

Supplementary Information

Folded Amphiphilic Homopolymer Micelles in Water: Uniform Self-Assembly beyond Amphiphilic Random Copolymers

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Experimental Section

Materials

For monomer synthesis, acryloyl chloride (TCI, purity >95%), triethylamine (TCI, purity >99%), poly(ethylene glycol) methyl ether acrylate ($\text{CH}_2=\text{CHCO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{Me}$, $M_n = 480$, $n = 9$ on average, Aldrich), dodecylamine (TCI, purity >97%), *n*-octylamine (TCI, purity >98%), butylamine (TCI, purity >99%), toluene (Wako, purity >99.7%), dichloromethane (Wako, dehydrated), and aluminum oxide 90, active basic (Merck) were used as received.

For polymerization, amphiphilic monomers (C_n-PEGAAm, C4-PEGAAm, C8-PEGAAm, C12-PEGAAm) were prepared as shown below. Poly(ethylene glycol) methyl ether acrylamide (PEGAAm) and *N*-dodecylacrylamide (DAAm) were prepared according to the literature.^{S1} 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 an inhibitor removal column (Aldrich) and degassed by triple vacuum-argon purge cycles before use. Ethyl 2-iodo-2-methylpropionate (EMA-I, TCI, purity >94%) and ethyl 2-chloro-2-phenylacetate (ECPA, Aldrich, purity >97%) were distilled under reduced pressure before use. $\text{Fe}_2(\text{CO})_4\text{Cp}_2$ (Cp: cyclopentadienyl, TCI, purity >96%), $\text{Ru}(\text{Ind})\text{Cl}(\text{PPh}_3)_2$ (Ind: indenyl, Aldrich), 2,2'-azobis(isobutyronitrile) (AIBN, Wako, purity >98%), and iodine (TCI, purity >98%) were 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 >98%, an internal standard for ¹H NMR analysis) was dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use. Tributylamine (TCI, purity >99%) was degassed by triple vacuum-argon purge cycles 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), and M_w/M_n ratio of the polymers were measured by size exclusion chromatography (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 = 4×10^6 ; particle size = 10 μm; pore size = 5000 Å; 0.8 cm i.d. × 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 11 standard poly(MMA) samples (PSS, Polymer Standard Service GmbH, Ready Cal Kit: $M_p = 2380 - 2200000$) or 14 standard poly(ethylene oxide) and poly(ethylene glycol) samples (Polymer Laboratories or Agilent Technologies: $M_p = 1470 - 863500$; $M_w/M_n = 1.02 - 1.16$). MWD curves,

M_n , M_p , and M_w/M_n of the polymers were also measured by SEC in H₂O containing 100 mM NaCl at 30 °C (flow rate: 1 mL/min) on a silica gel column (Shodex PROTEIN KW-804: exclusion limit = 5×10^5 (pullulan), particle size = 7 μm ; 0.8 cm i.d. \times 30 cm or Shodex PROTEIN LW-803 exclusion limit = 1×10^6 (protein), particle size = 3 μm ; 0.8 cm i.d. \times 30 cm) that was connected to the same pump and detectors as those used in DMF (UV/vis detector set at 345 nm). Both columns were calibrated against 11 standard poly(ethylene oxide) and poly(ethylene glycol) samples (Polymer Laboratories or Agilent Technologies: $M_p = 1470 - 298000$; $M_w/M_n = 1.03 - 1.07$). Before characterization, polymer samples were purified or fractionated by preparative SEC in DMF at 25 °C (flow rate: 15 mL/min) on TOSOH TSKgel α -3000 (exclusion limit = 1×10^5 ; particle size = 13 μm ; 5.5 cm i.d. \times 30 cm). ¹H NMR spectra were recorded in CDCl₃ on a JEOL JNM-ECA500 spectrometer operating at 500.16 MHz. Electrospray ionization mass spectrometry (ESI-MS) was performed on Waters Quattro micro API.

Absolute weight-average molecular weight (M_w) of the polymers in DMF or H₂O (100 mM NaCl) 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 H₂O containing 100 mM NaCl at 30 °C (flow rate: 1 mL/min) on a silica gel column (Shodex PROTEIN KW-804). Those 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.

Cloud point of the aqueous solutions of polymers was measured on V-750 (JASCO, optical path length = 1.0 cm, $\lambda = 670$ nm, heating/cooling rate: 1 °C/min, temperature range: 40 – 90 °C).

Small angle neutron scattering (SANS) measurements were performed on a BL15 TAIKAN in the Material and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC, Tokai, Japan).^{S2} We utilized the data from the small-angle detector bank. Temperature was controlled at 25 °C with a circulating bath (Ministat 125, Huber Co.). The sample solutions were contained in quartz cells (Starna Scientific Co.) with a 2 mm path length and low neutron absorption ability. The exposure time was around ~0.5 h. For data corrections, air, the empty cell, and D₂O filled in the cell were measured. All SANS data were normalized to an absolute intensity by the scattering of a glassy carbon standard after data corrections such as air and cell scattering. The scattering intensities from the cell and the solvent were subtracted with the measured transmission and the volume fraction of the solvent. Radius of gyration (R_g) of the polymer samples was determined by Guinier plots.

