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# Electronic Supplementary Information

## "Soldier–Sergeant–Soldier" Triblock Copolymers: Revealing the Folded Structure of Single-Chain Polymeric Nanoparticles

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## Materials and Methods

### 1. Materials.

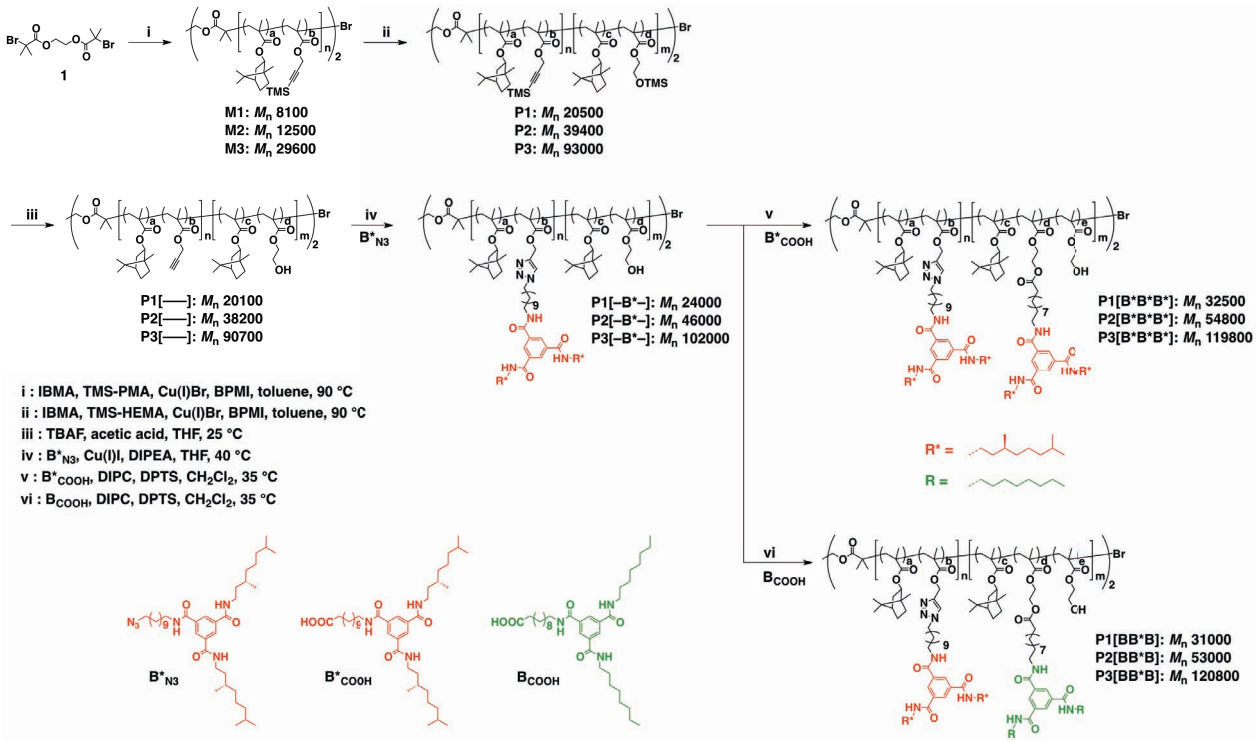
*N*,*N*'-Diisopropylcarbodiimide (DIPC) (99%) was purchased from Aldrich Chemicals and used as received. 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was prepared according to a reported procedure.[S1] CD and UV measurements were conducted in spectrophotometric grade 1,2-dichloroethane (DCE) from Acros Organics. Deuterated solvents for NMR spectroscopy were purchased from Cambridge Isotope Laboratories. Syntheses and characterizations of macroinitiator **M*n***, and triblock copolymer **P*n***, **P*n*[——]** and **P*n*[–B*–]** (*n* = 1, 2, and 3) are described in the literature previously published.[S2] **B*$_{N3}$** and **B*$_{COOH}$** were synthesized according a the literature procedure.[S2,S3] 11-Aminoundecanol was synthesized according to a literature procedure.[S4] All other materials were purchased from Aldrich Chemicals and used without any further purification.

### 2. General.

THF SEC-measurements were performed on a Shimadzu-system with two Polymer Laboratories columns in series (PLgel 5 $\mu$m mixed-C [200–2,000,000 Da] and PLgel 5 $\mu$m mixed-D [200–40,000 Da]) and equipped with a refractive index detector (Shimadzu RID-10A) and a diode array detector (Shimadzu SPD-M10A). The mobile phase was THF at a flow rate of 1.0 mL/min. Molecular weights and molecular weight distributions ($M_w/M_n$) were obtained relative to polystyrene standards (Polymer Laboratories, molecular weight range: 580–100,000 g/mol). $^1$H and $^{13}$C NMR spectra were recorded at 25°C on a Varian Mercury Vx 400 MHz, operating at 400 and 100 MHz, respectively, where chemical shifts ($\delta$ in ppm) were determined with respect to tetramethylsilane (TMS) as an internal reference. CD spectra were recorded on a Jasco J-815 CD spectrometer equipped with a Jasco PTC-348 WI temperature controller. Cells with an optical path length of 0.5 cm were applied.

## 3. Synthesis.

**Scheme S1**. Synthesis of **P*n*[BB*B]** and **P*n*[B*B*B*]** series of polymers (*n* = 1, 2, and 3).




*Abbreviations: Isobornyl methacrylate (IBMA), TMS-PMA (TMS-protected propargyl methacrylate), TMS-HEMA (TMS-protected hydroxylethyl methacrylate), N-(n-Butyl)-2-pyridylmethanimine (BPMI), N,N'-Diisopropylcarbodiimide (DIPC), 4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS).*

