

## Supplementary Information

### Self-assembly of amphiphilic block pendant polymers as microphase separation materials and folded flower micelles

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## Experimental Section

### Materials.

Poly(ethylene glycol) methyl ether methacrylate [PEGMA:  $\text{CH}_2=\text{CMeCO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{Me}$ ,  $M_n = 475$ ,  $n = 8.5$  on average] (Aldrich) and dodecyl methacrylate (DMA, Wako, purity >95%) were purified by inhibitor removal column (Aldrich) and were degassed by triple vacuum-argon purge cycles before use. Block monomers (DPEG10MA, DPEG23MA) were synthesized as shown below. Ethyl 2-chloro-2-phenylacetate (ECPA, Aldrich, purity >97%) and methacryloyl chloride (TCI, purity >90%) were distilled under reduced pressure before use.  $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$  ( $\text{Cp}^*$ : pentamethylcyclopentadieny, Aldrich) was used as received and handled in a glove box under moisture- and oxygen-free argon ( $\text{H}_2\text{O} < 1$  ppm;  $\text{O}_2 < 1$  ppm). Tetralin (1,2,3,4-tetrahydronaphthalene, TCI, purity >97%, an internal standard for  $^1\text{H}$  NMR analysis) was dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use. 4-Dimethylamino-1-butanol (4-DMAB, TCI, purity >98%), decaethylene glycol mono-dodecyl ether (DPEG10OH, Aldrich), polyoxyethylene(23) lauryl ether (Brij 35, DPEG23OH, Wako), triethylamine (Wako, purity >99%), and dichloromethane (Wako, dehydrated) were degassed before use. Toluene was purified before use by passing it through a purification column (Glass Contour Solvent Systems, Nikko Hansen & Co., Ltd).

### Characterization.

Molecular weight distribution (MWD) curves, number-average molecular weight ( $M_n$ ), peak top molecular weight ( $M_p$ ), and  $M_w/M_n$  ratio of the polymers were measured by SEC in DMF containing 10 mM LiBr at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L, exclusion limit =  $4 \times 10^6$ , particle size = 10  $\mu\text{m}$ , pore size = 5000 Å, 0.8 cm i.d.  $\times$  30 cm) that were connected to a Jasco PU-2080 precision pump, a Jasco RI-2031 refractive index detector, and a Jasco UV-2075 UV/vis detector set at 270 nm. The columns were calibrated against 10 standard poly(MMA) samples (Polymer Laboratories,  $M_p = 2680\text{--}1250000$ ,  $M_w/M_n = 1.02\text{--}1.09$ ) or 14 standard poly(ethylene oxide) samples (Polymer Laboratories,  $M_p = 1470\text{--}863500$ ,  $M_w/M_n = 1.02\text{--}1.16$ ). MWD curves,  $M_n$ ,  $M_p$ , and  $M_w/M_n$  of the polymers were also measured by SEC (Shodex GPC-104) in THF at 40 °C (flow rate: 0.3 mL/min). In the SEC system, three linear-type polystyrene gel columns (Shodex LF-404: exclusion limit =  $2 \times 10^6$ ; particle size = 6  $\mu\text{m}$ ; pore size = 3000 Å; 0.46 cm i.d.  $\times$  25 cm) were connected to a DU-2000 pump, a RI-74 refractive index detector, and a UV-41 ultraviolet detector set at 250 nm (all from Shodex). The columns were calibrated against 12 standard poly(MMA) samples (Polymer Laboratories:  $M_p = 625\text{--}1250000$ ;  $M_w/M_n = 1.02\text{--}1.30$ ). MWD curves,  $M_n$ ,  $M_p$ , and  $M_w/M_n$  of the polymers were also measured by

SEC in H<sub>2</sub>O at 30 °C (flow rate: 1 mL/min) on a silica gel column (TOSOH G4000SW<sub>XL</sub>, exclusion limit =  $7 \times 10^6$ , particle size = 8  $\mu\text{m}$ , 0.78 cm i.d.  $\times$  30 cm) that was connected to the same pump and detectors as those used in DMF. The column was calibrated against 11 standard poly(ethylene oxide) samples (Polymer Laboratories,  $M_p = 1470\text{--}298000$ ,  $M_w/M_n = 1.03\text{--}1.07$ ). To remove residual monomers and catalysts, polymer samples were purified by preparative SEC (column: TOSOH TSKgel  $\alpha$ -3000, exclusion limit =  $9 \times 10^4$ , particle size = 13  $\mu\text{m}$ , 5.5 cm i.d.  $\times$  30 cm) in DMF with a Jasco PU-2086 precision pump, a Jasco RI-2031 refractive index detector, and a Jasco UV-2075 UV/vis detector set at 270 nm. The purified polymers were employed for characterization. <sup>1</sup>H nuclear magnetic resonance (NMR) spectra were recorded in acetone-*d*<sub>6</sub> and CDCl<sub>3</sub> at 25 °C on a JEOL JNM-ECA500 spectrometer, operating at 500.16 (<sup>1</sup>H) MHz.

