Supporting information for

Normally Oriented Cylindrical Nanostructures in Amphiphilic PEO-LC Diblock Copolymer Films

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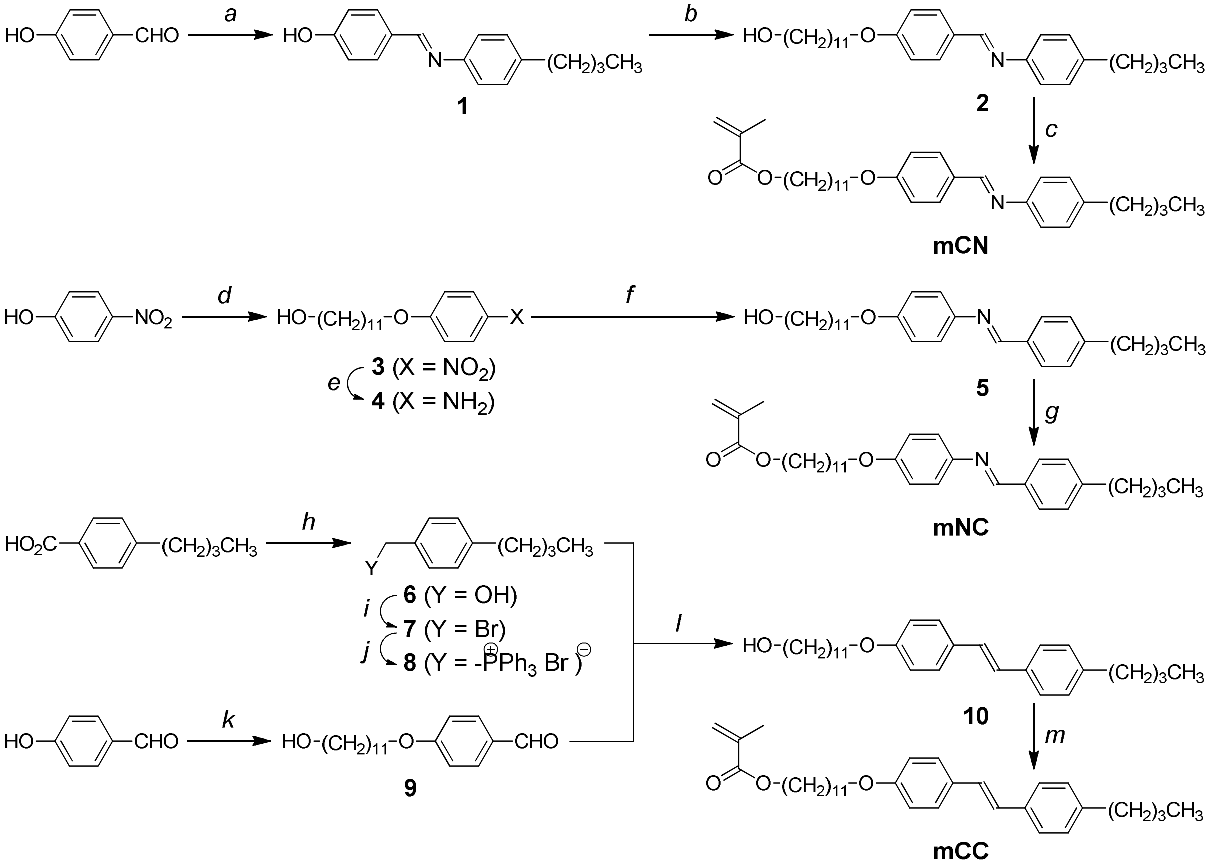
Table of contents.

1. Synthesis of liquid crystalline monomers

The monomers **mCN**, **mNC** and **mCC** were prepared via the synthetic route illustrated in Scheme S1 according to the following procedure;



Scheme S1. Synthesis of liquid crystalline monomers.
(a) 4-butylaniline/H_2O; (b) HO-$(CH_2)_{11}$-Br, K_2CO_3, KI/acetone; (c) CH_2=C(CH_3)CO_2H, DCC, DMAP/CH_2Cl_2; (d) HO-$(CH_2)_{11}$-Br, KOH/EtOH; (e) Na_2S/EtOH; (f) 4-butylbenzaldehyde/EtOH; (g) CH_2=C(CH_3)CO_2H, DCC, DMAP/CH_2Cl_2; (h) BF_3·Et_2O, $NaBH_4$/THF; (i) HBr; (j) PPh_3; (k) HO-$(CH_2)_{11}$-Br, K_2CO_3, KI, Et_3N/EtOH; (l) ^{t}BuOK/THF; (m) CH_2=C(CH_3)COCl, Et_3N/CH_2Cl_2

4-((*E*)-(4-Butylphenylimino)methyl)phenol (1). A mixture of 4-butylaniline (Wako, 20.6 g) and 4-hydroxybenzaldehyde (TCI, 25.0 g) in water (250 mL) was stirred at ambient temperature for 5 h. The yellow precipitates were collected by filtration, washed thoroughly with water and dried under reduced pressure. The crude product was purified by recrystallization from ethanol to afford pale yellow flakes (30.8 g, 88% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.37 (m, 2H), 1.61 (m, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 6.02 (br, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.6 Hz, 2H), 8.39 (s, 1H).

11-(4-((*E*)-(4-Butylphenylimino)methyl)phenoxy)undecan-1-ol (2). A mixture of **1** (20.8 g), potassium carbonate (17.7 g) and potassium iodide (700 mg) in acetone (200 mL) was heated at reflux temperature for 30 min. 11-Bromo-1-undecanol (Wako, 25.0 g) was added to the suspension and subject to reflux for 17 h. After removal of solvent under reduced pressure, the residual solid was washed with water and recrystallized from ethanol to give colorless flakes (21.1 g, 61% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.30-1.41 (m, 14H), 1.47 (m, 2H), 1.53-1.65 (m, 4H), 1.80 (m, 2H), 2.62 (t, *J* = 7.7 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 8.38 (s, 1H).

11-(4-((*E*)-(4-Butylphenylimino)methyl)phenoxy)undecyl methacrylate (monomer **mCN).** A mixture of **2** (21.0 g), *N,N'*-dicyclohexylcarbodiimide (12.6 g) and 4-(*N,N*-dimethylamino)pyridine (2.5 g) in dehydrated dichloromethane (200 mL) was stirred under Ar atmosphere for 30 min. The dehydrated dichloromethane (30 mL) solution of methacrylic acid (5.5 g) was added dropwise to the reaction mixture, which was then allowed to stir at ambient temperature for 17 h. After removal of the white precipitates by filtration, the filtrate was evaporated under reduced pressure. The residue was dissolved in chloroform, and washed with 5% $NaHCO_3$aq and brine. The organic layer was dried over $MgSO_4$ and evaporated to afford crude colorless solid, which was then subject to recrystallization from ethanol to give colorless flakes (19.9 g, 83% yield). ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.26-1.41 (m, 14H), 1.47 (m, 2H), 1.58-1.70 (m, 4H), 1.80 (m, 2H), 1.94 (m, 3H), 2.62 (t, *J* = 7.7 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 4.14 (t, *J* = 6.8 Hz, 2H), 5.54 (m, 1H), 6.10 (m, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 7.13 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.9 Hz, 2H), 8.39 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.11, 18.47, 22.49, 26.12, 26.15, 28.75, 29.32, 29.38, 29.51, 29.62, 29.66, 33.86, 35.32, 64.97, 68.32, 114.81, 120.91, 125.27, 129.20, 129.37, 130.51, 136.72, 140.54, 150.11, 159.14, 161.88, 167.72. MS (FAB) *m/z* (relative intensity) 493 (34), 492 (M^+ + H, 100), 491 (41), 490 (17). Anal. Calcd for $C_{32}H_{45}NO_3$: C, 78.17; H, 9.22; N, 2.85. Found: C, 78.09; H, 9.39; N, 2.92.

