

Supporting information to

Stable Macroscopic Nanocylinder Arrays in An Amphiphilic Diblock Liquid-Crystalline Copolymer with Successive Hydrogen Bonds

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Materials. 2-Bromo-2-methylpropionyl chloride, triethylamine, 4-hydroxybenzoic acid, 11-bromo-1-undecanol, methacrylic acid, N,N-dimethylformamide (DMF), 4-butylaniline, hydroquinone, toluenesulfonic acid, 4-dimethylaminopyridine (DMAP), N,N'-dicyclohexylcarbodiimide (DCC), commercially available (Kanto Chem. Co.), were used without further purification. Poly(ethylene glycol) monomethyl ether with a number-averaged molecular weight of about 5,000 (Aldrich) was dried by azeotropic distillation with toluene. Anisole and tetrahydrofuran (THF) were purified by distillation from sodium with benzophenone. The ligand, 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, Aldrich) was used as received without further purification. Catalyst Cu(I)Cl was washed successively with acetic acid and ether, then dried.

Preparation of poly(ethylene oxide) macroinitiator (PEO₁₁₄Br) : Similar to the previously reported method,¹⁻³ the macroinitiator was prepared by the Schotten-Baumann reaction between 2-bromo-2-methylpropionyl chloride and poly(ethylene glycol) monomethyl ether in CH₂Cl₂ with a yield of 32 %. The number-average molecular weight Mn (GPC) and the polydispersity index (Mw/Mn) were 7,400 and 1.02, respectively. MP: 64 °C. ¹H NMR (CDCl₃, δ, ppm): 4.33 (dd, 2H, -OCH₂COO-), 3.86 (t, 2H, CH₂CH₂OOC-), 3.73 (m, 158H, -CH₂CH₂-), 3.62 (t, 2H, CH₂CH₂OCH₃), 3.41(t, 2H, CH₂CH₂OCH₃), 3.38 (s, 3H, -OCH₃), 1.94 (s, 6H, ((CH₃)₂CBrCOO-).

4-(11-Hydroxyundecyloxy)benzoic acid : The compound was synthesized by the Williamson reaction of 4-hydroxybenzoic acid and 11-bromo-1-undecanol. The product was purified by recrystallization from ethanol, where a white solid was obtained with a yield of 42 %. MP: 110 °C. ¹H NMR (CDCl₃, δ, ppm): 12.60 (s, 1H, -COOH), 7.90 (d, 2H, -Ph-H), 6.92 (d, 2H, -Ph-H), 4.85 (s, 1H, HO-CH₂CH₂), 4.02 (t, 2H, CH₂CH₂O-Ph), 3.50 (t, 2H, HO-CH₂CH₂), 1.78-1.69 (m, 2H, CH₂CH₂O-Ph), 1.46-1.29 (m, 16 H, HOCH₂(CH₂)₈CH₂ CH₂-OPh).

4-(11-Methacryloyloxyundecyloxy)benzoic acid (M11BA) : M11BA was synthesized in toluene by the reaction of methacrylic acid and 4-(11-hydroxyundecyloxy)benzoic acid in the present of hydroquinone and toluenesulfonic acid. The product was recrystallized from ethanol to yield a white solid (81 %). MP: 114 °C. ¹H NMR (CDCl₃, δ, ppm): 8.06 (d, 2H, -Ph-H), 6.91 (d, 2H, -Ph-H), 6.10 (d, 1H, , H-C=), 5.55 (d, 1H, H-C=), 4.12 (t, 2H, -CH₂CH₂-OOC(CH₃)C=CH₂), 4.01 (t, 2H, CH₂CH₂O-Ph), 1.92 (s, 3H, -CH₂CH₂-OOC(CH₃)C=CH₂), 1.80-1.76 (m, 2H, -CH₂CH₂-OOC(CH₃)C=CH₂), 1.67-1.62 (m, 2H, -CH₂-CH₂OPh), 1.44-1.28 (m, 14H, OCH₂CH₂(CH₂)₇CH₂CH₂O-Ph).