**Hydroxyundecyl-3,5-bis(octylcarbamoyl)benzoate.** To a dry $CHCl_3$ solution (70 mL) of 1-aminooctane (5.3 mmol, 0.7 g), 11-aminoundecanol (5.3 mmol, 1.0 g), and triethylamine (26.7 mmol, 3.7 mL), dry $CHCl_3$ solution (12 mL) of benzene-1,3,5-tricarbonyl trichloride (4.5 mmol, 1.2 g) was added dropwise at 0 °C in a ice-water bath. The reaction mixture was stirred at 0 °C under Ar. When the ice-water bath was completely melted, the bath was removed and the solution was stirred at room temperature. After 12 hours, the solvent and excess of triethylamine were removed in a reduced pressure. The residue was dissolved in $CHCl_3$ (50 mL) and washed with 1M HCl (2 x 50 mL) and brine (1 x 50 mL). The organic phase was isolated and dried over anhydrous $MgSO_4$ and then evaporated to dryness under a reduced pressure. The residue was subjected to column chromatography ($SiO_2$, AcOEt/$CHCl_3$ 40/60, v/v) to allow isolation of hydroxyundecyl-3,5-bis(octylcarbamoyl)benzoate as a white sticky solid (0.54 g) in 20% yield. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.36 (s, 2H, Ar-*H*), 8.35 (s, 1H, Ar-*H*), 6.67 (m, 3H, N-*H*), 3.63 (m, 2H, -C*H*$_2$-OH), 3.44 (q, 6H, -NH-C*H*$_2$-), 1.67–1.48 (m, 8H, -NH-CH$_2$-C*H*$_2$-, -C*H*$_2$-CH$_2$-OH), 1.45–1.17 (m, 36H, aliphatic), 0.88 (t, 6H, -C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 165.8, 135.2, 128.0, 63.0, 40.4, 40.3, 32.7, 31.7, 29.5, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 29.1, 26.9, 26.8, 25.6, 22.6, 14.1.

**B$_{COOH}$**. To an acetone solution (4.5 mL) of hydroxyundecyl-3,5-bis(octylcarbamoyl)benzoate (0.30 g, 0.50 mmol), Jones reagent was added dropwise with stirring at room temperature. The solution turned blue immediately and then orange. After the solution became orange, the addition of Jones reagent was stopped and the solution was stirred for an additional 10 min at room temperature. Water (10 mL) was added and the resultant mixture was extracted with $CHCl_3$ (10 mL) three times. The combined organic phase was washed successively with water (10 mL) three times. The organic phase was isolated and dried over anhydrous $MgSO_4$ and then evaporated to dryness under a reduced pressure. The crude product was obtained as a white sticky solid (0.28 g) in 93% yield and used without further purification. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.60 (s, 2H, Ar-*H*), 8.47 (s, 1H, Ar-*H*), 7.55 (t, 1H, -N*H*-), 7.14 (t, 2H, -N*H*-), 3.43 (q, 6H, -NH-C*H*$_2$-), 2.35 (t, 2H, -C*H*$_2$-COOH), 1.70–1.50 (m, 8H, -NHCH$_2$C*H*$_2$-, -C*H*$_2$-CH$_2$-COOH), 1.43–1.15 (m, 36H, aliphatic), 0.87 (t, 6H, -C*H*$_3$). $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ (ppm) 176.7, 166.3, 165.9, 135.0, 134.7, 128.7, 128.3, 40.5, 40.2, 33.7, 31.8, 29.4, 29.3, 29.2, 28.8, 28.4, 28.3, 28.3, 28.2, 28.0, 27.0, 26.3, 24.4, 22.6, 14.1.

**P1[——].** The synthesis and characterization of this compound was described in a literature previousely published.[S2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.70–4.22 (m, 92.0H, -CO-O-C*H*$_2$-: PMA and -CO-O-C*H*-: IBMA), 4.20–3.97 (m, 12.8H, -CO-O-C*H*$_2$-CH$_2$-: HEMA), 3.92-3.76 (m, 12.8H, -CO-O-CH$_2$-C*H*$_2$-: HEMA), 2.43 (s, 3.8H, -CC*H*: PMA), 2.25–0.65 (m,

aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 20100 g/mol; $M_w/M_n$ = 1.25. DP = 93.6. Poly[(IBMA$_{25.8}$-*co*-HEMA$_{3.2}$)-*block*-(IBMA$_{31.9}$-co-PMA$_{3.8}$)-*block*-(IBMA$_{25.8}$-*co*-HEMA$_{3.2}$)].

**P2[——].** The synthesis and characterization of this compound was described in a literature previousely published.[S2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.70–4.22 (m, 162.5H, -CO-O-C$H_2$-: PMA and -CO-O-C*H*-: IBMA), 4.20–3.97 (m, 22.6H, -CO-O-C$H_2$-CH$_2$-: HEMA), 3.92-3.76 (m, 22.6H, -CO-O-CH$_2$-C$H_2$-: HEMA), 2.43 (s, 6.3H, -CC*H*: PMA), 2.25–0.65 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 38200 g/mol; $M_w/M_n$ = 1.34. DP = 169.9. Poly[(IBMA$_{49.9}$-*co*-HEMA$_{5.7}$)-*block*-(IBMA$_{52.6}$-*co*-PMA$_{6.3}$)-*block*-(IBMA$_{49.9}$-*co*-HEMA$_{5.7}$)].

**P3[——].** The synthesis and characterization of this compound was described in a literature previousely published.[S2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 4.70–4.22 (m, 403.5H, -CO-O-C$H_2$-: PMA and -CO-O-C*H*-: IBMA), 4.20–3.97 (m, 55.8H, -CO-O-C$H_2$-CH$_2$-: HEMA), 3.92-3.76 (m, 55.8H, -CO-O-CH$_2$-C$H_2$-: HEMA), 2.43 (s, 16.6H, -CC*H*: PMA), 2.25–0.65 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 90700 g/mol; $M_w/M_n$ = 1.53. DP = 421.5. Poly[(IBMA$_{121.3}$-*co*-HEMA$_{14.0}$)-*block*-(IBMA$_{134.5}$-*co*-PMA$_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-HEMA$_{14.0}$)].

**P1[–B*–].** The synthesis and characterization of this compound was described in a literature previousely published.[S2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.34 (br, 9.2H, aromatic: BTA), 7.68 (br, 2.8H, -C=C*H*-N-), 6.98–6.30 (br, 7.7H, amide: BTA), 5.12 (br, 3.1H, -O-C$H_2$-C=C-), 4.70–3.95 (m, 110H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-CH$_2$-: HEMA, and -C$H_2$-N<), 3.92-3.76 (m, 12.8H, -CO-O-CH$_2$-C$H_2$-: HEMA), 3.59–3.28 (br, 21.1H, -CO-N-C$H_2$-), 2.25–0.65 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 24000 g/mol; $M_w/M_n$ = 1.17. Poly[(IBMA$_{25.8}$-*co*-HEMA$_{3.2}$)-*block*-(IBMA$_{31.9}$-*co*-**B***$_{3.8}$)-*block*-(IBMA$_{25.8}$-*co*-HEMA$_{3.2}$)].