11-(4-nitrophenoxy)undecan-1-ol (3). Compounds **3** and **4** were prepared according to the similar procedure reported by Kosaka et al.[1]: A mixture of 4-nitrophenol (Wako, 14 g), 11-bromo-1-undecanol (25 g), potassium hydroxide (7 g) in 50% ethanol-water (180 mL) was heated at reflux temperature for 2 days. The reaction mixture was evaporated to concentrate under reduced pressure and extracted with ethyl acetate. The organic layer was washed with 5% $NaHCO_3$aq and brine, and then dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was recrystallized from methanol to give pale yellow powder (21.7 g, 71% yield). ^{1}H NMR ($CDCl_3$) δ 1.22-1.41 (m, 12H), 1.46 (m, 2H), 1.57 (m, 2H), 1.82 (m, 2H), 3.64 (m, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 6.93 (d, *J* = 9.2 Hz, 2H), 8.19 (d, *J* = 9.2 Hz, 2H).

11-(4-aminophenoxy)undecan-1-ol (4). To a suspension of **3** (21.7 g) in 50% ethanol-water (300 mL), sodium sulfide nonahydrate (34.0 g) was added and heated at reflux temperature for 40 h. The reaction mixture was evaporated to concentrate under reduced pressure, diluted with water (100 mL), and extracted with chloroform. After removal of precipitates formed in the extract by filtration, the filtrate was washed with brine and then dried over Na_2SO_4. After evaporation, the residue was recrystallized from toluene to afford pale orange solid (8.6 g, 44%). ^{1}H NMR ($CDCl_3$) δ 1.22-1.38 (m, 12H), 1.43 (m, 2H), 1.56 (m, 2H), 1.73 (m, 2H), 3.40 (br, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 3.87 (t, *J* = 6.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.6 Hz, 2H).

11-((*E*)-4-(4-butylbenzylideneamino)phenoxy)undecan-1-ol (5). A mixture of **4** (7.0 g) and 4-butylbenzaldehyde (TCI, 5 mL) in ethanol (100 mL) was heated at reflux temperature for 12 h. Pale yellow crystals were formed on cooling to ambient temperature, and collected by filtration. The crude crystals were thoroughly recrystallized from ethanol to give pale yellow flakes (8.9 g, 84% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.24-1.41 (m, 14H), 1.46 (m, 2H), 1.53-1.66 (m, 4H), 1.79 (m, 2H), 2.66 (t, *J* = 7.7 Hz, 2H), 3.64 (m, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.9 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 8.44 (s, 1H).

11-((*E*)-4-(4-butylbenzylideneamino)phenoxy)undecyl methacrylate (monomer **mNC).** Monomer **mNC** was prepared from **5** (5.5 g) and methacrylic acid (1.25 g) according to the same procedure as **mCN**. The crude product was purified on neutral alumina (Merck) short column chromatography eluted by mixed solvent of ethyl acetate and hexane (1:1) and recrystallized from ethanol to afford pale yellow powder (4.5 g, 71% yield). ^{1}H NMR ($CDCl_3$) δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.26-1.41 (m, 14H), 1.46 (m, 2H), 1.59-1.70 (m, 4H), 1.79 (m, 2H), 1.94 (m, 3H), 2.67 (t, *J* = 7.7 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 4.14 (t, *J* = 6.7 Hz, 2H), 5.54 (m, 1H), 6.09 (m, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 8.45 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 14.07, 18.48, 22.47, 26.12, 26.20, 28.76, 29.39, 29.47, 29.54, 29.63, 29.68, 33.55, 35.83, 64.98, 68.43, 115.12, 122.24, 125.28, 128.72, 128.98, 134.28, 136.72, 145.15, 146.59, 157.86, 158.51, 167.72. MS (FAB) *m/z* (relative intensity) 493 (33), 492 (M^+ + H, 100), 491 (63), 490 (20). Anal. Calcd for $C_{32}H_{45}NO_3$: C, 78.17; H, 9.22; N, 2.85. Found: C, 78.20; H, 9.00; N, 2.93.

4-butylbenzyl alcohol (6). To a suspension of sodium borohydride (5.5 g) in dehydrated THF (170 mL), 4-butylbenzoic acid (Wako, 25.0 g) was added portionwise under Ar atmosphere. Boron trifluoride diethyl etherate (Wako, 40 mL) was added dropwise at 0℃ and allowed to stir at ambient temperature for 12 h. The reaction mixture was poured onto ice, followed by extraction with ether. The organic layer was washed with 5% $NaHCO_3$aq, water, and brine, and then dried over $MgSO_4$. The crude product was purified on basic alumina (Merck) short column chromatography eluted by chloroform to give colorless liquid (21.4 g, 93% yield). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.2 Hz, 3H), 1.35 (m, 2H), 1.59 (m, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 4.65 (d, *J* = 5.8 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H).

4-butylbenzyl bromide (7). Compound **6** (21.4 g) was treated with 48% HBr (26 mL) at 120℃ for 12h. The reaction mixture was poured into 1N HCl and extracted with ether. The organic layer was washed thoroughly with 1N HCl and brine, and then dried over $MgSO_4$. The crude product was purified on silica gel (Merck, silica gel 60) column chromatography eluted by hexane to afford colorless liquid (25.2 g, 85% yield). ^{1}H NMR ($CDCl_3$) δ 0.92 (t, *J* = 7.3 Hz, 3H), 1.35 (m, 2H), 1.59 (m, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 4.49 (s, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H).

(4-butylbenzyl)triphenylphosphonium bromide (8). Triphenylphosphine (Wako, 35.0 g) was added to **7** (25.2 g), and heated at 90℃ for 30 min. The resulting solid was washed with hot hexane until the starting materials were completely removed. The white powder **8** was used without further purification. ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.3 Hz, 3H), 1.28 (m, 2H), 1.51 (m, 2H), 2.51 (m, 2H), 5.32 (d, J = 14.1 Hz, 2H), 6.91-7.00 (m, 4H), 7.58-7.80 (m, 15H).

