

## Supplementary Information

### Precisely Controlled yet Dynamically Exchanged Micelles via the Self-Assembly of Amphiphilic Acrylate Random Copolymers in Water

Hiroyuki Kono,<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

#### Contents

<b>Experimental Section</b>	S2
<b>Supporting Data</b>	
<b>1. Synthesis of Amphiphilic Random and Alternating Copolymers</b>	
<b>Scheme S1.</b> Synthesis of amphiphilic random/alternating copolymers	S7
<b>Figure S1.</b> Free radical copolymerization: time-conversion plots and SEC curves	S8
<b>Figure S2.</b> Fractionation of <b>Ran-D50-Py</b> or <b>Np</b> using preparative SEC	S9
<b>Figure S3.</b> Fractionation of <b>Ran-D40-Py</b> or <b>Np</b> and <b>Alt-D50</b> using preparative SEC	S10
<b>Table S1.</b> Characterization of fractionated <b>Ran-D50</b>	S11
<b>Table S2.</b> Characterization of fractionated <b>Ran-D50-Py</b> or <b>Np</b>	S12
<b>Table S3.</b> Characterization of fractionated <b>Ran-D40-Py</b> or <b>Np</b>	S13
<b>Table S4.</b> Characterization of fractionated <b>Alt-D50</b>	S14
<b>Figure S4.</b> <sup>13</sup> C NMR spectra of <b>Alt-D50</b>	S15
<b>Figure S5.</b> <sup>1</sup> H NMR spectra of <b>Ran-D50</b> and <b>Ran-D50-A – F</b>	S16
<b>Figure S6.</b> <sup>1</sup> H NMR spectra of <b>Ran-D50-Py</b> and <b>Ran-D50-Py-A – F</b>	S17
<b>Figure S7.</b> <sup>1</sup> H NMR spectra of <b>Ran-D50-Np</b> and <b>Ran-D50-Np-A – F</b>	S18
<b>Figure S8.</b> <sup>1</sup> H NMR spectra of <b>Ran-D40-Py</b> and <b>Ran-D40-Py-A – F</b>	S19
<b>Figure S9.</b> <sup>1</sup> H NMR spectra of <b>Ran-D40-Np</b> and <b>Ran-D40-Np-A – F</b>	S20
<b>Figure S10.</b> <sup>1</sup> H NMR spectra of <b>Alt-D50</b> and <b>Alt-D50-A – F</b>	S21
<b>2. Micelle Formation of Amphiphilic Random and Alternating Copolymers in Water</b>	
<b>Figure S11.</b> DLS of <b>Ran-D50</b> and <b>Ran-D50-Py</b> or <b>Np</b> micelles in H <sub>2</sub> O	S22
<b>Figure S12.</b> DLS of <b>Ran-D40-Py</b> or <b>Np</b> and <b>Alt-D50</b> micelles in H <sub>2</sub> O	S23
<b>Figure S13.</b> SEC curves of <b>Ran-D50-Py</b> or <b>Np</b> micelles in H <sub>2</sub> O	S24
<b>Figure S14.</b> SEC curves of <b>Ran-D40-Py</b> or <b>Np</b> and <b>Alt-D50</b> micelles in H <sub>2</sub> O	S25
<b>Figure S15.</b> CMC: Fluorescence spectra of pyrene with the copolymers in water	S26
<b>3. Dynamic Exchange of Polymer Chains between Micelles</b>	
<b>Figure S16.</b> Fluorescence spectra of binary <b>Ran-D50-Py-D</b> / <b>Ran-D50-Np-D</b> mixtures in H <sub>2</sub> O	S27
<b>Figure S17.</b> Fluorescence spectra of binary <b>Ran-D40-Py-D</b> / <b>Ran-D40-Np-D</b> mixtures in H <sub>2</sub> O	S27
<b>Figure S18.</b> Fluorescence spectra of binary <b>Ran-D50-Py-F</b> / <b>Ran-D50-Np-F</b> mixtures in H <sub>2</sub> O	S28
<b>Figure S19.</b> Normalized <i>I<sub>py</sub></i> and fitting curves for the chain exchange of <b>Ran-D40-Py-D</b> / <b>Ran-D40-Np-D</b>	S28
<b>Table S5.</b> Rate Constants for the Chain Exchange of the Random Copolymer Micelles	S29

## Experimental Section

### Materials.

Poly(ethylene glycol) methyl ether acrylate [PEGA:  $\text{CH}_2=\text{CHCO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{Me}$ ,  $M_n = 480$  g/mol,  $n = 9.0$  on average, TCI] and dodecyl acrylate (DA, TCI, purity >98%) were purified by an inhibitor removal column (Aldrich) and degassed by triple vacuum-argon purge cycles before use. 2-Naphthylmethyl acrylate (NpA) and 1-pyrenylmethyl acrylate (PyA) were prepared as shown below. Dodecyl vinyl ether (DVE, Aldrich, purity >98%) was degassed by argon bubbling before use. Tetralin (1,2,3,4-tetrahydronaphthalene: TCI; purity >98%; an internal standard for  $^1\text{H}$  NMR analysis) and triethylamine (TEA, TCI, purity >99%) were dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use. 2,2'-Azobis(isobutyronitrile) (AIBN, TCI, purity >98%) was degassed by triple vacuum-argon purge cycles before use. Toluene (Wako, deoxidized), methanol (Wako), distilled water (Wako), ultrapure Water (Wako), acetone (Wako), *N,N*-dimethylformamide (DMF, Wako), dichloromethane (DCM, Wako, super dehydrated), ethyl acetate (Wako), hexane (Wako), and NaCl (Wako, purity >99.5%) were used as received.

### Characterization.

Molecular weight distribution (MWD) curves, number-average molecular weight ( $M_n$ ), and dispersity ( $D$ ) 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 11 standard poly(MMA) samples (PSS, Polymer Standard Service GmbH, Ready Cal Kit:  $M_p = 2380 - 2200000$  g/mol) or 9 standard poly(ethylene oxide) and poly(ethylene glycol) samples (PSS, Polymer Standard Service GmbH, Ready Cal Kit:  $M_p = 238 - 504000$  g/mol). MWD curves,  $M_n$ , and  $D$  of the polymers were also measured by SEC in  $\text{H}_2\text{O}$  at 30 °C (flow rate: 1 mL/min) on a silica gel column (Shodex PROTEIN LW-803: exclusion limit =  $1 \times 10^6$  (protein), particle size = 3  $\mu\text{m}$ ; 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). The column was calibrated against 9 standard poly(ethylene oxide) and poly(ethylene glycol) samples (PSS, Polymer Standard Service GmbH, Ready Cal Kit:  $M_p = 238 - 504000$  g/mol). Before characterization, polymer samples were fractionated by preparative SEC in DMF at room temperature (flow rate: 15 mL/min) on TOSOH TSKgel  $\alpha$ -3000 (exclusion limit =  $9 \times 10^4$  (PEO), particle size = 13  $\mu\text{m}$ ; 5.5 cm i.d.  $\times$  30 cm).  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance (NMR) measurement was performed in  $\text{CDCl}_3$  or acetone- $d_6$  on a JEOL JNM-ECA500 spectrometer operating at 500 ( $^1\text{H}$ ) and 125 ( $^{13}\text{C}$ ) MHz.

Absolute weight-average molecular weight ( $M_w$ ) of the polymers in DMF or  $\text{H}_2\text{O}$  was determined by SEC equipped with multi-angle laser light scattering (MALLS) 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 (Shodex PROTEIN KW-804: exclusion limit =  $4 \times 10^6$  (protein), particle size = 7  $\mu$ m; 0.8 cm i.d.  $\times$  30 cm). The 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 350 nm.

Dynamic light scattering (DLS) was measured on Otsuka Photal ELSZ-0 equipped with a semiconductor laser (wavelength: 658 nm). The measuring angle was 165° and the data was analyzed by CONTIN method.

Fluorescence spectra were recorded on JASCO FP-8500 spectrofluorometer equipped with a peltier thermostatted cell holder (ETC-815, JASCO). Parameters for the FRET studies were set as follows: excitation slit width = 2.5 nm, emission slit width = 2.5 nm, response = 0.1 sec, scanning speed = 1000 nm/min, excitation wavelength = 290.0 nm, emission wavelength = 300.0 – 550.0 nm. Parameters for the measurements of critical micellar concentration (CMC) were set as follows: 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.

### Monomer Synthesis.

**2-Naphthylmethyl acrylate (NpA):** In a 100 mL round-bottomed flask filled with argon, acryloyl chloride (9.5 mmol, 0.77 mL) was added to the solution of 2-naphthalenemethanol (6.3 mmol, 1.0 g) and triethylamine (13 mmol, 1.8 mL) in dry dichloromethane (15 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 5 h and was poured into distilled water (50 mL). The aqueous phase was separated and extracted by dichloromethane (20 mL), and the extracts were combined with the organic layer. The combined organic phase was washed sequentially with a diluted HCl aqueous solution, a saturated solution of NaHCO<sub>3</sub>, and brine. After the dichloromethane was removed in vacuo, the crude product was purified by silica gel column chromatography with dichloromethane/hexane = 1/1 (v/v) as an eluent to give NpA as a white solid (1.2 g, 29% yield). <sup>1</sup>H NMR [500 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$  = 0 ppm (TMS)]:  $\delta$  7.89–7.81 (m, 4H, naphthalene ring), 7.52–7.47 (m, 3H, naphthalene ring), 6.47 (dd,  $J$  = 17.5, 1.4 Hz, 1H, CH<sub>2</sub>=), 6.14 (dd,  $J$  = 17.3, 10.5 Hz, 1H, CH<sub>2</sub>=CHCOO-), 5.67 (dd,  $J$  = 10.3, 1.4 Hz, 1H, CH<sub>2</sub>=), 5.32-5.40 (s, 2H, -COOCH<sub>2</sub>Np). <sup>13</sup>C NMR [125 MHz, CDCl<sub>3</sub>, 25 °C,  $\delta$  = 77.16 ppm (CHCl<sub>3</sub>)]:  $\delta$  166.1, 133.4, 133.3, 133.2, 131.3, 128.5, 128.4, 128.1, 127.8, 127.5, 126.4, 126.3, 125.0, 66.6.

**1-Pyrenylmethyl acrylate (PyA):** In a 100 mL round-bottomed flask filled with argon, acryloyl chloride (13 mmol, 1.1 mL) was added to the solution of 1-pyrenemethanol (8.6 mmol, 2.0 g) and triethylamine (18 mmol, 2.5 mL) in dry dichloromethane (30 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 5 h and was poured into distilled water (50 mL). The aqueous phase was separated and extracted by dichloromethane (20 mL), and the extracts were combined with the organic layer. The combined organic phase was washed sequentially with a diluted HCl aqueous solution, a saturated solution of NaHCO<sub>3</sub>, and brine. After the dichloromethane was removed in vacuo, the crude product

was purified by silica gel column chromatography with hexane/ethyl acetate = 4/1 (v/v) as an eluent to give PyA as a yellow solid (1.0 g, 37% yield).  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]:  $\delta$  8.30–7.97 (m, 9H, pyrene ring), 6.46 (dd,  $J = 17.3, 1.3$  Hz, 1H,  $\text{CH}_2=$ ), 6.18 (dd,  $J = 17.3, 10.5$  Hz, 1H,  $\text{CH}_2=\text{CHCOO-}$ ), 5.90 (s, 2H,  $-\text{COOCH}_2\text{Py}$ ), 5.83 (dd,  $J = 10.5, 1.3$  Hz, 1H,  $\text{CH}_2=$ ).  $^{13}\text{C}$  NMR [125 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 77.16$  ppm ( $\text{CHCl}_3$ )]:  $\delta$  166.2, 131.8, 131.4, 131.2, 130.7, 129.6, 128.8, 128.4, 128.3, 127.9, 127.8, 127.4, 126.1, 125.6, 125.5, 124.9, 124.7, 122.9, 64.9.

### Polymer Synthesis.

Polymer synthesis was carried out by syringe technique under argon in a round bottom flask equipped with a three-way stopcock.

**PEGA/DA (50/50) random copolymer (Ran-D50):** AIBN (0.075 mmol, 12 mg) was weighed in a 50 mL glass tube. Into the tube, DA (7.5 mmol, 2.0 mL), PEGA (7.5 mmol, 3.3 mL), toluene (9.5 mL), and tetralin (0.20 mL) were added sequentially at 25 °C under argon (the total volume: 15 mL). The tube was placed in an oil bath kept at 60 °C. After 21 h, the reaction was terminated by cooling the solution to  $-78$  °C. The conversion of PEGA and DA was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Conv. PEGA/DA = 86%/86%. The product was purified by preparative SEC in DMF as an eluent. The purified product was dried under vacuum at room temperature. SEC (DMF, PMMA std.):  $M_n = 33600$  g/mol,  $D = 2.27$ .  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]: 4.4–3.9 ( $-\text{COOCH}_2\text{CH}_2\text{O-}$ ,  $-\text{COOCH}_2\text{CH}_2\text{CH}_2-$ ), 3.8–3.7 ( $-\text{COOCH}_2\text{CH}_2\text{O-}$ ), 3.7–3.5 ( $-\text{OCH}_2\text{CH}_2\text{O-}$ ), 3.5–3.4 ( $-\text{CH}_2\text{OCH}_3$ ), 3.4–3.3 ( $-\text{OCH}_3$ ), 2.6–2.3 ( $-\text{CH}_2\text{CHCO-}$ ), 2.0–1.5 ( $-\text{CH}_2\text{CH-}$ ,  $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.5–1.2 ( $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.0–0.8 ( $-\text{COO}(\text{CH}_2)_{11}\text{CH}_3$ ).

**Py-Labeled PEGA/DA (50/50) random copolymer (Ran-D50-Py):** AIBN (0.050 mmol, 8.2 mg) and PyA (0.050 mmol, 14 mg) were weighed in a 50 mL glass tube. Into the tube, DA (49.5 mmol, 1.4 mL), PEGA (50 mmol, 2.2 mL), toluene (6.3 mL), and tetralin (0.20 mL) were added sequentially at 25 °C under argon (the total volume: 10 mL). The tube was placed in an oil bath kept at 60 °C. After 15 h, the reaction was terminated by cooling the solution to  $-78$  °C. The conversion of PEGA and DA was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Conv. PEGA/DA = 87%/87%. The product was purified by preparative SEC in DMF as an eluent. The purified product was dried under vacuum at room temperature. SEC (DMF, PMMA std.):  $M_n = 33000$  g/mol,  $D = 2.21$ .  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]: 8.4–8.0 (pyrene ring in PyA), 5.9–5.8 ( $-\text{COOCH}_2\text{Py}$ ), 4.4–3.9 ( $-\text{COOCH}_2\text{CH}_2\text{O-}$ ,  $-\text{COOCH}_2\text{CH}_2\text{CH}_2-$ ), 3.8–3.7 ( $-\text{COOCH}_2\text{CH}_2\text{O-}$ ), 3.7–3.5 ( $-\text{OCH}_2\text{CH}_2\text{O-}$ ), 3.5–3.4 ( $-\text{CH}_2\text{OCH}_3$ ), 3.4–3.3 ( $-\text{OCH}_3$ ), 2.6–2.3 ( $-\text{CH}_2\text{CHCO-}$ ), 2.0–1.5 ( $-\text{CH}_2\text{CH-}$ ,  $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.5–1.2 ( $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.0–0.8 ( $-\text{COO}(\text{CH}_2)_{11}\text{CH}_3$ ).