**P2[–B*–].** The synthesis and characterization of this compound was described in a literature previousely published.[S2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.34 (br, 11.1H, aromatic: BTA), 7.68 (br, 3.6H, -C=C*H*-N-), 6.98–6.30 (br, 5.4H, amide: BTA), 5.12 (br, 5.4H, -O-C$H_2$-C=C-), 4.70–3.95 (m, 177H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-CH$_2$-: HEMA, and -C$H_2$-N<), 3.92-3.76 (m, 22.6H, -CO-O-CH$_2$-C$H_2$-: HEMA), 3.59–3.28 (br, 24H, -CO-N-C$H_2$-), 2.25–0.65 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 46000 g/mol; $M_w/M_n$ = 1.30. Poly[(IBMA$_{49.9}$-*co*-HEMA$_{5.7}$)-*block*-(IBMA$_{52.6}$-*co*-**B***$_{6.3}$)-*block*-(IBMA$_{49.9}$-*co*-HEMA$_{5.7}$)].

**P3[–B*–].** The synthesis and characterization of this compound was described in a literature previousely published.[S2] $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.34 (br, 24.3H, aromatic: BTA), 7.68 (br, 10.3H, -C=C*H*-N-), 6.98–6.30 (br, 9.6H, amide: BTA), 5.12 (br, 7.4H, -O-C$H_2$-C=C-),

4.70–3.95 (m, 442H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-: HEMA, and -C$H_2$-N<), 3.92-3.76 (m, 55.8H, -CO-O-$CH_2$-C$H_2$-: HEMA), 3.59–3.28 (br, 72H, -CO-N-C$H_2$-), 2.25–0.65 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 102000 g/mol; $M_w/M_n$ = 1.48. Poly[(IBMA$_{121.3}$-*co*-HEMA$_{14.0}$)-*block*-(IBMA$_{134.5}$-*co*-**B***$_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-HEMA$_{14.0}$)].

**P1[BB*B].** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B_{COOH}}$ (8.3 $\mu$mol, 5.2 mg, excess amount) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (6.5 $\mu$mol, 1.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P1[–B*–]** (0.42 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at 35 °C for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P1[BB*B]** (10.0 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.42–7.85 (br, 18.1H, aromatic: BTA), 7.68 (br, 2.8H,-C=C*H*-N-), 7.20–6.40 (br, 18.6H, amide: BTA), 5.12 (br, 3.1H, -O-C$H_2$-C=C-), 4.62–3.94 (m, 80.6H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.43 (br, 36.3H, -CO-N-C$H_2$-), 2.33 (br, 12.9H, -C$H_2$-CO-O-), 2.22–0.63 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 31000 g/mol; $M_w/M_n$ = 1.20. The average incorporation number of $\mathbf{B_{COOH}}$ per chain was calculated to be 6.4 by complete consumption of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P1[–B*–]**. Poly[(IBMA$_{25.8}$-*co*-**B**$_{3.2}$)-*block*-(IBMA$_{31.9}$-*co*-**B***$_{3.8}$)-*block*-(IBMA$_{25.8}$-*co*-**B**$_{3.2}$)].

**P2[BB*B].** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B_{COOH}}$ (4.3 $\mu$mol, 2.6 mg, excess amount) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (6.5 $\mu$mol, 1.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P2[–B*–]** (0.22 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at 35 °C for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P2[BB*B]** (10.3 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.39–7.55 (br, 48.8H, aromatic: BTA, -C=C*H*-N-), 7.19–6.38 (br, 35.4H, amide: BTA), 5.12 (br, 5.4H, -O-C$H_2$-C=C-), 4.64–3.94 (m, 176.1H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.42 (br, 85.5H, -CO-N-C$H_2$-), 2.55–0.53 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 53000 g/mol; $M_w/M_n$ = 1.42. The average

incorporation number of $\mathbf{B}_{\mathbf{COOH}}$ per chain was calculated to be 11.4 by complete consumption of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P2[–B*–]**. Poly[(IBMA$_{49.9}$-*co*-$\mathbf{B}_{5.7}$)-*block*-(IBMA$_{52.6}$-*co*-$\mathbf{B}^*_{6.3}$)-*block*-(IBMA$_{49.9}$-*co*-$\mathbf{B}_{5.7}$)].

**P3[BB*B].** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B}_{\mathbf{COOH}}$ (8.1 $\mu$mol, 5.0 mg, excess amount) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (13 $\mu$mol, 2.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P3[–B*–]** (0.098 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at 35 °C for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P1[BB*B]** (11.2 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40–7.55 (br, 51.3H, aromatic: BTA, -C=C*H*-N-), 7.19–6.40 (br, 50.2H, amide: BTA), 5.12 (br, 7.4H, -O-C$H_2$-C=C-), 4.67–3.94 (m, 259.1H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.43 (br, 122.3H, -CO-N-C$H_2$-), 2.49–0.53 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 120800 g/mol; $M_w/M_n$ = 1.56. The average incorporation number of $\mathbf{B}_{\mathbf{COOH}}$ per chain was calculated to be 27.9 by complete consumption of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P3[–B*–]**. Poly[(IBMA$_{121.3}$-*co*-$\mathbf{B}_{14.0}$)-*block*-(IBMA$_{134.5}$-*co*-$\mathbf{B}^*_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-$\mathbf{B}_{14.0}$)].

**P1[B*B*B*].** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B}^*_{\mathbf{COOH}}$ (4.3 $\mu$mol, 2.8 mg, excess amount) and DPTS (3.4 $\mu$mol, 1.0 mg) was added DIPC (6.5 $\mu$mol, 1.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P2[–B*–]** (0.22 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at 35 °C for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P1[B*B*B*]** (7.1 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.42–7.85 (br, 16.8H, aromatic: BTA), 7.67 (br, 2.5H,-C=C*H*-N-), 7.16–6.35 (br, 16.6H, amide: BTA), 5.12 (br, 3.1H, -O-C$H_2$-C=C-), 4.63–3.98 (m, 67.4H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.45 (br, 31.9H, -CO-N-C$H_2$-), 2.34 (br, 12.9H, -C$H_2$-CO-O-), 2.20–0.63 (m, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 32500 g/mol; $M_w/M_n$ = 1.19. The average incorporation number of $\mathbf{B}^*_{\mathbf{COOH}}$ per chain was calculated to be 6.4 by complete

consumption of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P1[–B*–]**. Poly[(IBMA$_{25.8}$-*co*-**B***$_{3.2}$)-*block*-(IBMA$_{31.9}$-*co*-**B***$_{3.8}$)-*block*-(IBMA$_{25.8}$-*co*-**B***$_{3.2}$)].