4-(11-hydroxyundecyloxy)benzaldehyde (9). Compound **9** was synthesized according to the same procedure reported by Bustamante et al.[2]: A mixture of 4-hydroxybenzaldehyde (22.0 g) and 50% aqueous potassium hydroxide (20 mL) in ethanol (360 mL) were heated under reflux for 1 h. Potassium iodide (1.0 g), triethylamine (110 mL) and 11-bromo-1-undecanol (45.0 g) were added to the reaction mixture, which was then heated at reflux temperature for 48 h. The precipitate formed in the reaction mixture was filtered off and the solvent was removed under reduced pressure. The residue was diluted with water and extracted with ether. The organic layer was successively washed with water and brine, and dried over Na_2SO_4. The crude product was purified on silica gel (Merck, silica gel 60) short column chromatography eluted by dichloromethane and then recrystallized from the mixed solvent of hexane and ethyl acetate to give colorless fine needles (26.2 g, 50% yield). ^{1}H NMR (CDCl$_3$) δ 1.22-1.63 (m, 16H), 1.81 (m, 2H), 3.64 (t, *J* = 6.6 Hz, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 9.87 (s, 1H).

11-(4-((*E*)-4-butylstyryl)phenoxy)undecan-1-ol (10). To a suspension of compounds **8** (24.0 g) and **9** (13.8 g) in dehydrated THF (130 mL), potassium *t*-butoxide (10.5 g) was added portionwise at 0 ℃ under Ar atmosphere and allowed to stir at ambient temperature for 40 h. The reaction mixture was diluted by water (200 mL), neutralized with 1N HCl, and then extracted with chloroform. The organic layer was washed with water and brine, and dried over Na$_2$SO$_4$. The crude product was purified on silica gel (Cica, silica gel 60N) short column chromatography eluted by chloroform and then recrystallized from acetone to give colorless powder (7.3 g, 37% yield). ^{1}H NMR (CDCl$_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.26-1.40 (m, 14H), 1.46 (m, 2H), 1.53-1.64 (m, 4H), 1.78 (m, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 3.63 (t, *J* = 6.6 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 16.3 Hz, 1H), 7.01 (d, *J* = 16.3 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H).

11-(4-((*E*)-4-butylstyryl)phenoxy)undecyl methacrylate (monomer **mCC).** To the dehydrated dichloromethane (150 mL) solution of **10** (7.3 g) containing triethylamine (3.8 mL), methacryloyl chloride (2.7 g) solution in dehydrated dichloromethane (40 mL) was added dropwise at 0 ℃ under Ar atmosphere and allowed to stir at ambient temperature for 48 h. The solvent was evaporated under reduced pressure and the residue was dissolved in chloroform. The organic layer was washed with 5% NaHCO$_3$aq and brine, and then dried over Na$_2$SO$_4$. The crude product was purified on silica gel (Cica, silica gel 60N) column chromatography eluted by chloroform and then recrystallized from ethanol to give colorless fine needles (5.7 g, 68% yield). ^{1}H NMR (CDCl$_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.26-1.40 (m, 14H), 1.45 (m, 2H), 1.56-1.70 (m, 4H), 1.78 (m, 2H), 1.94 (m, 3H), 2.60 (t, *J* = 7.8 Hz, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 4.14 (t, *J* = 6.7 Hz, 2H), 5.54 (m, 1H), 6.10 (m, 1H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 16.3 Hz, 2H), 7.01 (d, *J* = 16.3 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (CDCl$_3$) δ 14.09, 18.46, 22.49, 26.12, 26.18, 28.75, 29.38, 29.42, 29.52, 29.63, 29.66, 33.72, 35.53, 64.96, 68.19, 114.83, 125.25, 126.28, 126.59, 127.48, 127.69, 128.85, 130.31, 135.27, 136.72, 142.23, 158.88, 167.69. MS (FAB) *m/z* (relative intensity) 492 (16), 491 (57), 490 (M$^+$, 100). Anal. Calcd for $C_{33}H_{46}O_3$: C, 80.77; H, 9.45. Found: C, 80.97; H, 9.50.

2. Synthesis of model compounds

11-(4-((*E*)-4-butylphenylazo)phenoxy)undecyl 2'-methypropionate (NN). To the dehydrated dichloromethane (20 mL) solution 11-(4-((*E*)-4-butylphenylazo)phenoxy)undecanol[3] (1 g) containing triethylamine (0.5 mL), the dehydrated dichloromethane (10 mL) solution of 2-methylpropionyl chloride (350 mg, Wako) was added dropwise and allowed to stir at ambient temperature for 20 h. The solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate. The organic layer was washed with 5% NaHCO$_3$aq and brine, and then dried over Na$_2$SO$_4$. The crude product was purified on silica gel (Cica, silica gel 60N) column chromatography eluted by chloroform and then recrystallized from ethanol to give orange flakes (1.0 g, 85% yield). ^{1}H NMR (CDCl$_3$) δ 0.94 (t, *J* = 7.3 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.26-1.41 (m, 14H), 1.48 (m, 2H), 1.64 (m, 4H), 1.81 (m, 2H), 2.53 (septet, *J* = 6.8 Hz, 1H), 2.68 (m, 2H), 4.04 (m, 4H), 6.98 (d, *J* = 9.1 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 9.1 Hz, 2H). MS (ESI-TOF) *m/z* (relative intensity) 517 (100, M$^+$ + Na), 518 (41), 519 (6).

11-(4-((*E*)-(4-butylphenylimino)methyl)phenoxy)undecyl 2'-methypropionate (CN). A model compound **CN** was prepared from **2** (1.0 g) and 2-methylpropionic acid (230 mg) according to the same procedure as **NN**. The crude product was purified on neutral alumina (Merck) short column chromatography eluted by mixed solvent of ethyl acetate and hexane (1:1) and recrystallized from ethanol to afford colorless fine needles (820 mg, 71% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.26-1.41 (m, 14H), 1.47 (m, 2H), 1.61 (m, 4H), 1.80 (m, 2H), 2.53 (septet, *J* = 6.8 Hz, 1H), 2.62 (m, 2H), 4.03 (m, 4H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 8.38 (s, 1H). MS (ESI-TOF) *m*/*z* (relative intensity) 516 (100, M^+ + Na), 517 (46), 518 (8).

11-((*E*)-4-(4-butylbenzylideneamino)phenoxy)undecyl 2'-methypropionate (NC). A model compound **NC** was prepared from **5** (1.0 g) and 2-methylpropionic acid (230 mg) according to the same procedure as **NN**. The crude product was purified on neutral alumina (Merck) short column chromatography eluted by mixed solvent of ethyl acetate and hexane (1:1) and recrystallized from ethanol to afford pale yellow powder (900 mg, 77% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.4 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.26-1.41 (m, 14H), 1.46 (m, 2H), 1.63 (m, 4H), 1.79 (m, 2H), 2.53 (septet, *J* = 6.8 Hz, 1H), 2.66 (m, 2H), 3.97 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 7.78 (d, *J* = 8.3 Hz, 2H), 8.44 (s, 1H). MS (ESI-TOF) *m*/*z* (relative intensity) 516 (100, M^+ + Na), 517 (33), 518 (6).

