Electronic supplementary information

Handwritable One Dimensional Photonic Crystals Prepared from Dendronized Brush Block Copolymers

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Contents

1. Experimental

Materials

Chemicals such as *n*-Bromodecane, *cis*-5-norbornene-*exo*-2,3-dicarboxylicanhydride, triethylamine, methyl gallate, tetrabutylammonium bromide (TBAB), ethyl gallate, 2-Aminoterephthalic acid, lithium aluminium hydride (LAH), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimidehydrochloride (EDC·HCl), benzyl bromide, ethyl-2-bromopropionate, 2-Amino-2-methyl-1,3-propanediol and 4-dimethylaminopyridine (DMAP) were purchased from Sigma Aldrich, and used without further purification. Dry solvents were purified by passing them through solvent purification columns. All other reagents were purchased from commercial sources and used as received unless otherwise noted.

Characterization

Nuclear magnetic resonance (NMR) spectroscopy was recorded on a Brucker Avance DPX 400 MHz Spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported as parts per million relative to tetramethylsilane. Ultra-small-angle X-ray scattering (USAXS) measurements were performed on Xeuss SAXS/USAXS equipment using 0.154 nm (Cu Kα radiation) and sample-to-detector distance was 6500 mm, and the wavelength of the X-ray was 0.154 nm, the beam area was 0.6×0.6 mm^2. Small-angle X-ray scattering (SAXS) data were collected at Shanghai Synchrotron Radiation Facility beamline BL17U. Working voltage: 11.96 keV, Wavelength: 1.037 Å, Sample-Detector Distance: 2646 mm, Detector Pixel Size 172.0 μm.

Synthesis of *n*-(2,5-dicarboxylphenyl)-*cis*-5-norbornene-*exo*-2,3-dicarboximide (1-a)

Compound 1-a was synthesized according to the reported method.[1] A 250 mL three-necked flask equipped with a stir bar was charged with *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (10.00g, 61.0 mmol) and glacial acetic acid (150.0 mL). 2-Aminoterephthalic acid (11.05 g, 61.0 mmol) was added stepwise to the reaction mixture at 120 °C within 30 min. The reaction mixture was refluxed for 18 h. After cooling to ambient temperature, the mixture was poured into cold water (~260.0 mL) and vigorously stirred for 2 h. The resulting white solid was filtered and dried under vacuum at room temperature to a constant weight. Yield: 76%.

^{1}H NMR (400 MHz, DMSO-d_6): δ 13.51(s, 2H), 8.10-7.76(m, 3H), 6.37-6.36(s, 2H), 3.31-3.18 (d, 2H), 2.88-2.84(d, 2H), 2.01-1.35(m, 2H).

Compound **1-b** and **1-c** was synthesized according to the reported method.[2,3]

Synthesis of ethyl 3,4,5-tris(decyloxy) benzoate (1-b)

A 250 mL round-bottomed flask equipped with a stir bar was charged with ethyl gallate (5.00 g, 23.56 mmol), anhydrous K_2CO_3 (16.10 g, 116.49 mmol), TBAB (2.28 g, 7.07 mmol), *n*-bromodecane (18.20 g, 82.29 mmol) and acetone (100.0 ml). The reaction mixture was heated to 65 °C for 24 h. Then the reaction mixture was poured into ice-water and extracted with diethyl ether for three times. The organic phase was washed with water followed by saturated brine, then dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by neutral alumina with hexanes followed by ethyl acetate/hexanes (1:2,v/v) as elution. Yield: 98%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26(s, 2H), 4.27-4.24(m, 2H), 4.03-4.00(m, 6H), 1.84-1.70(m, 6H), 1.51-1.24(m, 45H), 0.90-0.86(m, 9H).

Synthesis of (3,4,5-tris(decyloxy)phenyl)methanol (1-c)

A 250 mL round-bottomed flask equipped with a stir bar was charged with 1-b (14.00 g, 22.13 mmol) and dry tetrahydrofuran (THF, 50.0 mL). The suspension of LAH (1.26 g, 33.20 mmol) in dry THF was added dropwise into the above mentioned solution at 0 °C. The solution was stirred for 24 h at room temperature. The reaction mixture was washed with water (1.6 mL) and then 10% sodium hydroxide aqueous solution (5.0 mL) and dried over anhydrous Na_2SO_4. The mixture solution was filtered and concentrated. The residue was purified by a silica gel chromatography with ethyl acetate/petroleum ether (1:5,v/v) as the eluent. Yield: 92%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.56(s, 2H), 4.56(s, 2H), 3.98-4.03(m, 6H), 1.82-1.70(m, 6H),1.51-1.27(m, 42H), 0.90-0.86(m, 9H).