**P2[B*B*B*].** To a dry $CH_2Cl_2$ solution (0.5 mL) of **B*$_{COOH}$** (4.3 $\mu$mol, 2.9 mg, excess amount) and DPTS (3.4 $\mu$mol, 1.0 mg) was added DIPC (6.5 $\mu$mol, 1.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P1[–B*–]** (0.42 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at 35 °C for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P2[B*B*B*]** (9.0 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40–7.86 (br, 45.5H, aromatic: BTA), 7.67 (br, 3.6H, -C=C*H*-N-), 7.19–6.40 (br, 42.0H, amide: BTA), 5.12 (br, 5.4H, -O-C$H_2$-C=C-), 4.65–3.94 (m, 172.6H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.45 (br, 89.1H, -CO-N-C$H_2$-), 2.49–0.41 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 54800 g/mol; $M_w/M_n$ = 1.43. The average incorporation number of **B*$_{COOH}$** per chain was calculated to be 11.4 by complete consumption of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P2[–B*–]**. Poly[(IBMA$_{49.9}$-*co*-**B***$_{5.7}$)-*block*-(IBMA$_{52.6}$-*co*-**B***$_{6.3}$)-*block*-(IBMA$_{49.9}$-*co*-**B***$_{5.7}$)].

**P3[B*B*B*].** To a dry $CH_2Cl_2$ solution (0.5 mL) of **B*$_{COOH}$** (4.9 $\mu$mol, 3.3 mg, excess amount) and DPTS (3.4 $\mu$mol, 1.0 mg) was added DIPC (6.5 $\mu$mol, 1.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P3[–B*–]** (0.098 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at 35 °C for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P3[B*B*B*]** (6.6 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.40–7.55 (br, 55.6H, aromatic: BTA, -C=C*H*-N-), 7.19–6.40 (br, 53.7H, amide: BTA), 5.12 (br, 7.4H, -O-C$H_2$-C=C-), 4.67–3.94 (m, 219.5H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.44 (br, 106.8H, -CO-N-C$H_2$-), 2.49–0.53 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 119800 g/mol; $M_w/M_n$ = 1.70. The average incorporation number of **B*$_{COOH}$** per chain was calculated to be 27.9 by complete consumption of

hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P3[–B*–]**. Poly[(IBMA$_{121.3}$-*co*-**B***$_{14.0}$)-*block*-(IBMA$_{134.5}$-*co*-**B***$_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-**B***$_{14.0}$)].

**P3[BB*B]a.** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B_{COOH}}$ (0.98 $\mu$mol, 0.6 mg) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (13 $\mu$mol, 2.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P3[–B*–]** (0.098 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at room temperature for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P3[BB*B]a** (10.2 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.42–7.54 (br, 27.2H, aromatic: BTA, -C=C*H*-N-), 7.20–6.40 (br, 17.2H, amide: BTA), 5.12 (br, 7.4H, -O-C$H_2$-C=C-), 4.64–3.96 (m, 253.2H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.84 (br, 28.5H, -CO-O-$CH_2$-C$H_2$-OH: HEMA), 3.46 (br, 43.8H, -CO-N-C$H_2$-), 2.50–0.47 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 103000 g/mol; $M_w/M_n$ = 1.53. The average incorporation number of $\mathbf{B_{COOH}}$ per chain was calculated to be 6.4 by consumption rate (22.8%) of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P3[–B*–]**. Poly[(IBMA$_{121.3}$-*co*-HEMA$_{10.8}$-*co*-**B**$_{3.2}$)-*block*-(IBMA$_{134.5}$-*co*-**B***$_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-HEMA$_{10.8}$-*co*-**B**$_{3.2}$)].

**P3[BB*B]b.** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B_{COOH}}$ (1.5 $\mu$mol, 0.9 mg) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (13 $\mu$mol, 2.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P3[–B*–]** (0.098 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at room temperature for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P3[BB*B]b** (10.0 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.42–7.54 (br, 22.4H, aromatic: BTA, -C=C*H*-N-), 7.20–6.40 (br, 14.9H, amide: BTA), 5.12 (br, 7.4H, -O-C$H_2$-C=C-), 4.64–3.96 (m, 210.3H, -CO-O-C*H*-: IBMA, -CO-O-C$H_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C$H_2$-O-CO-), 3.83 (br, 25.5H, -CO-O-$CH_2$-C$H_2$-OH: HEMA), 3.45 (br, 41.4H, -CO-N-C$H_2$-), 2.51–0.47 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 104500 g/mol; $M_w/M_n$ = 1.54. The average incorporation number of $\mathbf{B_{COOH}}$ per chain was

calculated to be 8.6 by consumption rate (30.9%) of hydroxyethyl group (-CO-O-$CH_2$-C*H*$_2$-OH: HEMA) referring to **P3[–B*–]**. Poly[(IBMA$_{121.3}$-*co*-HEMA$_{9.7}$-*co*-**B**$_{4.3}$)-*block*-(IBMA$_{134.5}$-*co*-**B***$_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-HEMA$_{9.7}$-*co*-**B**$_{4.3}$)].

**P3[BB*B]c.** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B_{COOH}}$ (2.0 $\mu$mol, 1.2 mg) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (13 $\mu$mol, 2.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P3[–B*–]** (0.098 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at room temperature for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P3[BB*B]c** (10.0 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.42–7.54 (br, 29.9H, aromatic: BTA, -C=C*H*-N-), 7.17–6.35 (br, 20.0H, amide: BTA), 5.12 (br, 7.4H, -O-C*H*$_2$-C=C-), 4.64–3.96 (m, 244.7H, -CO-O-C*H*-: IBMA, -CO-O-C*H*$_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C*H*$_2$-O-CO-), 3.83 (br, 23.2H, -CO-O-$CH_2$-C*H*$_2$-OH: HEMA), 3.45 (br, 46.4H, -CO-N-C*H*$_2$-), 2.51–0.47 (m, -C*H*$_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 105900 g/mol; $M_w/M_n$ = 1.51. The average incorporation number of $\mathbf{B_{COOH}}$ per chain was calculated to be 10.4 by consumption rate (37.1%) of hydroxyethyl group (-CO-O-$CH_2$-C*H*$_2$-OH: HEMA) referring to **P3[–B*–]**. Poly[(IBMA$_{121.3}$-*co*-HEMA$_{8.8}$-*co*-**B**$_{5.2}$)-*block*-(IBMA$_{134.5}$-*co*-**B***$_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-HEMA$_{8.8}$-*co*-**B**$_{5.2}$)].

