# **Supplementary Information**

# Self-assembly and salt-induced thermoresponsive properties of amphiphilic PEG/cation random terpolymers in water

Rikuto Kanno,<sup>1</sup> Makoto Ouchi,<sup>1</sup> and Takaya Terashima<sup>1\*</sup>

<sup>1</sup> Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University

Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

\*Correspondence to: terashima.takaya.2e@kyoto-u.ac.jp

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## **Experimental Section**

#### Materials.

Poly(ethylene glycol) methyl ether methacrylate [PEGMA:  $CH_2=CMeCO_2(CH_2CH_2O)_nMe$ ,  $M_n =$ 475, n = 8.5 on average, Aldrich], dodecyl methacrylate (DMA, Wako, purity >95%), and N,Ndimethyl amino ethyl methacrylate (DMAEMA, TCI, purity >98.5%) were purified by an inhibitor removal column (Aldrich) and degassed by triple vacuum-argon purge cycles before use. Ethyl 2chloro-2-phenylacetate (ECPA, Aldrich, purity >97%) was distilled under reduced pressure before use. Triethylamine (TCI, purity >99%) and 1,2,3,4-tetrahydronaphthalene (tetralin, TCI, purity >98%; an internal standard for <sup>1</sup>H NMR analysis) were dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use. Ru(Ind)Cl(PPh<sub>3</sub>)<sub>2</sub> (Aldrich) and Ru(Cp\*)Cl(PPh<sub>3</sub>)<sub>2</sub> (Aldrich) were used as received and handled in a glove box under moisture- and oxygen-free argon (H<sub>2</sub>O < 1 ppm, O<sub>2</sub> < 1 ppm). 4-Dimethylamino-1-butanol (4-DMAB, TCI, purity > 98%) and tributylamine (TCI, purity >99%) were degassed by triple vacuum-argon purge cycles before use. Ethanol (Wako, dehydrated), toluene (Wako, deoxidized), distilled water (Wako), ultrapure water (Wako), chloroform (Wako, purity >99%), N,N-dimethylformamide (Wako, purity >99.5%), THF (Wako, purity >99.5%), acetonitrile (Wako, purity >99.5%), iodomethane (Wako, purity >99.5%), NaNO<sub>3</sub> (Wako, purity >99.5%), NaCl (Wako, purity >99.5%), Na<sub>2</sub>SO<sub>4</sub> (Wako, purity >99%), NaI (Wako, purity >99.5%), and CH<sub>3</sub>COONa (Wako, purity 98%) were used as received.

#### Characterization.

Molecular weight distribution (MWD) curves,  $M_n$ , and  $M_w/M_n$  of the DMAEMA-based precursors of PEG/cation random terpolymers and a cation copolymer were measured by size exclusion chromatography (SEC) in THF containing 20 mM triethylamine at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex K-805L: exclusion limit = 4 × 10<sup>6</sup>; 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-1531 refractive index detector, and a Jasco UV-970 UV/vis detector set at 250 nm. The columns were calibrated against 11 standard poly(MMA) samples (PSS, Polymer Standard Service GmbH, Ready Cal Kit:  $M_p = 2380-2200000$ ). MWD curves, number-average molecular weight ( $M_n$ ), and  $M_w/M_n$  ratio of a PEG copolymer 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 × 10<sup>6</sup>; 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:  $M_p = 2380-2200000$ ). MWD curves, number-average molecular weight ( $M_n$ ), and  $M_w/M_n$  ratio of all the polymer micelles were measured by SEC in water containing 100 mM NaNO<sub>3</sub> at 30 °C (flow rate: 1 mL/min) on a polymethacrylate gel column (TOSOH TSKgel G5000PW<sub>XL</sub>-CP: exclusion limit = 1 × 10<sup>6</sup>; particle size = 10 µm; pore size = 1000 Å; 0.78 cm i.d. × 30 cm) that was connected to a Jasco PU-4180 precision pump, a Jasco RI-4030 refractive index detector, a Jasco FP-4020 FL detector set at 336 and 396 nm (excitation wavelength = 290 nm), and a Jasco UV-4075 UV/vis detector set at 346 nm. The columns were calibrated against 11 standard poly(ethylene oxide) and poly(ethylene glycol) samples (Agilent Technologies: M<sub>p</sub> = 238–504000;  $M_w/M_n$  = 1.00–1.08). Before characterization, the DMAEMA-based precursors of PEG/cation random terpolymers and a cation copolymer were purified by preparative SEC in CHCl<sub>3</sub> containing 50 mM triethylamine at room temperature (flow rate: 10 mL/min) on Shodex KF-5003 (exclusion limit = 7 × 10<sup>4</sup>; particle size = 20 µm; 5.0 cm i.d. × 30 cm). The PEG copolymer was purified by preparative SEC in DMF at room temperature (flow rate: 15 mL/min) on TOSOH TSKgel α-3000 (exclusion limit = 1 × 10<sup>5</sup>; particle size = 13 µm; 5.5 cm i.d. × 30 cm). <sup>1</sup>H NMR measurement was performed in CDCl<sub>3</sub>, acetone-*d*<sub>6</sub>, and DMSO-*d*<sub>6</sub> on a JEOL JNM-ECA500 spectrometer operating at 500.16 MHz.