11-(4-((*E*)-4-butylstyryl)phenoxy)undecyl 2'-methypropionate (CC). A model compound **CC** was prepared from **10** (1.0 g) and 2-methylpropionyl chloride (350 mg) according to the same procedure as **NN**. The crude product was purified on silica gel (Cica, silica gel 60N) column chromatography eluted by chloroform and then recrystallized from ethanol to give colorless fine needles (920 mg, 79% yield). ^{1}H NMR ($CDCl_3$) δ 0.93 (t, *J* = 7.3 Hz, 3H), 1.16 (d, *J* = 6.8 Hz, 6H), 1.26-1.41 (m, 14H), 1.45 (m, 2H), 1.60 (m, 4H), 1.78 (m, 2H), 2.53 (septet, *J* = 6.8 Hz, 1H), 2.60 (m, 2H), 3.96 (t, *J* = 6.6 Hz, 2H), 4.05 (t, *J* = 6.6 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 16.1 Hz, 2H), 7.01 (d, *J* = 16.1 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H). MS (ESI-TOF) *m*/*z* (relative intensity) 515 (100, M^+ + Na), 516 (34), 517 (9).

3. Synthesis of initiators

The initiators, benzyl 2-bromo-2-methylpropionate (BzO-BMP) and α-methoxy-poly(ethylene oxide)-ω-(2-bromo-2-methylpropionate) (PEO-BMP), were synthesized by esterification of benzyl alcohol (Wako) and poly(ethylene oxide) monomethyl ether (M_W = 5000, NOF), respectively, with 2-bromo-2-methylpropionyl bromide (TCI) according to the similar procedure as reported previously;[3]

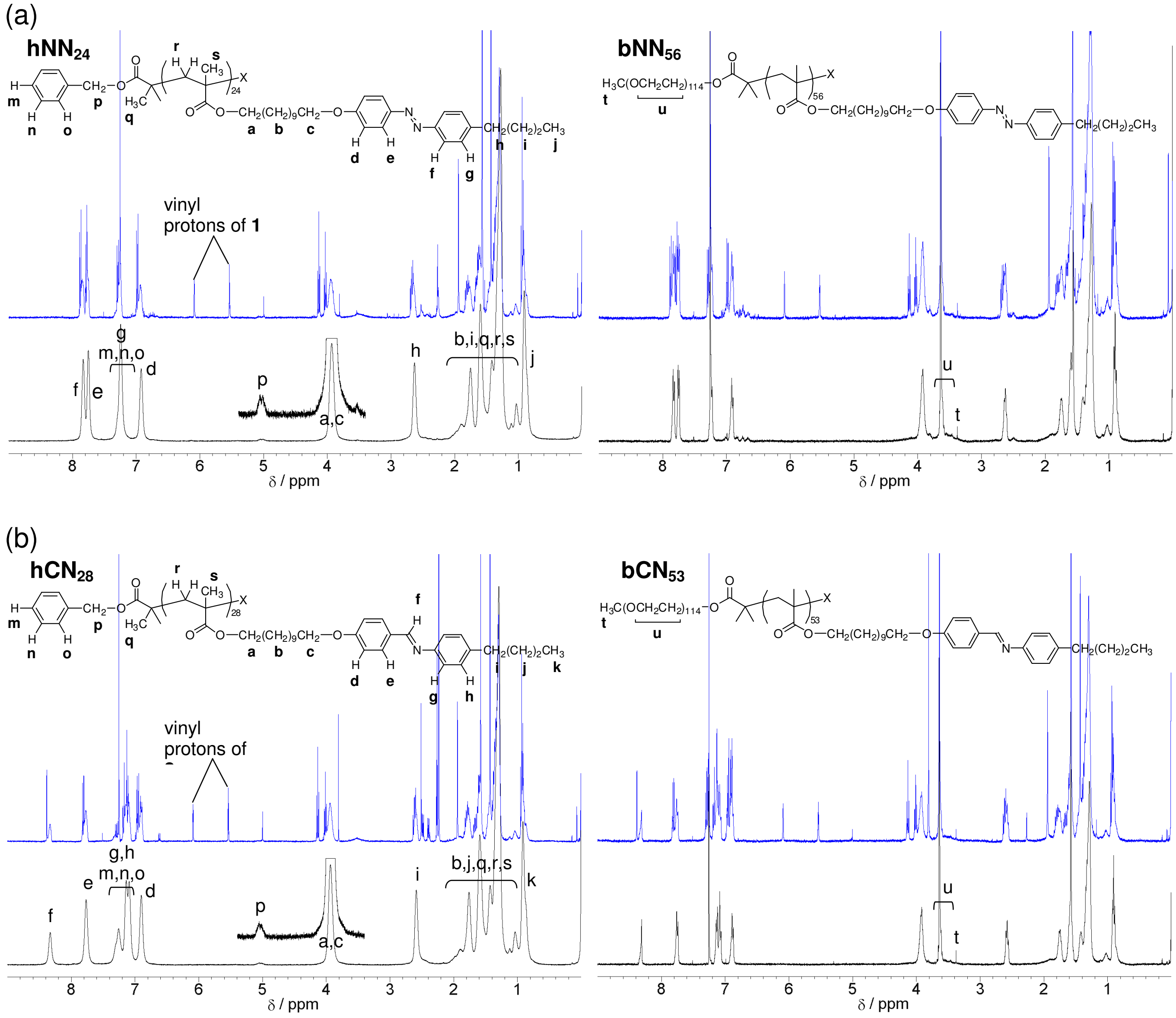
benzyl 2-bromo-2-methylpropionate (BzO-BMP). To the dehydrated THF (100 mL) solution of benzyl alcohol (12 g) containing triethylamine (25 mL), a dehydrated THF (25 mL) solution of 2-bromo-2-methylpropionyl bromide (25 g) was added dropwise under Ar atmosphere and allowed to stir at ambient temperature for 20 h. The solvent was removed under reduced pressure and the residue was dissolved in ethyl acetate. The organic layer was washed with water, 5% $NaHCO_3$aq and brine, and then dried over Na_2SO_4. The crude product was purified on silica gel (Cica, silica gel 60N) column chromatography eluted by hexane to give colorless liquid (22.5 g, 80% yield). ^{1}H NMR ($CDCl_3$) δ 5.21 (s, 2H), 7.37 (m, 5H). MS (ESI-TOF) *m*/*z* (relative intensity) 281 (12), 280 (100), 279 (13), 278 (94, M^+ + Na). Anal. Calcd for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.10; Br, 31.08. Found: C, 51.16; H, 4.92; Br, 30.80.