**P3[BB*B]d.** To a dry $CH_2Cl_2$ solution (0.5 mL) of $\mathbf{B_{COOH}}$ (2.9 $\mu$mol, 1.8 mg) and DPTS (3.4 $\mu$mol, 1.0 mg) was successively added DIPC (13 $\mu$mol, 2.0 $\mu$L, excess amount), and the mixture was stirred at room temperature under Ar until all the reagents were dissolved. **P3[–B*–]** (0.098 $\mu$mol, 10 mg) was added to the resulting solution, and the mixture was stirred at room temperature for 12 hours under Ar. The reaction mixture was poured into methanol (20 mL), and the precipitate formed was collected by centrifugation (2000 rpm, 30 min) and decantation. The product was dissolved in THF (1 mL) again and precipitated in methanol (20 mL) at room temperature. This reprecipitation procedure was repeated three times. The precipitate collected by the centrifugation and decantation was then dried at room temperature under a reduced pressure to give **P3[BB*B]d** (11.2 mg) as a white powder. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ (ppm) 8.41–7.56 (br, 46.4H, aromatic: BTA, -C=C*H*-N-), 7.15–6.39 (br, 43.8H, amide: BTA), 5.12 (br, 7.4H, -O-C*H*$_2$-C=C-), 4.64–3.96 (m, 244.7H, -CO-O-C*H*-: IBMA, -CO-O-C*H*$_2$-$CH_2$-O-CO-, and -CO-O-$CH_2$-C*H*$_2$-O-CO-), 3.83 (br, 10.4H, -CO-O-$CH_2$-C*H*$_2$-OH: HEMA), 3.45 (br, 71.5H, -CO-N-

C$H_2$-), 2.51–0.47 (m, -C$H_2$-CO-O-, aliphatic). SEC analysis (THF, polystyrene standards): $M_n$ = 110300 g/mol; $M_w/M_n$ = 1.55. The average incorporation number of $\mathbf{B_{COOH}}$ per chain was calculated to be 20.1 by consumption rate (71.9%) of hydroxyethyl group (-CO-O-$CH_2$-C$H_2$-OH: HEMA) referring to **P3[–B*–]**. Poly[(IBMA$_{121.3}$-*co*-HEMA$_{3.9}$-*co*-$\mathbf{B}_{10.1}$)-*block*-(IBMA$_{134.5}$-*co*-$\mathbf{B^*}_{16.6}$)-*block*-(IBMA$_{121.3}$-*co*-HEMA$_{3.9}$-*co*-$\mathbf{B}_{10.1}$)].

**Table S1. Data for Triblock Copolymers.**

| Polymer | $\boldsymbol{n}_{\mathbf{BTA}}$ in each [A–B–A] block[1] | Total $\boldsymbol{n}_{\mathbf{BTA}}$/chain | $f_{\mathbf{B^*}}$[2] | $M_n$ g/mol ($Đ$)[3] |
|---|---|---|---|---|
| **P1[BB*B]** | $[3.2_{\mathbf{B}} – 3.8_{\mathbf{B^*}} – 3.2_{\mathbf{B}}]$ | 10.2 | 37% | 31000 (1.20) |
| **P2[BB*B]** | $[5.7_{\mathbf{B}} – 6.3_{\mathbf{B^*}} – 5.7_{\mathbf{B}}]$ | 17.7 | 36% | 53000 (1.42) |
| **P3[BB*B]** | $[14.0_{\mathbf{B}} – 16.6_{\mathbf{B^*}} – 14.0_{\mathbf{B}}]$ | 44.6 | 37% | 120800 (1.56) |
| **P1[B*B*B*]** | $[3.2_{\mathbf{B^*}} – 3.8_{\mathbf{B^*}} – 3.2_{\mathbf{B^*}}]$ | 10.2 | 100% | 32500 (1.19) |
| **P2[B*B*B*]** | $[5.7_{\mathbf{B^*}} – 6.3_{\mathbf{B^*}} – 5.7_{\mathbf{B^*}}]$ | 17.7 | 100% | 54800 (1.43) |
| **P3[B*B*B*]** | $[14.0_{\mathbf{B^*}} – 16.6_{\mathbf{B^*}} – 14.0_{\mathbf{B^*}}]$ | 44.6 | 100% | 119800 (1.70) |

[1] Number of BTA groups. [2] Sergeant fraction. [3] $M_w/M_n$.

**Table S2. Data for P3[BB*B] Polymers with Various Numbers of B.**

| Polymer | $\boldsymbol{n}_{\mathbf{BTA}}$ in each [A–B–A] block[1] | Total $\boldsymbol{n}_{\mathbf{BTA}}$/chain | $f_{\mathbf{B^*}}$[2] | $M_n$ g/mol ($Đ$)[3] |
|---|---|---|---|---|
| **P3[–B*–]** | $[0 – 16.6_{\mathbf{B^*}} – 0]$ | 16.6 | 100% | 102000 (1.48) |
| **P3[BB*B]a** | $[3.2_{\mathbf{B}} – 16.6_{\mathbf{B^*}} – 3.2_{\mathbf{B}}]$ | 23.0 | 72% | 103000 (1.53) |
| **P3[BB*B]b** | $[4.3_{\mathbf{B}} – 16.6_{\mathbf{B^*}} – 4.3_{\mathbf{B}}]$ | 25.2 | 66% | 104500 (1.54) |
| **P3[BB*B]c** | $[5.2_{\mathbf{B}} – 16.6_{\mathbf{B^*}} – 5.2_{\mathbf{B}}]$ | 27.0 | 62% | 105900 (1.51) |
| **P3[BB*B]d** | $[10.1_{\mathbf{B}} – 16.6_{\mathbf{B^*}} – 10.1_{\mathbf{B}}]$ | 36.7 | 45% | 110300 (1.55) |
| **P3[BB*B]** | $[14.0_{\mathbf{B}} – 16.6_{\mathbf{B^*}} – 14.0_{\mathbf{B}}]$ | 44.6 | 37% | 120800 (1.56) |

[1] Number of BTA groups. [2] Sergeant fraction. [3] $M_w/M_n$.