Aqueous solutions of polymers utilized for SEC and light scattering were prepared as follows: bulk polymers were mixed with water, and the aqueous solutions were sonicated for several minutes and filtrated with PTFE membrane filter (0.45  $\mu\text{m}$  pore, Merck Millipore) before analysis. Absolute weight-average molecular weight ( $M_w$ ) of polymers in DMF or H<sub>2</sub>O was determined by multi-angle laser light scattering (MALLS) equipped with SEC on a Dawn HELEOS II instrument (Wyatt Technology, semiconductor laser,  $\lambda = 663$  nm). The SEC was performed in DMF containing 10 mM LiBr at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L) or in H<sub>2</sub>O at 30 °C (flow rate: 1 mL/min) on a silica gel column (TOSOH G4000SW<sub>XL</sub>). These columns were connected to a Jasco PU-2080 precision pump, a Jasco RI-1530 refractive index detector, and a Jasco UV-1570 UV/vis detector set at 270 nm. Refractive index ( $dn/dc$ ) of the samples in DMF or H<sub>2</sub>O was directly determined by the on-line RI detector that was equipped in the SEC-MALLS instrument.

Cloud point of the aqueous solutions of copolymers was measured on UV-1800 (Shimadzu, optical path length = 1.0 cm,  $\lambda = 670$  nm, heating/cooling rate: 1 °C/min, temperature range: 20 – 80 °C).

Differential scanning calorimetry (DSC) was performed for polymer samples (ca. 1 – 4 mg in an aluminum pan) under dry nitrogen flow on a DSCQ200 calorimeter (TA Instruments) equipped with a RCS 90 electric freezing machine. The heating and cooling rates were performed at 10 °C/min and -10 °C/min, respectively, between -80 °C and 150 °C. The first cooling and second heating scans were employed as data in this work.

Small angle X-ray scattering (SAXS) measurements were performed at RIKEN beamline BL45XU of SPring-8, Japan. The X-ray wavelength, sample to detector distance, and the detector used at BL45XU were 0.1 nm, 2500 nm, and PILATUS 3X 2M, respectively. The obtained 2-dimensional data were circularly averaged and corrected for background of cell and electronic noise of detector.

## Monomer Synthesis.

**Poly(ethylene glycol)(10) dodecyl ether methacrylate (DPEG10MA).** In a 300 mL round-bottomed flask filled with argon, methacryloyl chloride (22 mmol, 2.1 mL) was added to the solution of decaethylene glycol mono-dodecyl ether (DPEG10OH, 14 mmol, 9.0 g) and triethylamine (29 mmol, 4.0 mL) in dry dichloromethane (100 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 22 h. Into the mixture, methanol (35 mL) was added to quench the reaction. After 6 h, the mixture was evaporated. Into the crude product, dichloromethane (60 mL) was added. The solution was washed with diluted HCl aqueous solution and a saturated solution of NaHCO<sub>3</sub>. The aqueous phase was separated and extracted by dichloromethane, and the dichloromethane extracts were combined with the organic layer. The combined organic phase was washed sequentially with brine and dried with NaSO<sub>4</sub>. After the dichloromethane was removed in vacuo, the product was purified by silica gel column chromatography with dichloromethane/methanol (10/0 – 9/1, v/v) as an eluent to give DPEG10MA (8.5 g, 85% yield). <sup>1</sup>H NMR [500 MHz, CDCl<sub>3</sub>, 25 °C, δ = 7.26 (CHCl<sub>3</sub>)]: δ 6.13 (s, 1H, CH<sub>2</sub>=), 5.57 (s, 1H, CH<sub>2</sub>=), 4.30 (t, 2H, *J* = 4.8 Hz, COOCH<sub>2</sub>-), 3.76 – 3.41 (40H, -CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>9</sub>CH<sub>2</sub>-), 1.94 (s, 3H, CH<sub>2</sub>=C(CH<sub>3</sub>)COO-), 1.57 (quin, 2H, *J* = 7.3 Hz), 1.34 – 1.21 (br, 18H), 0.88 (t, 3H, *J* = 6.8 Hz). <sup>13</sup>C NMR [125 MHz, CDCl<sub>3</sub>, 25 °C, δ = 77.16 (chloroform)]: δ 167.2, 136.1, 125.6, 71.4, 70.5, 69.9, 69.0, 63.7, 31.8, 29.5, 29.4, 29.2, 26.0, 22.6, 18.2, 14.0.