Monomer Synthesis

Amphiphilic monomers (Cn-PEGAAm) were synthesized as follows.

C4-PEG amine: In a 200mL round-bottomed flask, basic alumina (5.0 g) was weighted. Poly(ethylene glycol) methyl ether acrylate (20 mmol, 8.8 mL) and toluene (50 mL) were added in the flask and stirred under 0 °C for 20 minutes. Then, butylamine (60 mmol, 8.4 mL) was added to the solution. The mixture was stirred at 50 °C for overnight. After the removal of alumina by filtration, the filtrate was evaporated under reduced pressure. The concentrated crude was purified with silica gel column chromatography (CH₂Cl₂/MeOH = 90/10, v/v). ¹H NMR [500 MHz, CDCl₃, r.t., δ = 0 ppm (TMS)]: δ 4.24 (t, 2 H, -COOCH₂CH₂O-, J = 4.5 Hz), 3.65-3.49 (m, 34 H, -COOCH₂CH₂O-, -(OCH₂CH₂)₈O-), 3.38 (s, 3 H, -OCH₃), 2.88 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 6.5 Hz), 2.60 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 7.3 Hz), 2.55 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 6.8 Hz), 1.46 (quin, 2 H, -CH₂CH₂CH₂CH₃, J = 7.3 Hz), 1.35 (sext, 2 H, -CH₂CH₂CH₂CH₃, J = 7.4 Hz), 0.91 (t, 3 H, -CH₃, J = 7.3 Hz) (Figure S1a). ¹³C NMR [500 MHz, CDCl₃, r.t., δ = 77.2 ppm (CHCl₃)]: δ 172.8, 72.0, 70.6, 69.1, 63.6, 59.1, 49.5, 45.1, 34.7, 32.2, 20.5, 14.0 ppm. Yield: 9.8 g (89% from PEGA).

C4-PEGAAm: In a 300 mL round-bottomed flask filled with argon, acryloyl chloride (21 mmol, 1.7 mL) was added dropwise to the solution of C4-PEGamine (18 mmol, 9.8 g, crude) and triethylamine (21 mmol, 3.0 mL) in dry dichloromethane (150 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3.0 h and then evaporated under reduced pressure. The concentrated solution was filtrated to remove precipitated solids. After the evaporation of the filtrate, the crude solid was purified with silica gel column chromatography (ethyl acetate/MeOH = 100/0, v/v (1 min), 100/0 – 80/20, v/v (29 min), flow rate: 85 mL/min, Redisep Rf GOLD) on CombiFlash Rf 200 (TELEDYNE ISCO). ¹H NMR [500 MHz, CDCl₃, r.t., δ = 0 ppm (TMS)]: δ 6.63-6.50, 6.37-6.33, 5.71-5.66 (olefin, 3 H), 4.23 (t, 2 H, -COOCH₂CH₂O-, J = 4.5 Hz), 3.72-3.55 (m, 36 H, -COOCH₂CH₂O-, -(OCH₂CH₂)₈O-, -CH₂N(CO)CH₂CH₂COO-), 3.38 (s, 3 H, -OCH₃), 3.36 (t, 2 H, -CH₂N(CO)CH₂CH₂COO-, J = 8.0 Hz), 2.70-2.62 (m, 2 H, -CH₂N(CO)CH₂CH₂COO-), 1.56 (quin, 2 H, -CH₂CH₂CH₂CH₃, J = 7.5 Hz), 1.31-1.26 (sext, 2 H, -CH₂CH₂CH₂CH₃, J = 7.5 Hz), 0.95 (t, 3 H, -CH₂CH₂CH₂CH₃, J = 7.0 Hz) (Figure S2a). ¹³C NMR [500 MHz, CDCl₃, r.t., δ = 77.2 ppm (CHCl₃)]: δ 172.1, 166.2, 128.0, 127.6, 72.0, 70.6, 69.1, 63.8, 59.1, 48.8, 43.1, 32.8, 31.8, 20.0, 13.8 ppm. ESI-MS m/z ([M + Na]⁺): calcd for C₂₉H₅₅NO₁₂, 632.37; found, 632.37.

C8-PEG amine: In a 200mL round-bottomed flask, basic alumina (5.0 g) was weighted. Poly(ethylene glycol) methyl ether acrylate (20 mmol, 8.8 mL) and toluene (50 mL) were added in the flask and stirred under 0 °C for 20 minutes. Then, octylamine (60 mmol, 9.9 mL) was added to the solution. The mixture was stirred at 50 °C for overnight. After the removal of alumina by filtration, the filtrate was evaporated under reduced pressure. The concentrated crude was purified