4-(11-Methacryloyloxyundecyloxy)benzoic 4-butylbenzene amide (M11BABC4) : A solution of N,N'-dicyclohexylcarbodiimide (DCC, 0.6 g, 3.0 mmol) in N,N-dimethylformamide (DMF, 5 mL) was added dropwise at room temperature to a solution of M11BA (1.0 g, 2.7 mmol), 4-butylaniline (0.4 g, 2.7

mmol), 4-dimethylaminopyridine (DMAP, 0.3 g, 2.6 mmol) dissolved in DMF (10 mL), the reaction mixture was stirred at room temperature for 24 h, and then was filtered to obtain a solution which was poured into water to precipitate the product. The crude solid was purified by recrystallization from methanol to yield 1.1 g (79 %) white needle crystal. MP: 72 °C. MS (FAB): 508 (MH⁺). ¹H NMR (CDCl₃, δ, ppm): 7.82 (d, 2H, -Ph-H), 7.70 (s, 1H, -Ph-CO-NH-Ph-), 7.52 (d, 2H, -Ph-H), 7.16 (d, 2H, -Ph-H), 6.94 (d, 2H, -Ph-H), 6.10 (d, 1H, H-C=), 5.54 (d, 1H, H-C=), 4.14 (t, 2H, -CH₂CH₂-OOC(CH₃)C=CH₂), 4.02 (t, 2H, CH₂CH₂O-Ph), 2.59 (t, 2H, Ph-CH₂CH₂CH₂CH₃), 1.89 (s, 3H, -CH₂CH₂-OOC(CH₃)C=CH₂), 1.78 (m, 4H, Ph-OCH₂CH₂(CH₂)₇CH₂CH₂OOC(CH₃)C=CH₂), 1.62-1.25 (m, 18H, Ph-OCH₂CH₂(CH₂)₇CH₂CH₂, Ph-CH₂CH₂CH₂CH₃), 0.93 (t, 3H, Ph-CH₂CH₂CH₂CH₃).

Diblock copolymer : In a 20 mL ampule bottle, Cu(I)Cl (7.5 mg, 0.075 mmol), PEO₁₁₄Br (0.125 g, 0.025 mmol) and M11BABC4 (1.01 g, 2.0 mmol) were mixed, degassed and filled with argon. HMTETA (20.4 μL, 0.075 mmol) in anisole (6.0 mL) was added through a syringe. The mixture was degassed by three freeze-pump-thaw cycles and sealed under vacuum. After 30 min stirring at room temperature, the ampule bottle was placed in an oil bath preheated at 80 °C for 24 h. Exposing the mixture to air stopped the reaction, and then the solution was passed through a neutral Al₂O₃ column with THF as eluent to remove the catalyst. The white filtrate was concentrated under reduced pressure and reprecipitated into methanol and then into hot ethanol. The copolymer was collected by filtration and dried under vacuum. Yield: 0.96 g (85 %). Mn (GPC): 42,400, Mw/Mn: 1.15. ¹H NMR (CDCl₃, δ, ppm): 8.40 (s, 1H, -Ph-CO-NH-Ph-), 7.74 (d, 2H, -Ph-H), 7.52 (d, 2H, -Ph-H), 7.5 (d, 2H, -Ph-H), 6.74 (d, 2H, -Ph-H), 3.87 (s, 4H, Ph-OCH₂CH₂(CH₂)₇CH₂CH₂OC=O), 3.65 (s, 4H, -CH₂CH₂O-), 2.52 (s, 2H, Ph-CH₂CH₂CH₂CH₃), 1.73-1.21 (m, 27H, Ph-OCH₂(CH₂)₉CH₂, Ph-CH₂CH₂CH₂CH₃, -CH₂(CH₃)C-), 0.89 (m, 3H, Ph-CH₂CH₂CH₂CH₃).

Characterization ¹H NMR spectra were measured using a Lambda-300 spectrometer operating at 300 MHz with tetramethylsilane as an internal reference for chemical shifts. The molecular weights of the

polymers were determined by GPC (JASCO) and referenced against standard polystyrenes with chloroform as eluent. The thermodynamic properties of the monomers and polymers were analyzed by DSC (Seiko) at a heating and cooling rate of 10 °C/min. At least three scans were performed to check the reproducibility. The LC phases were evaluated by POM (Olympus BH-2). The UV-Vis spectra were measured in a chloroform solution or as a spin-coated film on a quartz substrate using a JASCO V-550 spectrophotometer. The FTIR spectrum of a spin-coated film was obtained on a KBr crystal substrate with a JASCO FTIR-3 spectrophotometer. AFM images of the block copolymer films in tapping mode were detected with a scanning probe microscope (Veeco, Nanoscope IV) at room temperature.

