

Supplementary Information

Amphiphilic random and random block terpolymers with PEG, octadecyl, and oleyl pendants for controlled crystallization and microphase separation

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Experimental Section

Materials

Poly(ethylene glycol) methyl ether acrylate [PEGA: $\text{CH}_2=\text{CHCO}_2(\text{CH}_2\text{CH}_2\text{O})_n\text{Me}$, $M_n = 480$, $n = 9.0$ on average, TCI] and octadecyl acrylate (ODA, TCI, purity >97%) were purified by an inhibitor removal column (Aldrich) and degassed by triple vacuum-argon purge cycles before use. Oleyl acrylate (OLA) and benzyl 2-bromo-2-methylpropanoate (BzMA-Br)^{S1} were prepared as shown below. $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ (Cp^* : pentamethylcyclopentadienyl, Aldrich, purity >97%) was used as received and handled in a glove box under moisture- and oxygen-free argon ($\text{H}_2\text{O} < 1$ ppm; $\text{O}_2 < 1$ ppm). Tetralin (1,2,3,4-tetrahydronaphthalene, TCI, purity >97%, an internal standard for ^1H NMR analysis) was dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use. Triethylamine (TEA, TCI, purity >99%) was purified by distillation before use. $n\text{-Bu}_3\text{N}$ (TBAI, TCI, purity >98%) was degassed by triple vacuum-argon purge cycles before use. Toluene (solvent) was purified before use by passing it through a purification column (Glass Contour Solvent Systems, Nikko Hansen & Co., Ltd.). Oleyl alcohol (TBAI, purity >60%), 2-bromoisobutyryl bromide (TBAI, purity >98%), benzyl alcohol (TBAI, purity >99%), CH_2Cl_2 (Wako, purity >99.5%), and THF (Wako, purity >99.5%) were used as received.

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, TOSOH, HLC-8320 GPC) in THF at 40 °C (flow rate: 0.35 mL/min). In the SEC system, two linear-type polystyrene gel columns (TOSOH, TSKgel SuperMultiporeHZ-M: exclusion limit = 2×10^6 ; particle size = 4 μm ; 0.46 cm i.d. \times 15 cm) were connected to a pump, a UV detector set at 254 nm, and a refractive index detector (all from TOSOH). The columns were calibrated against 12 standard poly(MMA) samples (Polymer Laboratories: $M_p = 625\text{--}955000$). To remove the residue of catalysts and unreacted monomers, polymer samples were purified by preparative SEC in CHCl_3 at 25 °C (flow rate: 10 mL/min) on Shodex K-5003 (exclusion limit = 7×10^4 , particle size = 15 μm , 50 mm i.d. \times 300 mm) before characterization. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , CD_2Cl_2 , and acetone- d_6 on a JEOL JNM-ECA500 spectrometer operating at 500 (^1H) and 125 (^{13}C) MHz. Electrospray ionization mass spectrometry (ESI-MS) was performed on Exactive Plus (Thermo Fisher Scientific).

Differential scanning calorimetry (DSC) was performed for polymer samples (ca. 1 – 4 mg in an aluminum pan) under dry nitrogen flow on a DSCQ200 calorimeter (TA Instruments) equipped with a RCS 90 electric freezing machine. The samples were first heated from 40 °C to 150 °C to erase the thermal history. The samples were then cooled to -80 °C and again heated to 150 °C. The heating and

cooling rates were performed at 10 °C/min and -10 °C/min, respectively. The first cooling scans from 150 °C to -80 °C and the second heating scans from -80 °C to 150 °C were used as data. Powder X-ray diffractometry (PXRD) was performed on a Rigaku SmartLab Diffractometer, using a Cu anode and a K_{α} monochromator ($\lambda = 0.154$ nm). SAXS measurements were performed at the beamline BL05XU at SPring-8. The X-ray wavelength λ and the sample-detector distance were 0.1 nm and 840 mm, respectively. The scattering images were detected by PILATUS 1M (Dectris Ltd.) with an exposure time of 1.0 s.