Synthesis of norbornene alkyl monomer (NAM)

A 250 mL round-bottomed flask equipped with a stir bar was charged with 1-c (13.00 g, 22.55 mmol), 1-a (3.07 g, 9.40 mmol), EDC·HCl (5.00 g, 26.08 mmol), DMAP (0.17 g, 1.39 mmol) and dichloromethane (DCM, 100.0 mL). The mixture solution was stirred for 24 h at room temperature. Then the mixture solution was washed with 1M HCl, saturated $NaHCO_3$ followed by saturated brine and dried over anhydrous Na_2SO_4. The mixture solution was filtered and concentrated. The residue was purified by a silica gel chromatography with DCM/petroleum ether

(5:1,v/v) as the eluent. Yield: 60%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29-8.09(s, 2H), 7.88(s, 1H), 6.66-6.48(m, 4H), 6.24 (s, 2H), 5.10(s, 4H), 4.01-3.88(m, 12H), 3.35(m, 2H), 2.52(m, 2H), 1.88-1.67(m, 12H), 1.55-1.18(m, 86H), 0.95-0.79 (t, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 176.80, 164.52, 164.01, 153.30, 138.50, 137.88, 132.28, 131.77, 130.37, 130.25, 130.20, 129.74,107.29, 73.46, 69.22, 68.17, 67.92, 53.40, 48.24, 45.44, 43.41, 31.94, 31.92, 30.36, 29.75, 29.68, 29.66, 29.62, 29.59, 29.51, 29.43, 29.40, 29.36, 26.13, 22.69, 14.11. MS (ESI), $[M+Na]^+$ calculated:1467.1, found 1467.1.

Synthesis of norbornene diol (2-a)

The synthesis of compound 2-a was following the similar procedures reported.[4] *Cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (9 g, 54.82 mmol), 2-amino-2-methyl-1,3-propanediol (5.76 g, 54.86 mmol) were mixed with 150.0 mL dry toluene in a 250 mL round-bottomed flask fitted with a Dean-Stark trap. The toluene was removed on a rotary evaporator after refluxed for 24 h. The residue was purified by a silica gel chromatography with ethyl acetate/petroleum ether (1:2,v/v) as the eluent. Yield: 35%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.29(s, 2H), 4.35(d, 2 H), 3.69-3.76(m, 4 H),3.27(m, 2 H), 2.66(s, 2H), 1.51-1.56(dd, 2H), 1.28 (s, 3H).

Compound **2-b** and **2-c** were synthesized according to the reported method.[5]

Synthesis of methyl 3,4,5-tribenzylbenzoate (2-b)

Methyl gallate (5.0 g, 27.15 mmol), benzyl bromide (23.17 mL, 94.72 mmol), potassium carbonate (16.20 g, 114.25 mmol), and TBAB (2.28 g, 7.07 mmol) were mixed with 100.0 mL acetone in a 250 mL round-bottomed flask. After refluxing the mixture for 24 h, the reaction solution was cooled and diluted with water (100 mL), and then extracted with diethyl ether (3×100mL). The organic phase was washed with water followed by 50% brine, then dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by passing through basic alumina with acetone as elution. Yield: 95%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.4 (m, 6H), 7.40-7.2 (m, 9H), 7.28-7.23(m, 2H), 5.16-5.14(d, 6H), 4.23(s, 3H).

Synthesis of 3,4,5-tribenzylbenzoic acid (2-c)

Sodium hydroxide (13.60 g, 340 mmol) and 2-b (11.00 g, 24.22 mmol) were mixed with 95% EtOH (140 mL) in a 250 mL round-bottomed flask. The mixture solution was stirred for 5 h at

85°C.The reaction was cooled to room temperature and stirred for 1 h. The resulting suspension was filtered and the solid was washed with cold 95% EtOH. The solid was transferred to a 500 mL beaker and diethyl ether (200 mL) was added. Then the concentrated HCl (12 mL) was added into the above mentioned beaker, followed by filtration. The filtrate was washed with water and dissolved in acetone, then dried over anhydrous Na_2SO_4 and concentrated. Yield: 62%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.42(m, 6H), 7.42-7.32(m, 9H), 7.28-7.22(m, 2H), 5.16-5.14(d, 6H).