with silica gel column chromatography (CH₂Cl₂/MeOH = 90/10, v/v). ¹H NMR [500 MHz, CDCl₃, r.t., δ = 0 ppm (TMS)]: δ 4.24 (t, 2 H, -COOCH₂CH₂O-, J = 5.0 Hz), 3.66-3.50 (m, 34 H, -COOCH₂CH₂O-, -(OCH₂CH₂)₈O-), 3.38 (s, 3 H, -OCH₃), 2.88 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 6.8 Hz), 2.59 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 7.3 Hz), 2.55 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 6.5 Hz), 1.47 (quin, 2 H, -CH₂CH₂(CH₂)₅CH₃, J = 7.5 Hz), 1.33-1.22 (m, 10 H, -CH₂CH₂(CH₂)₅CH₃), 0.88 (t, 3 H, -CH₃, J = 7.3 Hz) (Figure S1b). ¹³C NMR [500 MHz, CDCl₃, r.t., δ = 77.2 ppm (CHCl₃)]: δ 172.9, 72.0, 70.7, 70.6, 69.2, 63.6, 59.1, 49.9, 45.2, 34.8, 31.9, 30.2, 29.6, 29.3, 29.6, 27.4, 22.7, 14.2 ppm. Yield: 11.2 g (92% from octylamine).

C8-PEGAam: In a 300 mL round-bottomed flask filled with argon, acryloyl chloride (22 mmol, 1.8 mL) was added dropwise to the solution of C8-PEGamine (18 mmol, 11 g, crude) and triethylamine (22 mmol, 3.0 mL) in dry dichloromethane (150 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then evaporated under reduced pressure. The concentrated solution was filtrated to remove precipitated solids. After the evaporation of the filtrate, the crude solid was purified with silica gel column chromatography (ethyl acetate/MeOH = 100/0, v/v (1 min), 100/0 – 80/20, v/v (29 min), flow rate: 85 mL/min, Redisep Rf GOLD) on CombiFlash Rf 200 (TELEDYNE ISCO). ¹H NMR [500 MHz, CDCl₃, r.t., δ = 0 ppm (TMS)]: δ 6.63-6.48, 6.37-6.32, 5.70-5.65 (olefin, 3 H), 4.23 (t, 2 H, -COOCH₂CH₂O-, J = 6.0 Hz), 3.71-3.54 (m, 36 H, -COOCH₂CH₂O-, -(OCH₂CH₂)₈O-, -CH₂N(CO)CH₂CH₂COO-), 3.37 (s, 3 H, -OCH₃), 3.34 (t, 2 H, -CH₂N(CO)CH₂CH₂COO-, J = 9.8 Hz), 2.70-2.60 (m, 2 H, -CH₂N(CO)CH₂CH₂COO-), 1.55 (m, 2 H, -CH₂CH₂(CH₂)₅CH₃), 1.33-1.22 (m, 10 H, -CH₂CH₂(CH₂)₅CH₃), 0.89 (t, 3 H, -CH₃, J = 8.3 Hz) (Figure S2b). ¹³C NMR [500 MHz, CDCl₃, r.t., δ = 77.2 ppm (CHCl₃)]: δ 172.1, 166.2, 129.0, 128.2, 71.9, 70.6, 69.0, 59.0, 49.0, 43.0, 32.7, 31.7, 29.7, 29.3, 29.2, 26.7, 22.6, 21.4, 14.1 ppm. ESI-MS m/z ([M + Na]⁺): calcd for C₃₃H₆₃NO₁₂, 688.44; found, 688.40.

C12-PEG amine: In a 300mL round-bottomed flask, basic alumina (12 g) was weighted. Poly(ethylene glycol) methyl ether acrylate (30 mmol, 13 mL) and toluene (75 mL) were added in the flask and stirred under 0 °C for 20 minutes. Then, dodecylamine (60 mmol, 11 mL) was added to the solution. The mixture was stirred at 50 °C for overnight. After the removal of alumina by filtration, the filtrate was evaporated under reduced pressure. The concentrated crude was purified with silica gel column chromatography (CH₂Cl₂/MeOH = 91/9, v/v). ¹H NMR [500 MHz, CDCl₃, r.t., δ = 0 ppm (TMS)]: δ 4.24 (t, 2 H, -COOCH₂CH₂O-, J = 5.0 Hz), 3.65-3.50 (m, 34 H, -COOCH₂CH₂O-, -(OCH₂CH₂)₈O-), 3.38 (s, 3 H, -OCH₃), 2.88 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 6.5 Hz), 2.59 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 7.0 Hz), 2.55 (t, 2 H, -CH₂NHCH₂CH₂COO-, J = 6.5 Hz), 1.47 (quin, 2 H, -CH₂CH₂(CH₂)₉CH₃, J = 7.0 Hz), 1.31-1.23 (m, 18 H, -CH₂CH₂(CH₂)₉CH₃), 0.88 (t, 3 H, -CH₃, J = 6.8 Hz) (Figure S1c). ¹³C NMR [500 MHz, CDCl₃, r.t., δ = 77.2 ppm

(CHCl₃): δ 172.8, 72.0, 70.6, 70.6, 70.4, 69.2, 63.6, 59.1, 49.9, 45.1, 34.7, 32.0, 30.2, 29.7, 29.7, 29.6, 29.4, 27.4, 22.7, 14.2 ppm. Yield: 14.0 g (70% from PEGA).