**Poly(ethylene glycol)(23) dodecyl ether methacrylate (DPEG23MA).** In a 300 mL round-bottomed flask filled with argon, methacryloyl chloride (12 mmol, 1.2 mL) was added to the solution of polyoxyethylene(23) lauryl ether (DPEG23OH, 7.9 mmol, 9.5 g) and triethylamine (16 mmol, 2.2 mL) in dry dichloromethane (100 mL) at 0 °C. The reaction mixture was stirred at 25 °C overnight. Into the mixture, methanol (0.5 mL) was added to quench the reaction. The organic solution was washed with diluted HCl aqueous solution (twice) and brine, and dried with NaSO<sub>4</sub>. After the dichloromethane was removed in vacuo, the solid product (DPEG23MA) was obtained (4.8 g, 53% yield). <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C, δ = 2.04 (acetone)]: δ 6.07 (m, 1H, CH<sub>2</sub>=), 5.63 (m, 1H, CH<sub>2</sub>=), 4.25 (m 2H, COOCH<sub>2</sub>-), 3.73 – 3.40 (92H, -CH<sub>2</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>22</sub>CH<sub>2</sub>-), 1.91 (m, 3H, CH<sub>2</sub>=C(CH<sub>3</sub>)COO-), 1.53 (quin, 2H, *J* = 6.8 Hz), 1.37 – 1.22 (br, 18H), 0.87 (t, 3H, *J* = 7.0 Hz). <sup>13</sup>C NMR [125 MHz, CDCl<sub>3</sub>, 25 °C, δ = 77.16 (chloroform)]: δ 167.3, 136.2, 125.7, 71.6, 70.6, 70.1, 69.2, 63.9, 31.9, 29.6, 29.5, 29.4, 26.1, 22.7, 18.3, 14.1.

## Polymer Synthesis.

The synthesis of amphiphilic block pendant (co)polymers (**P1-P11**) was carried out by syringe technique under argon in glass flasks or tubes equipped with a three-way stopcock.

**DPEG23MA homopolymer (P1):** In 30 mL glass tube, RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.013 mmol, 10.4 mg) was dissolved with ethanol (2.6 mL) to prepare a stock solution of the ruthenium catalyst ([Ru] = 5 mM in ethanol). Into another 30 mL glass tube, DPEG23MA (633 mg, 0.50 mmol) was placed under air and purged by argon. Into this tube, ethanol (1.1 mL), tetralin (0.04 mL), a 500 mM ethanol solution of 4-DMAB (0.04 mL, 4-DMAB = 0.02 mmol), the 5 mM stock ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.2 mL, Ru = 0.001 mmol), and a 30.4 mM ethanol solution of ECPA (0.13 mL, ECPA = 0.004 mmol) were added at 25 °C under argon (the total volume: 2.1 mL). The flask was placed in an oil bath kept at 40 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to -78°C. The monomer conversion was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. = 84% at 23 h. The crude product was dried under vacuum at room temperature and purified by preparative SEC in DMF to give **P1**. SEC (DMF, PMMA std.):  $M_n = 53900$ ,  $M_w/M_n = 1.18$ . <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C,  $\delta = 2.04$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-).  $M_n = (\text{NMR}, \alpha) = 137000$ .