**Np-Labeled PEGA/DA (50/50) random copolymer (Ran-D50-Np):** AIBN (0.050 mmol, 8.2 mg) and NpA (0.050 mmol, 10 mg) were weighed in a 50 mL glass tube. Into the tube, DA (49.5 mmol, 1.4 mL), PEGA (50 mmol, 2.2 mL), toluene (6.3 mL), and tetralin (0.20 mL) were added sequentially at 25 °C under argon (the total volume: 10 mL). The tube was placed in an oil bath kept at 60 °C. After 15 h, the reaction was terminated by cooling the solution to  $-78$  °C. The conversion of PEGA and DA

was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Conv. PEGA/DA = 84%/84%. The product was purified by preparative SEC in DMF as an eluent. The purified product was then dried under vacuum at room temperature. SEC (DMF, PMMA std.):  $M_n = 34000$  g/mol,  $D = 2.43$ .  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]: 8.1–7.9 and 7.7–7.5 (naphthalene ring in NpA), 5.3–5.2 ( $-\text{COOCH}_2\text{Np}$ ), 4.4–3.9 ( $-\text{COOCH}_2\text{CH}_2\text{O}-$ ,  $-\text{COOCH}_2\text{CH}_2\text{CH}_2-$ ), 3.8–3.7 ( $-\text{COOCH}_2\text{CH}_2\text{O}-$ ), 3.7–3.5 ( $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 3.5–3.4 ( $-\text{CH}_2\text{OCH}_3$ ), 3.4–3.3 ( $-\text{OCH}_3$ ), 2.6–2.3 ( $-\text{CH}_2\text{CHCO}-$ ), 2.0–1.5 ( $-\text{CH}_2\text{CH}-$ ,  $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.5–1.2 ( $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.0–0.8 ( $-\text{COO}(\text{CH}_2)_{11}\text{CH}_3$ ).

**Py-Labeled PEGA/DA (60/40) random copolymer (Ran-D40-Py):** AIBN (0.10 mmol, 16 mg) and PyA (0.050 mmol, 14 mg) were weighed in a 50 mL glass tube. Into the tube, DA (39.5 mmol, 1.1 mL), PEGA (60 mmol, 2.6 mL), toluene (6.1 mL), and tetralin (0.20 mL) were added sequentially at 25 °C under argon (the total volume: 10 mL). The tube was placed in an oil bath kept at 60 °C. After 22 h, the reaction was terminated by cooling the solution to  $-78$  °C. The conversion of PEGA and DA was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Conv. PEGA/DA = 86%/86%. The product was purified by preparative SEC in DMF as an eluent. The purified product was then dried under vacuum at room temperature. SEC (DMF, PMMA std.):  $M_n = 29600$  g/mol,  $D = 2.05$ .  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]: 8.4–8.0 (pyrene ring in PyA), 5.9–5.8 ( $-\text{COOCH}_2\text{Py}$ ), 4.4–3.9 ( $-\text{COOCH}_2\text{CH}_2\text{O}-$ ,  $-\text{COOCH}_2\text{CH}_2\text{CH}_2-$ ), 3.8–3.7 ( $-\text{COOCH}_2\text{CH}_2\text{O}-$ ), 3.7–3.5 ( $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 3.5–3.4 ( $-\text{CH}_2\text{OCH}_3$ ), 3.4–3.3 ( $-\text{OCH}_3$ ), 2.6–2.3 ( $-\text{CH}_2\text{CHCO}-$ ), 2.0–1.5 ( $-\text{CH}_2\text{CH}-$ ,  $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.5–1.2 ( $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.0–0.8 ( $-\text{COO}(\text{CH}_2)_{11}\text{CH}_3$ ).

**Np-Labeled PEGA/DA (60/40) random copolymer (Ran-D40-Np):** AIBN (0.10 mmol, 16 mg) and NpA (0.050 mmol, 10 mg) were weighed in a 50 mL glass tube. Into the tube, DA (39.5 mmol, 1.1 mL), PEGA (60 mmol, 2.6 mL), toluene (6.1 mL), and tetralin (0.20 mL) were added sequentially at 25 °C under argon (the total volume: 10 mL). The tube was placed in an oil bath kept at 60 °C. After 22 h, the reaction was terminated by cooling the solution to  $-78$  °C. The conversion of PEGA and DA was determined by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard: Conv. PEGA/DA = 85%/85%. The product was purified by preparative SEC in DMF as an eluent. The purified product was then dried under vacuum at room temperature. SEC (DMF, PMMA std.):  $M_n = 23400$  g/mol,  $D = 2.08$ .  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]: 8.1–7.9 and 7.7–7.5 (naphthalene ring in NpA), 5.3–5.2 ( $-\text{COOCH}_2\text{Np}$ ), 4.4–3.9 ( $-\text{COOCH}_2\text{CH}_2\text{O}-$ ,  $-\text{COOCH}_2\text{CH}_2\text{CH}_2-$ ), 3.8–3.7 ( $-\text{COOCH}_2\text{CH}_2\text{O}-$ ), 3.7–3.5 ( $-\text{OCH}_2\text{CH}_2\text{O}-$ ), 3.5–3.4 ( $-\text{CH}_2\text{OCH}_3$ ), 3.4–3.3 ( $-\text{OCH}_3$ ), 2.6–2.3 ( $-\text{CH}_2\text{CHCO}-$ ), 2.0–1.5 ( $-\text{CH}_2\text{CH}-$ ,  $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.5–1.2 ( $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_9\text{CH}_3$ ), 1.0–0.8 ( $-\text{COO}(\text{CH}_2)_{11}\text{CH}_3$ ).

**PEGA/DVE alternating copolymer (Alt-D50):** AIBN (0.38 mmol, 62 mg) was weighed in a 300 mL round bottom flask. Into the flask, DVE (260 mmol, 66 mL), PEGA (7.5 mmol, 3.3 mL), toluene (78 mL), and tetralin (3.0 mL) were added sequentially at 25 °C under argon (the total volume: 150 mL). The flask was placed in an oil bath kept at 60 °C. After 4 h, the reaction was terminated by cooling the solution to  $-78$  °C. The conversion of PEGA and DVE was determined to be >99% and 3.0%,

respectively, by  $^1\text{H}$  NMR in  $\text{CDCl}_3$  with tetralin as an internal standard. The product was purified by dialysis in acetone and by preparative SEC in DMF as an eluent. The purified product was then dried under vacuum at room temperature. SEC (DMF, PMMA std.):  $M_n = 33500$  g/mol,  $D = 1.72$ .  $^1\text{H}$  NMR [500 MHz,  $\text{CDCl}_3$ , 25 °C,  $\delta = 0$  ppm (TMS)]: 4.3–4.1 (-COOCH<sub>2</sub>CH<sub>2</sub>O-), 3.8–3.5 (-COOCH<sub>2</sub>CH<sub>2</sub>O-, -OCH<sub>2</sub>CH<sub>2</sub>O-), 3.4–3.2 (-OCH<sub>3</sub>, -OCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.2–3.0 (-CH<sub>2</sub>CHO-), 2.8–2.3 (-CH<sub>2</sub>CHCO-), 2.0–1.1 (-CH<sub>2</sub>CHO-, -CH<sub>2</sub>CHCO-, -OCH<sub>2</sub>(CH<sub>2</sub>)<sub>10</sub>CH<sub>3</sub>), 0.9–0.8 (-CHO(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub>).

### Preparation of Polymer Micelles in Water.

The dichloromethane solution of a random or alternating copolymer was evaporated, and the resulting bulk polymer was dissolved in water. The aqueous solution was sonicated for 3 minutes at 25 °C and kept for 1 h at 25 °C. The solution was then filtrated with a PTFE membrane filter (pore size = 0.45  $\mu\text{m}$ ) before SEC, DLS, and fluorescence measurements.

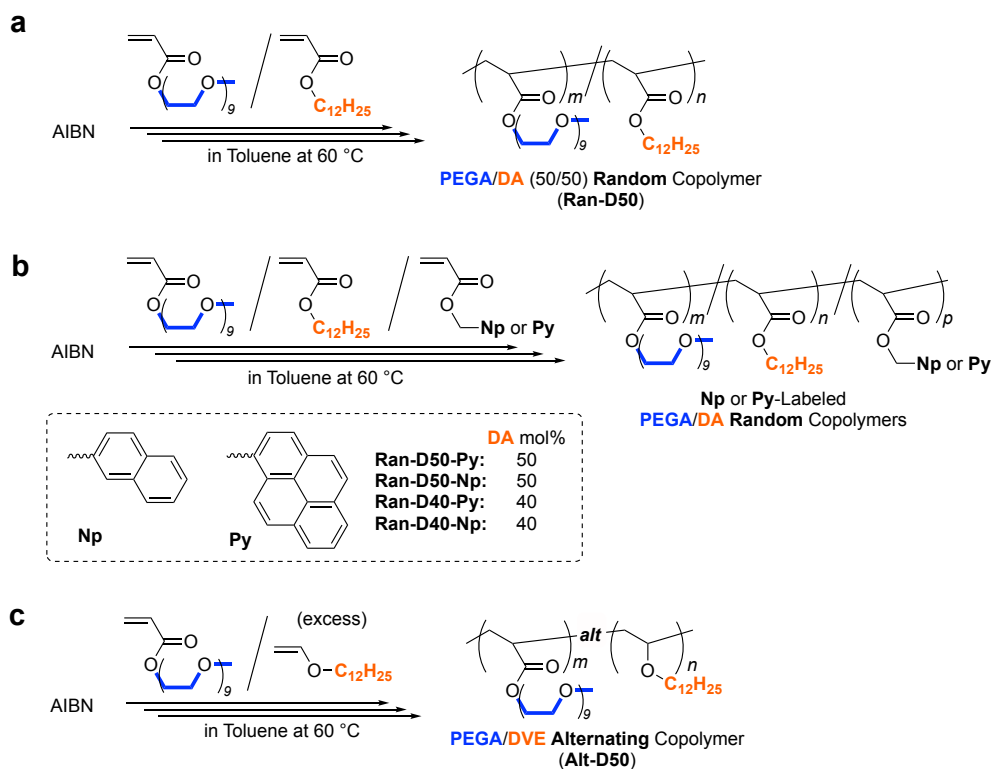
### Critical Micelle Concentration (CMC) of Random or Alternating Copolymers in Water.

CMC of the random or alternating copolymers was determined by fluorescence spectroscopy of pyrene in the presence of the copolymers in water. Aqueous solutions of the copolymers with 14 different concentrations between  $1.0 \times 10^{-4}$  mg/mL and  $1.0 \times 10^{-1}$  mg/mL (each volume: 2 mL) were prepared in vials. Into the solutions, a DMSO solution of pyrene ( $1 \times 10^{-4}$  M, 10  $\mu\text{L}$ ) 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. 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 intensity ratio of the first ( $I_1$ , 373 nm) and the third ( $I_3$ , 384 nm) vibronic bands of pyrene emission, was plotted as a function of polymer concentration. CMC was determined as the concentration at which  $I_1/I_3$  started to decrease.

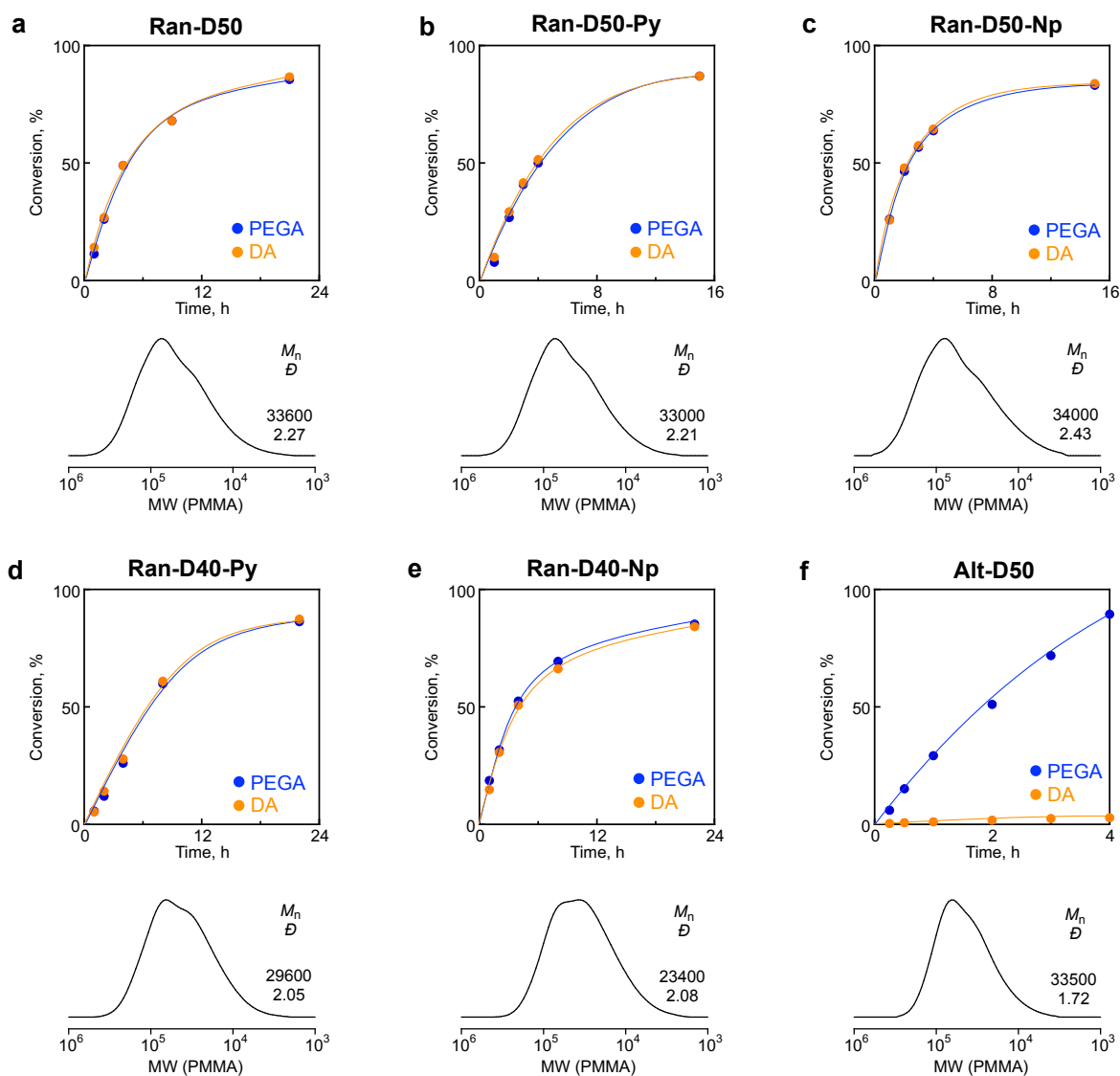
### Dynamic Polymer Exchange between Micelles.