Synthesis of Initiators and Monomers

Benzyl 2-bromo-2-methylpropanoate (BzMA-Br): In 50 mL round-bottomed flask equipped with a three-way stopcock, benzyl alcohol (11 mmol, 1.1 mL), triethylamine (23 mmol, 3.2 mL), and CH_2Cl_2 (30 mL) were added at 25 °C under argon. Into the solution, 2-bromo-2-methylpropanoyl bromide (15 mmol, 1.9 mL) was added dropwise at 0 °C. The mixture was stirred at 25 °C for 2 days. Then, the reaction was terminated by adding water. The organic layer was washed with saturated aqueous Na_2CO_3 solutions (50 mL) twice, dilute aqueous HCl solutions (150 mL) twice, water (100 mL) three times, and brine (100 mL) once, and was dried on sodium sulfate for 1 min. After evaporating the organic solution, the resulting crude was purified by column chromatography (hexane/ethyl acetate = 9/1) to give benzyl 2-bromo-2-methylpropanoate (BzMA-Br). Yield 1.7 g (66 %). ^1H NMR [500 MHz, CD_3OD , r.t., $\delta = 3.31$ ppm (CD_2HOD)]: δ 7.6-7.1 (m, 5H, aromatic), 5.3-5.1 (s, 2H, benzyl), 2.0-1.8 (s, 6H, methyl). ^{13}C NMR [125 MHz, CD_3OD , r.t., $\delta = 49.0$ ppm (CD_3OD)]: δ 172.7 (-O-CO-), 137.0, 129.6, 129.3, 129.0 (C_6H_5 -), 68.5 (-O- CH_2 - C_6H_5), 56.9 (-CO-C(CH_3) $_2$ -Br), 31.1 ((CH_3) $_2$ -CBr-CO-).

Oleyl acrylate (OLA): In a 300 mL round-bottomed flask equipped with a three-way stopcock, oleyl alcohol (43 mmol, 13.5 mL), triethylamine (51 mmol, 7.1 mL), and CH_2Cl_2 (100 mL) were added at 25 °C under argon. Into the solution, acryloyl chloride (51 mmol, 4.1 mL) was added dropwise at 0 °C. The mixture was stirred at 25 °C for 16 h. Then, the reaction was terminated by adding water. The organic layer was washed with the mixture of water (100 mL) and EtOH (10 mL) once. After evaporating the organic layer, the resulting crude was purified by column chromatography (hexane/dichloromethane = 1/1) to give oleyl acrylate. Yield 4.3 g (32 %). ^1H NMR [500 MHz, CDCl_3 , r.t., $\delta = 7.26$ ppm (CHCl_3)]: δ 6.5-6.3 (d, $J = 17.3$ Hz, 1H, olefin), 6.2-6.0 (dd, $J = 17.5$ Hz, 10.5 Hz, 1H, olefin), 5.9-5.7 (d, $J = 10.0$ Hz, 1H, olefin), 5.5-5.2 (m, 2H, olefin), 4.2-4.1 (t, $J = 6.5$ Hz, 2H, $\text{CH}_2\text{CHCOOCH}_2$ -), 2.2-1.9 (m, 4H, $-\text{CH}_2\text{CH}=\text{CHCH}_2$ -), 1.7-1.6 (m, 2H, $-\text{COOCH}_2\text{CH}_2$ -), 1.5-1.1 (m, 22H, $-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_5\text{CH}_2\text{CH}=\text{CHCH}_2(\text{CH}_2)_6\text{CH}_3$), 1.0-0.8 (t, $J = 7.0$ Hz, 3H, $-\text{CH}_2\text{CH}_3$). ^{13}C NMR [125 MHz, CDCl_3 , r.t., $\delta = 77.2$ ppm (CDCl_3)]: δ 166.4 (-CO-), 130.5 (CH_2 -CH-COO-), 130.1, 129.9 ($-\text{CH}_2$ -CHCH- CH_2 -), 128.8 (-CHCOO-), 64.8 (-O- CH_2 -), 32.0 ($-\text{CH}_2$ -CHCH- CH_2 -), 30.1-26.0

(-COO-CH₂-CH₂-(CH₂)₅-CH₂-CH-CH-CH₂-(CH₂)₅-CH₂-CH₃), 22.8 (-CH₂-CH₃), 14.2 (-CH₂-CH₃). ESI-MS m/z ([M + Na]⁺): calcd for C₂₁H₃₈O₂, 345.2764; found, 345.2773.