Synthesis of norbornene benzyl monomer (NBzM)

A 100 mL schlenk flask equipped with a stir bar was charged with 2-a (1.43 g, 5.70 mmol), 2-c (6.00 g, 13.60 mmol), EDC·HCl (3.00 g, 15.65 mmol), DMAP (0.23 g, 1.90 mmol) and DCM (50.0 mL). The mixture solution was stirred for 24 h at room temperature under nitrogen atmosphere. Then the mixture solution was washed with 1M HCl (2×50mL), saturated $NaHCO_3$ (2×50mL) followed by saturated brine and dried over anhydrous Na_2SO_4. The mixture solution was filtered and concentrated. The residue was purified by a silica gel chromatography with DCM as the eluent. Yield: 67%.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.40(m, 12H), 7.39-7.28(m, 18H), 7.27-7.24(m, 4H), 6.24(s, 2H), 5.12(s, 12H), 4.91(d, 2H), 4.75(d, 2H), 3.20(s, 2H), 2.55(s, 2H), 1.72(s, 3H), 1.54(d, 1H), 1.29(d, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 178.81, 165.37, 152.59, 142.73, 137.74, 137.42, 136.68, 128.55, 128.23, 128.16, 127.51, 124.58, 109.24, 75.16, 71.23, 65.49, 62.13, 47.50, 45.89, 42.67, 19.41. MS (ESI), $[M+Na]^+$ calculated:1118.4, found 1118.4.

2. Figures and schemes

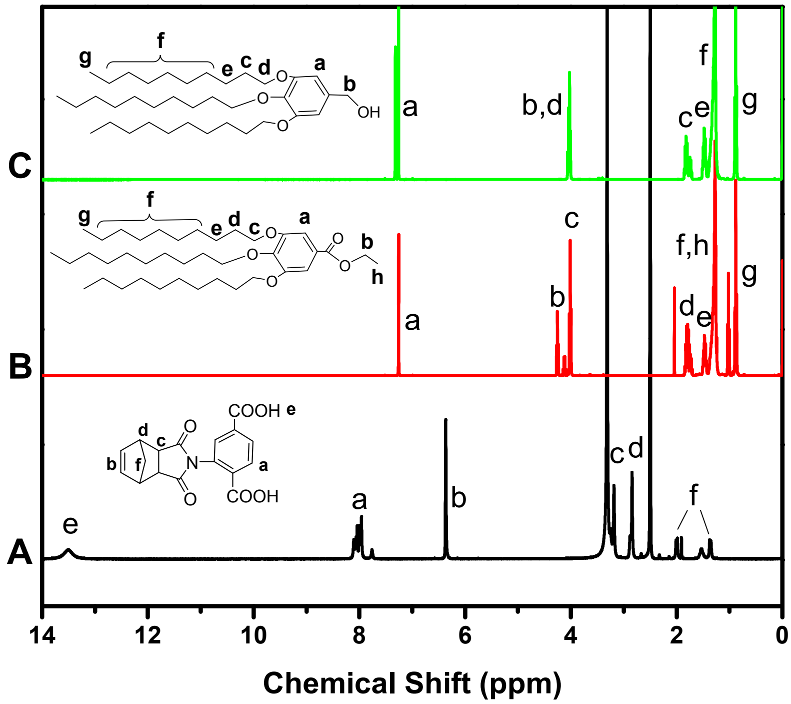

Figure S1. ^{1}H NMR spectra of (A) 1-a in DMSO-d$_6$ and (B) 1-b, (C) 1-c in CDCl$_3$。