## Supplementary Figures

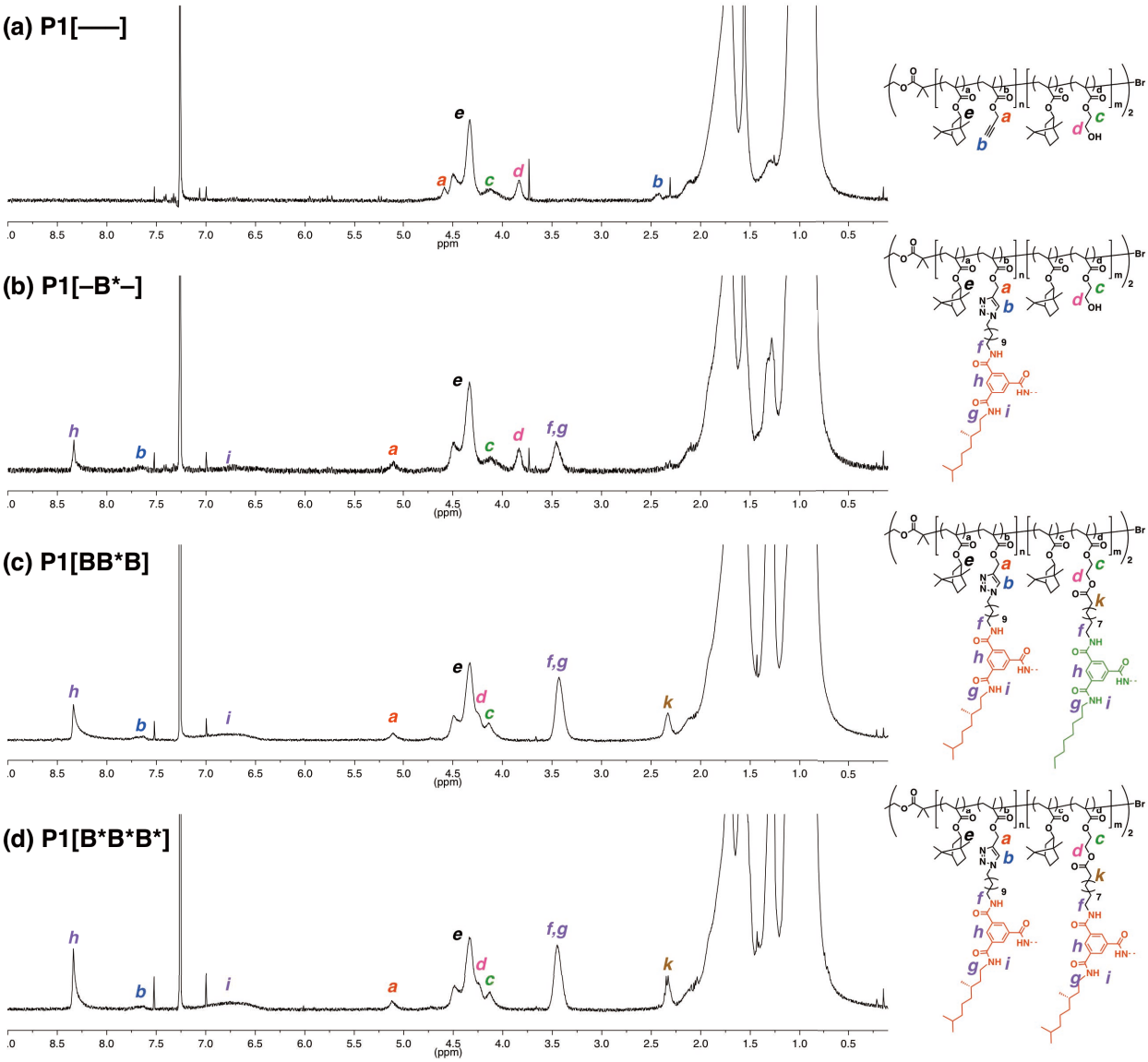



**Figure S1.** NMR Spectra of (a) **P1[——]**, (b) **P1[–B*–]**, (c) **P1[BB*B]**, and (d) **P1[B*B*B*]** in Chloroform-d at room temperature.