α-methoxy-poly(ethylene oxide)-ω-(2-bromo-2-methylpropionate) (PEO-BMP). An optimized procedure to achieve quantitative esterification is as follows; A poly(ethylene oxide) monomethyl ether (2.0 g) was dissolved to dehydrated dichloromethane (20 mL) containing dehydrated pyridine (560 mg) at 50 ℃, and then a dehydrated dichloromethane (20 mL) solution of 2-bromo-2-methylpropionyl bromide (950 mg) was added dropwise under Ar atmosphere. The reaction mixture was allowed to stir at 50 ℃ for 3 h. After the precipitate formed in the reaction mixture was filtered off, the filtrate was concentrated under reduced pressure and then precipitated in ether. The crude product was purified by recrystallization from ethanol to give colorless powder (1.56 g, 76% yield). ^{1}H NMR (CD_3OD) δ 1.92 (s, 6H), 3.35 (s, 3H), 3.49 (m, 2H), 3.54 (m, 2H), 3.56-3.72 (m, (4n – 10)H), 3.75 (m, 2H), 3.77 (m, 2H), 4.30 (m, 2H); M_N = 8990; M_W/M_N = 1.05. The quantitative introduction was confirmed by precise comparison of observed ratio of protons on two methyl groups of 2-bromo-2-methylpropionyl unit (6H, 1.92 ppm) to those on a terminal methylene group of poly(ethylene oxide) adjacent to the ester unit (2H, 4.30 ppm) in 500MHz ^{1}H NMR spectra.

4. Polymerization

All the block copolymers were synthesized via ATRP according to a typical procedure as follows; A mixture of copper chloride(I) (17 mg, 172 μmol) and 1,1,4,7,10,10-hexamethylenetetramine (HMTETA, 50 μL, 184 μmol) in anisole (1 mL) was added to the anisole (4 mL) solution containing PEO-BMP (87 mg, 17 μmol) and monomer **mCN** (492 mg, 1 mmol) under argon atmosphere. The reaction mixture was sealed in the tube and then heated at 80 ℃ for 22 h. The reaction mixture was passed through an activated basic alumina (Merck) column using chloroform as eluent to remove the copper complex. After the solvent was removed under reduced pressure, the residue was taken for ^{1}H NMR measurement in order to determine the conversion. The residual solid was washed with hot hexane repeatedly to remove the remaining monomer. The residue was then dissolved in a minimum amount of chloroform and reprecipitated in methanol to give $\mathbf{bCN_{53}}$ as colorless powder (265 mg, 46%), which was served as an isolated polymer sample for characterization. All the homopolymers were prepared according to the same procedure by using BzO-BMP as an initiator.

The polymerization condition and properties of all homo- and copolymers were summarized in Table 1. The typical ^{1}H NMR spectra of homopolymers and diblock copolymers were shown in Figure S1. The polymerization degrees (DPs) of homo- and copolymers were determined from the ratio of the peak area corresponding to the four methylene protons at the both ends (**a** and **c**) of the undecyl linker in each monomer unit against that to the two α-methylene proton (**p**) of benzyl unit and that to the four methylene units (**u**) in each monomer unit of poly(ethylene oxide), respectively.


(a)
hNN24
bNN56
vinyl protons of 1
f
e
g
m,n,o
d
p
a,c
h
b,i,q,r,s
j
u
t
δ / ppm
8 7 6 5 4 3 2 1
(b)
hCN28
bCN53
vinyl protons of
f
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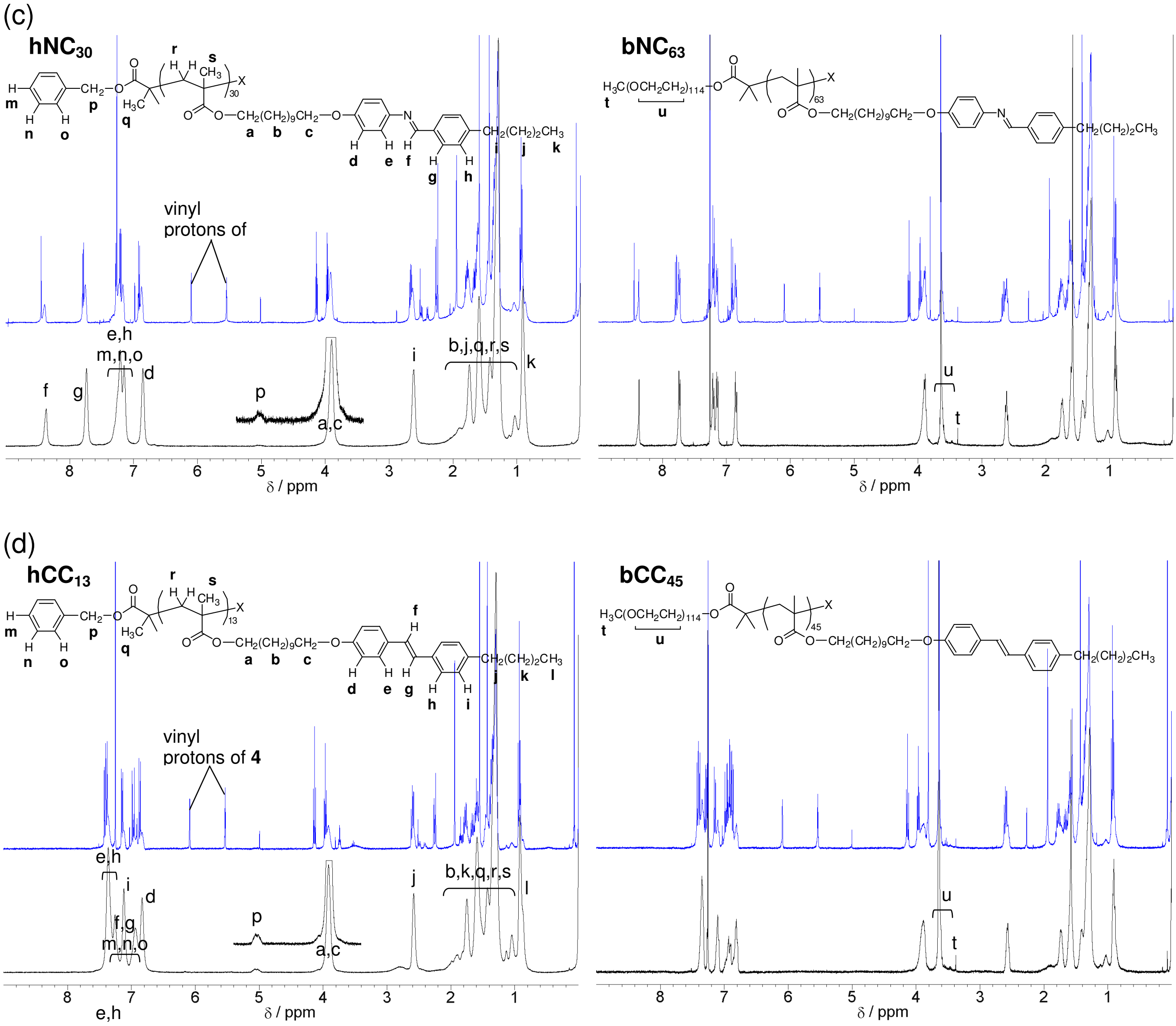
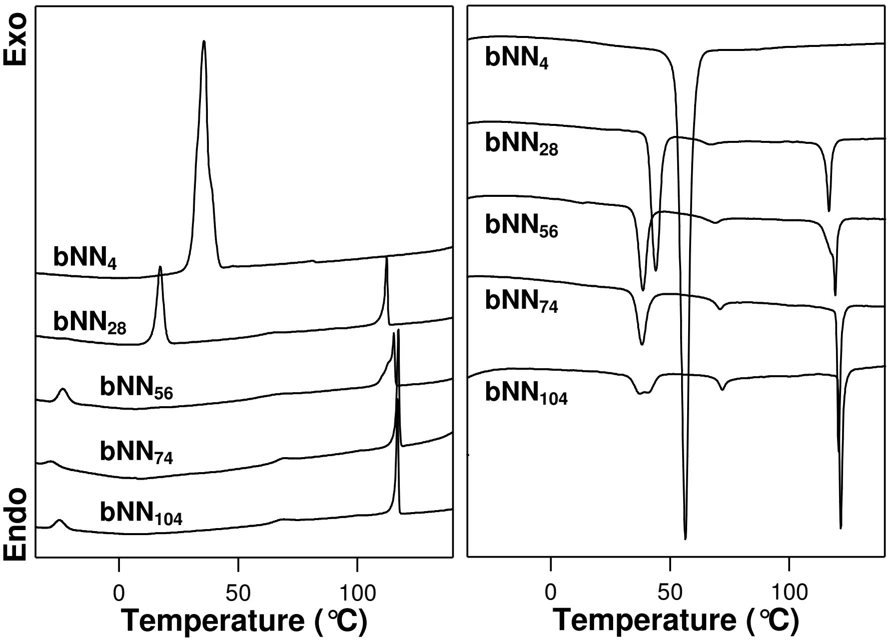


