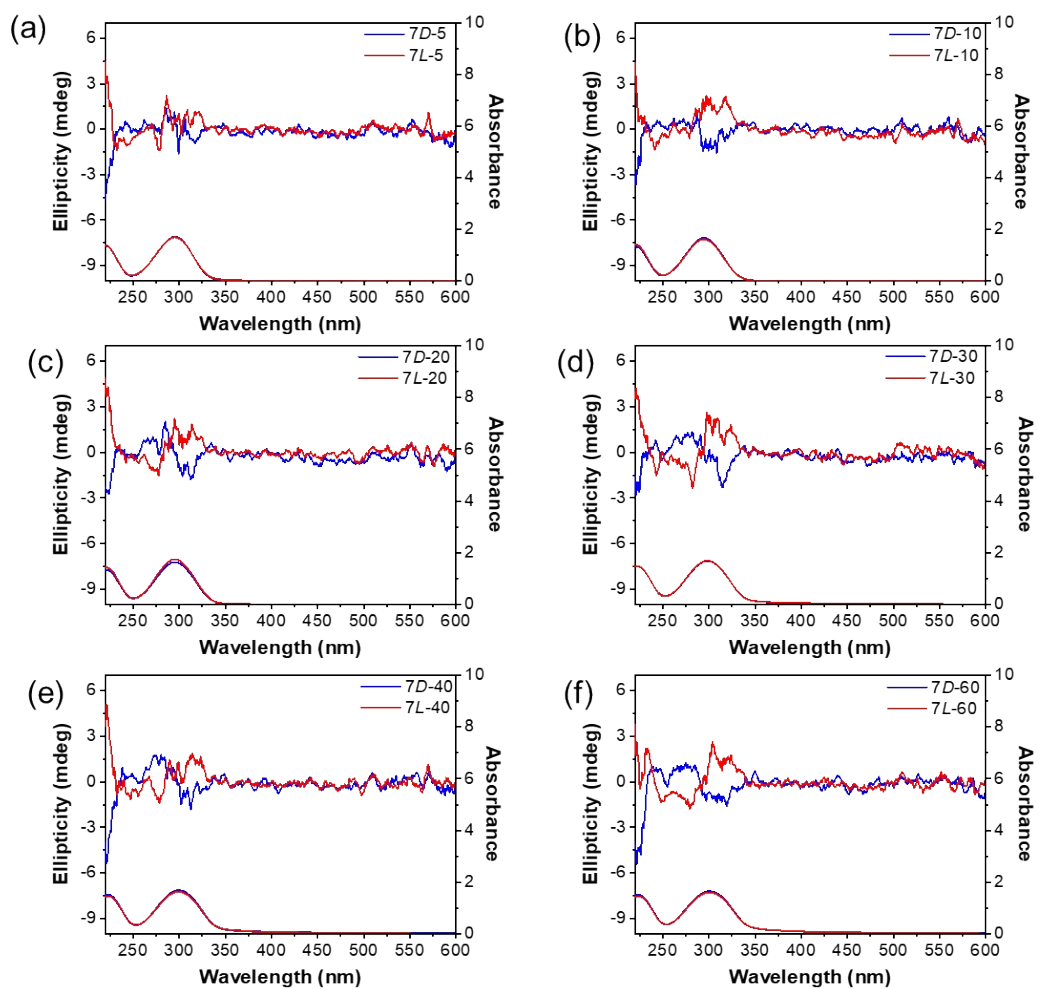
Fig. S3. (a) Synthesis route for PMAA<sub>63</sub> macro-CTA;  $^1\text{H}$  NMR spectra of (b) PMAA<sub>63</sub> macro-CTA and (c) PMAA<sub>63</sub> macro-CTA after chemical modification; (d) GPC curve of the PMAA<sub>63</sub> macro-CTA after chemical modification.