Absolute weight-average molecular weight ( $M_w$ ) of polymers in DMF or 100 mM NaNO<sub>3</sub>aq 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 water containing 100 mM NaNO<sub>3</sub> at 30 °C (flow rate: 1 mL/min) on a polymethacrylate gel column (TOSOH TSKgel G5000PW<sub>XL</sub>-CP). These columns were connected to a Jasco PU-4180 precision pump, a Jasco RI-4030 refractive index detector, and a Jasco UV-4075 UV/vis detector set at 250 nm (for DMF) or 346 nm (for 100 mM NaNO<sub>3</sub>aq). *dn/dc* of their polymer micelles in 100 mM NaNO<sub>3</sub> aqueous solutions was determined by OPTILAB DSP Interferometric Refractrometer (Wyatt Technology,  $\lambda = 690$  nm).

Cloud point measurement of the aqueous solutions of polymer micelles was performed on Jasco V-750 spectrophotometer equipped with a peltier thermostatted cell holder (ETCS-761, JASCO). To determine cloud point, transmittance of the aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 90 or 100 °C: optical path length = 1.0 cm, heating or cooling rate = 1.0 or -1.0 °C/min.

Dynamic light scattering (DLS) was measured on ELSZ-0 (Otsuka Electronics, Semiconductor laser:  $\lambda = 658$  nm). The measuring angle was 165° and the data was analyzed by CONTIN method.

#### **Polymer Synthesis.**

The synthesis of P/C-1/0 and the DMAEMA-based precursors of P/C-2/1, P/C-1/1, P/C-1/2, P/C-1/3, and P/C-0/1 was carried out by syringe technique under argon in glass tubes equipped with a three-way stopcock. Typical procedures were shown below.

The DMAEMA-based precursor of P/C-1/1: Ru(Cp\*)Cl(PPh<sub>3</sub>)<sub>2</sub> (0.0080 mmol, 6.4 mg) was placed in a 50 mL round bottom flask. Then, ethanol (4.4 mL), tetralin (0.080 mL), a 500 mM toluene solution of 4-DMAB (4-DMAB = 0.16 mmol, 0.32 mL), PEGMA (2.0 mmol, 0.88 mL), DMAEMA (2.0 mmol, 0.35 mL), DMA (4.0 mmol, 1.2 mL), and a 39 mM ethanol solution of ECPA (ECPA = 0.050 mmol, 1.3 mL) were added sequentially into the tube at 25 °C under argon (total volume: 10 mL). The flask was placed in an oil bath kept at 40 °C. After 23 h, the reaction was terminated by cooling the solution to -78 °C. The conversion of PEGMA, DMAEMA, and DMA was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. PEGMA/DMAEMA/DMA = 71%/73%/77%. The quenched mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl<sub>3</sub> containing 50 mM Et<sub>3</sub>N as an eluent to remove their unreacted monomers and the catalyst residue. SEC (THF, 20 mM Et<sub>3</sub>N, PMMA std.):  $M_n = 44200$ ,  $M_w/M_n =$ 1.15. <sup>1</sup>H NMR [500 MHz, acetone- $d_6$ , 25 °C,  $\delta = 2.05$  (acetone)]:  $\delta 8.5-8.0$  (pyrene unit in PyMA), 7.4-7.2 (Ph in ECPA), 4.2-4.1 (-COOCH2CH2O-), 4.1-4.0 (-COOCH2CH2N-), 4.0-3.9 (-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.8–3.7 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.7–3.5 (-OCH<sub>2</sub>CH<sub>2</sub>O-), 3.5-3.4 (-CH<sub>2</sub>OCH<sub>3</sub>), 3.4-3.3 (-OCH<sub>3</sub>), 2.6-2.4 (-COOCH<sub>2</sub>CH<sub>2</sub>N-), 2.3-2.1 (-N(CH<sub>3</sub>)<sub>2</sub>), 2.1-1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.8-1.6 (- $COOCH_2CH_2(CH_2)_9CH_3$ , 1.6-1.2 (- $COOCH_2CH_2(CH_2)_9CH_3$ ), 1.2–0.8 (- $COO(CH_2)_{11}CH_3$ , -CH<sub>2</sub>C(CH<sub>3</sub>)-). PEGMA/DMAEMA/DMA = 43/42/92. *M*<sub>n</sub> (NMR) = 50600.