**PEGMA/DPEG23MA random copolymer (P2):** In 30 mL glass tube, a 278 mM ethanol solution of DPEG23MA (1.8 mL, 0.50 mmol), PEGMA (0.22 mL, 0.50 mmol), tetralin (0.05 mL), a 500 mM ethanol solution of 4-DMAB (0.05 mL, 4-DMAB = 0.025 mmol), a 10.5 mM ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.12 mL, Ru = 0.0013 mmol), and a 30.4 mM ethanol solution of ECPA (0.26 mL, ECPA = 0.008 mmol) were added at 25 °C under argon (the total volume: 2.5 mL). The flask was placed in an oil bath kept at 40 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to -78°C. The monomer conversion was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Total Conv. = 86% at 24 h. The crude product was dried under vacuum at room temperature and purified by preparative SEC in DMF to give **P2**. SEC (DMF, PMMA std.):  $M_n = 51900$ ,  $M_w/M_n = 1.33$ . <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C,  $\delta = 2.04$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.0 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 3.4–3.3 (-OCH<sub>3</sub>), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). PEGMA/DPEG23MA = 53/56,  $M_n = (\text{NMR}, \alpha) = 96400$ .

**DMA/DPEG23MA random copolymer (P3):** In 30 mL glass tube, a 278 mM ethanol solution of DPEG23MA (1.9 mL, 0.52 mmol), DMA (0.15 mL, 0.52 mmol), tetralin (0.054 mL), a 500 mM ethanol solution of 4-DMAB (0.054 mL, 4-DMAB = 0.027 mmol), a 10.5 mM ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.12 mL, Ru = 0.0013 mmol), and a 30.4 mM ethanol solution of ECPA (0.27 mL, ECPA = 0.0082 mmol) were added at 25 °C under argon (the total volume: 2.5 mL). The flask was placed in an oil bath kept at 40 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to -78°C. The monomer conversion was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. (DMA/DPEG23MA) = 88%/78% at 24 h. The crude product was dried under vacuum at room temperature and purified by preparative SEC in DMF to give **P3**. SEC (DMF, PMMA std.):  $M_n = 57300$ ,  $M_w/M_n = 1.31$ . <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C,  $\delta = 2.04$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.0 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 4.0–3.9 (-COOCH<sub>2</sub>CH<sub>2</sub>-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.7–1.6 (-COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). DMA/DPEG23MA = 53/51,  $M_n$  (NMR,  $\alpha$ ) = 78300.

**DPEG10MA homopolymer (P4):** In 30 mL glass tube, a 705 mM ethanol solution of DPEG10MA (1.42 mL, 1.0 mmol), ethanol (0.20 mL), tetralin (0.04 mL), a 500 mM ethanol solution of 4-DMAB (0.04 mL, 4-DMAB = 0.02 mmol), a 5 mM ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.20 mL, Ru = 0.001 mmol), and a 42.5 mM ethanol solution of ECPA (0.094 mL, ECPA = 0.004 mmol) were added at 25 °C under argon (the total volume: 2.0 mL). The flask was placed in an oil bath kept at 40 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to -78°C. The monomer conversion was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. = 77% at 26 h. The crude product was dried under vacuum at room temperature and purified by preparative SEC to give **P4**. SEC (THF, PMMA std.):  $M_n = 62400$ ,  $M_w/M_n = 1.31$ . <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C,  $\delta = 2.04$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-).  $M_n$  (NMR,  $\alpha$ ) = 144000.

**PEGMA/DPEG10MA random copolymer (P5):** In 30 mL glass tube, a 680 mM ethanol solution of DPEG10MA (0.91 mL, 0.61 mmol), PEGMA (0.41 mL, 0.93 mmol), ethanol (1.07 mL), tetralin (0.06 mL), a 500 mM ethanol solution of 4-DMAB (0.06 mL, 4-DMAB = 0.030 mmol), a 7.5 mM ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.20 mL, Ru = 0.0015 mmol), and a 42.5 mM ethanol solution of ECPA (0.29 mL, ECPA = 0.012 mmol) were added at 25 °C under argon (the total volume: 3.0 mL). The flask was placed in an oil bath kept at 40 °C. At predetermined intervals, the

mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to  $-78^{\circ}\text{C}$ . The monomer conversion was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Total Conv. = 81% at 40 h. The crude product was dried under vacuum at room temperature and purified by preparative SEC in DMF to give **P5**. SEC (DMF, PMMA std.):  $M_n = 31400$ ,  $M_w/M_n = 1.16$ .  $^1\text{H}$  NMR [500 MHz, acetone- $d_6$ ,  $25^{\circ}\text{C}$ ,  $\delta = 2.1$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 3.4–3.3 (-OCH<sub>3</sub>), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). PEGMA/DPEG10MA = 67/45,  $M_n = (\text{NMR}, \alpha) = 67000$ .  $dn/dc = 0.048$  (DMF), 0.122 (H<sub>2</sub>O).