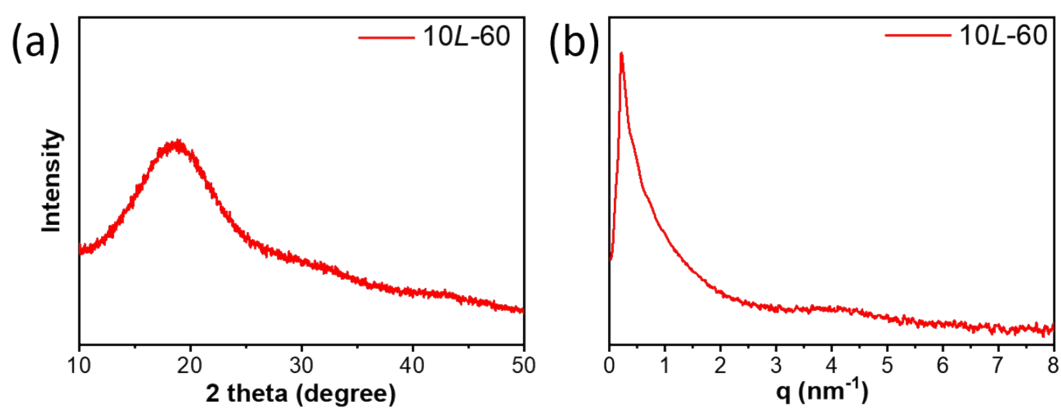
**Fig. S4.** (a-f) GPC curves of the  $mL-x$  BCP ( $m = 3, 6, 7, 8, 9$  and  $10$ .  $x = 5, 30$  and  $60$ ). All of the BCPs were fully esterified using benzyl chloride with TMG as a promoter.



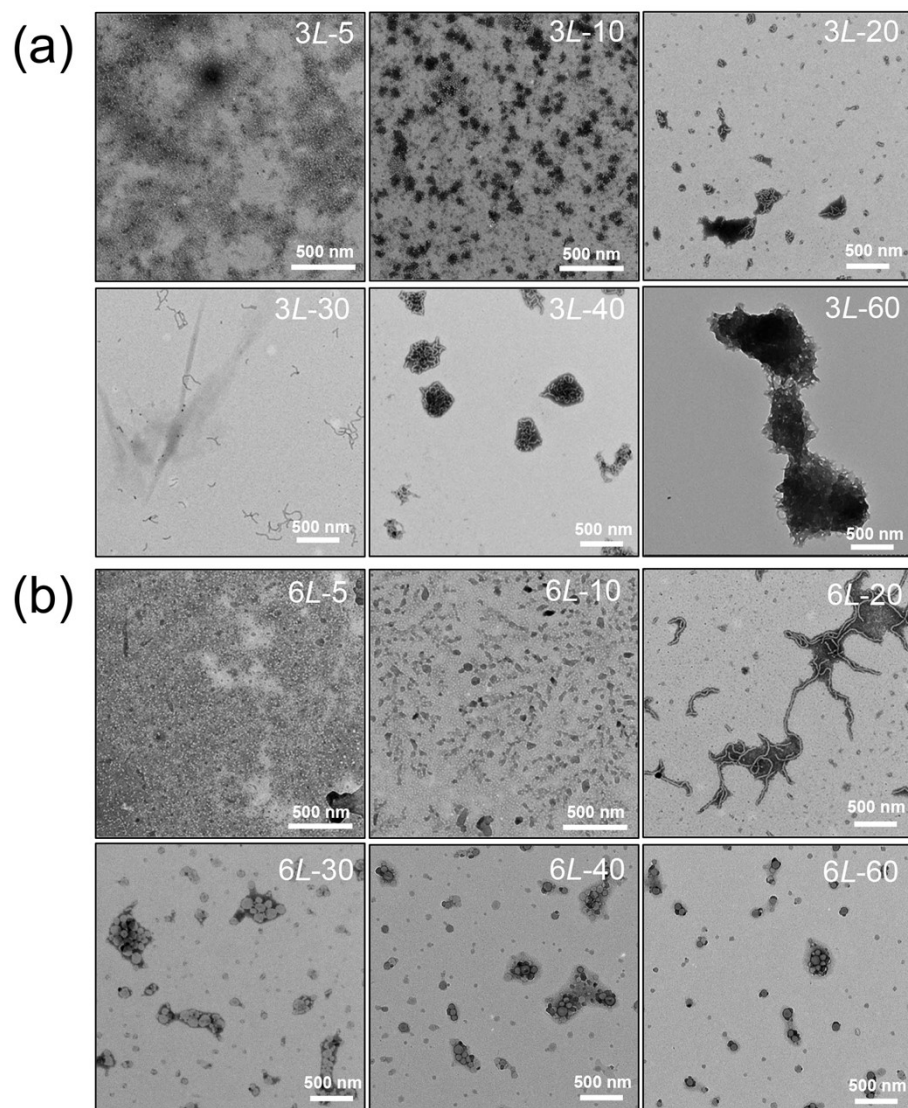
**Fig. S5.** (a)  $^1H$  NMR spectra of the  $7D-60$  BCP assembly with different polymerization time in ethanol, using deuterated solvents  $CDCl_3/DMSO-d_6$  (6/4, v/v); (b) The corresponding  $\ln([M]_0/[M])$ -Time and Conversion-Time curves.