C12-PEGAAm: In a 300 mL round-bottomed flask filled with argon, acryloyl chloride (26 mmol, 4.6 mL) was added dropwise to the solution of C12-PEGamine (21 mmol, 14 g, crude) and triethylamine (26 mmol, 3.6 mL) in dry dichloromethane (150 mL) at 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then evaporated under reduced pressure. The concentrated solution was filtrated to remove precipitated solids. After the evaporation of the filtrate, the crude solid was purified with silica gel column chromatography (CH₂Cl₂/MeOH = 100/0, v/v (1 min), 100/0 – 90/10, v/v (29 min), flow rate: 85 mL/min, Redisep Rf GOLD) on CombiFlash Rf 200 (TELEDYNE ISCO). ¹H NMR [500 MHz, CDCl₃, r.t., δ = 0 ppm (TMS)]: δ 6.62-6.49, 6.37-6.32, 5.70-5.65 (olefin, 3 H), 4.22 (t, 2 H, -COOCH₂CH₂O-, J = 5.0 Hz), 3.70-3.54 (m, 36 H, -COOCH₂CH₂O-, -(OCH₂CH₂)₈O-, -CH₂N(CO)CH₂CH₂COO-), 3.37 (s, 3 H, -OCH₃), 3.34 (t, 2 H, -CH₂N(CO)CH₂CH₂COO-, J = 7.5 Hz), 2.70-2.60 (m, 2 H, -CH₂N(CO)CH₂CH₂COO-), 1.55 (m, 2 H, -CH₂CH₂(CH₂)₉CH₃), 1.31-1.23 (m, 18 H, -CH₂CH₂(CH₂)₉CH₃), 0.88 (t, 3 H, -CH₃, J = 7.0 Hz) (Figure S2c). ¹³C NMR [500 MHz, CDCl₃, r.t., δ = 77.2 ppm (CHCl₃): δ = 172.3, 166.3, 128.1, 127.7, 72.1, 70.7, 69.2, 59.2, 49.2, 32.9, 32.1, 29.9, 29.8, 29.7, 29.6, 29.5, 26.9, 22.8, 14.3 ppm. ESI-MS m/z ([M + Na]⁺): calcd for C₃₇H₇₁NO₁₂, 744.50; found, 744.38.

Polymer Synthesis

The synthesis of amphiphilic homopolymers and random copolymers was carried out by syringe technique under argon in glass tubes equipped with a three-way stopcock as shown below.

P1: Fe₂(CO)₄Cp₂ (0.05 mmol, 17.6 mg) was charged in a 20 mL glass tube. Then, toluene (0.84 mL), tetralin (0.05 mL), a 150 mM toluene solution of iodine (0.083 mL, iodine = 0.0125 mmol), a 859 mM toluene solution of C4-PEGAAm (1.46 mL, C4-PEGAAm = 1.25 mmol), and a 512 mM toluene solution of EMA-I (0.049 mL, EMA-I = 0.025 mmol) were added sequentially into the tube at 25 °C under argon (the total volume: 2.5 mL). The glass tube was placed in an oil bath kept at 60 °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 ¹H NMR in CDCl₃ with tetralin as an internal standard (Conv. 60%, 18 h). The quenched mixture was evaporated to dryness. The final crude product was purified by preparative SEC. The product was dried under vacuum at room temperature. SEC (DMF, PMMA std.): M_n = 13400, M_w/M_n = 1.36. ¹H NMR [500 MHz, CDCl₃, 25 °C, δ = 0 ppm (TMS)] δ 4.25-4.15 (-COOCH₂CH₂O-), 3.8-3.5 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -N(CO)CH₂CH₂COO-), 3.38 (-OCH₃), 3.30-3.00 (-CH₂N(CO)CH₂CH₂COO-), 2.80-2.20 (-N(CO)CH₂CH₂COO-, -CH₂CH(CO)-),

2.0-1.4 (-CH₂CH(CO)-, -CH₂CH₂CH₂CH₃), 1.4-1.2 (-CH₂CH₂CH₂CH₃), 0.93 (-CH₃). dn/dc = 0.0489 (DMF, 10mM LiBr), 0.112 (H₂O, 100 mM NaCl).