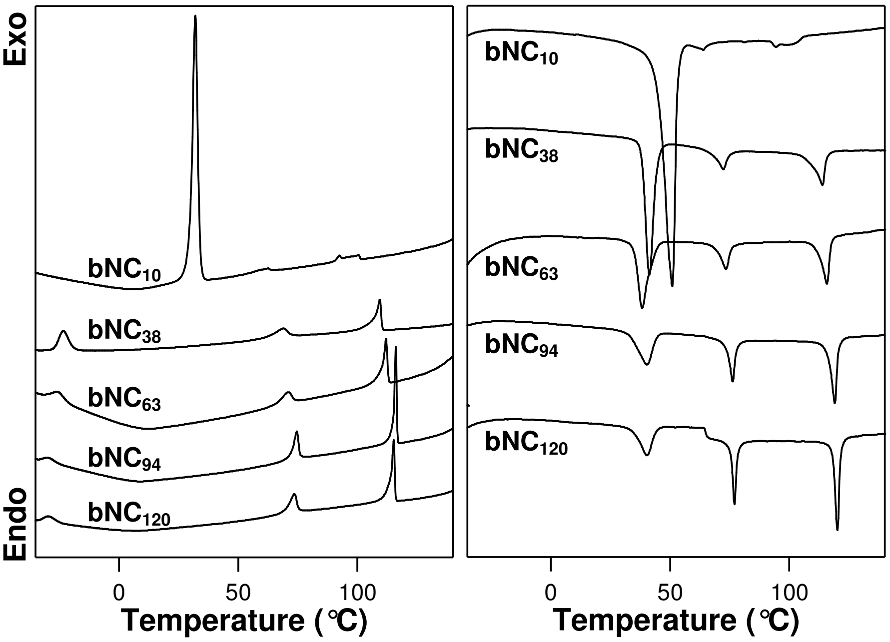
Figure S1. ^{1}H NMR spectra of reaction mixtures after polymerization (upper traces) and purified (lower traces) homopolymers (left) and diblock copolymers (right) synthesized via ATRP of the monomers (a) **mNN**, (b) **mCN**, (c) **mNC** and (d) **mCC**.

5. DSC curves of amphiphilic diblock copolymers

(a)



(b)



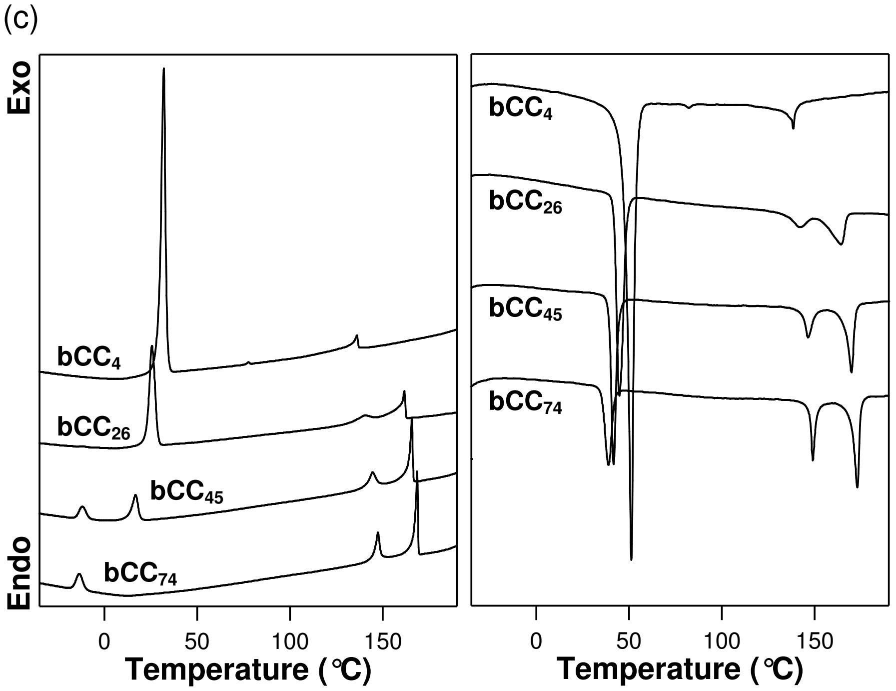


Figure S2. DSC curves of amphiphilic diblock copolymers (a) **bNN**s, (b) **bNC**s and (c) **bCC**s on 1st cooling (left) and 2nd heating (right) processes with heating/cooling rate of ±10 °C/min.