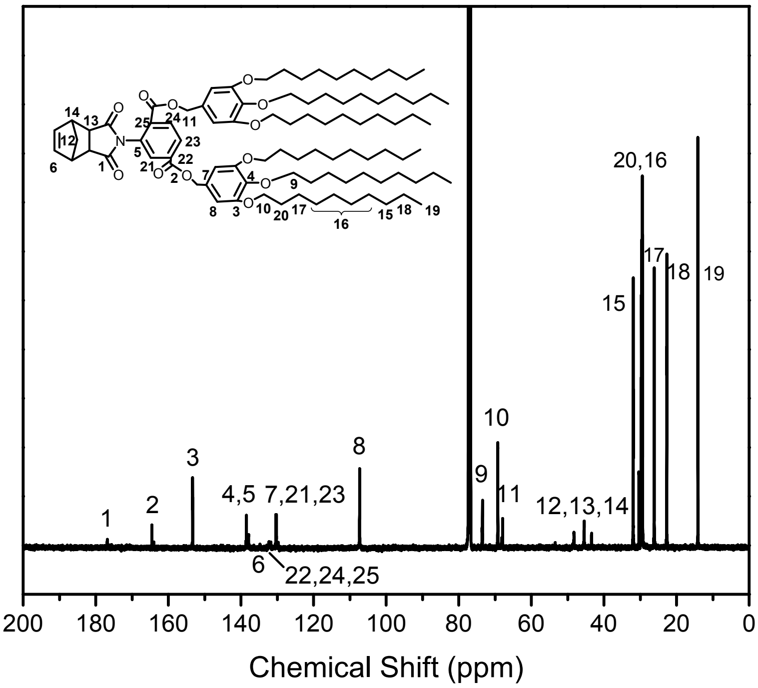

Figure S2. ^{13}C NMR spectrum of NAM monomer in CDCl$_3$.

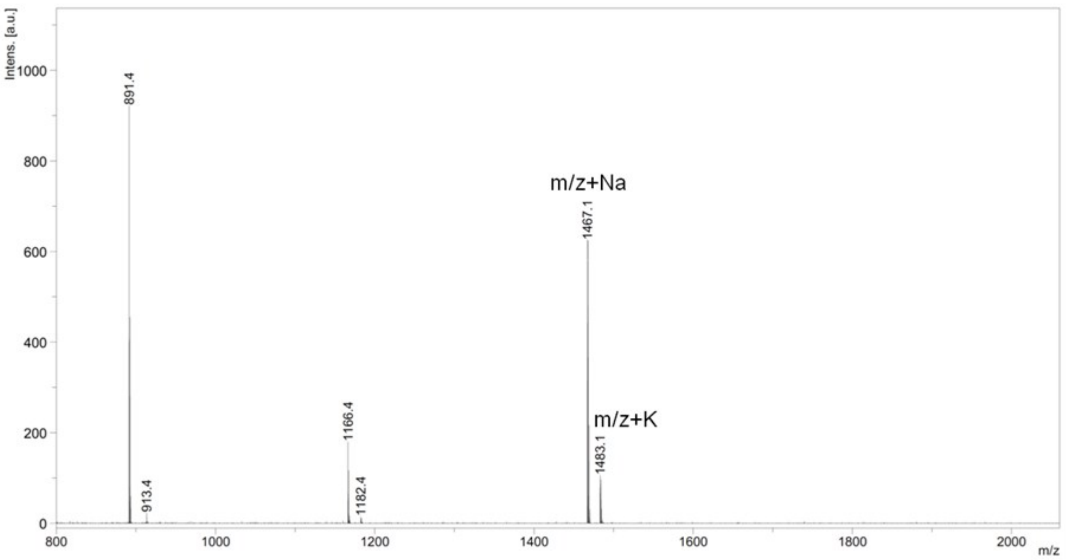

Figure S3. Mass spectrum of NAM monomer.