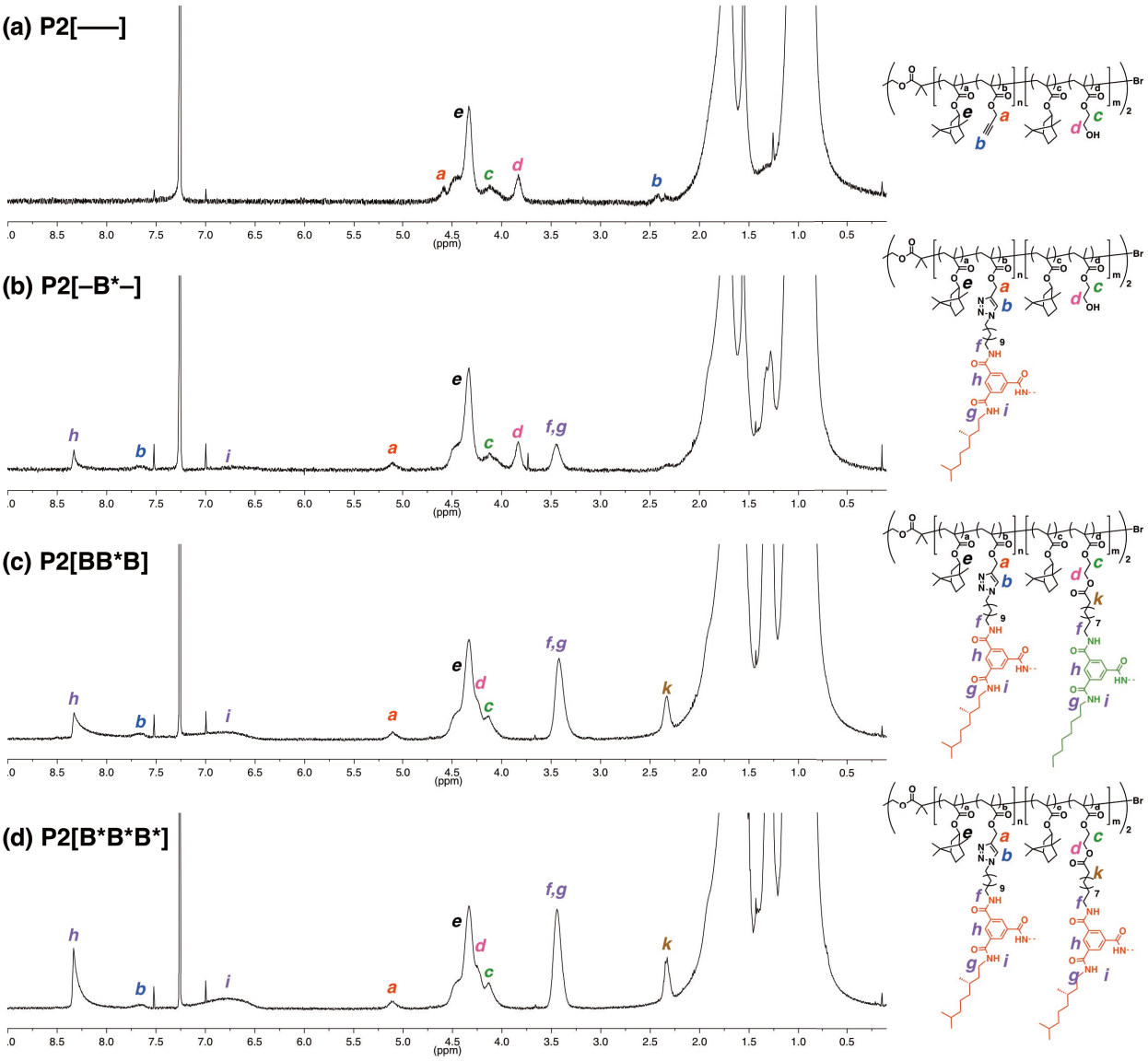



**Figure S2.** NMR Spectra of (a) **P2[——]**, (b) **P2[–B*–]**, (c) **P2[BB*B]**, and (d) **P2[B*B*B*]** in Chloroform-d at room temperature.

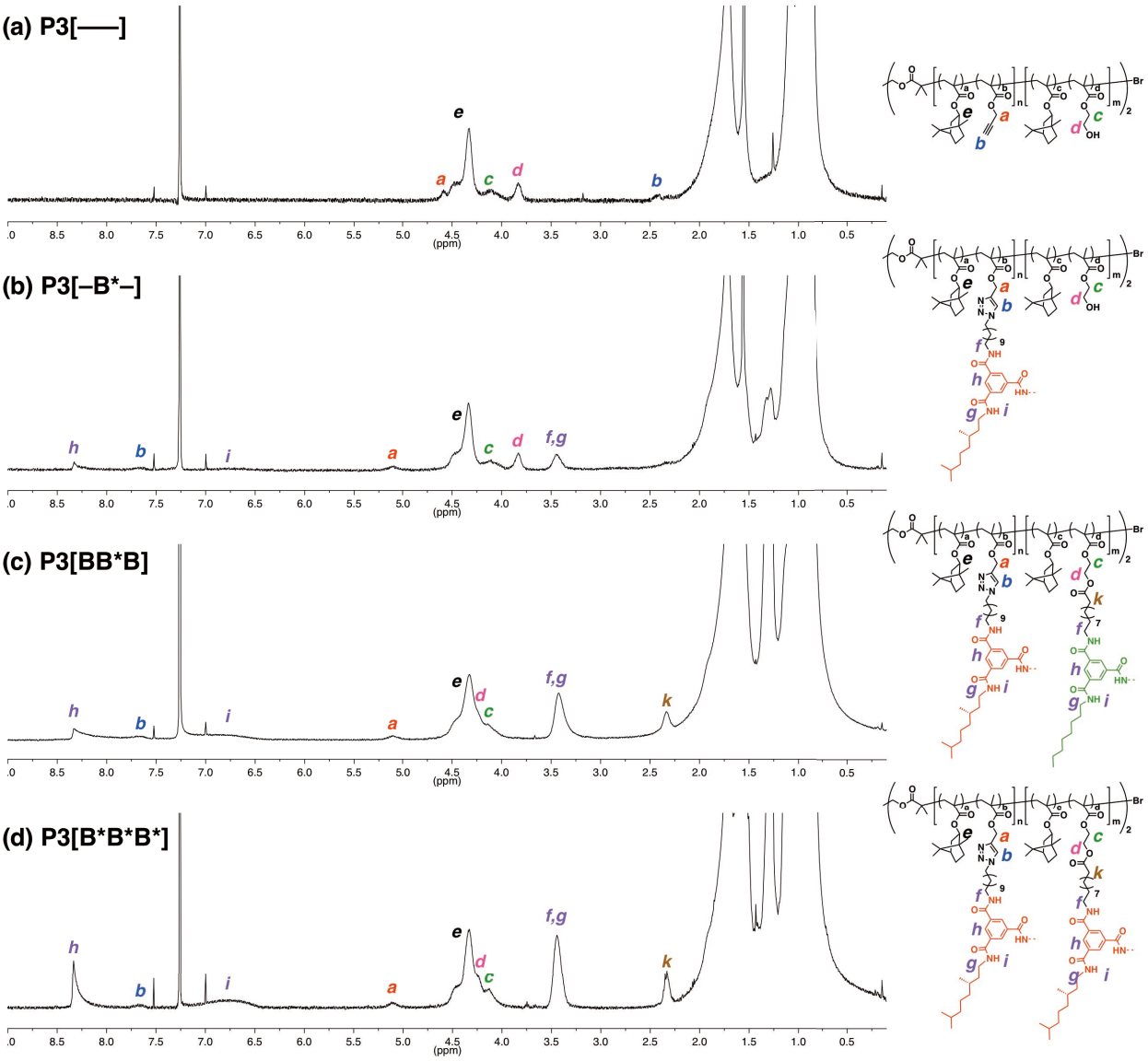



**Figure S3.** NMR Spectra of (a) **P3[——]**, (b) **P3[–B*–]**, (c) **P3[BB*B]**, and (d) **P3[B*B*B*]** in Chloroform-d at room temperature.