6. SAXS profiles of amphiphilic diblock copolymers

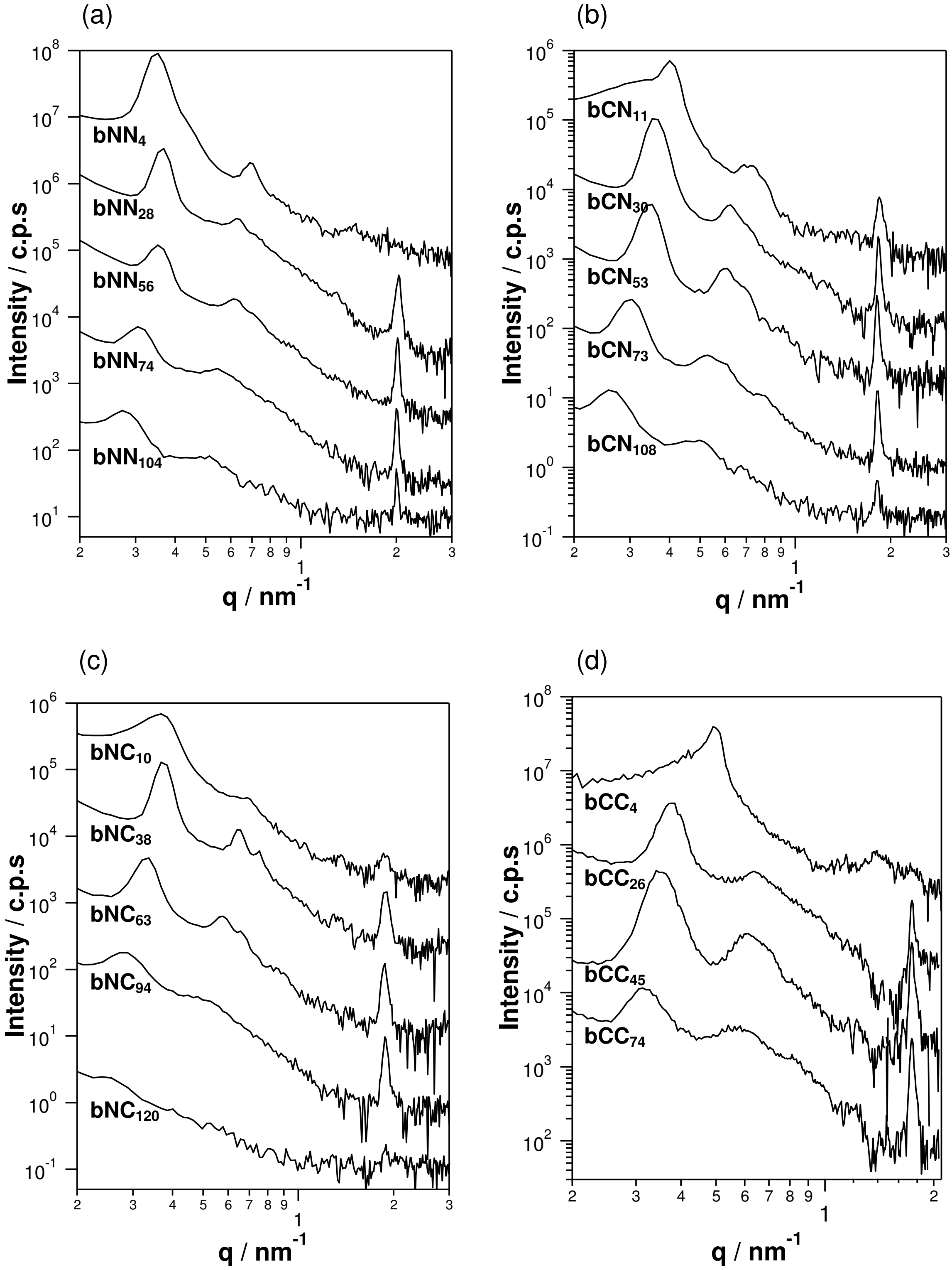


Figure S3. SAXS profiles of bulk pellets of (a) **bNN**s, (b) **bCN**s and (c) **bNC**s annealed at 140 ℃, and that of **bCC**s annealed at 190 ℃.

7. 'Intra-layer' regularity of LC mesogens

A relatively broad peak was also observed for all the homopolymers at around 20°, which was originated from the lateral correlation among the mesogens in the side chain. The inter-mesogen distance (d_{M}s) were calculated to be almost comparable at 45 ℃ of 4.33-4.36 Å for all the homopolymers, and increased upon heating up to 4.72-4.90 Å at the higher temperature than 1st transition peaks. The d_{M} values were plotted as a function of temperature in Figure S4. The slopes of the plots were not uniform but changed remarkably at the two liquid crystalline transition temperatures, suggesting that these increases in d_{M} values is not simply based on the thermal expansion. These broad peaks in liquid crystalline phase become sharper in the lower temperature region than the 2nd transition peaks on cooling in the DSC curves at 66-81 ℃ for **hNN$_{57}$**, **hCN$_{69}$** and **hNC$_{69}$**, and around 150 ℃ for **hCC$_{31}$**, respectively. Applying the Scherrer equation[4] to the half-width of the diffraction peaks, the scattering domain sizes (D) along the scattering direction can be estimated;

$$D = K\lambda(\beta\cos\theta)^{-1}$$

, where K is the shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle. The 'intra-layer' regularity as a persistent length based on the mesogen ordering (D_{M}) of homopolymers were estimated to be 6 nm for **hNN$_{57}$**, 19 nm for **hCN$_{69}$**, 13 nm for **hNC$_{69}$** and 15 nm for **hCC$_{31}$** at 45 ℃. The D_{M} value of **hNN$_{57}$** was obviously smaller than that of the other homopolymers. The phase transition from smectic A to C in **hNN$_{57}$** induces the tilt of side chains, of which direction might not be uniform. Such a multidirectional tilt of side chains might reduce the lateral mesogen ordering in each liquid crystalline layer. Although the D_{M} values were almost comparable for all the homopolymers in the isotropic phase (2 nm) and smectic A phase (2-3 nm), they suddenly increased at the 2nd transition temperature, implying the formation of long-range bond orientational order in the intra-layer mesogen arrangements.

The d_{M} and D_{M} values for the block copolymers **bNN$_{56}$**, **bCN$_{53}$**, **bNC$_{63}$** and **bCC$_{45}$** were also estimated and plotted against temperature as shown in Figure S5. Although the order in the domain sizes for copolymers were unchanged from homopolymers, these D_{M} values at the ambient temperature were considerably smaller than that of corresponding homopolymers, implying that the growth of the quasi-crystalline region in the intra-layer direction should be restricted by the regularly arranged cylindrical domains with 17-18 nm of distances between them. The d_{M} values showed the discontinuous change against the temperature and their slopes were obviously changed at the two LC phase transition temperature. It should be emphasized here again that the D_{M} values were dramatically increased at the 2nd LC transition temperature, suggesting the intra-layer correlations were substantially improved more than the corresponding smectic phase above the 2nd LC transition temperature. As far as the nature of these first-order transitions, they could be assigned as the transitions between the hexatic type of phase and the corresponding smectic phase.