Into a cuvette containing the 1 mL aqueous solution of a Py-labeled micelle at measuring temperature, a 1 mL aqueous solution of a Np-labeled micelle at the same temperature was added quickly with stirring. The fluorescence spectra of the resulting solution were immediately recorded at the predetermined temperature for 2 h. The collected fluorescence spectra were fitted by eq.1 (in the main text) to calculate  $k_{\text{obs}}$ . The  $k_{\text{obs}}$  values were applied to Arrhenius Plot to calculate activation energy ( $E_a$ ) for the exchange process of polymer chains between their micelles.

## Supporting Data

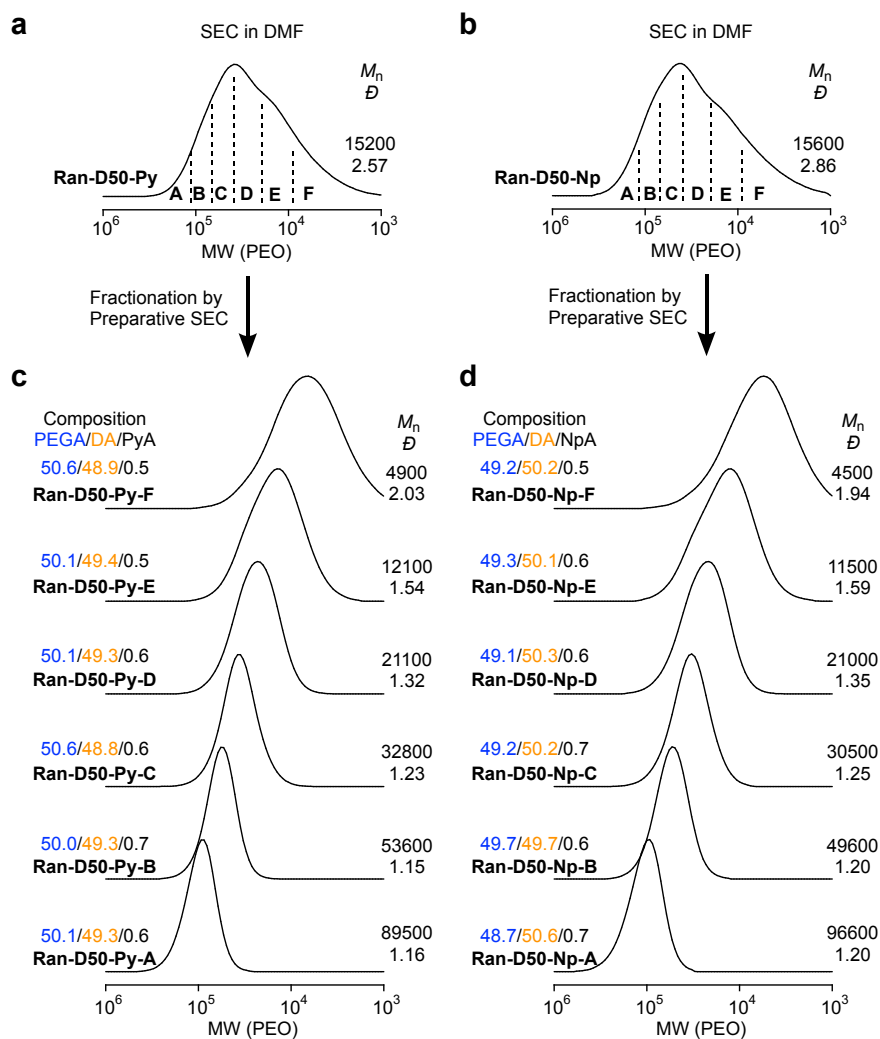


**Scheme S1.** Synthesis of (a) a PEGA/DA (50/50) random copolymer, (b) Np or Py-labeled PEGA/DA random copolymers, and (c) a PEGA/DVE alternating copolymer.

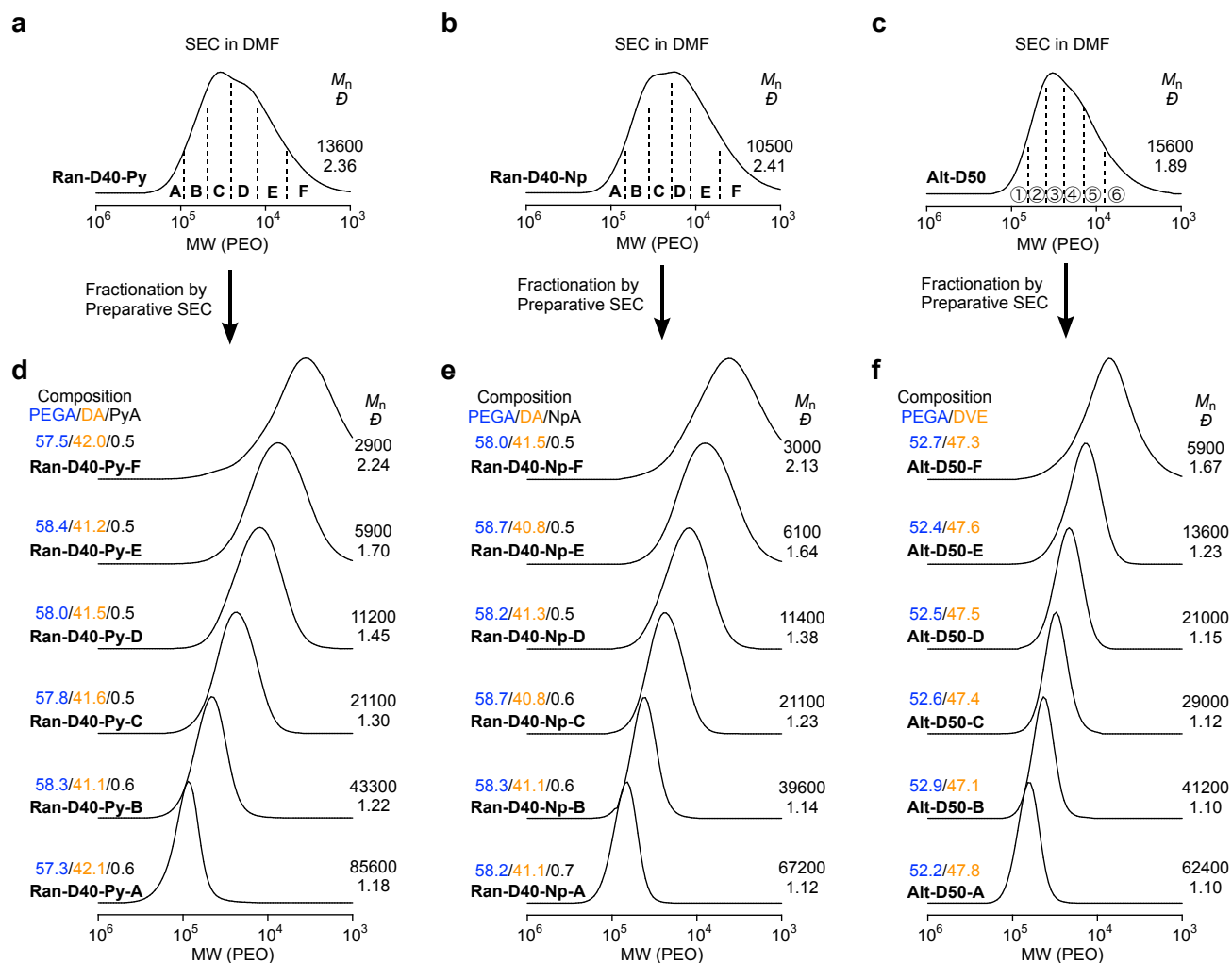


**Figure S1.** Synthesis of PEGA/DA/PyA or NpA random copolymers (a: **Ran-D50**, b: **Ran-D50-Py**, c: **Ran-D50-Np**, d: **Ran-D40-Py**, e: **Ran-D40-Np**) or a PEGA/DVE alternating copolymer (f: **Alt-D50**,) via free radical copolymerization of PEGA, DA, and PyA or NpA. Upper: time conversion plots, lower: SEC curves of the final products.  $[PEGA]_0/[DA]_0/[AIBN]_0 = 500/500/5.0$  mM (**Ran-D50**),  $[PEGA]_0/[DA]_0/[PyA (NpA)]_0/[AIBN]_0 = 500/495/5.0/5.0$  mM (**Ran-D50-Py** or **Np**),  $[PEGA]_0/[DA]_0/[PyA (NpA)]_0/[AIBN]_0 = 600/395/5.0/10$  mM (**Ran-D40-Py** or **Np**), or  $[PEGA]_0/[DVE]_0/[AIBN]_0 = 50/1700/2.5$  mM (**Alt-D50**) in toluene at 60 °C. The final products in (a–f) were purified by preparative SEC. The in-set  $M_n$  and  $\bar{D}$  values are determined with PMMA standard calibration.





**Figure S2.** SEC curves,  $M_n$ , and  $\bar{D}$  of (a) **Ran-D50-Py** and (b) **Ran-D50-Np** in DMF (10 mM LiBr) with PEO standard calibration. These polymers were fractionated into six samples with different molecular weights (A–F) by preparative SEC. SEC curves,  $M_n$ , and  $\bar{D}$  of fractionated (c) **Ran-D50-Py-A – F** and (d) **Ran-D50-Np-A – F** in DMF (10 mM LiBr) with PEO standard calibration.



**Figure S3.** SEC curves,  $M_n$ , and  $\bar{D}$  of (a) **Ran-D40-Py**, (b) **Ran-D40-Np**, and (c) **Alt-D50** in DMF (10 mM LiBr) with PEO standard calibration. These polymers were fractionated into six samples with different molecular weights (A–F) by preparative SEC. SEC curves,  $M_n$ , and  $\bar{D}$  of fractionated (d) **Ran-D40-Py-A – F**, (e) **Ran-D40-Np-A – F**, and (f) **Alt-D50-A – F** in DMF (10 mM LiBr) with PEO standard calibration.

**Table S1. Characterization of PEGA/DA Random Copolymers<sup>a</sup>**

Polymer	DA <sup>b</sup> (mol%)	DP <sup>c</sup>	<i>m/n</i> <sup>c</sup>	<i>M<sub>n,DMF</sub></i> <sup>d</sup> (g/mol, SEC)	<i>dn/dc</i> <sup>e</sup> (DMF)	<i>M<sub>w,DMF</sub></i> <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>DMF</sub> <sup>e</sup> (MALLS)	<i>dn/dc</i> <sup>e</sup> (H <sub>2</sub> O)	<i>M<sub>w,H2O</sub></i> <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>H2O</sub> <sup>e</sup> (MALLS)	<i>N<sub>agg</sub></i> <sup>f</sup>	<i>R<sub>h,H2O</sub></i> <sup>g</sup> (nm)
<b>Ran-D50</b>	50.7	n.d.	n.d.	15,400	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.0
<b>Ran-D50-A</b>	50.8	799	393/406	90,700	0.0475	327,000	1.14	0.133	393,000	1.15	1.2	7.7
<b>Ran-D50-B</b>	50.8	457	225/232	49,700	0.0424	181,000	1.10	0.134	236,000	1.09	1.3	6.2
<b>Ran-D50-C</b>	50.7	270	133/137	31,600	0.0424	110,000	1.13	0.133	210,000	1.08	1.9	5.7
<b>Ran-D50-D</b>	50.7	201	99/102	22,400	0.0438	84,600	1.18	0.132	206,000	1.09	2.4	5.9
<b>Ran-D50-E</b>	50.5	121	60/61	12,600	0.0418	54,200	1.25	0.133	204,000	1.10	3.8	5.7
<b>Ran-D50-F</b>	50.7	55	27/28	4,500	0.0416	31,600	1.60	0.131	208,000	1.14	6.6	6.1

<sup>a</sup> A PEGA/DVE copolymer (**Ran-D50**) was synthesized by free radical copolymerization of PEGA and DA with AIBN: [PEGA]<sub>0</sub>/[DA]<sub>0</sub>/[AIBN]<sub>0</sub> = 500/500/5.0 mM in toluene at 60 °C. **Ran-D50-A – F** were obtained from the fractionation of **Ran-D50** by preparative SEC.

<sup>b</sup> DA content in the copolymers determined by <sup>1</sup>H NMR.

<sup>c</sup> Degree of polymerization (DP) and the copolymer composition (*m/n*: DP of PEGA and DVE determined by <sup>1</sup>H NMR, *M<sub>w,DMF</sub>* (MALLS), and *D*<sub>DMF</sub> (MALLS). n.d.: not determined.

<sup>d</sup> Number-average molecular weight (*M<sub>n</sub>*) determined by SEC in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl) with PEO standard calibration.

<sup>e</sup> Absolute weight-average molecular weight (*M<sub>w</sub>*) and dispersity (*D*) determined by SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl). n.d.: not determined. Refractive Index Increment (*dn/dc*) of the polymers was determined by the on-line RI detector of SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl).

<sup>f</sup> Aggregation number of their micelles in H<sub>2</sub>O: *N<sub>agg</sub>* = *M<sub>w,H2O</sub>* (MALLS)/*M<sub>w,DMF</sub>* (MALLS). n.d.: not determined.

<sup>g</sup> Hydrodynamic radius of their micelles determined by DLS in H<sub>2</sub>O at 25 °C: [polymer] = 1.0 mg/mL.