**P/C-1/0**: Ru(Ind)Cl(PPh<sub>3</sub>)<sub>2</sub> (0.010 mmol, 7.8 mg) was placed in a 50 mL round bottom flask. Then, toluene (7.3 mL), tetralin (0.10 mL), a 400 mM toluene solution of *n*-Bu<sub>3</sub>N (*n*-Bu<sub>3</sub>N = 0.10 mmol, 0.25 mL), PEGMA (2.5 mmol, 1.1 mL), DMA (2.5 mmol, 0.73 mL), and a 40 mM toluene solution of ECPA (ECPA = 0.02 mmol, 0.50 mL) were added sequentially into the tube at 25 °C under argon (total volume: 5.0 mL). The glass tube was placed in an oil bath kept at 80 °C. After 37 h, the reaction was terminated by cooling the solution to -78 °C. The conversion of PEGMA and DMA was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. PEGMA/DMA = 79%/78%. The quenched mixture was evaporated to dryness. The crude product was purified by preparative SEC in DMF as an eluent to remove their unreacted monomers and the catalyst residue. SEC (DMF, 10 mM LiBr, PMMA):  $M_n = 37350$ ,  $M_w/M_n = 1.27$ . dn/dc (DMF) = 0.043. SEC-MALLS (DMF, 0.01 M LiBr):  $M_{w,DMF} = 82100$ . <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C,  $\delta = 2.05$  (acetone)]:  $\delta$  7.4-7.2 (Ph in ECPA), 4.2-4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 4.0-3.9 (-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.8-3.7 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.7-3.5 (-OCH<sub>2</sub>CH<sub>2</sub>O-), 3.5-3.4 (-CH<sub>2</sub>OCH<sub>3</sub>), 3.4-3.3 (-OCH<sub>3</sub>), 2.6-2.4 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 2.3-2.1 (-N(CH<sub>3</sub>)<sub>2</sub>), 2.1-1.8 (-COO(CH<sub>2</sub>C(H<sub>3</sub>)-), 1.8-1.6 (-COOCH<sub>2</sub>CH<sub>2</sub>O)-). PEGMA/DMA = 1.27 (COOCH<sub>2</sub>CH<sub>2</sub>O)-). PEGMA/DMA = 1.27 (COOCH<sub>2</sub>CH<sub>3</sub>O)-). PEGMA/DMA = 1.27 (COOCH<sub>2</sub>CH<sub>3</sub>)-). PEGMA/DMA = 1.27 (COOCH<sub>3</sub>)-). PEGMA/D

90/89.  $M_n$  (NMR) = 65800.  $M_{w,calcd} = M_n$  (NMR) x  $M_w/M_n = 83300$ .

The DMAEMA-based precursor of **P/C-0/1**: Ru(Ind)Cl(PPh<sub>3</sub>)<sub>2</sub> (0.015 mmol, 12 mg) was placed in a 50 mL round bottom flask. Then, toluene (12 mL), tetralin (0.15 mL), a 400 mM toluene solution of *n*-Bu<sub>3</sub>N (*n*-Bu<sub>3</sub>N = 0.15 mmol, 0.38 mL), DMAEMA (3.8 mmol, 0.63 mL), DMA (3.8 mmol, 1.10 mL), and a 40 mM toluene solution of ECPA (ECPA = 0.030 mmol, 0.75 mL) were added sequentially into the tube at 25 °C under argon (total volume: 10 mL). The flask was placed in an oil bath kept at 80 °C. After 47 h, the reaction was terminated by cooling the solution to -78 °C. The conversion of DMAEMA and DMA was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. DMAEMA/DMA = 73%/70%. The quenched mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl<sub>3</sub> containing 50 mM Et<sub>3</sub>N, PMMA std.): *M*<sub>n</sub> = 33900, *M*<sub>w</sub>/*M*<sub>n</sub> = 1.27. <sup>1</sup>H NMR [500 MHz, acetone-*d*<sub>6</sub>, 25 °C,  $\delta$  = 2.05 (acetone)]:  $\delta$  7.4-7.2 (Ph in ECPA), 4.1–4.0 (-COOCH<sub>2</sub>CH<sub>2</sub>N-), 4.0–3.9 (-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 2.6-2.4 (-COOCH<sub>2</sub>CH<sub>2</sub>N-), 2.3-2.1 (-N(CH<sub>3</sub>)<sub>2</sub>), 2.1–1.8 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.8-1.6 (-COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.6-1.2 (-COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.2–0.8 (-COO(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). DMAEMA/DMA = 98/90. *M*<sub>n</sub> (NMR) = 38400.