References

1. Y. Tian, K. Watanabe, X. Kong, J. Abe, T. Iyoda, *Macromolecules* 2002, **35**, 3739-3727
2. H. F. Yu, A. Shishido, T. Ikeda, and T. Iyoda, *Macromol. Rapid Commun.*, 2005, **26**, 1594-1598.
3. H. F. Yu, T. Iyoda and T. Ikeda, *J. Am. Chem. Soc.*, 2006, **128**, 11010-11011.

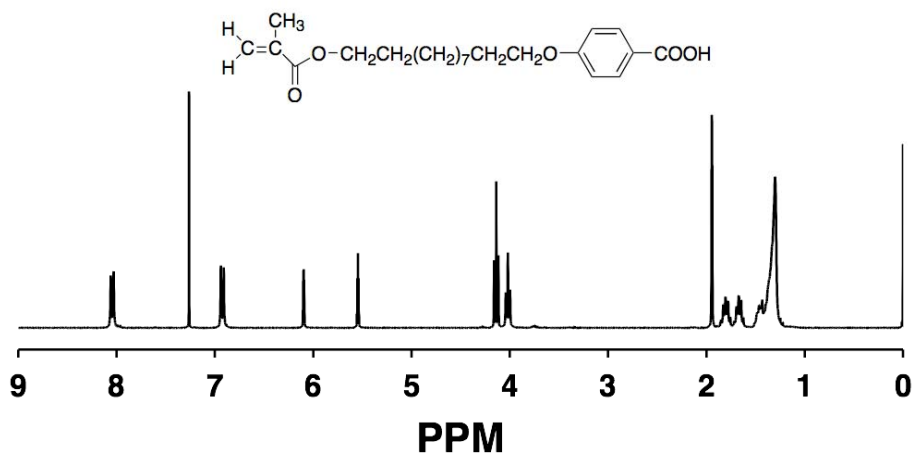


Figure S1. ¹H NMR of the compound M11BA.