P2: Fe₂(CO)₄Cp₂ (0.052 mmol, 18.3 mg) was charged in a 20 mL glass tube. Then, toluene (0.59 mL), tetralin (0.05 mL), a 150 mM toluene solution of iodine (0.083 mL, iodine = 0.0125 mmol), a 733 mM toluene solution of C8-PEGAAm (1.71 mL, C8-PEGAAm = 1.25 mmol), and a 512 mM toluene solution of EMA-I (0.049 mL, EMA-I = 0.025 mmol) were added sequentially into the tube at 25 °C under argon (the total volume: 2.5 mL). The glass tube was placed in an oil bath kept at 60 °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 ¹H NMR in CDCl₃ with tetralin as an internal standard (Conv. 66%, 18 h). The quenched mixture was evaporated to dryness. The final crude product was purified by preparative SEC. The product was dried under vacuum at room temperature. SEC (DMF, PMMA std.): M_n = 14000, M_w/M_n = 1.31. ¹H NMR [500 MHz, CDCl₃, 25 °C, δ = 0 ppm (TMS)] δ 4.3-4.1 (-COOCH₂CH₂O-), 3.8-3.5 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -N(CO)CH₂CH₂COO-), 3.38 (-OCH₃), 3.3-2.9 (-CH₂N(CO)CH₂CH₂COO-), 2.8-2.1 (-N(CO)CH₂CH₂COO-, -CH₂CH(CO)-), 1.9-1.4 (-CH₂CH(CO)-, -CH₂CH₂(CH₂)₅CH₃), 1.4-1.1 (-CH₂CH₂(CH₂)₅CH₃), 0.88 (-CH₃). dn/dc = 0.0531 (DMF, 10mM LiBr), 0.139 (H₂O, 100 mM NaCl).

P3: Fe₂(CO)₄Cp₂ (0.104 mmol, 37.0 mg) was charged in a 30 mL glass tube. Then, toluene (0.53 mL), tetralin (0.10 mL), a 150 mM toluene solution of iodine (0.34 mL, iodine = 0.051 mmol), a 658 mM toluene solution of C12-PEGAAm (3.97 mL, C12-PEGAAm = 2.61 mmol), and a 461 mM toluene solution of EMA-I (0.23 mL, EMA-I = 0.106 mmol) were added sequentially into the tube at 25 °C under argon (the total volume: 5.2 mL). The glass tube was placed in an oil bath kept at 60 °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 ¹H NMR in CDCl₃ with tetralin as an internal standard (Conv. 49%, 48 h). The quenched mixture was evaporated to dryness. The final crude product was purified by preparative SEC. The product was dried under vacuum at room temperature. SEC (DMF, PMMA std.): M_n = 9300, M_w/M_n = 1.28. ¹H NMR [500 MHz, CDCl₃, 25 °C, δ = 0 ppm (TMS)] δ = 4.3-4.1 (-COOCH₂CH₂O-), 3.8-3.5 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -N(CO)CH₂CH₂COO-), 3.38 (-OCH₃), 3.3-2.9 (-CH₂N(CO)CH₂CH₂COO-), 2.9-2.2 (-N(CO)CH₂CH₂COO-, -CH₂CH(CO)-), 1.9-1.4 (-CH₂CH(CO)-, -CH₂CH₂(CH₂)₉CH₃), 1.4-1.1 (-CH₂CH₂(CH₂)₉CH₃), 0.88 (-CH₃). dn/dc = 0.0502 (DMF, 10mM LiBr), 0.130 (H₂O, 100 mM NaCl).

P4 was prepared according to the literature.^{S1}

P5: Ru(Ind)Cl(PPh₃)₂ (0.096 mmol, 74.4 mg) was weighed in a 100mL round-bottomed flask. Into the tube, toluene (27.0 mL), tetralin (0.96 mL), a 400 mM toluene solution of *n*-Bu₃N (2.4 mL,

n-Bu₃N = 0.96 mmol), PEGMA (21.6 mmol, 9.49 mL), DMA (14.4 mmol, 4.21 mL), and a 37.5 mM toluene solution of ECPA (3.84 mL, ECPA = 0.144 mmol) were added sequentially at 25 °C under argon (total volume: 50 mL). The flask was placed in an oil bath kept at 80 °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 ¹H NMR in CDCl₃ with tetralin as an internal standard (Conv. PEGMA/DMA = 22%/21%, 8 h). The quenched mixture was evaporated to dryness. The crude product was purified by preparative SEC in DMF as an eluent (Figure S3). SEC (DMF, PMMA std.): *M*_n = 18100, *M*_w/*M*_n = 1.23. ¹H NMR [500 MHz, acetone-*d*₆, 25 °C, δ 2.05 ppm (acetone)]: δ = 7.3 (-COCHPh-), 4.2-4.1 (-COOCH₂CH₂O-), 4.1-3.9 (-COOCH₂(CH₂)₁₀CH₃), 3.8-3.5 (-COOCH₂CH₂O-, -CH₂CH₂O-), 3.3 (-OCH₃), 3.2 (-COCHPh-), 2.1-1.6 (-CH₂CCH₃(CO)-), 1.7-1.2 (-CH₂(CH₂)₁₀CH₃), 1.2-1.0 (-CH₂CCH₃(CO)-), 0.9 (-(CH₂)₁₁CH₃). *dn/dc* = 0.0498 (DMF, 10mM LiBr), 0.138 (H₂O, 100 mM NaCl).

Sample Preparation for Micelles in Water

Polymer micelles were prepared as follows: In vials, amphiphilic polymers were mixed with water at 25 °C and the polymer solutions (1 mg/mL) were sonicated at 40 °C for 30 min (AS ONE, MCD-2, 40 kHz). Then, the resulting homogeneous solutions were filtrated with a membrane filter (Merck, PTFE, 0.45 μm) before analysis.