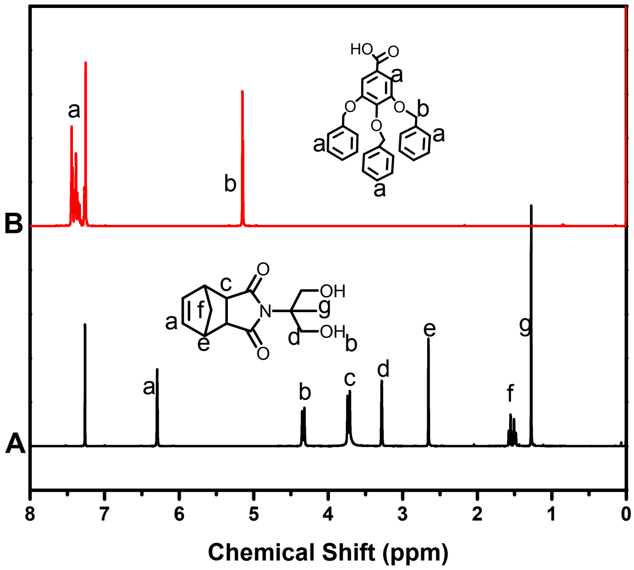

Figure S4. ^{1}H NMR spectra of (A) 2-a, (B) 2-c in $CDCl_3$

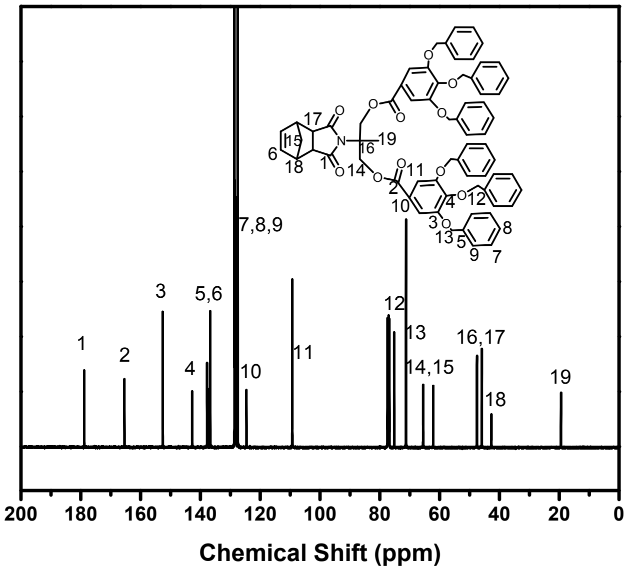

Figure S5. ^{13}C NMR spectrum of NBzM monomer in $CDCl_3$。

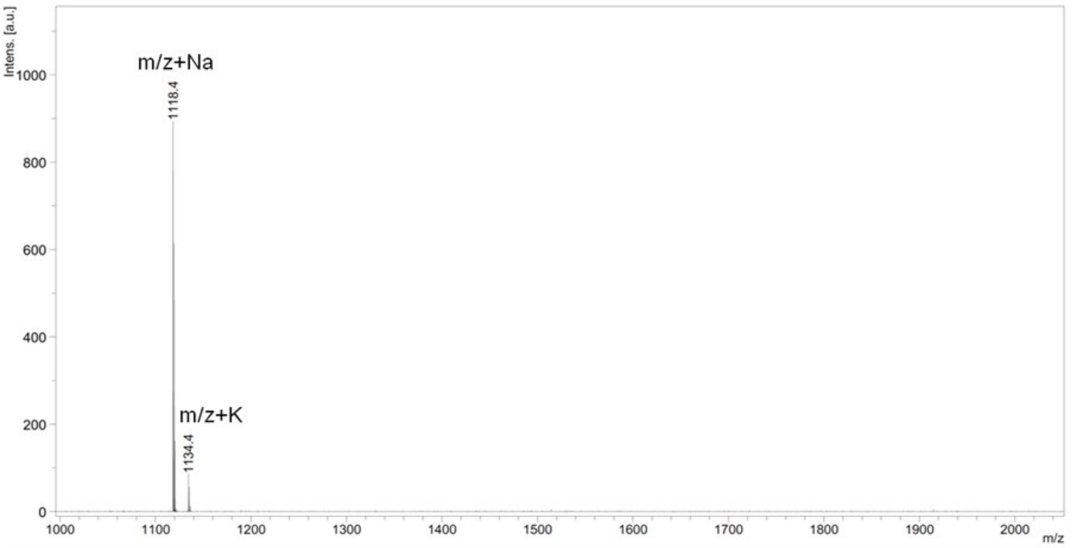

Figure S6. Mass spectrum of monomer NBzM.