The DMAEMA-based precursors of PEG/cation (1/1) terpolymers with different DPs: Ru(Cp\*)Cl(PPh<sub>3</sub>)<sub>2</sub> (0.030 mmol, 24 mg) was placed in a 100 mL round bottom flask. Then, ethanol (20 mL), tetralin (0.30 mL), a 500 mM toluene solution of 4-DMAB (4-DMAB = 0.60 mmol, 0.60 mmolmL), PEGMA (7.5 mmol, 3.3 mL), DMAEMA (7.5 mmol, 1.3 mL), DMA (15 mmol, 4.4 mL), and a 570 mM ethanol solution of ECPA (ECPA = 0.15 mmol, 0.26 mL) were added sequentially into the tube at 25 °C under argon (total volume: 30 mL). The flask was placed in an oil bath kept at 40 °C. The polymerization solution (about 10 mL) was sampled by a syringe at 5 h and 10 h and cooled to -78 °C to terminate the reaction. At 17 h, the remaining solution was also cooled to -78 °C to terminate the reaction. The conversion of PEGMA, DMAEMA, and DMA was determined by <sup>1</sup>H NMR in CDCl<sub>3</sub> with tetralin as an internal standard: Conv. PEGMA/DMAEMA/DMA = 29%/32%/35% (5 h), 45%/50%/53% (10 h), and 63%/68%/69% (17 h). The quenched mixtures were evaporated to dryness. The crude products were purified by preparative SEC in CHCl<sub>3</sub> containing 50 mM Et<sub>3</sub>N as an eluent to remove their unreacted monomers and the catalyst residue. SEC (THF containing 20 mM Et<sub>3</sub>N, PMMA std.):  $M_n = 18600, 26100, 32100; M_w/M_n = 1.12, 1.13, 1.17.$ <sup>1</sup>H NMR [500 MHz, acetone- $d_6$ , 25 °C,  $\delta$  = 2.05 (acetone)]:  $\delta$  8.5–8.0 (pyrene unit in PyMA), 7.4-7.2 (Ph in ECPA), 4.2–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 4.1–4.0 (-COOCH<sub>2</sub>CH<sub>2</sub>N-), 4.0–3.9 (-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.8-3.7 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.7-3.5 (-OCH<sub>2</sub>CH<sub>2</sub>O-), 3.5-3.4 (-CH<sub>2</sub>OCH<sub>3</sub>), 3.4-3.3 (-OCH<sub>3</sub>), 2.6-2.4 (-COOCH<sub>2</sub>C<u>H</u><sub>2</sub>N-), 2.3-2.1 (-N(C<u>H</u><sub>3</sub>)<sub>2</sub>), 2.1–1.8 (-C<u>H</u><sub>2</sub>C(CH<sub>3</sub>)-), 1.8-1.6 (-COOCH<sub>2</sub>C<u>H</u><sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.6-1.2  $(-COOCH_2CH_2(CH_2)_9CH_3),$ 1.2 - 0.8(-COO(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). PEGMA/DMAEMA/DMA = 17/17/41, 25/25/57, 36/31/71. *M*<sub>n</sub> (NMR) = 21500, 30700, 39000.