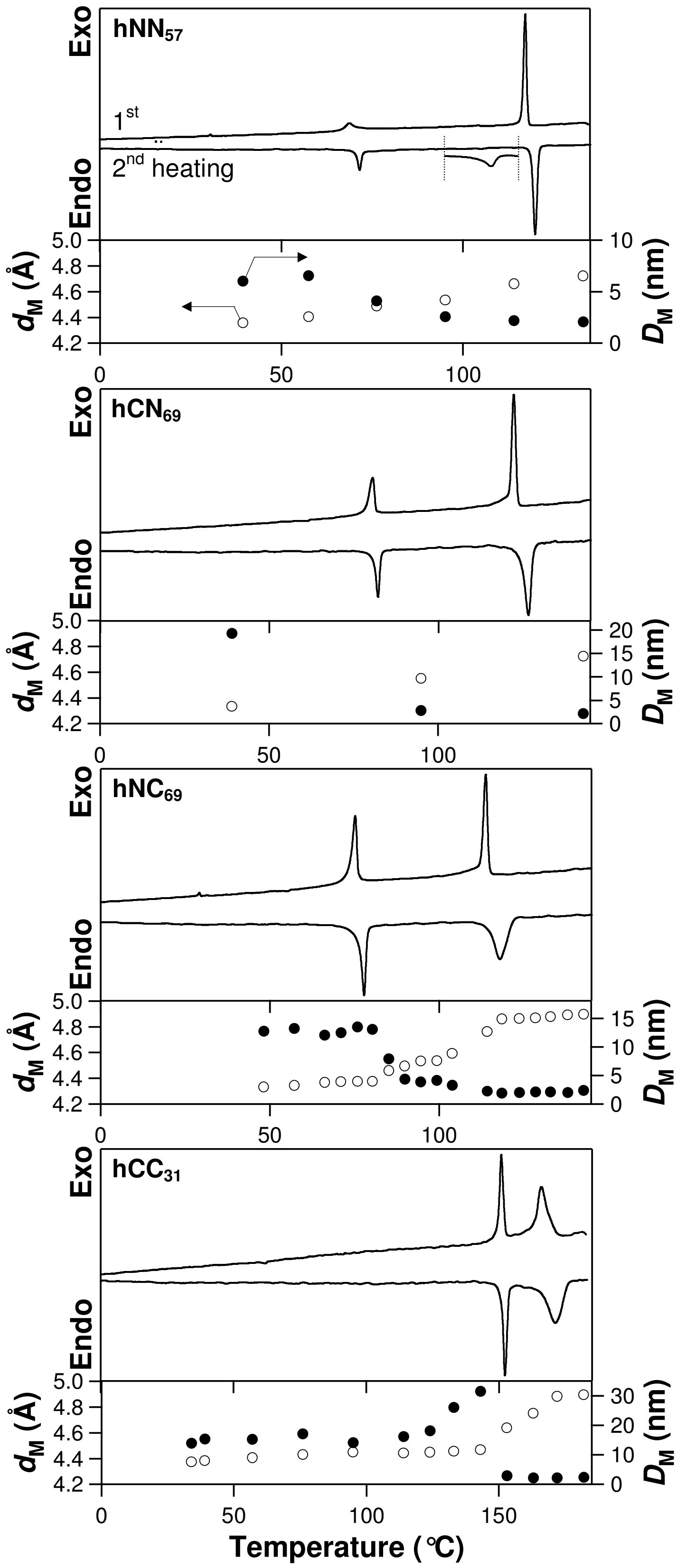


Figure S4 DSC curves of homopolymers on 1st cooling and 2nd heating processes with heating/cooling rate of ±10 °C/min (upper traces) together with the plots of inter-mesogen distances (d_M: open circles) and persistent lengths based on mesogen ordering (D_M: closed circles) as a function of temperature (lower traces).

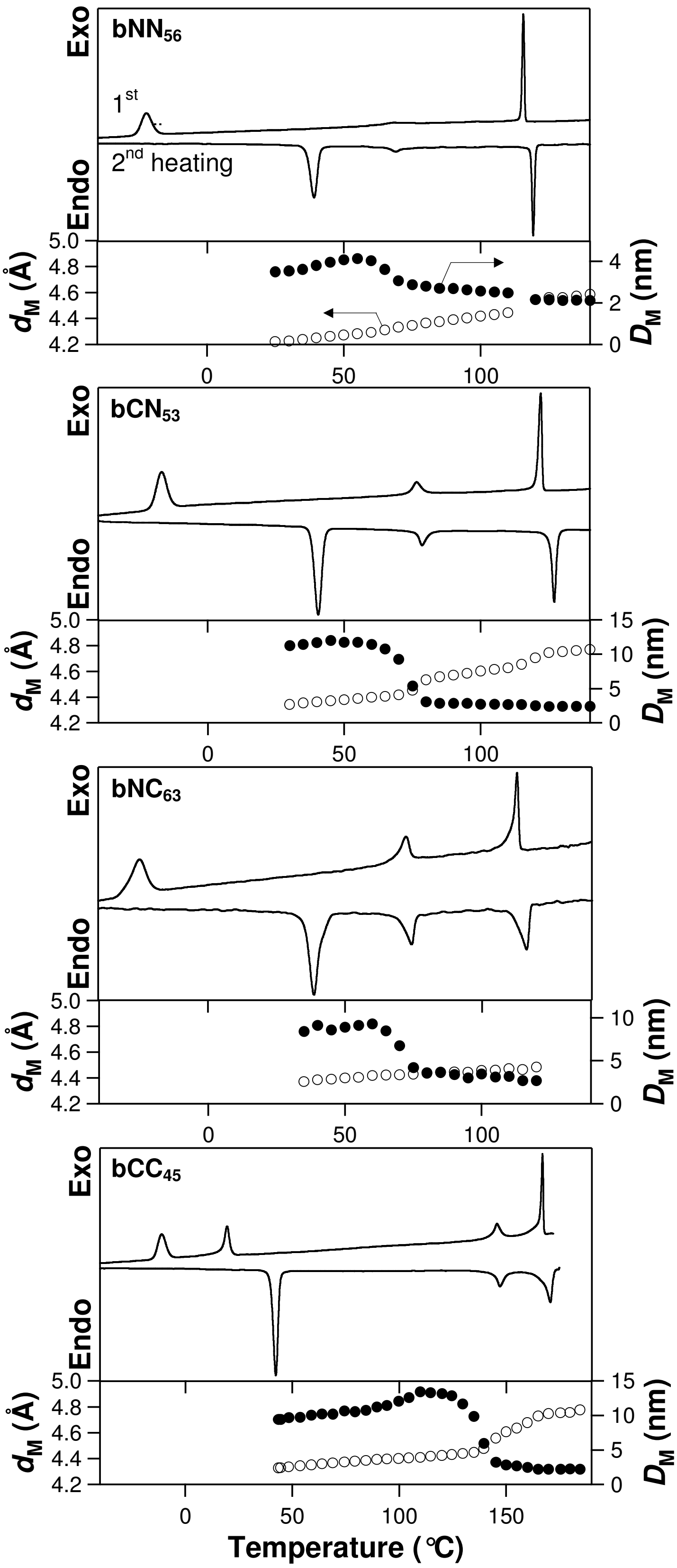


Figure S5 DSC curves of amphiphilic diblock copolymers on 1st cooling and 2nd heating processes with heating/cooling rate of ±10 °C/min (upper traces) together with the plots of inter-mesogen distances (d_M: open circles) and persistent lengths based on mesogen ordering (D_M: closed circles) as a function of temperature (lower traces).

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