**Fig. S6.** (a-f) CD and UV-vis spectra of 7L-x and 7D-x ( $x = 5, 10, 20, 30, 40$  and  $60$ ) BCP assemblies in ethanol.

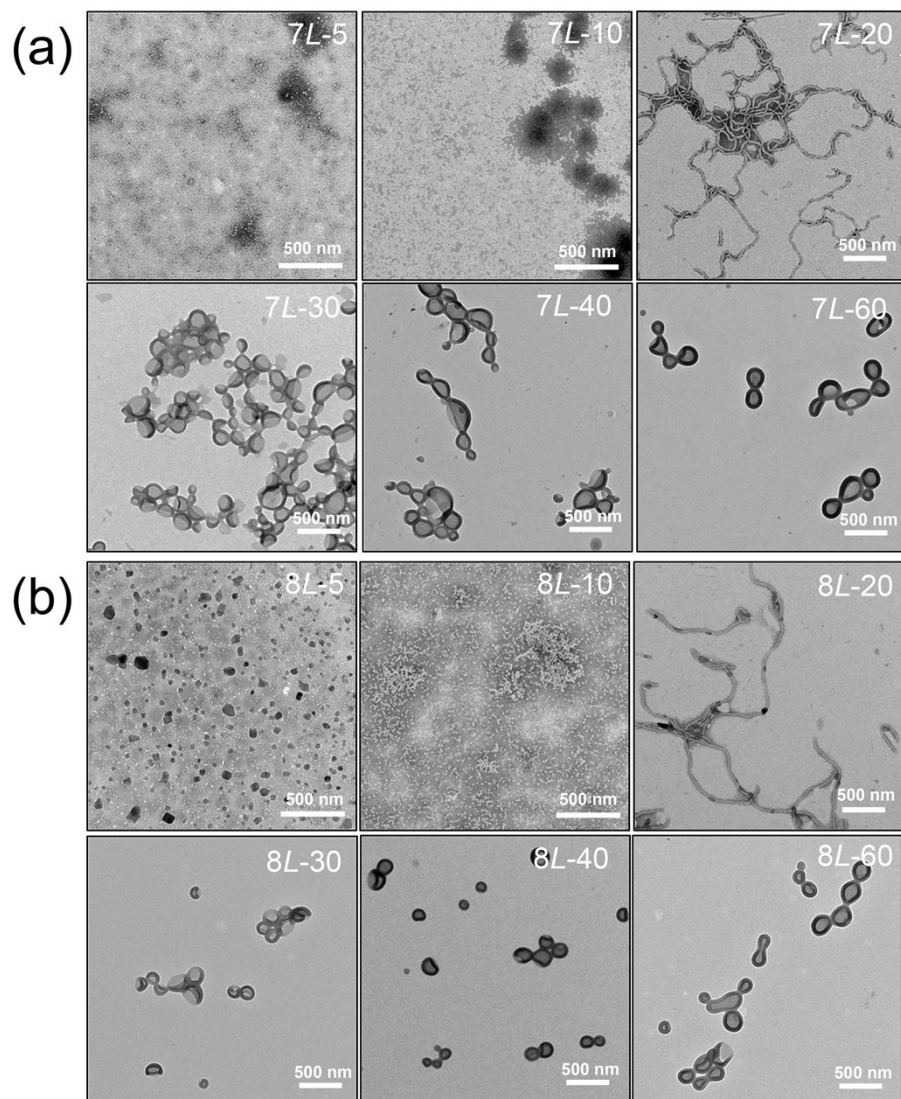


**Fig. S7.** (a) WAXD pattern of 10L-60 BCP; (b) SAXS pattern of 10L-60 BCP.

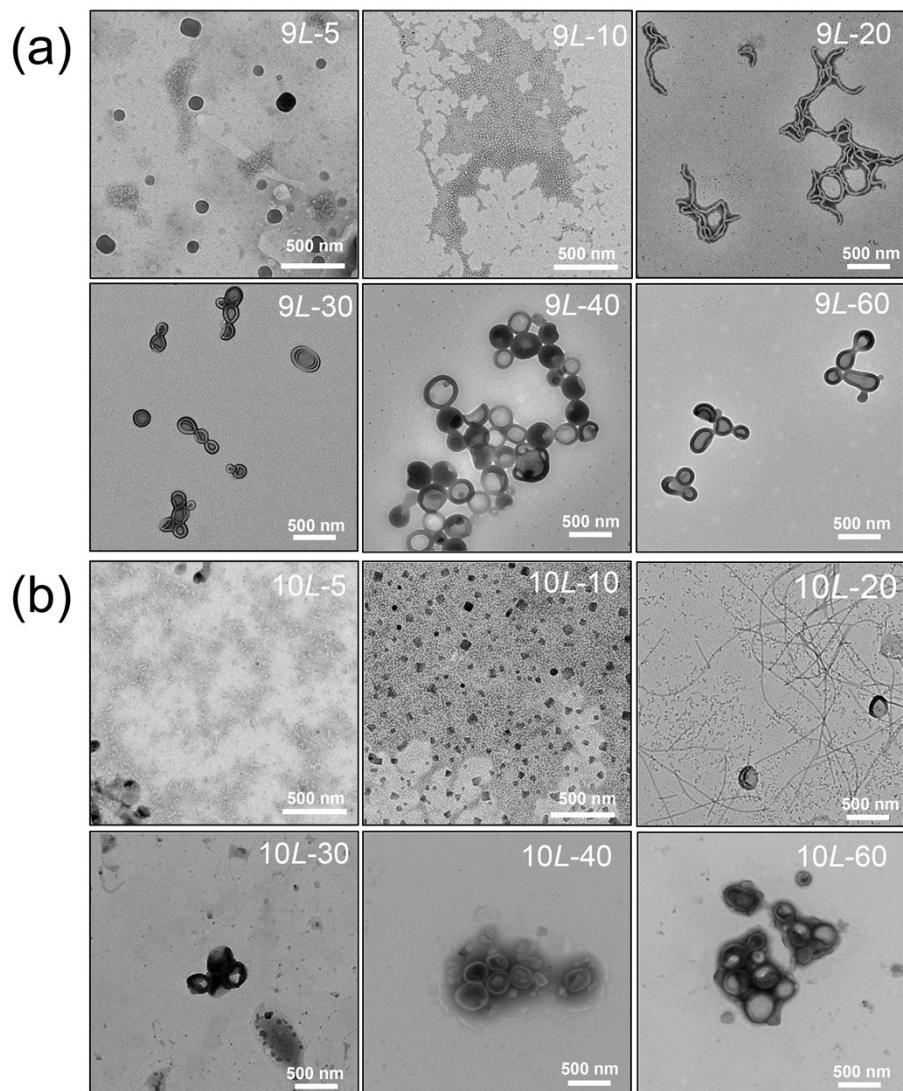


**Fig. S8.** TEM images of (a) 3L-x and (b) 6L-x (x = 5, 10, 20, 30, 40 and 60) BCP assemblies over DP of CB blocks.





**Fig. S9.** TEM images of (a) 7L-x and (b) 8L-x (x = 5, 10, 20, 30, 40 and 60) BCP assemblies over DP of CB blocks.



**Fig. S10.** TEM images of (a) 9L-x and (b) 10L-x (x = 5, 10, 20, 30, 40 and 60) BCP assemblies over DP of CB blocks.

### References

1. W. Xie, B. Zou, D. Pei, D. Ma, *Org. Lett.* **2005**, *7*, 2775-2777.
2. J. del Barrio, R. M. Tejedor, L. S. Chinelatto, C. Sánchez, M. Piñol, L. Oriol, *J. Mater.Chem.* **2009**, *19*, 4922-4930.
3. Y. B. Q. Li, H. Wang, F. Du, Q. Li, B. Jin, R. Bai, *Poly. Chem.* **2013**, *4*, 2891-2897.