#### Quaternization of DMAEMA-Based Precursors for PEG/Cation or Cation Ter(co)polymers.

A typical procedure to produce **P/C-1/1** was given: In a 50 mL round-bottomed flask, the dichloromethane solution of the DMAEMA-based precursor (100 mg/mL, 11 mL,  $M_n$  (NMR) = 50600) was added and evaporated to dryness. The resulting polymer (1.1 g, 0.022 mmol, DMAEMA unit = 0.9 mmol) was dissolved in THF/acetonitrile (1/1, v/v, 22 mL). Into the solution, iodomethane (3.0 mL, 48 mmol; [CH<sub>3</sub>I]/[DMAEMA] = 50/1, mol/mol) was added. The mixture was stirred at 0 °C overnight. After removing THF, acetonitrile, and iodomethane in vacuo, **P/C-1/1** was obtained. <sup>1</sup>H NMR [500 MHz, DMSO-*d*<sub>6</sub>, 25 °C,  $\delta$  = 2.50 (DMSO)] (Figure S2):  $\delta$  7.4-7.1 (Ph in ECPA), 4.7-4.2 (-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>-), 4.1-3.9 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.9-3.7 (-COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.57-3.45 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.57-3.45 (-OCH<sub>2</sub>CH<sub>2</sub>O-), 3.45-3.4 (-CH<sub>2</sub>OCH<sub>3</sub>), 3.3-3.1 (-OCH<sub>3</sub>, -COOCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>-, -N<sup>+</sup>(CH<sub>3</sub>)<sub>3</sub>), 2.0-1.7 (-CH<sub>2</sub>C(CH<sub>3</sub>)-), 1.6-1.5 (-COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.4-1.1 (-COOCH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.1-0.7 (-COO(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>, -CH<sub>2</sub>C(CH<sub>3</sub>)-). The quantitative quaternization of the DMAEMA-based precursors with iodomethane was confirmed by <sup>1</sup>H NMR.

The counter anions of the P/C-1/1 micelle measured in SEC-MALLS would be changed from I<sup>-</sup> into NO<sub>3</sub><sup>-</sup> that is originating from NaNO<sub>3</sub> included in the eluent of the SEC system, because the concentration of the NaNO<sub>3</sub> is higher than that of the original counter anion (I<sup>-</sup>) of P/C-1/1. To determine the aggregation number ( $N_{agg}$ ) of the P/C-1/1 micelle, we herein estimated  $M_n$  (NMR) and  $M_{w,calcd}$  of P/C-1/1, assuming that all the counter anions are NO<sub>3</sub><sup>-</sup>. P/C-1/1 with NO<sub>3</sub><sup>-</sup> as counter anions:  $M_n$  (NMR) = 50600 ( $M_n$  (NMR) of the precursor) + 42 (m) x 77 (Fw, -CH<sub>3</sub>NO<sub>3</sub>) = 56600.  $M_{w,calcd} = M_n$  (NMR) x  $M_w/M_n = 61900$  (Table 2). Other DMAEMA-based precursors were also treated similarly to produce corresponding PEG/cation or cation random ter(co)polymers.

#### **Preparation of Polymer Micelles.**

Micelles of P/C-1/0, P/C-2/1, P/C-1/1, P/C-1/2, P/C-1/3, and P/C-0/1 were prepared in pure water or water containing 2 M NaCl and those aqueous solutions were employed for SEC-MALLS and cloud point measurements. The micelle solutions in water containing 100 mM NaNO<sub>3</sub>, 1M CH<sub>3</sub>COONa, NaCl, NaI, NaNO<sub>3</sub>, and Na<sub>2</sub>SO<sub>4</sub>, and 2 M NaCl were prepared for DLS measurements. Typical preparation procedures of polymer micelles were shown below.

**PEG/cation random terpolymer micelles.** The dichloromethane solution of a terpolymer (e.g., **P/C-**1/1, **P/C-2/1**, **P/C-2/1**, and **P/C-1/3**) was evaporated, and the resulting polymer was dissolved in ultrapure water or in water containing 100 mM NaNO<sub>3</sub> or 2 M NaCl. The solution was sonicated for 10 minutes at room temperature. Then, the solution was placed in a water bath kept at 50 or 40 °C. After 24 h, the solution was gradually cooled at room temperature and used for SEC-MALLS, cloud point, and DLS measurements.

**PEG random copolymer micelles.** The dichloromethane solution of **P/C-1/0** was evaporated, and the resulting polymer was dissolved in ultrapure water or in water containing 100 mM NaNO<sub>3</sub> or 2 M NaCl. The solution was sonicated for 10 minutes at room temperature. Then, the solution was placed at room temperature for one hour before SEC-MALLS, cloud point, and DLS measurements. **Cation random copolymer micelles.** A solid **P/C-0/1** was dissolved in ultrapure water or in water containing 100 mM NaNO<sub>3</sub> or 2 M NaCl, and the solution was sonicated for 10 minutes at room temperature. Then, the solution was placed in a water bath kept at 50 °C. After 24 h, the solution was gradually cooled at room temperature and and used for SEC-MALLS, cloud point, and DLS measurements.

#### dn/dc of Polymer Micelles

To determine  $M_w$  of the polymer micelles by SEC-MALLS (Tables 1 and S1), dn/dc of their polymer micelles in water containing 100 mM NaNO<sub>3</sub> was determined by Refractrometer. To calculate  $M_w$  of the PEG/cation (1/1) terpolymer micelles with different DPs (DP = 76, 107, and 135), we used the dn/dc value of the P/C-1/1 micelle, since the composition of three monomer units is almost identical each other.