**Table S2. Characterization of Py or Np-Labeled PEGA/DA (50/50) Random Copolymers<sup>a</sup>**

Polymer	DA <sup>b</sup> (mol%)	DP <sup>c</sup>	<i>m/n/p</i> <sup>c</sup>	<i>M<sub>n,DMF</sub></i> <sup>d</sup> (g/mol, SEC)	<i>dn/dc</i> <sup>e</sup> (DMF)	<i>M<sub>w,DMF</sub></i> <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>DMF</sub> <sup>e</sup> (MALLS)	<i>dn/dc</i> <sup>e</sup> (H <sub>2</sub> O)	<i>M<sub>w,H2O</sub></i> <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>H2O</sub> <sup>e</sup> (MALLS)	<i>N<sub>agg</sub></i> <sup>f</sup>	<i>R<sub>h,H2O</sub></i> <sup>g</sup> (nm)
<b>Ran-D50-Py</b>	49.0	167	84/82/0.9	15,200	0.0464	110,000	1.82	0.130	230,000	1.19	2.1	6.5
<b>Ran-D50-Py -A</b>	49.3	685	343/338/4.2	89,500	0.0459	279,000	1.13	0.135	336,000	1.15	1.2	8.8
<b>Ran-D50-Py -B</b>	49.3	423	212/209/2.8	53,600	0.0456	171,000	1.12	0.135	223,000	1.09	1.3	6.5
<b>Ran-D50-Py -C</b>	49.8	266	135/130/1.6	32,800	0.0441	112,000	1.16	0.132	196,000	1.08	1.7	6.2
<b>Ran-D50-Py -D</b>	49.3	172	86/85/1.0	21,100	0.0454	76,200	1.23	0.135	186,000	1.09	2.4	5.4
<b>Ran-D50-Py -E</b>	49.4	105	53/52/0.5	12,100	0.0455	51,800	1.36	0.132	185,000	1.10	3.6	6.0
<b>Ran-D50-Py -F</b>	48.9	68	34/33/0.3	4,900	0.0458	34,700	1.42	0.134	187,000	1.14	5.4	6.3
<b>Ran-D50-Np</b>	50.3	187	92/94/1.2	15,600	0.0454	134,000	1.99	0.134	235,000	1.17	1.8	7.0
<b>Ran-D50-Np-A</b>	50.6	716	349/363/4.9	96,600	0.0456	317,000	1.24	0.134	372,000	1.17	1.2	10
<b>Ran-D50-Np-B</b>	49.7	324	161/161/2.1	49,600	0.0452	148,000	1.27	0.134	235,000	1.09	1.6	7.0
<b>Ran-D50-Np-C</b>	50.2	259	126/128/1.7	30,500	0.0445	104,000	1.13	0.133	207,000	1.09	2.0	6.0
<b>Ran-D50-Np-D</b>	50.3	170	83/85/1.0	21,000	0.0452	74,300	1.22	0.134	198,000	1.10	2.7	5.6
<b>Ran-D50-Np-E</b>	50.1	97	48/49/0.5	11,500	0.0459	48,000	1.38	0.136	193,000	1.12	4.0	6.5
<b>Ran-D50-Np-F</b>	50.2	38	19/19/0.2	4,500	0.0438	24,400	1.80	0.134	201,000	1.16	8.3	6.1

<sup>a</sup> Py or Np-labeled PEGA/DVE copolymers (**Ran-D50-Py** or **Ran-D50-Np**) were synthesized by free radical copolymerization of PEGA, DA, and Py(Np)A with AIBN: [PEGA]<sub>0</sub>/[DA]<sub>0</sub>/[Py(Np)A]<sub>0</sub>/[AIBN]<sub>0</sub> = 500/495/5.0/5.0 mM in toluene at 60 °C. **Ran-D50-Py-A – F** and **Ran-D50-Np-A – F** were obtained from the fractionation of **Ran-D50-Py** and **Ran-D50-Np** by preparative SEC, respectively.

<sup>b</sup> DA content in the copolymers determined by <sup>1</sup>H NMR.

<sup>c</sup> DP and the copolymer composition (*m/n/p*: DP of PEGA, DVE, and Py(Np)A) determined by <sup>1</sup>H NMR, *M<sub>w,DMF</sub>* (MALLS), and *D*<sub>DMF</sub> (MALLS).

<sup>d</sup> *M<sub>n</sub>* determined by SEC in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl) with PEO standard calibration.

<sup>e</sup> Absolute weight-average molecular weight (*M<sub>w</sub>*) and dispersity (*D*) determined by SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl). Refractive Index Increment (*dn/dc*) of the polymers was determined by the on-line RI detector of SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl).

<sup>f</sup> Aggregation number of their micelles in H<sub>2</sub>O: *N<sub>agg</sub>* = *M<sub>w,H2O</sub>* (MALLS)/*M<sub>w,DMF</sub>* (MALLS).

<sup>g</sup> Hydrodynamic radius of their micelles determined by DLS in H<sub>2</sub>O at 25 °C: [polymer] = 1.0 mg/mL.

**Table S3. Characterization of Py or Np-Labeled PEGA/DA (60/40) Random Copolymers<sup>a</sup>**

Polymer	DA <sup>b</sup> (mol%)	DP <sup>c</sup>	<i>m/n/p</i> <sup>c</sup>	<i>M<sub>n,DMF</sub></i> <sup>d</sup> (g/mol, SEC)	<i>dn/dc</i> <sup>e</sup> (DMF)	<i>M<sub>w,DMF</sub></i> <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>DMF</sub> <sup>e</sup> (MALLS)	<i>dn/dc</i> <sup>e</sup> (H <sub>2</sub> O)	<i>M<sub>w,H2O</sub></i> <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>H2O</sub> <sup>e</sup> (MALLS)	<i>N<sub>agg</sub></i> <sup>f</sup>	<i>R<sub>h,H2O</sub></i> <sup>g</sup> (nm)
<b>Ran-D40-Py</b>	41.5	n.d.	n.d.	13,600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.8
<b>Ran-D40-Py -A</b>	42.1	715	410/301/4.1	85,600	0.0424	301,000	1.11	0.131	316,000	1.14	1.0	8.0
<b>Ran-D40-Py -B</b>	41.1	319	186/131/1.8	43,400	0.0443	140,000	1.16	0.131	166,000	1.17	1.2	6.5
<b>Ran-D40-Py -C</b>	41.6	157	91/65/0.9	21,100	0.0447	72,400	1.21	0.132	115,000	1.09	1.6	5.3
<b>Ran-D40-Py -D</b>	41.5	91	53/38/0.5	11,200	0.0453	42,800	1.23	0.133	103,000	1.06	2.4	4.7
<b>Ran-D40-Py -E</b>	41.2	70	41/29/0.3	5,900	0.0411	35,100	1.32	0.135	101,000	1.05	2.9	4.7
<b>Ran-D40-Py -F</b>	42.0	50	29/21/0.2	2,900	0.0435	27,100	1.45	0.131	120,000	1.07	4.4	4.9
<b>Ran-D40-Np</b>	40.8	n.d.	n.d.	10,500	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5.4
<b>Ran-D40-Np-A</b>	41.1	470	274/193/3.4	67,200	0.0436	192,000	1.07	0.134	225,000	1.10	1.2	6.9
<b>Ran-D40-Np-B</b>	41.1	295	172/121/1.7	39,600	0.0411	120,000	1.07	0.131	131,000	1.07	1.1	6.1
<b>Ran-D40-Np-C</b>	40.8	153	90/62/0.8	21,100	0.0429	65,600	1.13	0.132	102,000	1.04	1.6	5.4
<b>Ran-D40-Np-D</b>	41.3	82	48/34/0.4	11,400	0.0435	39,300	1.26	0.130	98,800	1.05	2.5	5.3
<b>Ran-D40-Np-E</b>	40.8	53	31/22/0.2	6,100	0.0418	28,600	1.41	0.131	100,000	1.06	3.5	5.3
<b>Ran-D40-Np-F</b>	41.5	32	19/13/0.2	3,000	0.0426	19,400	1.59	0.131	113,000	1.07	5.8	4.9

<sup>a</sup> Py or Np-labeled PEGA/DVE copolymers (**Ran-D40-Py** or **Ran-D40-Np**) were synthesized by free radical copolymerization of PEGA, DA, and Py(Np)A with AIBN: [PEGA]<sub>0</sub>/[DA]<sub>0</sub>/[Py(Np)A]<sub>0</sub>/[AIBN]<sub>0</sub> = 600/395/5.0/10 mM in toluene at 60 °C. **Ran-D40-Py-A – F** and **Ran-D40-Np-A – F** were obtained from the fractionation of **Ran-D40-Py** and **Ran-D40-Np** by preparative SEC, respectively.

<sup>b</sup> DA content in the copolymers determined by <sup>1</sup>H NMR.

<sup>c</sup> DP and the copolymer composition (*m/n/p*: DP of PEGA, DVE, and Py(Np)A) determined by <sup>1</sup>H NMR, *M<sub>w,DMF</sub>* (MALLS), and *D*<sub>DMF</sub> (MALLS). n.d.: not determined.

<sup>d</sup> *M<sub>n</sub>* determined by SEC in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl) with PEO standard calibration.

<sup>e</sup> Absolute weight-average molecular weight (*M<sub>w</sub>*) and dispersity (*D*) determined by SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl). n.d.: not determined. Refractive Index Increment (*dn/dc*) of the polymers was determined by the on-line RI detector of SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl).

<sup>f</sup> Aggregation number of their micelles in H<sub>2</sub>O: *N<sub>agg</sub>* = *M<sub>w,H2O</sub>* (MALLS)/*M<sub>w,DMF</sub>* (MALLS). n.d.: not determined.

<sup>g</sup> Hydrodynamic radius of their micelles determined by DLS in H<sub>2</sub>O at 25 °C: [polymer] = 1.0 mg/mL.

**Table S4. Characterization of PEGA/DVE Alternating Copolymers<sup>a</sup>**

Polymer	DVE <sup>b</sup> (mol%)	DP <sup>c</sup>	<i>m/n</i> <sup>c</sup>	<i>M<sub>n</sub></i> ,DMF <sup>d</sup> (g/mol, SEC)	<i>dn/dc</i> <sup>e</sup> (DMF)	<i>M<sub>w</sub></i> ,DMF <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>DMF</sub> <sup>e</sup> (MALLS)	<i>dn/dc</i> <sup>e</sup> (H <sub>2</sub> O)	<i>M<sub>w</sub></i> ,H <sub>2</sub> O <sup>e</sup> (g/mol, MALLS)	<i>D</i> <sub>H<sub>2</sub>O</sub> <sup>e</sup> (MALLS)	<i>N<sub>agg</sub></i> <sup>f</sup>	<i>R<sub>h</sub></i> ,H <sub>2</sub> O <sup>g</sup> (nm)
<b>Alt-D50</b>	47.4	n.d.	n.d.	15,600	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.8
<b>Alt-D50-A</b>	47.8	497	259/238	62,400	0.0424	183,000	1.04	0.130	205,000	1.06	1.1	6.5
<b>Alt-D50-B</b>	47.1	325	172/153	41,200	0.0417	120,000	1.04	0.133	129,000	1.05	1.1	5.2
<b>Alt-D50-C</b>	47.4	228	120/108	29,000	0.0419	83,900	1.04	0.131	96,900	1.04	1.2	4.4
<b>Alt-D50-D</b>	47.5	161	85/77	21,000	0.0422	61,200	1.08	0.132	87,900	1.03	1.4	4.3
<b>Alt-D50-E</b>	47.6	109	57/52	13,600	0.0413	43,800	1.14	0.131	82,600	1.01	1.9	4.2
<b>Alt-D50-F</b>	47.3	60	32/28	5,900	0.0411	28,600	1.35	0.133	82,500	1.01	2.9	4.1

<sup>a</sup> A PEGA/DVE copolymer (**Alt-D50**) was synthesized by free radical copolymerization of PEGA and DVE with AIBN: [PEGA]<sub>0</sub>/[DVE]<sub>0</sub>/[AIBN]<sub>0</sub> = 50/1700/2.5 mM in toluene at 60 °C. **Alt-D50-A – F** were obtained from the fractionation of **Alt-D50** by preparative SEC.

<sup>b</sup> DVE content in the copolymers determined by <sup>1</sup>H NMR.

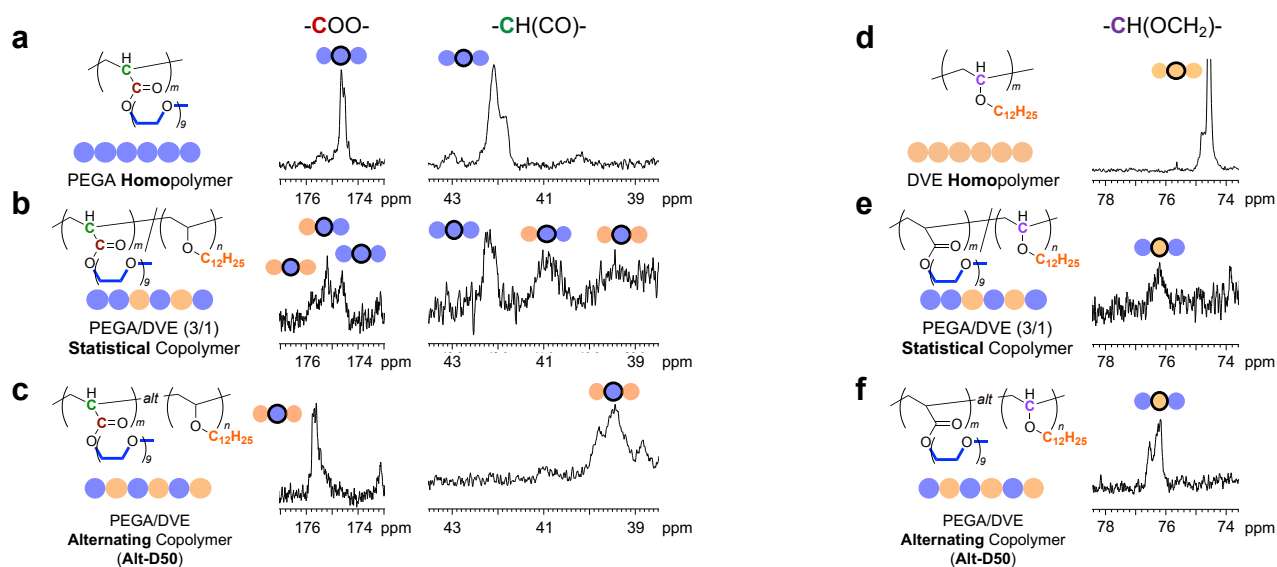
<sup>c</sup> DP and the copolymer composition (*m/n*: DP of PEGA and DVE determined by <sup>1</sup>H NMR, *M<sub>w</sub>*,DMF (MALLS), and *D*<sub>DMF</sub> (MALLS). n.d.: not determined.

<sup>d</sup> *M<sub>n</sub>* determined by SEC in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl) with PEO standard calibration.