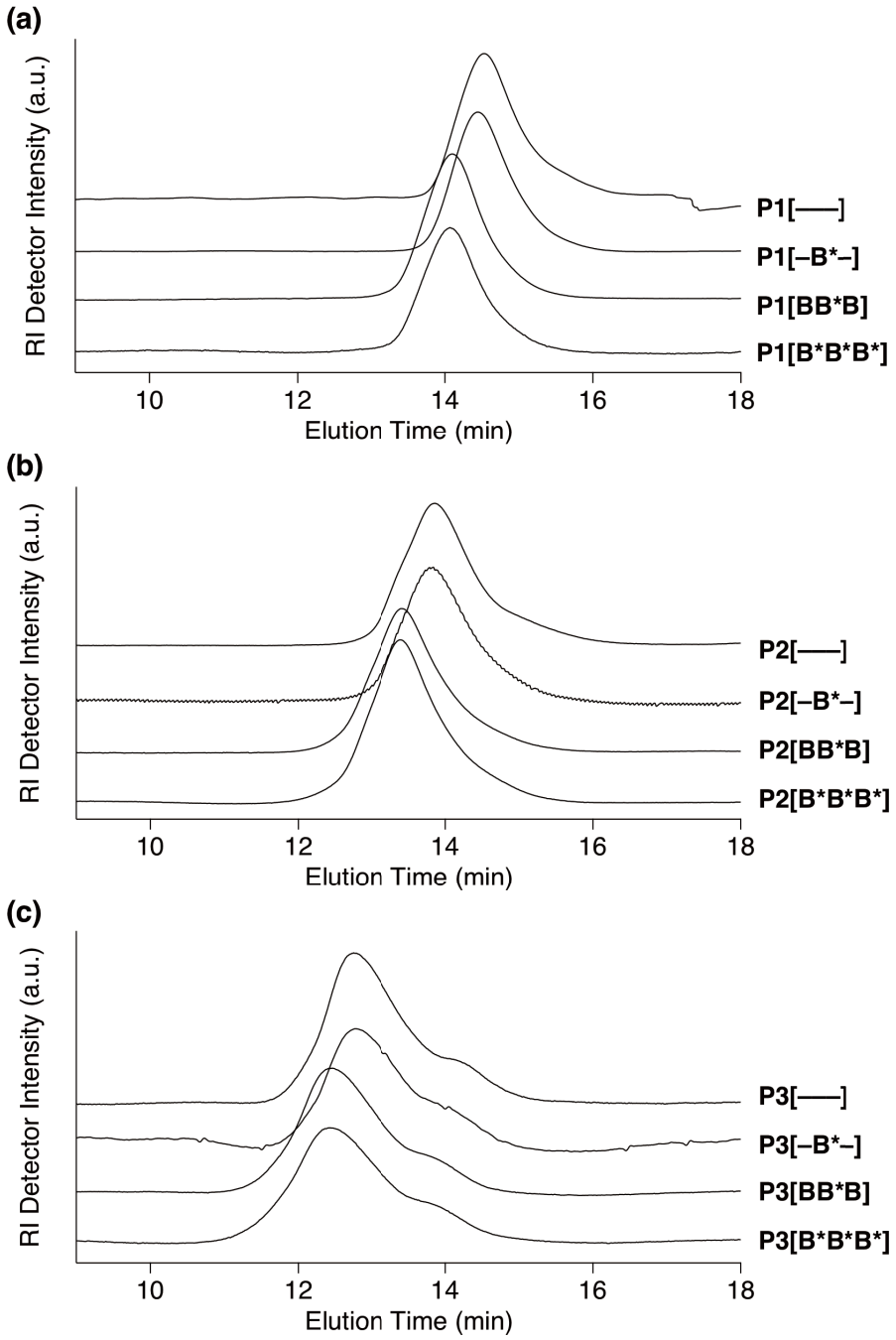



**Figure S4.** SEC traces of (a) **P1**, (b) **P2**, and (c) **P3** series of polymers (eluent: THF, 1 mL/min).

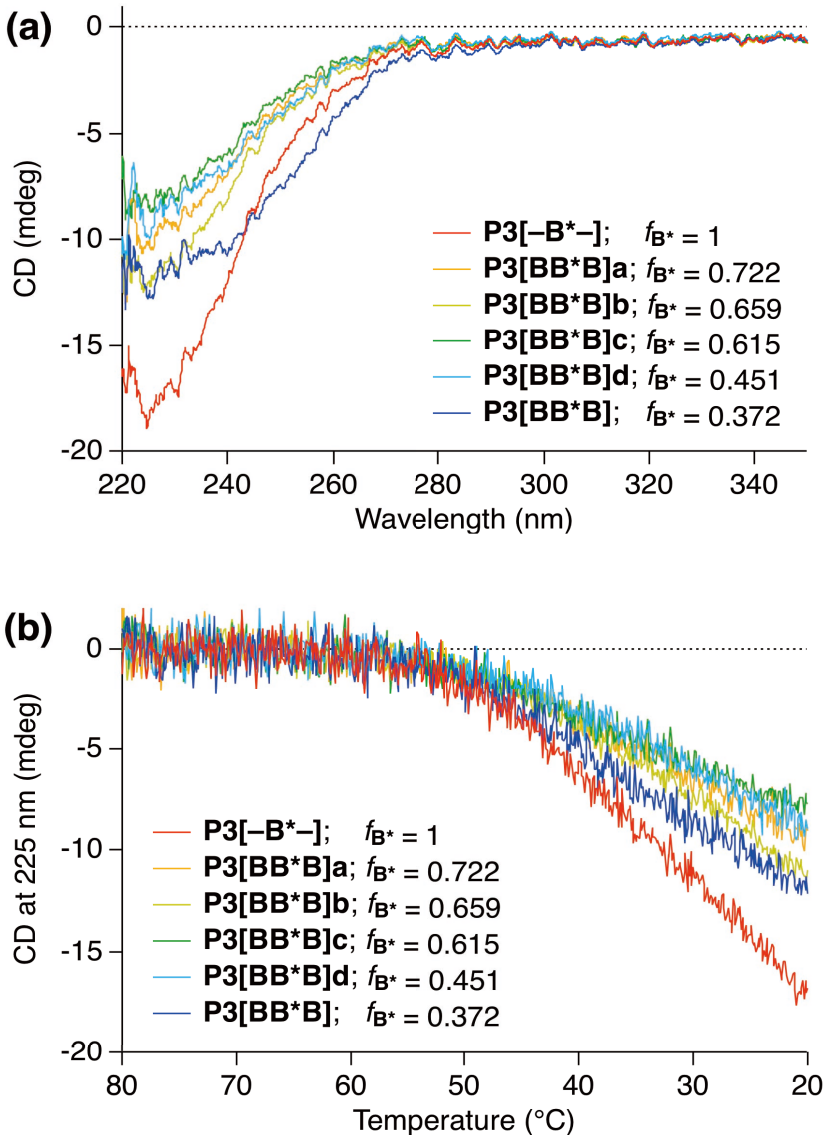



**Figure S5.** (a) CD spectra and (b) cooling curves for **P3[BB*B]** polymers with various $f_{B*}$ ($c_{BTA}$ = 50 $\mu$M in 1,2-DCE; cooling rate: –1 °C/min).

**Supporting References**


(S1) J. S. Moore, S. I. Stupp, *Macromolecules*, 1990, **23**, 65.

(S2) N. Hosono, M. A. J. Gillissen, Y. Li, S. S. Sheiko, A. R. A. Palmans, E. W. Meijer, *J. Am. Chem. Soc.*, 2013, **135**, 501.

(S3) N. Hosono, P. J. M. Stals, A. R. A. Palmans, E. W. Meijer, *Chem. Asian J.*, 2014, **9**, 1099.

(S4) T. Terashima, T. Mes, T. F. A. de Greef, M. A. J. Gillissen, P. Besenius, A. R. A. Palmans, E. W. Meijer, *J. Am. Chem. Soc.*, 2011, **133**, 4742.