P/C-1/0 micelle: dn/dc = 0.140, P/C-2/1 micelle: dn/dc = 0.142, P/C-1/1 micelle: dn/dc = 0.145, P/C-1/2 micelle: dn/dc = 0.148, P/C-1/3 micelle: dn/dc = 0.154, P/C-0/1 micelle: dn/dc = 0.154.

## **Supporting Data**



Scheme S1. (a) Synthesis of PEG/cation random terpolymers (P/C-2/1, -1/1, -1/2, -1/3, and PEG/cation = 1/1 with different DPs) via Ru-catalyzed living radical terpolymerization of PEGMA, DMAEMA, and DMA, followed by the quaternization of the resulting terpolymer with methyl iodide. (b) Synthesis of a PEG random copolymer (P/C-1/0) via Ru-catalyzed living radical copolymerization of PEGMA, and DMA. (c) Synthesis of a cation random copolymer (P/C-0/1) via Ru-catalyzed living radical copolymerization of DMAEMA, and DMA, followed by the quaternization of DMAEMA, and DMA, followed by the quaternization of DMAEMA, and DMA, followed by the quaternization of the resulting terpolymer with methyl iodide.



Figure S1. (a-h) Ru-catalyzed living radical copolymerization of PEGMA, DMAEMA, and DMA for the precursors of (a, b) P/C-1/1, (c, d) P/C-1/2, (e, f) P/C-2/1, (g, h) PEG/cation (1/1) random terpolymers with different DPs (76, 107, 135), and (i. j) P/C-1/3: [PEGMA]<sub>0</sub>/[DMAEMA]<sub>0</sub>/  $[DMA]_0/[ECPA]_0/[Ru(Cp^*)Cl(PPh_3)]_0/[4-DMAB]_0 = (a, b) 250/250/500/4.0/1.0/20 mM, (c, d)$ 167/333/500/4.0/1.0/20 mM, (e, f) 333/167/500/4.0/1.0/20 mM, (g, h) 250/250/500/5.0/1.0/20 mM, and (i, j) 125/375/500/4.0/1.0/20 mM in ethanol at 40 °C. (k, l) Ru-catalyzed living radical copolymerization of PEGMA and DMA for **P/C-1/0**: [PEGMA]<sub>0</sub>/[DMA]<sub>0</sub>/[ECPA]<sub>0</sub>/  $[Ru(Ind)Cl(PPh_3)]_0/[n-Bu_3N]_0 = 250/250/2.0/1.0/10$  mM in toluene at 80 °C. (m, n) Ru-catalyzed living radical copolymerization of DMAEMA and DMA for the precursor of P/C-0/1:  $[DMAEMA]_0/[DMA]_0/[ECPA]_0/[Ru(Ind)Cl(PPh_3)]_0/[n-Bu_3N]_0 = 250/250/2.0/1.0/10 \text{ mM in toluene}$ at 80 °C. (a, c, e, g, i, k, m) Time-conversion curves and (b, d, f, h, j, l, n) SEC curves of the products. The final products (b, d, f, h, j, l, n) and the intermediates (h) were purified by preparative SEC and used as the precursors of P/C-1/1, P/C-1/2, P/C-2/1, PEG/cation (1/1) random terpolymers with different DPs (76, 107, 135), and P/C-1/3 or P/C-1/0.



**Figure S2.** <sup>1</sup>H NMR spectra of (a) a PEGMA/DMAEMA/DMA random terpolymer (the precursor of P/C-1/1) in acetone- $d_6$  and (b) P/C-1/1 in DMSO- $d_6$  at 25 °C: [polymer] = 20 mg/mL.



Figure S3. <sup>1</sup>H NMR spectrum of P/C-1/0 in acetone- $d_6$  at 25 °C: [polymer] = 20 mg/mL.