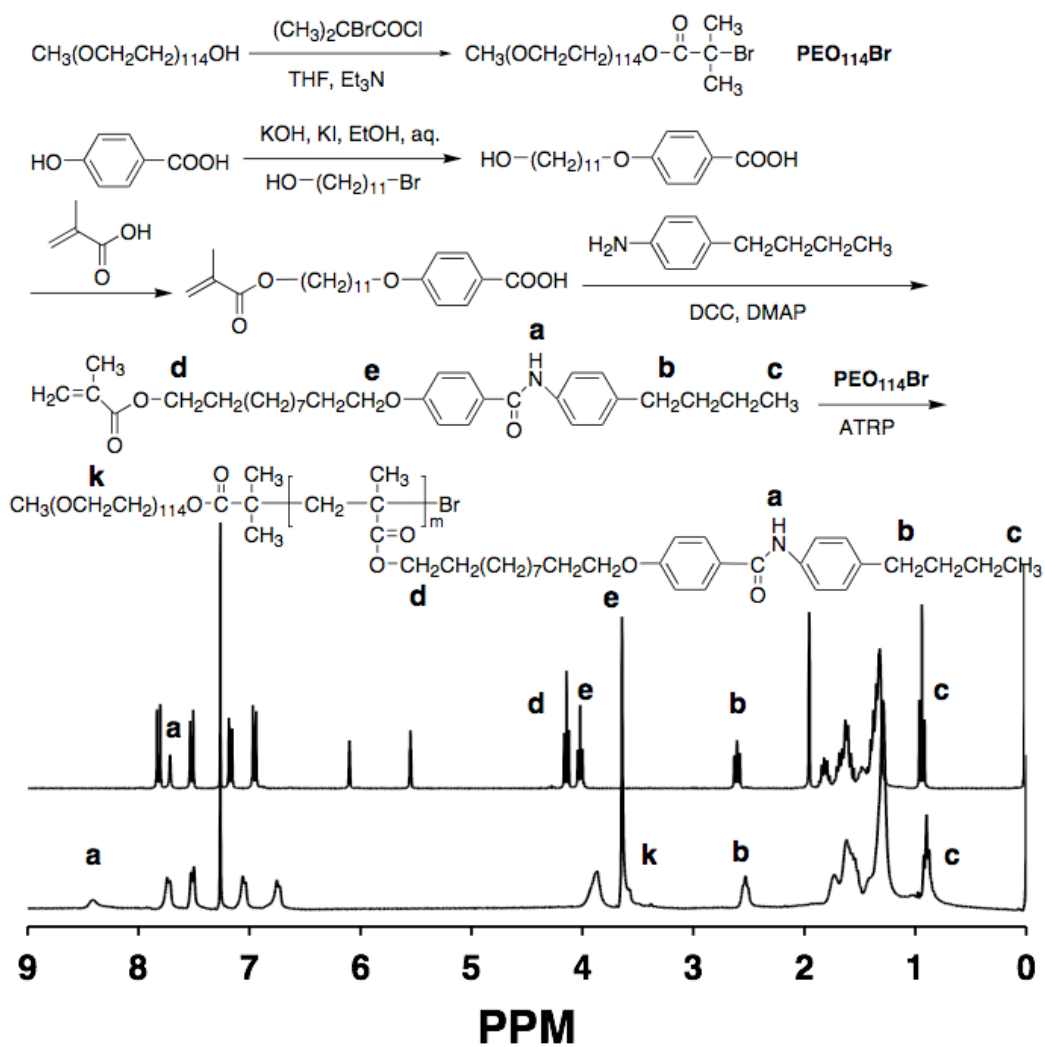


Figure S2. Synthetic route and ^1H NMR spectra of the monomer and the diblock copolymer.

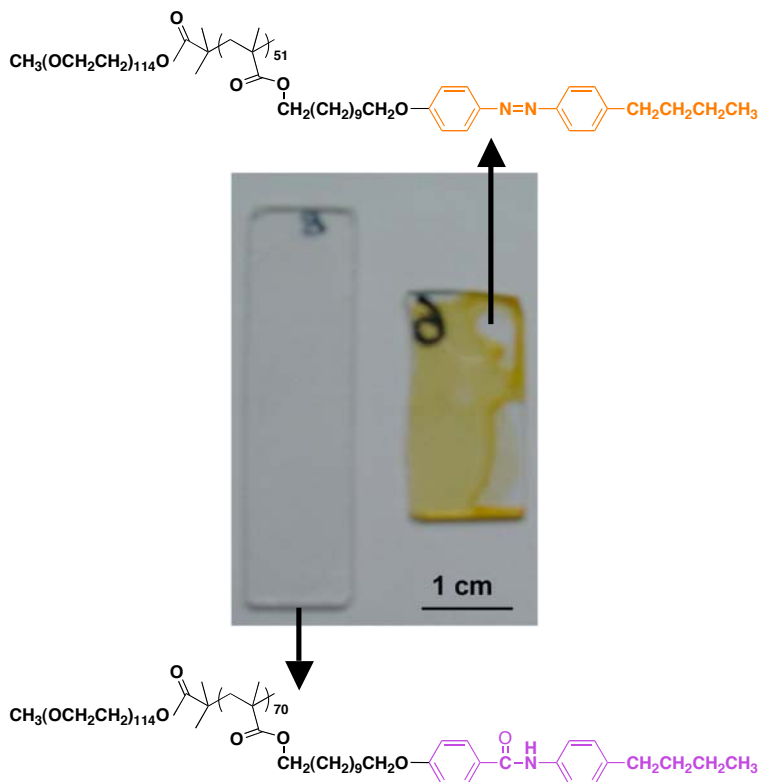


Figure S3. The photograph of block copolymer films exposed to room light for six months.

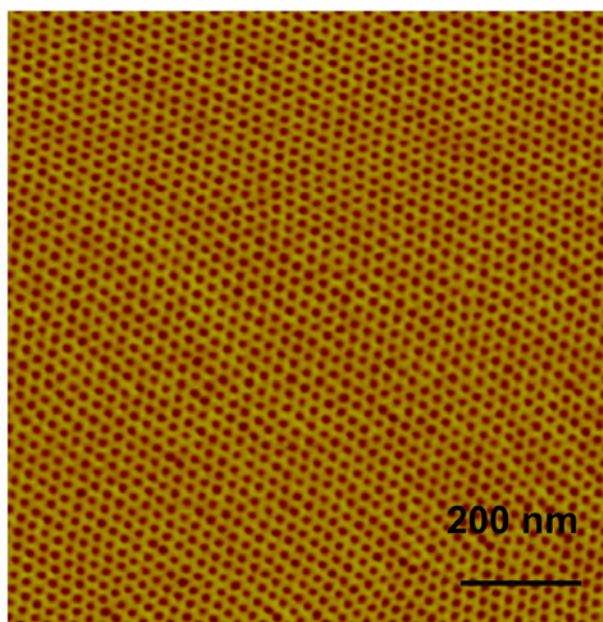


Figure S4. AFM phase image of the aramid block copolymer film exposed to room light for six months.