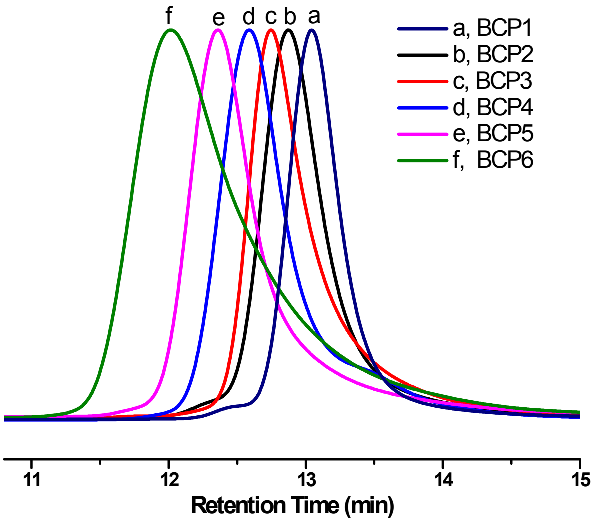

Figure S7. GPC curves of dendronized PNAM-*b*-PNBzM, (a) BCP1, (b) BCP2, (c) BCP3, (d) BCP4, (e) BCP5, (f) BCP6.

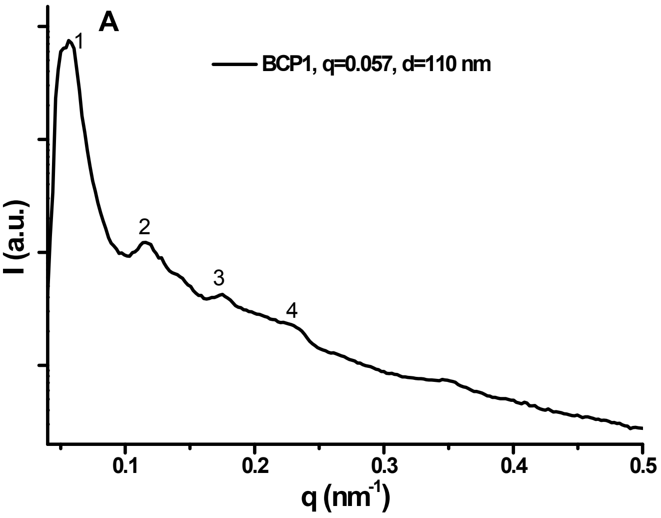

Figure S8. The SAXS profile of the 1D PC thin film prepared by BCP1.

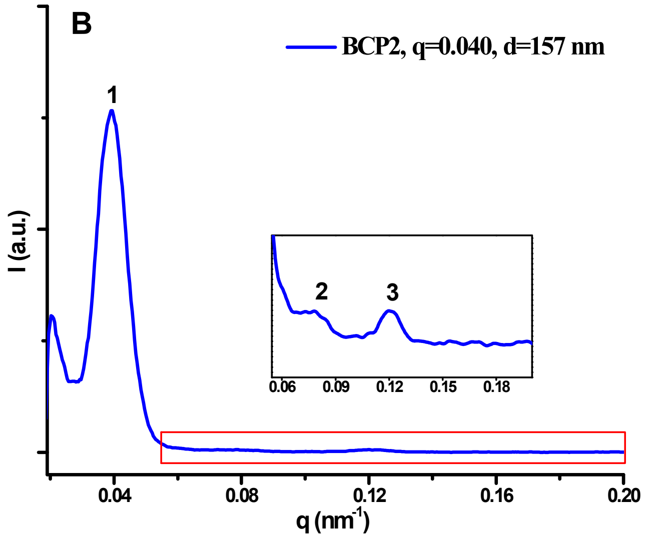

Figure S9. The USAXS profiles of the 1D PC thin film prepared by BCP2.

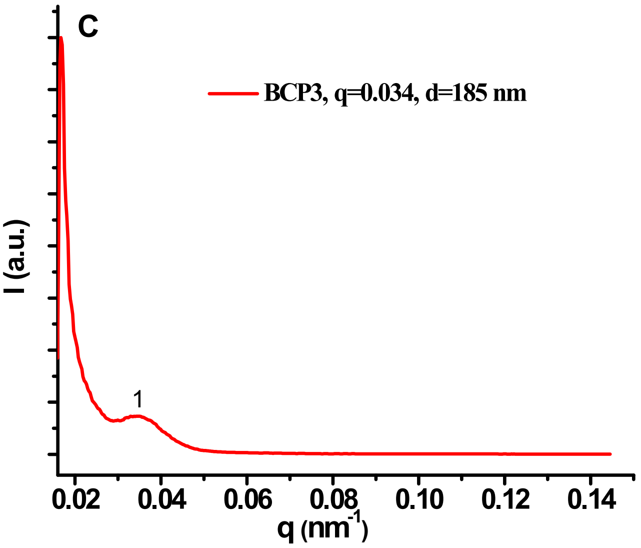

Figure S10. The USAXS profiles of the 1D PC thin film prepared by BCP3.