Supporting Data

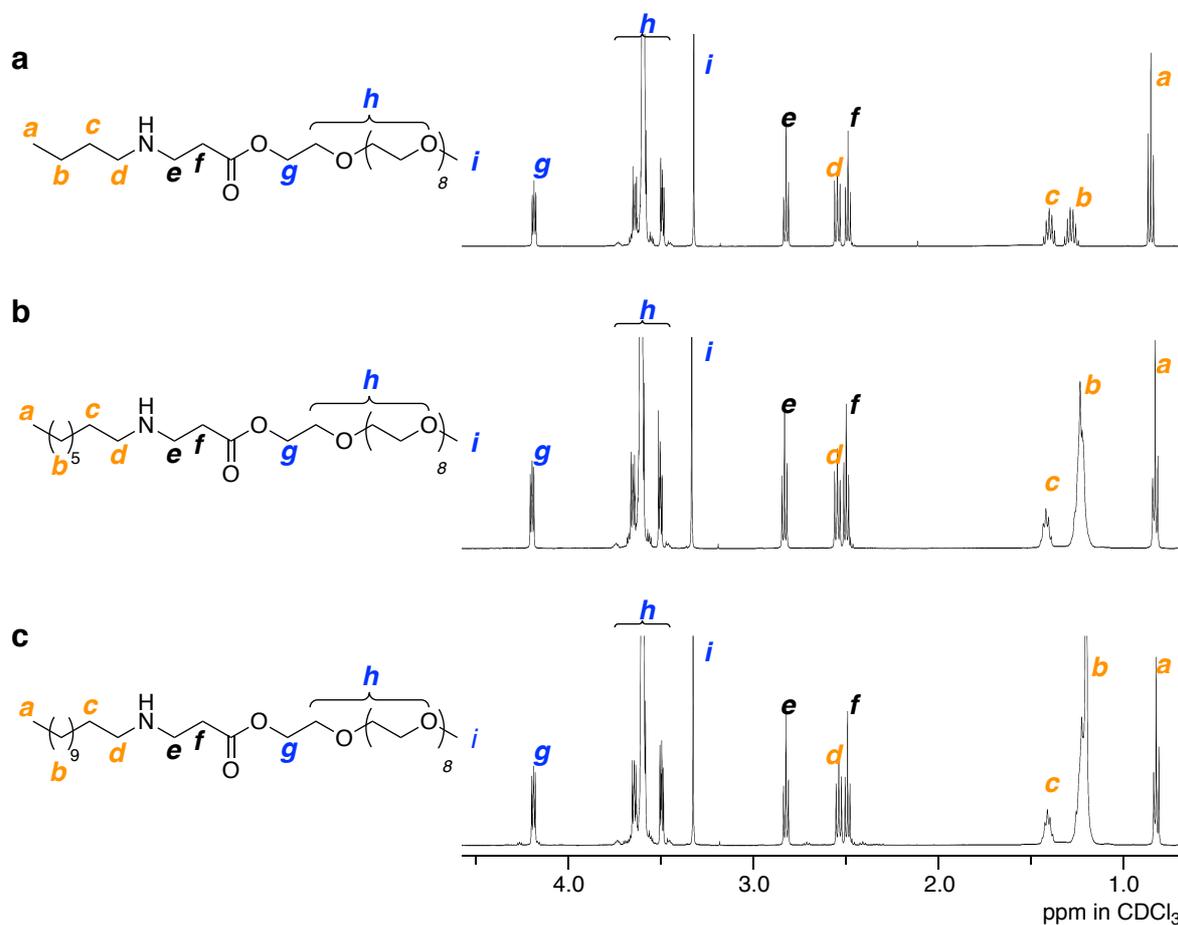


Figure S1. ^1H NMR spectra of (a) C4-PEG amine, (b) C8-PEG amine, and (c) C12-PEG amine in CDCl_3 at 25°C .