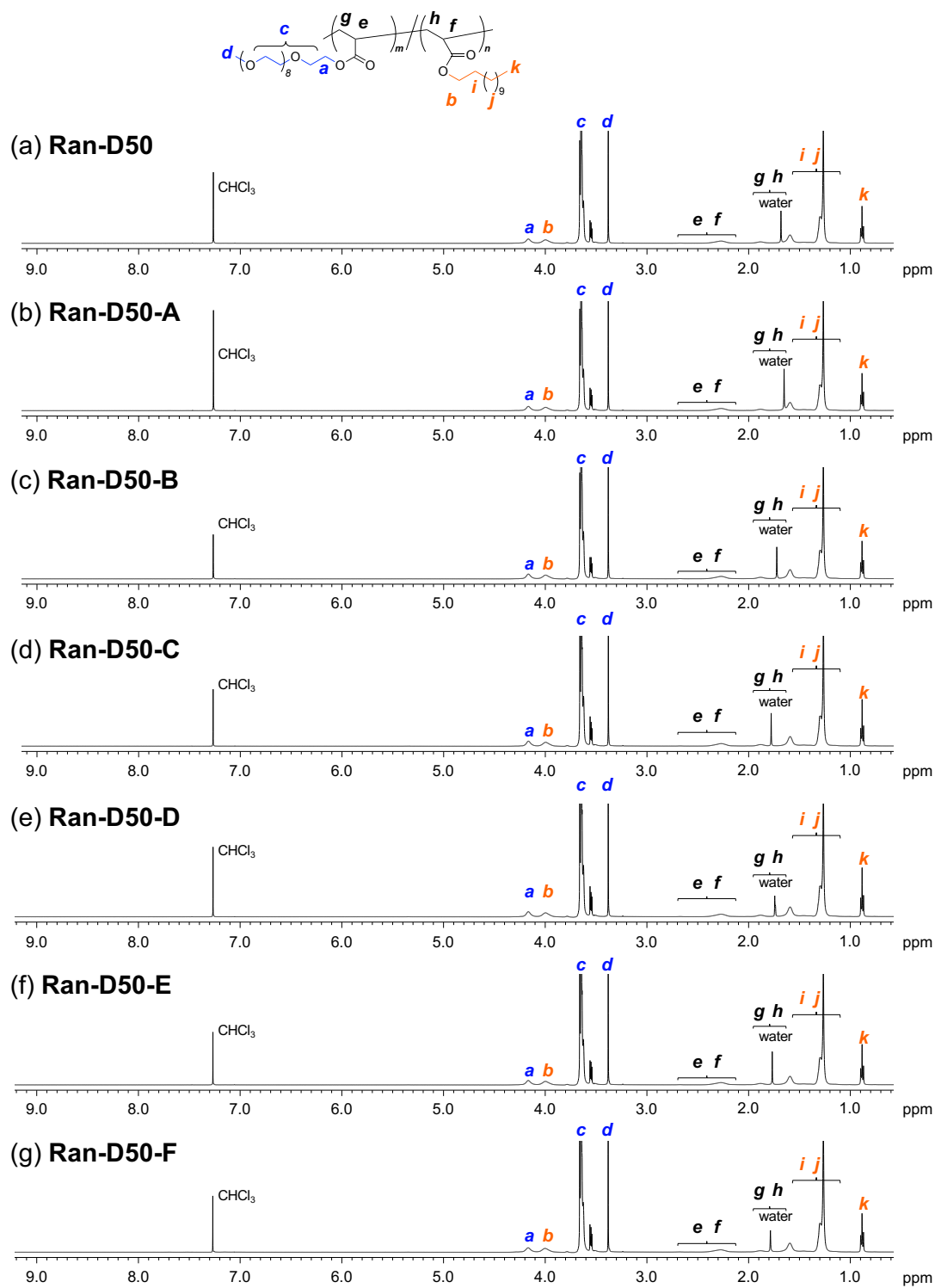
<sup>e</sup> Absolute weight-average molecular weight (*M<sub>w</sub>*) and dispersity (*D*) determined by SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl). n.d.: not determined. Refractive Index Increment (*dn/dc*) of the polymers was determined by the on-line RI detector of SEC-MALLS in DMF (10 mM LiBr) or H<sub>2</sub>O (100 mM NaCl).

<sup>f</sup> Aggregation number of their micelles in H<sub>2</sub>O: *N<sub>agg</sub>* = *M<sub>w</sub>*,H<sub>2</sub>O (MALLS)/*M<sub>w</sub>*,DMF (MALLS). n.d.: not determined.

<sup>g</sup> Hydrodynamic radius of their micelles determined by DLS in H<sub>2</sub>O at 25 °C: [polymer] = 1.0 mg/mL.

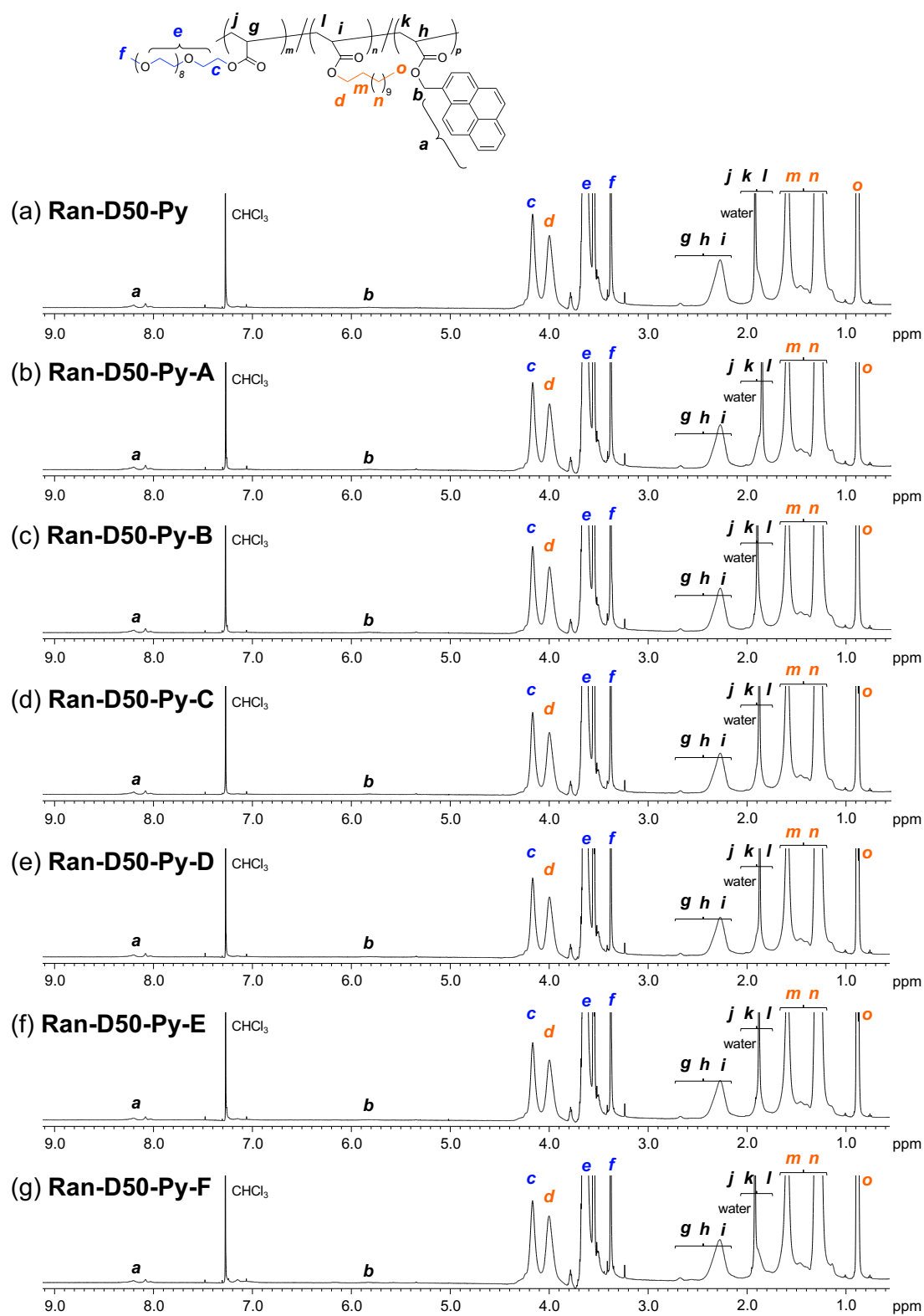


**Figure S4.**  $^{13}\text{C}$  NMR spectra of the carbonyl or methine carbons in the PEGA units of (a) a PEGA homopolymer ( $M_n = 12,000$  g/mol,  $D = 1.21$  by SEC with PMMA std.), (b) a PEGA/DVE (3/1) statistical copolymer ( $M_n = 33,000$  g/mol,  $D = 1.82$  by SEC with PMMA std.), and (c) **Alt-D50** in toluene- $d_8$  at 55 °C: [polymer] = 200 mg/mL.  $^{13}\text{C}$  NMR spectra of the methine carbons in the DVE units of (d) a DVE homopolymer ( $M_n = 16,000$  g/mol,  $D = 1.03$  by SEC with PMMA std.), (e) a PEGA/DVE (3/1) statistical copolymer, and (f) **Alt-D50** in toluene- $d_8$  at 55 °C: [polymer] = 200 mg/mL.

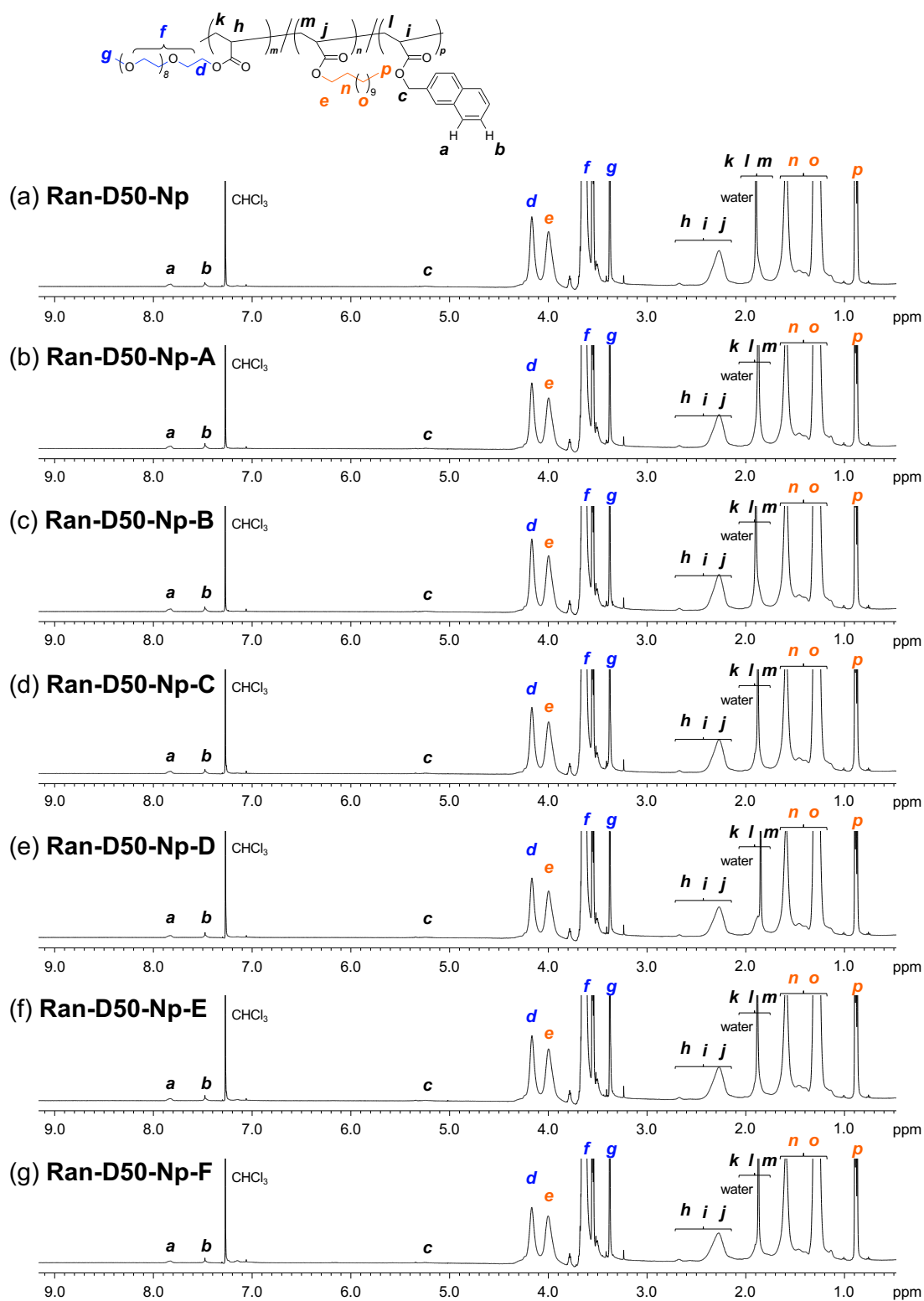


**Figure S5.** (a–g)  $^1\text{H}$  NMR spectra of **Ran-D50** and **Ran-D50-A – F** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : [polymer] = 30 mg/mL.