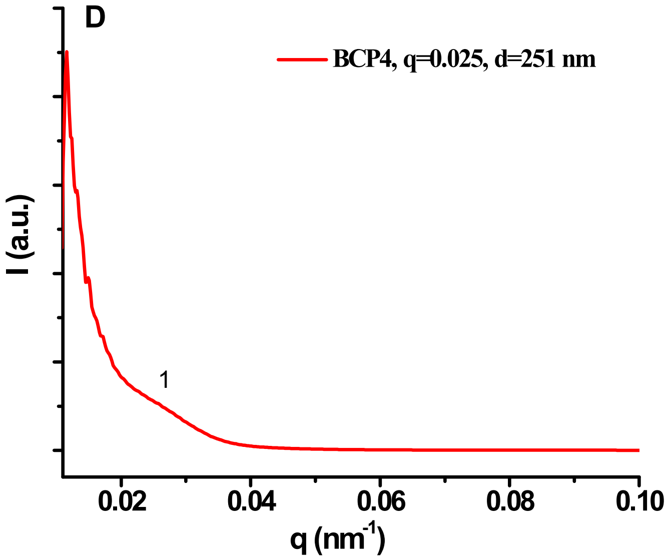

Figure S11. The USAXS profiles of the 1D PC thin film prepared by BCP4.

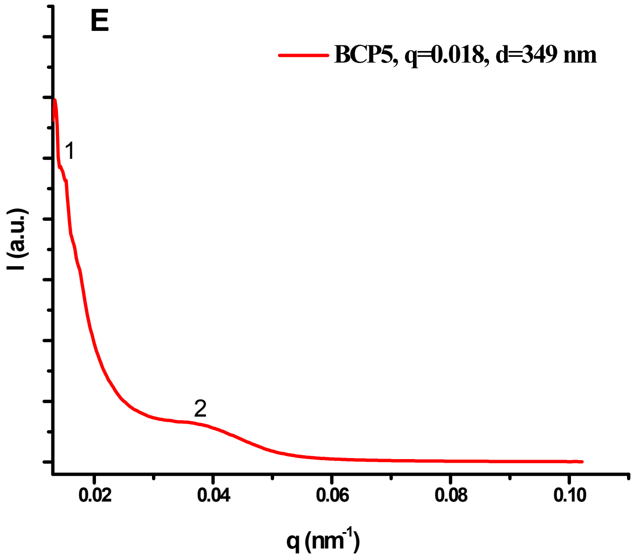

Figure S12. The USAXS profiles of the 1D PC thin film prepared by BCP5.

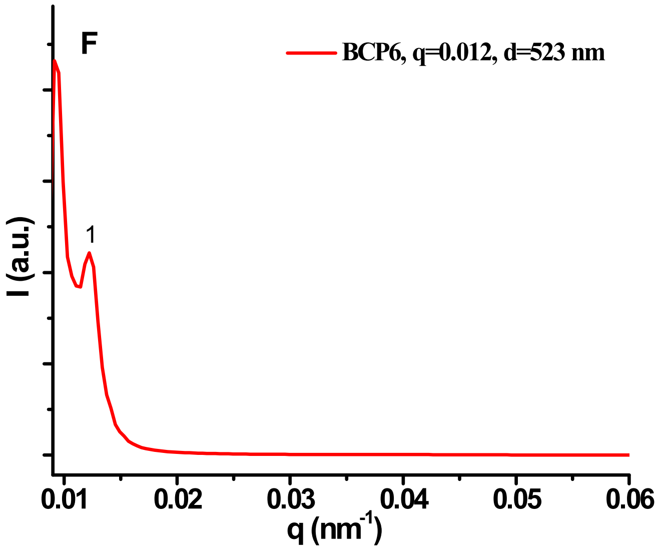

Figure S13. The USAXS profiles of the 1D PC thin film prepared by BCP6.

3. References

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