**PEGMA/DPEG10MA random copolymer (P9)**: In 30 mL glass tube, a 680 mM ethanol solution of DPEG10MA (1.10 mL, 0.75 mmol), PEGMA (0.33 mL, 0.75 mmol), ethanol (0.97 mL), tetralin (0.06 mL), a 500 mM ethanol solution of 4-DMAB (0.06 mL, 4-DMAB = 0.030 mmol), a 7.5 mM ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.20 mL, Ru = 0.0015 mmol), and a 42.5 mM ethanol solution of ECPA (0.28 mL, ECPA = 0.012 mmol) were added at  $25^{\circ}\text{C}$  under argon (the total volume: 3.0 mL). The flask was placed in an oil bath kept at  $40^{\circ}\text{C}$ . At predetermined intervals, the mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to  $-78^{\circ}\text{C}$ . The monomer conversion was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Total Conv. = 83% at 40 h. The crude product was dried under vacuum at room temperature and purified by preparative SEC in DMF to give **P9**. SEC (DMF, PMMA std.):  $M_n = 29700$ ,  $M_w/M_n = 1.16$ .  $^1\text{H}$  NMR [500 MHz, acetone- $d_6$ ,  $25^{\circ}\text{C}$ ,  $\delta = 2.1$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 3.4–3.3 (-OCH<sub>3</sub>), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). PEGMA/DPEG10MA = 60/59,  $M_n = (\text{NMR}, \alpha) = 70100$ .  $dn/dc = 0.047$  (DMF), 0.112 (H<sub>2</sub>O). **P6-P8** and **P10** were similarly prepared. **P6**:  $dn/dc = 0.047$  (DMF), 0.114 (H<sub>2</sub>O). **P7**:  $dn/dc = 0.047$  (DMF), 0.103 (H<sub>2</sub>O). **P8**:  $dn/dc = 0.046$  (DMF), 0.114 (H<sub>2</sub>O). **P10**:  $dn/dc = 0.047$  (DMF), 0.129 (H<sub>2</sub>O).

**PEGMA/DPEG10MA random copolymer (P11)**: In 30 mL glass tube, a 680 mM ethanol solution of DPEG10MA (1.10 mL, 0.75 mmol), PEGMA (0.22 mL, 0.50 mmol), ethanol (0.64 mL), tetralin (0.05 mL), a 500 mM ethanol solution of 4-DMAB (0.05 mL, 4-DMAB = 0.025 mmol), a 6.3 mM ethanol solution of RuCp\*Cl(PPh<sub>3</sub>)<sub>2</sub> (0.20 mL, Ru = 0.0013 mmol), and a 42.5 mM ethanol solution of ECPA (0.24 mL, ECPA = 0.010 mmol) were added at  $25^{\circ}\text{C}$  under argon (the total volume: 2.5 mL). The flask was placed in an oil bath kept at  $40^{\circ}\text{C}$ . At predetermined intervals, the mixture was sampled with a syringe under dry argon, and the reaction was terminated by cooling the solution to  $-78^{\circ}\text{C}$ . The monomer conversion was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Total Conv. = 80% at 41 h. The crude product was dried under vacuum at

room temperature and purified by preparative SEC in DMF to give **P11**. SEC (DMF, PMMA std.):  $M_n = 25500$ ,  $M_w/M_n = 1.18$ .  $^1\text{H NMR}$  [500 MHz, acetone- $d_6$ , 25 °C,  $\delta = 2.1$  (acetone)]:  $\delta$  7.4–7.2 (aromatic), 4.2–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>-), 3.4–3.3 (-OCH<sub>3</sub>), 2.2–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6–1.5 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4–1.2 (-OCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-O(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). PEGMA/DPEG10MA = 50/72,  $M_n = (\text{NMR}, \alpha) = 74400$ .  $dn/dc = 0.046$  (DMF), 0.121 (H<sub>2</sub>O).