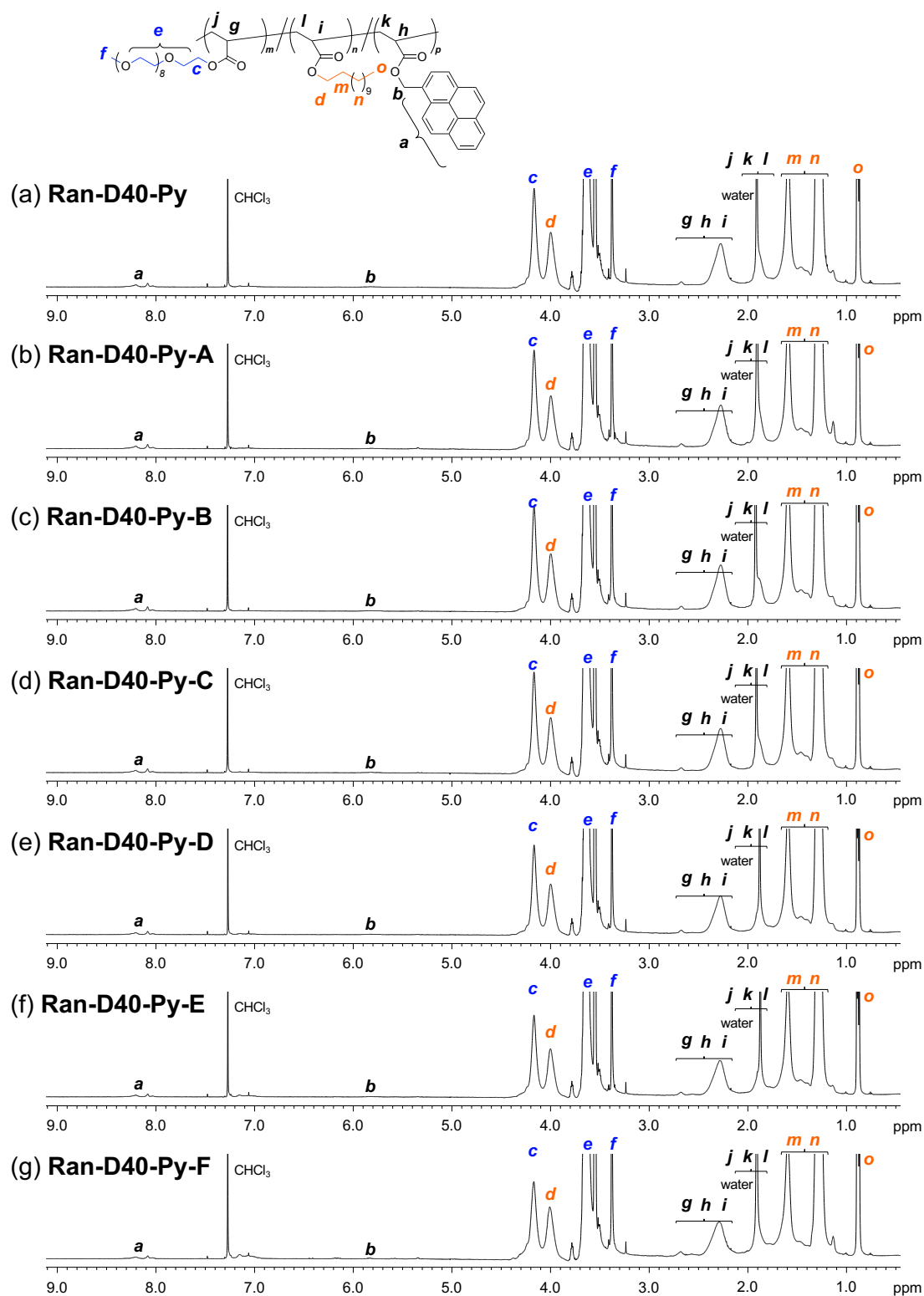




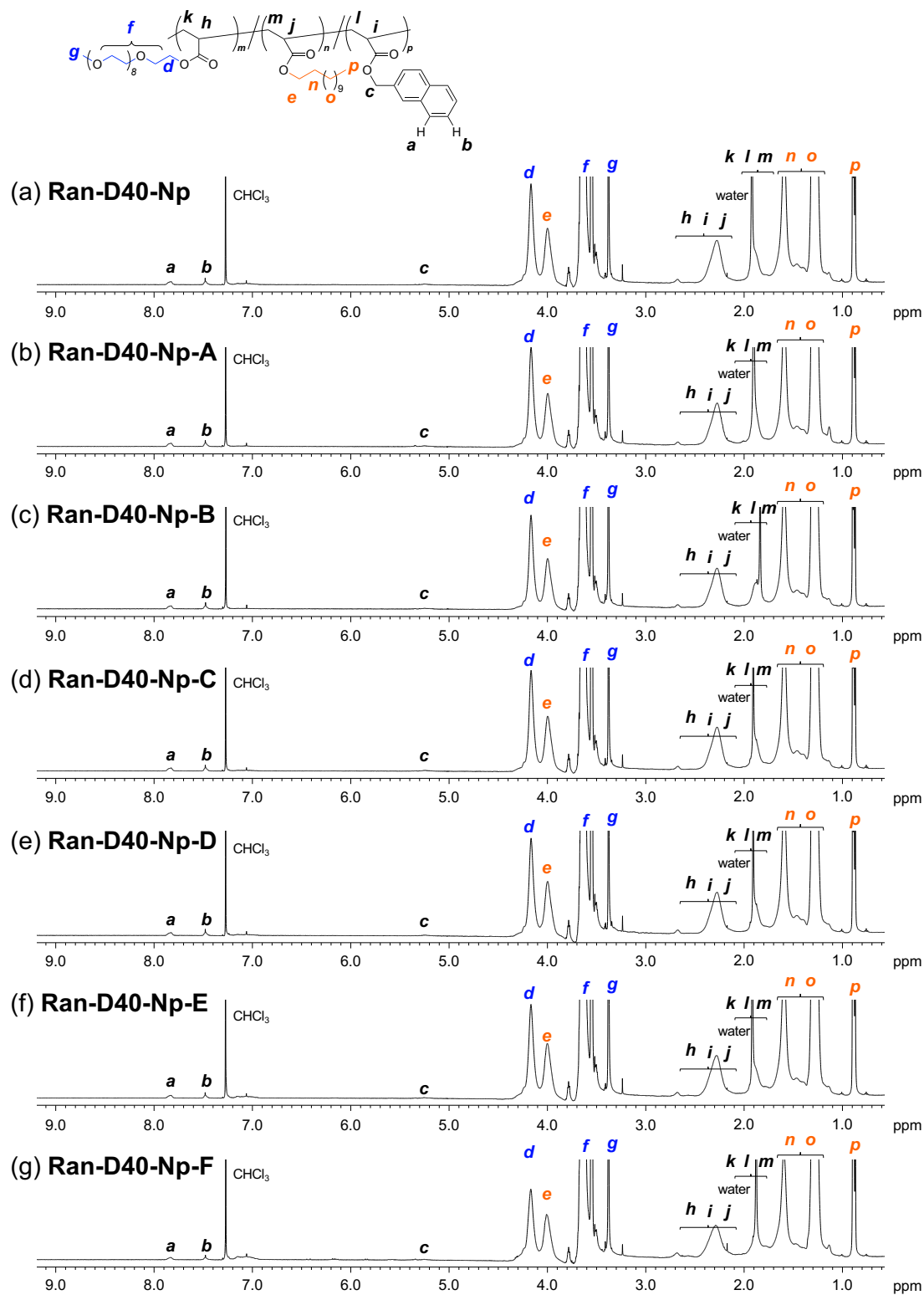
**Figure S6.** (a–g)  $^1\text{H}$  NMR spectra of Ran-D50-Py and Ran-D50-Py-A – F in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : [polymer] = 30 mg/mL.



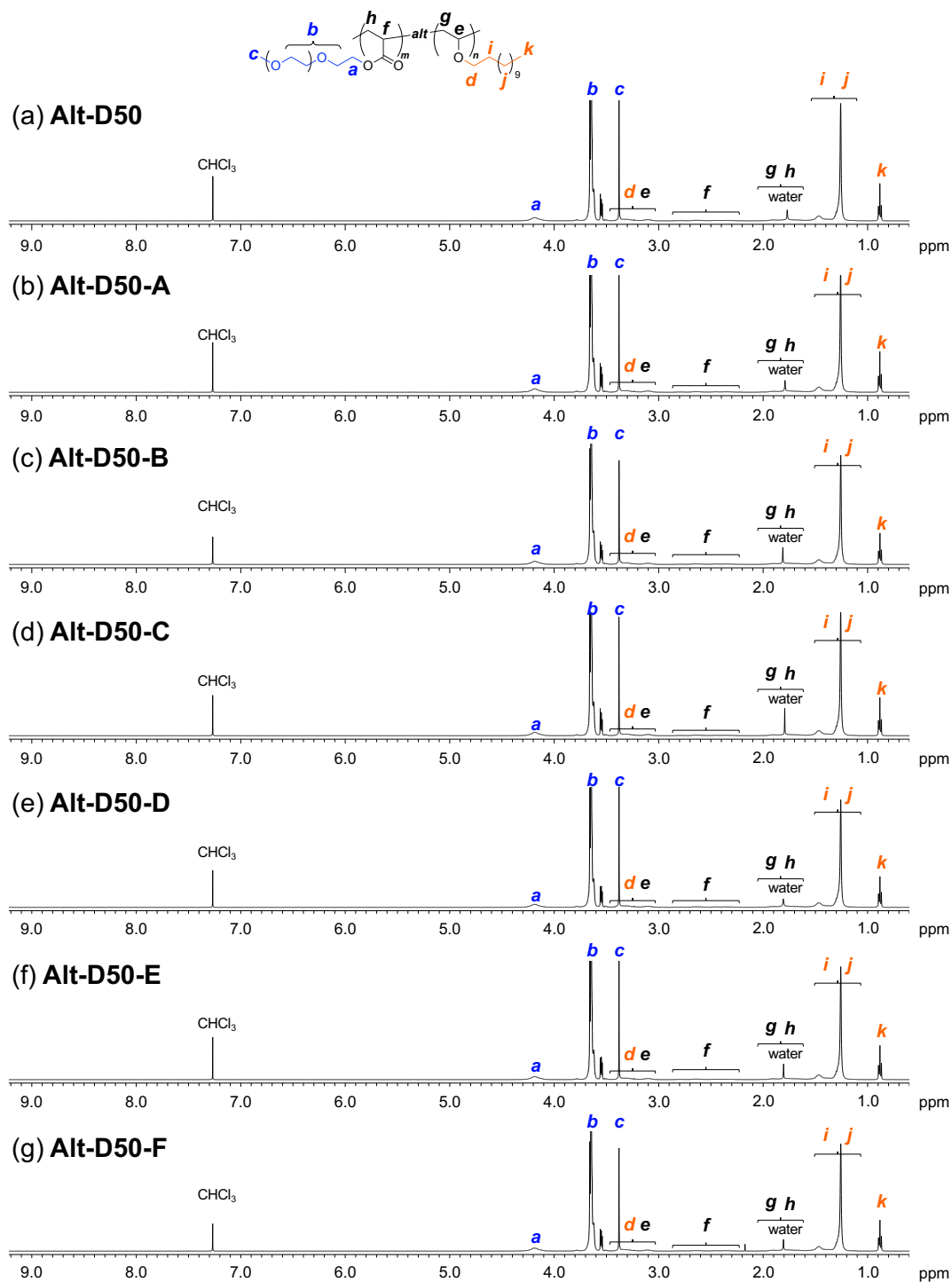
**Figure S7.** (a–g)  $^1\text{H}$  NMR spectra of **Ran-D50-Np** and **Ran-D50-Np-A – F** in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : [polymer] = 30 mg/mL.



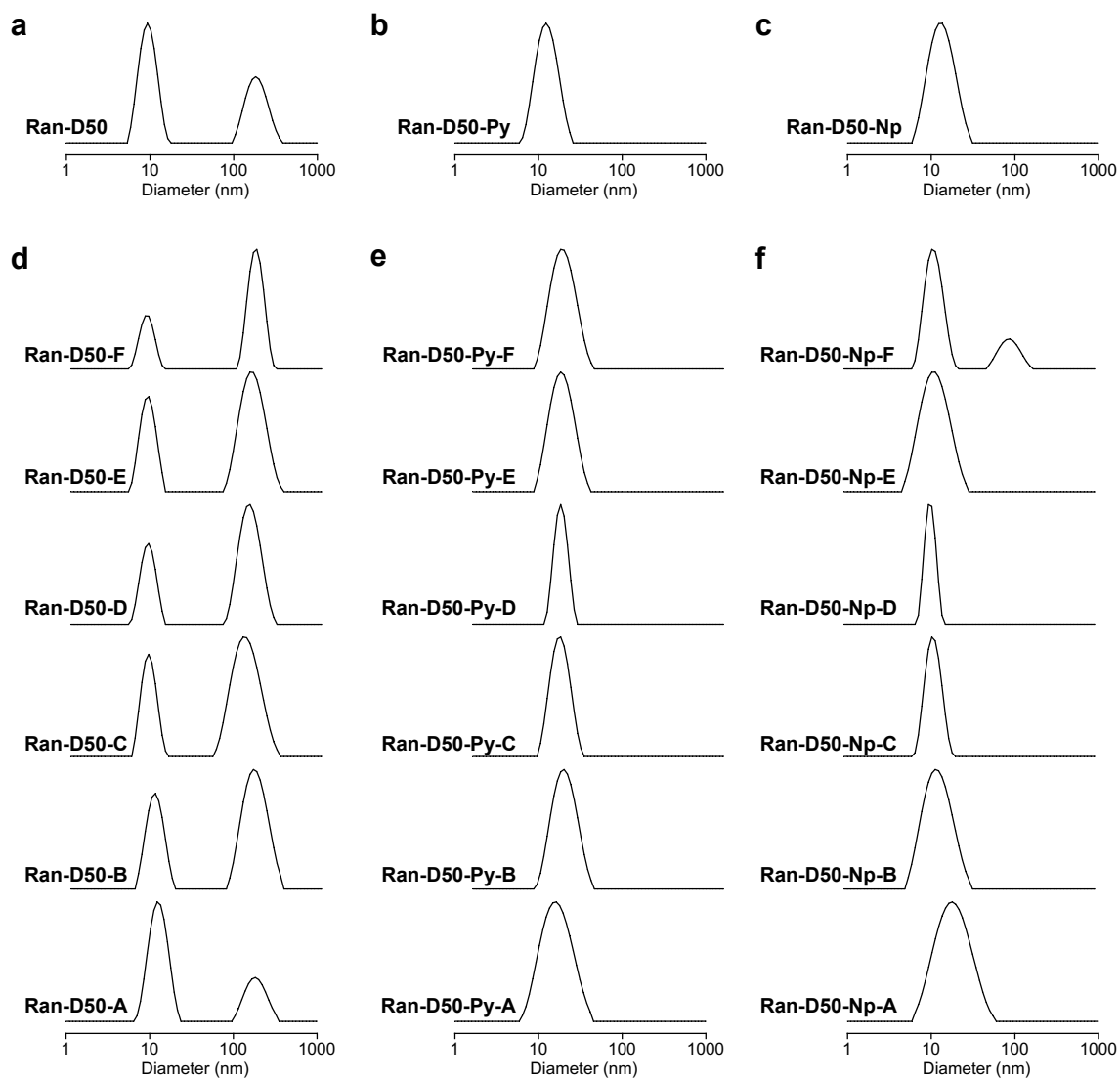
**Figure S8.** (a–g)  $^1\text{H}$  NMR spectra of Ran-D40-Py and Ran-D40-Py-A – F in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : [polymer] = 30 mg/mL.