**Figure S4.** <sup>1</sup>H NMR spectra of (a) a DMAEMA/DMA random copolymer (the precursor of P/C-0/1) in acetone- $d_6$  and (b) P/C-0/1 in DMSO- $d_6$  at 25 °C: [polymer] = 20 mg/mL.

| $\mathrm{D}\mathrm{P}^{b}$ | <i>l/m/n<sup>b</sup></i> | $M_{\rm n}{}^c$ | $M_{\rm w}/M_{\rm n}^{\ c}$ | $M_{\rm n}{}^d$ | $M_{\rm w}{}^e$ | $M_{ m w,H2O}^{f}$ | $N_{\rm agg}{}^{\rm g}$ | $\mathbf{C}\mathbf{p}^{\mathrm{h}}$ |
|----------------------------|--------------------------|-----------------|-----------------------------|-----------------|-----------------|--------------------|-------------------------|-------------------------------------|
|                            | (NMR)                    | (SEC)           | (SEC)                       | (NMR)           | (calcd)         | (MALLS)            |                         | (°C)                                |
| 76                         | 17/17/41                 | 18600           | 1.12                        | 24000           | 25600           | 618000             | 24                      | 57                                  |
| 107                        | 25/25/57                 | 26100           | 1.13                        | 34200           | 36900           | 414000             | 11                      | 56                                  |
| 135                        | 34/31/71                 | 32100           | 1.15                        | 43400           | 48400           | 355000             | 7.3                     | 55                                  |

Table S1. Characterization of PEG/Cation (1/1) Random Terpolymers and Their Micelles<sup>a</sup>

<sup>*a*</sup> PEG/cation (1/1) random terpolymers with different DPs (76, 107, and 135) were synthesized by living radical copolymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA), 2-(dimethylamino)ethyl methacrylate (DMAEMA), and dodecyl methacrylate (DMA), followed by the quaternization of the terpolymers with methyl iodide.

<sup>b</sup> The total degree of polymerization (DP) of the copolymers and DP of the PEGMA (l), DMAEMA (m), and DMA (n) units determined by <sup>1</sup>H NMR.

<sup>*c*</sup> Number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the DMAEMA-based terpolymer precursors determined by SEC in THF (20 mM Et<sub>3</sub>N) with PMMA standard calibration.

<sup>*d*</sup> Number-average molecular weight ( $M_n$ ) of the PEG/cation random terpolymers bearing PEG, quaternary ammonium salts [-CH<sub>2</sub>N(CH<sub>3</sub>)<sub>3</sub>I], and dodecyl groups determined by <sup>1</sup>H NMR.

<sup>*e*</sup> Weight-average molecular weight of the polymer chains calculated with  $M_n$  (NMR) and  $M_w/M_n$  (SEC):  $M_w$  (calcd) =  $M_n$  (NMR) x  $M_w/M_n$  (SEC).  $M_n$  (NMR) used for  $M_w$  (calcd) was re-calculated, assuming that all the counter anions on their micelles were changed to NO<sub>3</sub><sup>-</sup> originating from NaNO<sub>3</sub> included in the eluent of SEC-MALLS.

<sup>*f*</sup> Absolute weight-average molecular weight of the polymer micelles ( $M_{w,H2O}$ ) was determined by SEC-MALLS in H<sub>2</sub>O containing 100 mM NaNO<sub>3</sub>.

<sup>g</sup> Aggregation number ( $N_{agg}$ ) of the terpolymer micelles was estimated as follows:  $N_{agg} = M_{w,H2O}$  (MALLS)/ $M_w$  (calcd).

<sup>*h*</sup> Cloud point ( $C_p$ ) temperature was determined by monitoring the transmittance of the aqueous solutions of their polymer micelles ([polymer] = 4 mg/mL in pure water) at 670 nm upon heating from 25 °C to 90 °C. Cp was defined as a temperature, at which the transmittance became 90%.



Figure S5. DLS intensity distribution of (a, g) P/C-1/0, (b, h) P/C-2/1, (c, i) P/C-1/1, (d, j) P/C-1/2, (e, k) P/C-1/3, and (f, l) P/C-0/1 in water containing (a-e) 100 mM NaNO<sub>3</sub> or (f-j) 2 M NaCl: [polymer] = 1.0 mg/mL.



**Figure S6.** Cloud point measurements on a P/C-1/1 micelle in water with various concentrations of NaCl [(a) 0, (b) 0.1, (c) 0.2, (d) 0.5, (e) 1.0, (f) 1.5, and (g) 2.0 M]. The transmittance of their aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 90 or 100 °C (red solid line: heating, blue dashed line: cooling): Heating or cooling rate = 1 or - 1 °C /min, [polymer] = 4.0 mg/mL.



**Figure S7.** Cloud point measurements on a P/C-1/0 micelle in water with various concentrations of NaCl [(a) 0, (b) 0.1, (c) 0.2, (d) 0.5, (e) 1.0, (f) 1.5, and (g) 2.0 M]. The transmittance of their aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 70 °C (red solid line: heating, blue dashed line: cooling): Heating or cooling rate = 1 or -1 °C /min, [polymer] = 4.0 mg/mL.