## Supporting Data

**Table S1. Thermal Properties of Block Pendant Polymers and Monomers<sup>a</sup>**

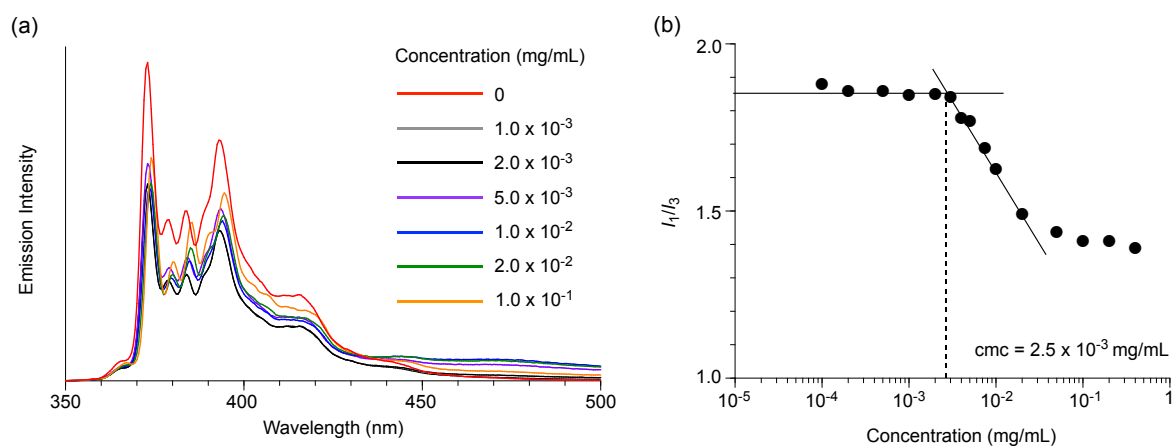
entry	sample	$T_c$ (°C)	$T_m$ (°C)	enthalpy of melting (J/g)
1	DPEG23OH	12.9	39.8	164
2	DPEG23MA	11.4	32.7	107
3	PDPEG23MA ( <b>P1</b> )	10.5	29.1	70.4
4	PEGMA/DPEG23MA random copolymer ( <b>P2</b> )	-12.3	17.1	44.3
5	DPEG10OH	-0.77	24.1	94.8
6	DPEG10MA	-13.2	4.60	80.4
7	PDPEG10MA ( <b>P4</b> )	-7.74	-1.88	44.3
8	PEGMA/DPEG10MA random copolymer ( <b>P9</b> )	-22.1	-8.42	16.7

<sup>a</sup> Crystallization and melting temperature of the samples ( $T_c$ ,  $T_m$ ) were determined by DSC measurement: heating/cooling rate: 10 °C/min; temperature range = -80 °C – 150 °C.  $T_c$ : determined from first cooling scan from 150 °C,  $T_m$ : determined from second heating scan from -80 °C.



## Critical micelle concentration (CMC) of an amphiphilic block pendant polymers in water

CMC of **P8** (Table 3) was determined by fluorescence spectroscopy of pyrene in the presence of the copolymers in water (Figure S1).<sup>S1</sup> Aqueous solutions of the copolymer with 15 different concentrations between  $1.0 \times 10^{-4}$  mg/mL and  $4.0 \times 10^{-1}$  mg/mL (each volume: 2 mL) were prepared in vials. Into the solutions, a DMSO solution of pyrene ( $1 \times 10^{-4}$  M, 10  $\mu$ L) was added. The resulting mixtures were sonicated for 2 min and allowed to equilibrate for 20 h at room temperature before fluorescence measurement. The final concentration of pyrene was  $5 \times 10^{-7}$  M, which is lower than the saturation concentration of pyrene in water at 25 °C.<sup>S2</sup> All steady-state fluorescence spectra were recorded on a fluorescence spectrometer, JASCO FP-8500, under the following conditions: excitation slit width = 2.5 nm, emission slit width = 1 nm, response = 0.1 sec, scanning speed = 500 nm/min, excitation wavelength = 334.0 nm, emission wavelength = 350.0 – 500.0 nm, temperature = 25 °C.  $I_1/I_3$ , the ratio between the intensities of the first ( $I_1$ , ~ 373 nm) and the third ( $I_3$ , ~ 384 nm) vibronic bands of pyrene emission, were plotted as a function of polymer concentration. CMC was determined as the concentration at which  $I_1/I_3$  started to decrease.



**Figure S1.** Determination of CMC of **P8**: (a) emission spectra of pyrene ( $5 \times 10^{-7}$  M: normalized at  $I_1$ ) with **P8** in water and (b)  $I_1/I_3$  plots as a function of the polymer concentration ( $1.0 \times 10^{-4}$  –  $4.0 \times 10^{-1}$  mg/mL).

## References

- S1) Kalyanasundaram, K.; Thomas, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 2039-2044.  
S2) Mackay, D; Shiu, W. Y. *J. Chem. Eng. Data.* **1977**, *22*, 399-402.