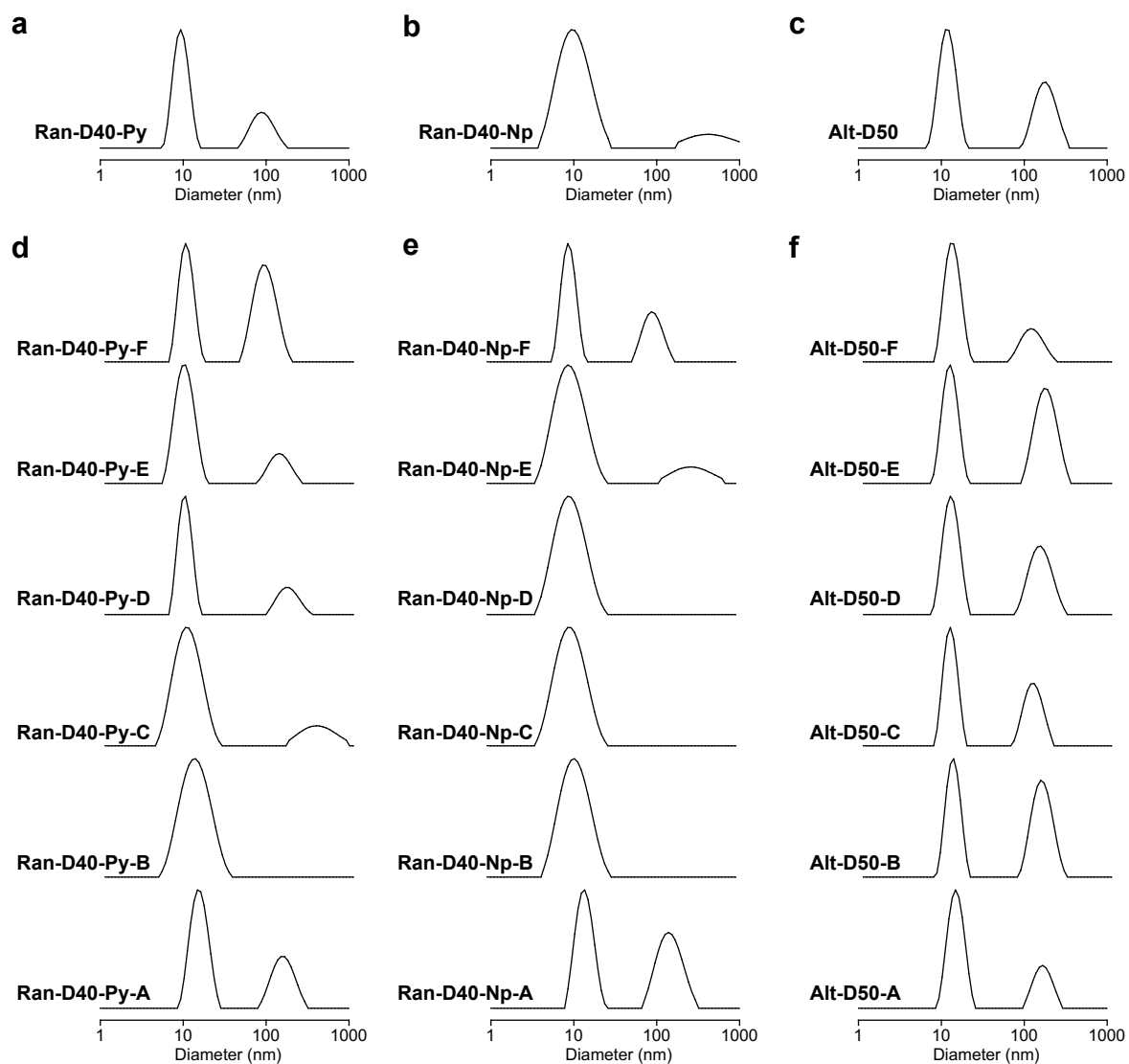
**Figure S9.** (a–g)  $^1\text{H}$  NMR spectra of Ran-D40-Np and Ran-D40-Np-A – F in  $\text{CDCl}_3$  at  $25^\circ\text{C}$ : [polymer] = 30 mg/mL.



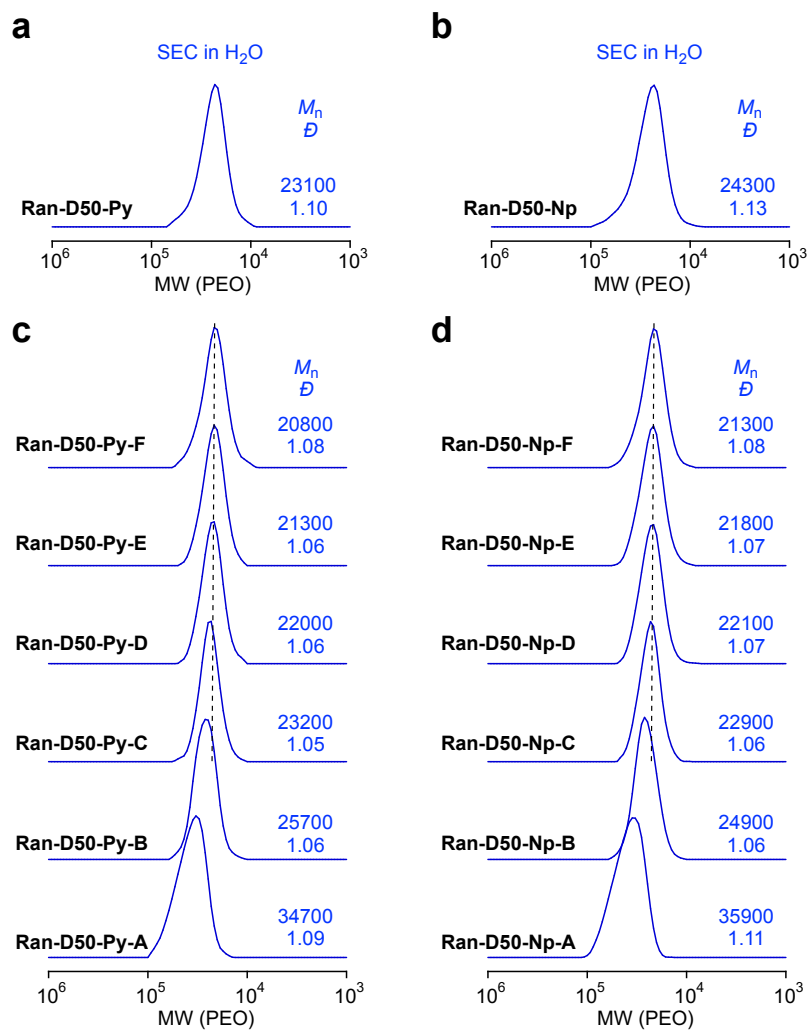
**Figure S10.** (a–g)  $^1\text{H}$  NMR spectra of Alt-D50 and Alt-D50-A – F in  $\text{CDCl}_3$  at 25  $^\circ\text{C}$ : [polymer] = 30 mg/mL.



**Figure S11.** DLS intensity distribution of (a) **Ran-D50**, (b) **Ran-D50-Py**, (c) **Ran-D50-Np**, (d) **Ran-D50-A – F**, (e) **Ran-D50-Py-A – F**, and (f) **Ran-D50-Np-A – F** micelles in H<sub>2</sub>O at 25 °C: [polymer] = 1.0 mg/mL. Several samples contain aggregates with about or above 100 nm diameter, whereas the volume fraction of the aggregates was below 2%.

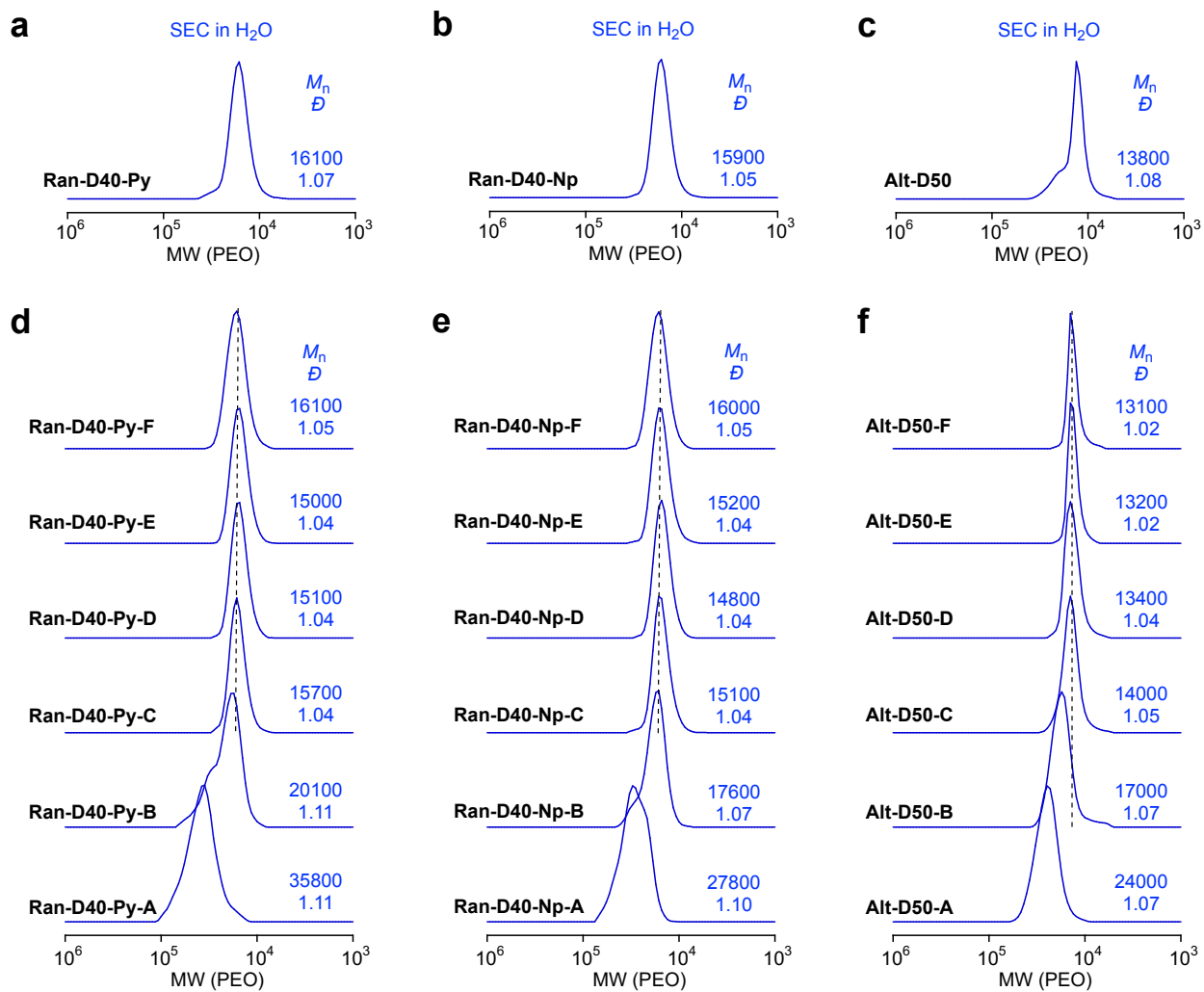


**Figure S12.** DLS intensity distribution of (a) **Ran-D40-Py**, (b) **Ran-D40-Np**, (c) **Alt-D50**, (d) **Ran-D40-Py-A – F**, (e) **Ran-D40-Np-A – F**, and (f) **Alt-D50-A – F** micelles in H<sub>2</sub>O at 25 °C: [polymer] = 1.0 mg/mL. Several samples contain aggregates with about or above 100 nm diameter, whereas the volume fraction of the aggregates was below 2%.

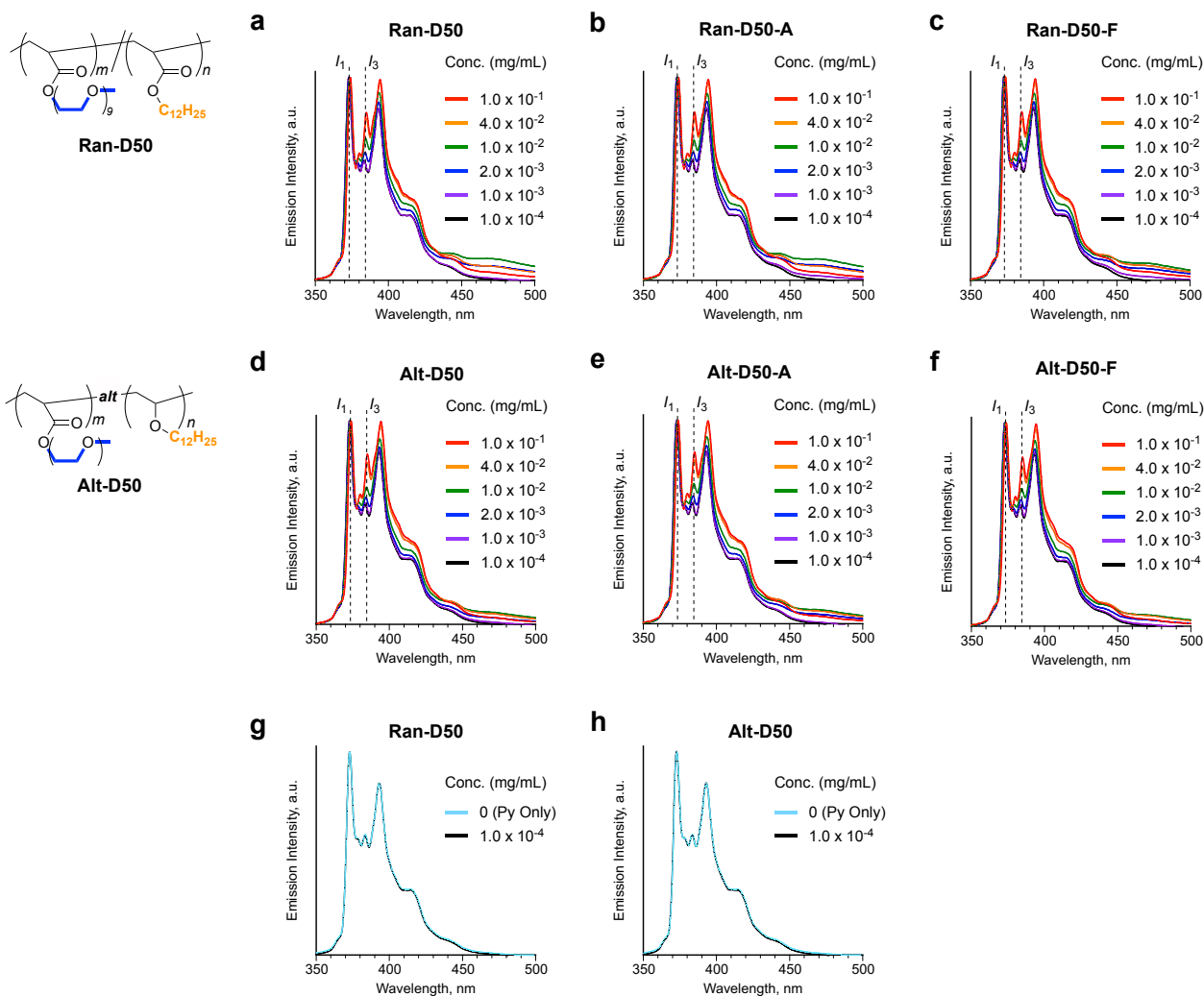


**Figure S13.** SEC curves,  $M_n$ , and  $\bar{D}$  of (a) **Ran-D50-Py**, (b) **Ran-D50-Np**, (c) **Ran-D50-Py-A – F**, and (d) **Ran-D50-Np-A – F** in H<sub>2</sub>O (10 mM LiBr) with PEO standard calibration.