**Figure S8.** Cloud point measurements on a P/C-2/1 micelle in water with various concentrations of NaCl [(a) 0, (b) 0.1, (c) 0.2, (d) 0.5, (e) 1.0, (f) 1.5, and (g) 2.0 M]. The transmittance of their aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 90 or 100 °C (red solid line: heating, blue dashed line: cooling): Heating or cooling rate = 1 or - 1 °C /min, [polymer] = 4.0 mg/mL.



**Figure S9.** Cloud point measurements on a P/C-1/2 micelle in water with various concentrations of NaCl [(a) 0, (b) 0.1, (c) 0.2, (d) 0.5, (e) 1.0, (f) 1.5, and (g) 2.0 M]. The transmittance of their aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 90 or 100 °C (red solid line: heating, blue dashed line: cooling): Heating or cooling rate = 1 or - 1 °C /min, [polymer] = 4.0 mg/mL.



Figure S10. (a, b) Cloud point measurements on a P/C-1/3 micelle in (a) pure water or (b) water with 2 M NaCl. (c, d) Cloud point measurements on a P/C-0/1 micelle in (c) pure water or (d) water with 2 M NaCl. The transmittance of their aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 90 or 100 °C (red solid line: heating, blue dashed line: cooling): Heating or cooling rate = 1 or -1 °C /min, [polymer] = 4.0 mg/mL.



Figure S11. Cloud point measurements on a P/C-1/1 micelle in water with 1 M (a) Na<sub>2</sub>SO<sub>4</sub>, (b) NaNO<sub>3</sub>, (c) NaI, and (d) CH<sub>3</sub>COONa. The transmittance of their aqueous solutions was monitored at 670 nm upon heating or cooling in the temperature range between 25 °C and 90 or 100 °C (red solid line: heating, blue dashed line: cooling): Heating or cooling rate = 1 or -1 °C /min, [polymer] = 4.0 mg/mL.



**Figure S12.** DLS intensity distribution of **P/C-1/1** micelles in water containing 1 M (a) CH<sub>3</sub>COONa, (b) NaCl, (c) NaI, (d)NaNO<sub>3</sub>, or (e) Na<sub>2</sub>SO<sub>4</sub> at 25 °C: [polymer] = 1.0 mg/mL.



**Figure S13.** DLS intensity distribution of **P/C-1/1** micelles in water containing (a-f) 100 mM NaNO<sub>3</sub> or (g-l) 2 M NaCl at (a, g) 25 °C, (b, h) 30 °C, (c, i) 40 °C, (d, j) 50 °C, (e, k) 60 °C, and (f, l) 70 °C: [polymer] = 1.0 mg/mL.



**Figure S14.** DLS intensity distribution of **P/C-2/1** micelles in water containing (a-g) 100 mM NaNO<sub>3</sub> or (h-n) 2 M NaCl at (a, h) 25 °C, (b, i) 30 °C, (c, j) 40 °C, (d, k) 50 °C, (e, l) 60 °C, (f, n) 70 °C, and (g, n) 80 °C: [polymer] = 1.0 mg/mL.



Figure S15. DLS intensity distribution of P/C-1/2 in water containing (a-g) 100 mM NaNO<sub>3</sub> or (h-n) 2 M NaCl at (a, h) 25 °C, (b, i) 30 °C, (c, j) 40 °C, (d, k) 50 °C, (e, l) 60 °C, (f, n) 70 °C, and (g, n) 80 °C: [polymer] = 1.0 mg/mL.



Figure S16. DLS intensity distribution of P/C-1/3 in water containing (a-g) 100 mM NaNO<sub>3</sub> or (h-n) 2 M NaCl at (a, h) 25 °C, (b, i) 30 °C, (c, j) 40 °C, (d, k) 50 °C, (e, l) 60 °C, (f, n) 70 °C, and (g, n) 80 °C: [polymer] = 1.0 mg/mL.



Figure S17. DLS intensity distribution of P/C-0/1 in water containing (a-g) 100 mM NaNO<sub>3</sub> or (h-n) 2 M NaCl at (a, h) 25 °C, (b, i) 30 °C, (c, j) 40 °C, (d, k) 50 °C, (e, l) 60 °C, (f, n) 70 °C, and (g, n) 80 °C: [polymer] = 1.0 mg/mL.



**Figure S18.** Hydrodynamic diameters of **P/C-2/1** micelles and aggregates in water containing 100 mM NaNO<sub>3</sub> (black circles) or 2 M NaCl (green squares) at various temperatures (25, 30, 40, 50, 60, 70, and 80 °C): [polymer] = 1.0 mg/mL.