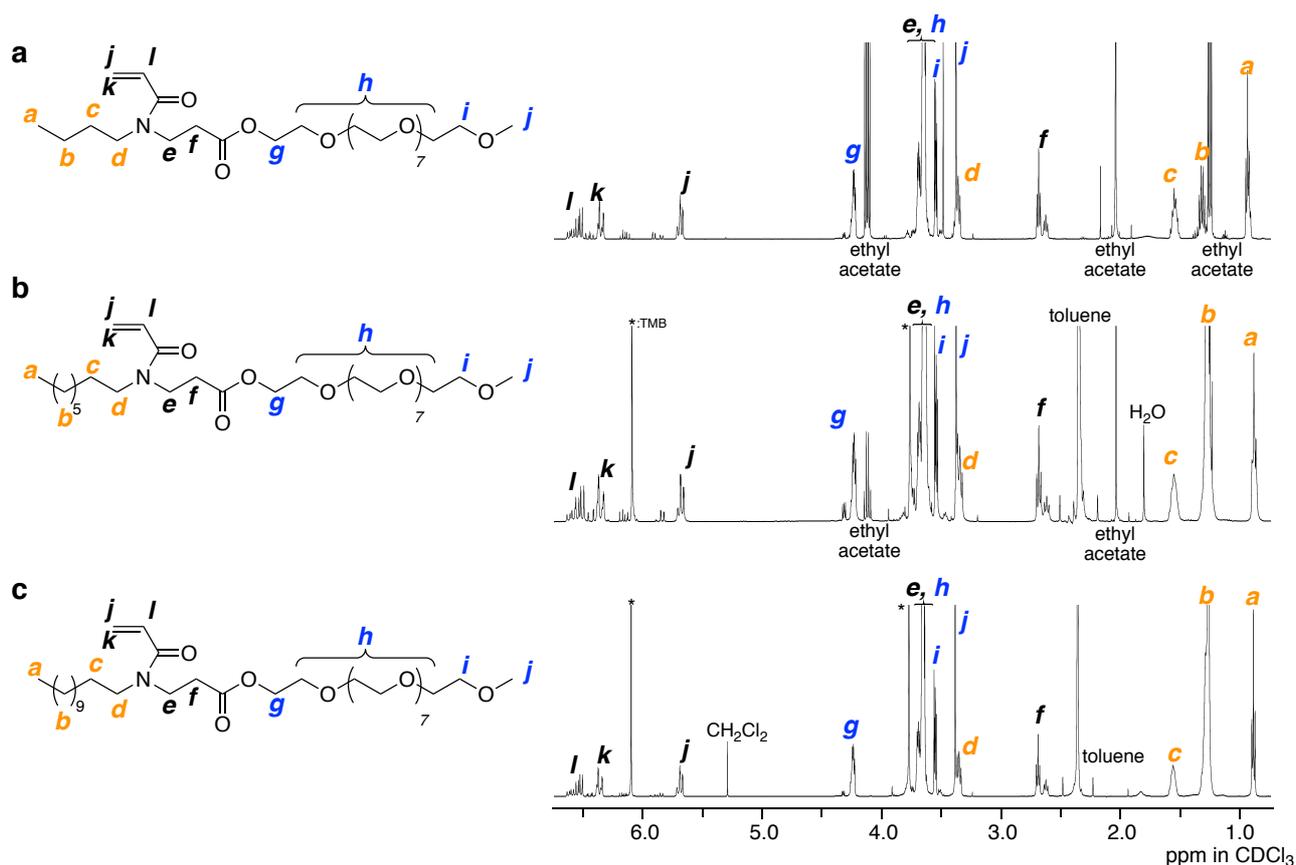


Figure S2. ^1H NMR spectra of (a) C4-PEGAAm, (b) C8-PEGAAm, and (c) C12-PEGAAm in CDCl_3 at 25 $^\circ\text{C}$. Figures S2b and S2c were obtained from NMR measurements of the toluene solutions of C8-PEGAAm or C12-PEGAAm containing 1,3,5-trimethoxybenzene (TMB). The toluene solutions were prepared to determine the monomer concentration using TMB. To avoid unexpected polymerization, the monomers were roughly dried after column chromatography and analyzed by NMR. Therefore, the monomers slightly contain ethyl acetate or dichloromethane used as eluents in column chromatography.