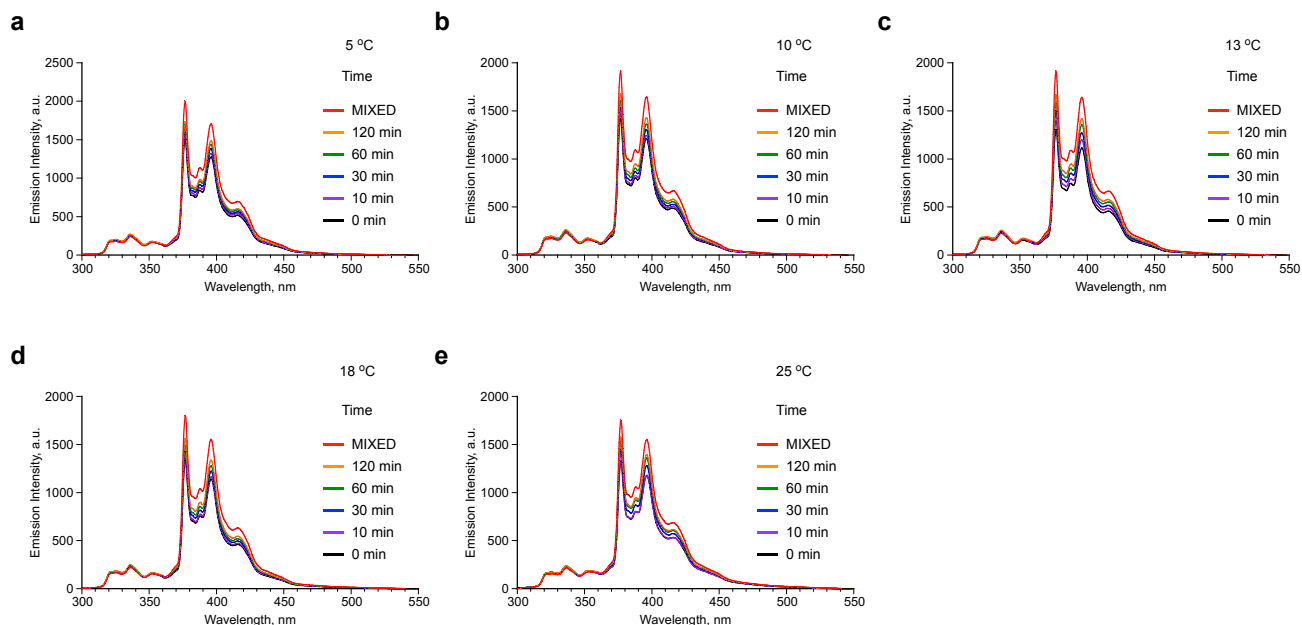




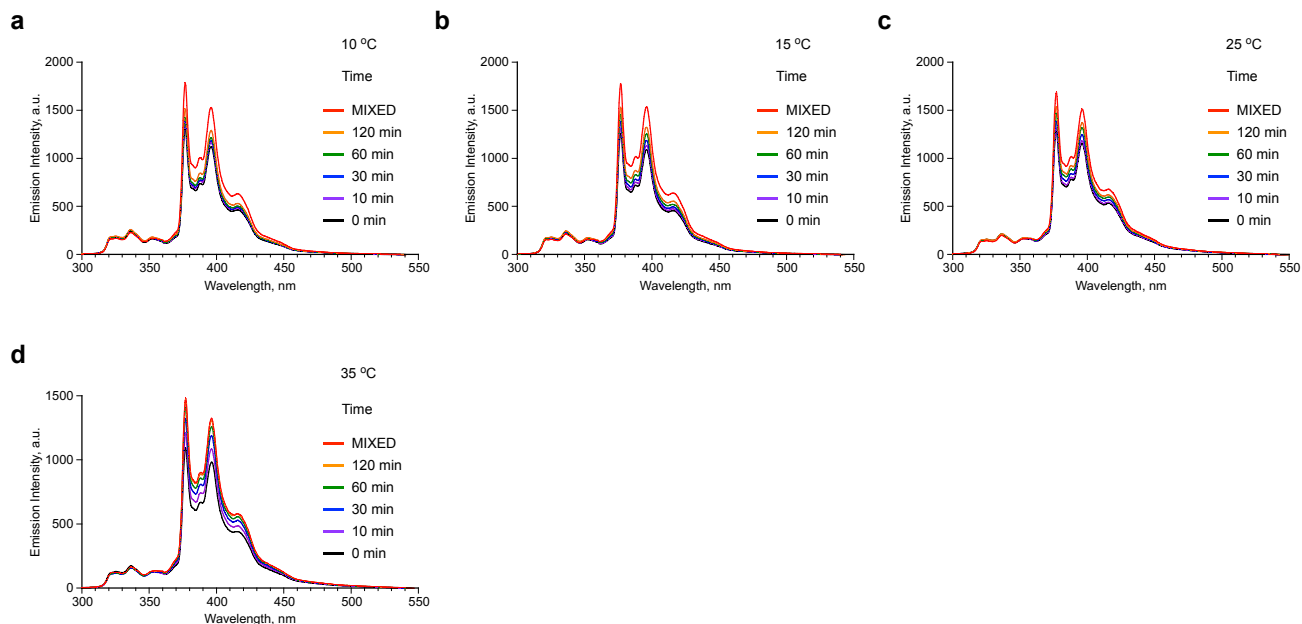
**Figure S14.** SEC curves,  $M_n$ , and  $D$  of (a) Ran-D40-Py, (b) Ran-D40-Np, (c) Alt-D50, (d) Ran-D40-Py-A – F, (e) Ran-D40-Np-A – F, and (f) Alt-D50-A – F in H<sub>2</sub>O (10 mM LiBr) with PEO standard calibration.



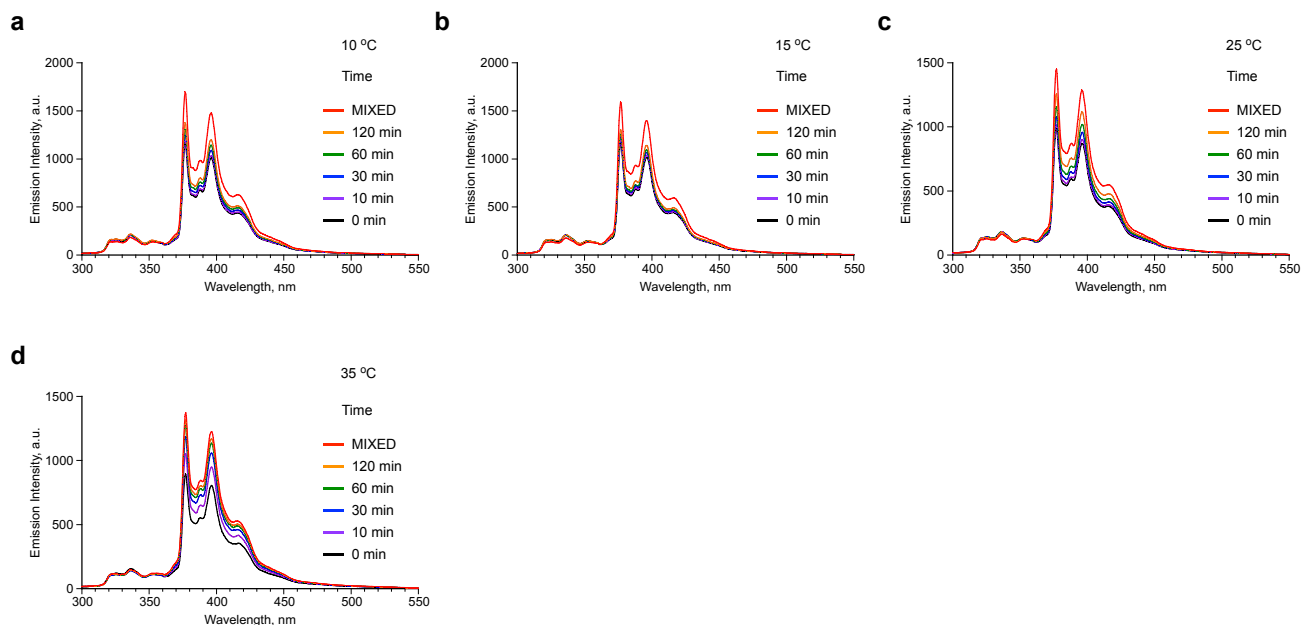
**Figure S15.** (a–h) Emission spectra of the aqueous solutions of pyrene ( $5 \times 10^{-7}$  M: normalized at  $I_1$ ) with (a) **Ran-D50**, (b) **Ran-D50-A**, (c) **Ran-D50-F**, (d) **Alt-D50**, (e) **Alt-D50-A**, and (f) **Alt-D50-F** at 25 °C [polymer] =  $1.0 \times 10^{-4} - 1.0 \times 10^{-1}$  mg/mL in H<sub>2</sub>O. (g, h) Emission spectra of the aqueous solutions of pyrene ( $5 \times 10^{-7}$  M: normalized at  $I_1$ ) in the presence or absence of (g) **Ran-D50** and (h) **Alt-D50** at 25 °C: [polymer] =  $1.0 \times 10^{-4}$  (black) or 0 (light blue) mg/mL.



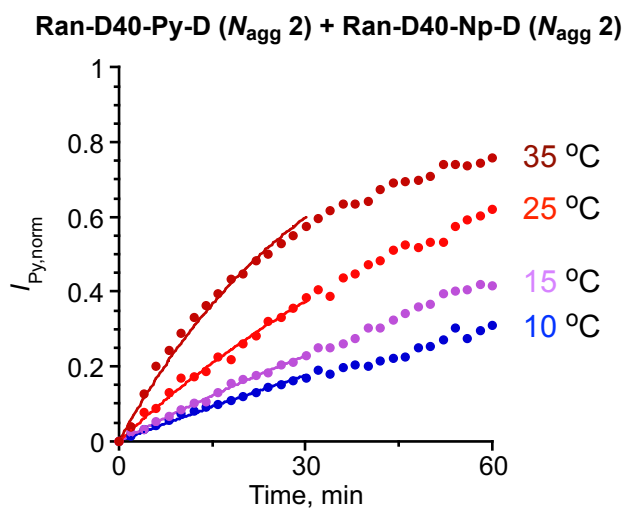
**Figure S16.** (a–e) Fluorescence spectra of the aqueous mixtures of a **Ran-D50-Py-D** micelle and a **Ran-D50-Np-D** micelle by the excitation at 290 nm at (a) 5 °C, (b) 10 °C, (c) 13 °C, (d) 18 °C, and (e) 25 °C: [polymer] = 1.0 mg/mL. The fluorescence intensity was monitored at 396 nm ( $I_{Py}$ ) and 336 nm ( $I_{Np}$ ) after mixing the two micelles.



**Figure S17.** (a–d) Fluorescence spectra of the aqueous mixtures of a **Ran-D40-Py-D** micelle and a **Ran-D40-Np-D** micelle by the excitation at 290 nm at (a) 10 °C, (b) 15 °C, (c) 25 °C, and (d) 35 °C: [polymer] = 1.0 mg/mL. The fluorescence intensity was monitored at 396 nm ( $I_{Py}$ ) and 336 nm ( $I_{Np}$ ) after mixing the two micelles.



**Figure S18.** (a–d) Fluorescence spectra of the aqueous mixtures of a **Ran-D50-Py-F** micelle and a **Ran-D50-Np-F** micelle by the excitation at 290 nm at (a) 10 °C, (b) 15 °C, (c) 25 °C, and (d) 35 °C: [polymer] = 1.0 mg/mL. The fluorescence intensity was monitored at 396 nm ( $I_{Py}$ ) and 336 nm ( $I_{Np}$ ) after mixing the two micelles.



**Figure S19.** Normalized  $I_{Py}$  ( $I_{Py, norm}$ ) and fitting curves for the chain exchange of the binary mixtures of **Ran-D40-Py-D** micelle ( $N_{agg} = 2$ ) + **Ran-D40-Np-D** micelle ( $N_{agg} = 2$ ) in water at 10–35 °C: [polymer] = 1.0 mg/mL.

**Table S5. Rate Constant for the Chain Exchange of PEGA/DA Random Copolymer Micelles**

Polymer Mixtures	$k_{\text{obs}}$ (min <sup>-1</sup> ) <sup>a</sup>					
	10 °C	13 °C	15 °C	18 °C	25 °C	35 °C
<b>Ran-D50-Py-D</b> ( $N_{\text{agg}} = 2$ ) +	$8.0 \times 10^{-3}$	$9.2 \times 10^{-3}$	n.d.	$1.2 \times 10^{-2}$	$1.6 \times 10^{-2}$	$3.0 \times 10^{-2}$
<b>Ran-D50-Np-D</b> ( $N_{\text{agg}} = 2$ )						
<b>Ran-D40-Py-D</b> ( $N_{\text{agg}} = 2$ ) +	$6.2 \times 10^{-3}$	n.d.	$8.2 \times 10^{-3}$	n.d.	$1.4 \times 10^{-2}$	$3.0 \times 10^{-2}$
<b>Ran-D40-Np-D</b> ( $N_{\text{agg}} = 2$ )						
<b>Ran-D50-Py-F</b> ( $N_{\text{agg}} = 5$ ) +	$1.0 \times 10^{-2}$	n.d.	$1.3 \times 10^{-2}$	n.d.	$2.2 \times 10^{-2}$	$4.6 \times 10^{-2}$
<b>Ran-D50-Np-F</b> ( $N_{\text{agg}} = 8$ )						

<sup>a</sup> Rate constant ( $k_{\text{obs}}$ ) of the chain exchange between PEGA/DA random copolymer micelles determined from fitting the normalized emission intensity ( $I_{\text{Py,norm}}$ ) by a single exponential kinetic model (Figures 7 and S19): [polymer] = 1.0 mg/mL in H<sub>2</sub>O; n.d.: not determined.