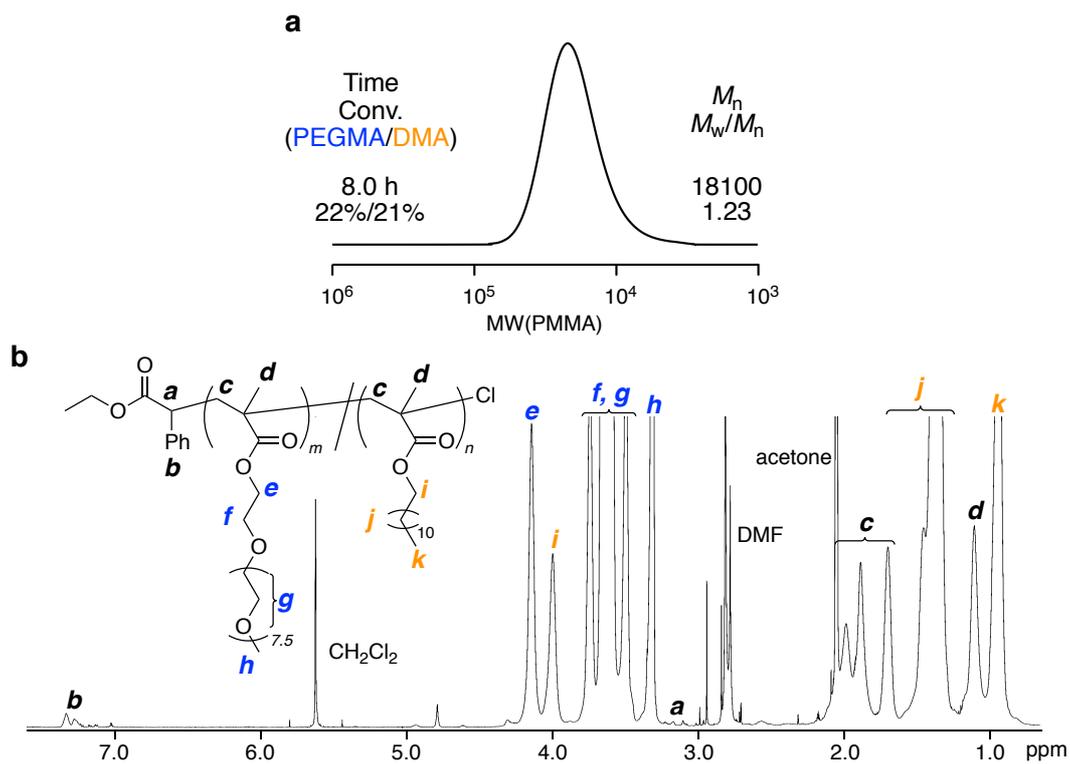


Figure S3. (a) A SEC curve of **P5** in DMF (10 mM LiBr) and (b) a ¹H NMR spectrum of **P5** in acetone-*d*₆ at 25 °C.

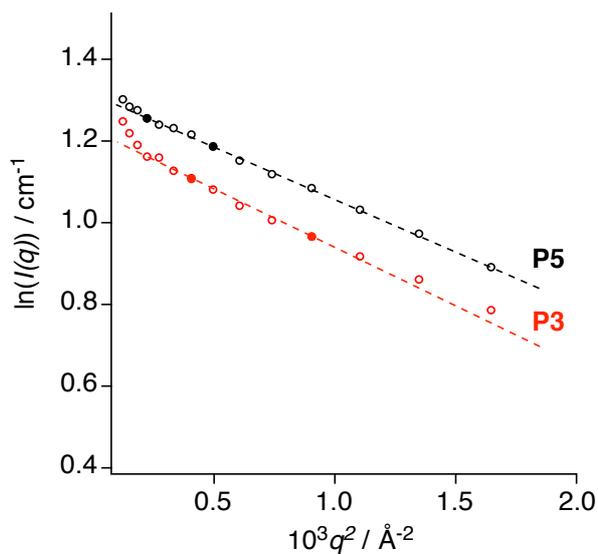


Figure S4. Guinier plots of the SANS profiles of **P3** (red) or **P5** (black) in water at 25 °C (open circles: raw data, filled circles: fit ranges, dot lines: fit lines).

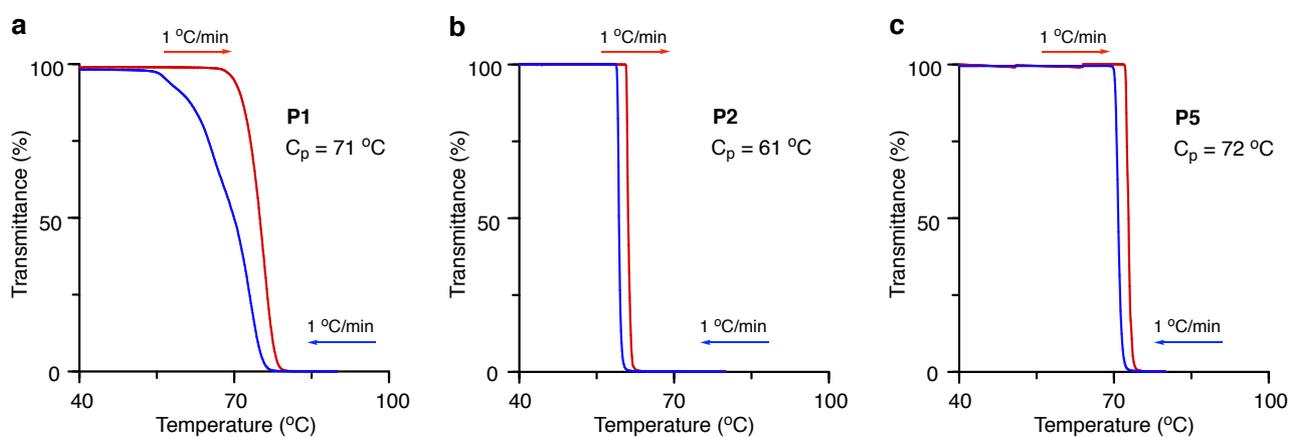


Figure S5. Transmittance of the aqueous solutions of (a) **P1**, (b) **P2**, and (c) **P5** (heating: red, cooling: blue) monitored by changing temperature between 40 and 80 °C: [polymer] = 4 mg/mL, heating/cooling rate: 1 °C/min, $\lambda = 670$ nm.

References

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- (S2) Takata, S.; Suzuki, J.; Shinohara, T.; Oku, T.; Tominaga, T.; Ohishi, K.; Iwase, H.; Nakatani, T.; Inamura, Y.; Ito, T.; Suzuya, K.; Aizawa, K.; Arai, M.; Otomo, T.; Sugiyama, M. The Design and q Resolution of the Small and Wide Angle Neutron Scattering Instrument (TAIKAN) in J-PARC, *JPS Conf. Proc.* **2015**, *8*, 036020.