Synthesis of Amphiphilic Random and Random Block Copolymers

The synthesis of random and random block copolymers was carried out by syringe technique under argon in glass tubes equipped with a three-way stopcock. Typical procedures were given:

P4, PEGA/ODA/OLA (32/33/14) random terpolymer: RuCp*Cl(PPh₃)₂ (0.0030 mmol, 2.4 mg) was added in a 30 mL glass tube. Then, toluene (0.87 mL), tetralin (0.080 mL), a 400 mM toluene solution of *n*-Bu₃N (0.12 mmol, 0.30 mL), PEGA (1.2 mmol, 0.53 mL), a 1670 mM toluene solution of ODA (1.3 mmol, 0.76 mL), a 2100 mM toluene solution of OLA (0.55 mmol, 0.26 mL), and a 140 mM toluene solution of BzMA-Br (0.030 mmol, 0.21 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 3 mL). The glass tube was placed in an oil bath kept at 80 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon; 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. PEGA/ODA+OLA = 65%/64%, 160 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl₃ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): *M_n* = 16600, *M_w*/*M_n* = 1.28. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.4–7.3 (aromatic), 5.1–5.0 (benzyl), 4.4–4.1 (-COOCH₂CH₂O-), 4.1–3.8 (-COOCH₂CH₂CH₂-), 3.8–3.4 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -CH₂OCH₃), 3.4–3.3 (-OCH₃), 2.5–2.1 (-CH₂CHCO-), 2.1–2.0 (-COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃), 2.0–1.5 (-CH₂CHCO-), 1.7–1.5 (-COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.4–1.1 (-COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 0.9–0.8 (-COO(CH₂)₁₇CH₃, -COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃).

¹H NMR [500 MHz, CDCl₃, 25 °C, δ = 7.26 (CHCl₃)]: δ 5.4–5.3 (-COO(CH₂)₈CH=CH(CH₂)₇CH₃), 5.1–5.0 (benzyl), 4.3–4.1 (-COOCH₂CH₂O-), 4.1–3.8(-COOCH₂CH₂CH₂-), 3.7–3.5 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -CH₂OCH₃), 3.4–3.3 (-OCH₃), 2.5–2.2 (-CH₂CHCO-), 2.1–2.0 (-COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃), 2.0–1.5 (-CH₂CHCO-), 1.7–1.5 (-COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.4–1.1 (-COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.0–0.8 (-COO(CH₂)₁₇CH₃, -COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃).

P2, **P3**, **P5**, and **P6** were similarly synthesized.

P7, PEGA/OLA (14/23) random copolymer: RuCp*Cl(PPh₃)₂ (0.0041 mmol, 3.3 mg) was added in a 30 mL glass tube. Then, toluene (1.34 mL), tetralin (0.10 mL), a 400 mM toluene solution of *n*-Bu₃N (0.080 mmol, 0.20 mL), PEGA (1.6 mmol, 0.71 mL), a 1750 mM toluene solution of OLA (2.4 mmol, 1.37 mL), and a 140 mM toluene solution of BzMA-Br (0.039 mmol, 0.28 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 4 mL). The glass tube was placed in an oil bath kept at 80 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon; 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. PEGA/OLA = 39%/39%, 214 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl₃ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): *M_n* = 12500, *M_w*/*M_n* = 1.36. ¹H NMR [500 MHz, acetone-*d*₆, 25 °C, δ = 2.05 (CD₂HCOCD₃)]: δ 7.5–7.3 (aromatic), 5.5–5.3 (-COO(CH₂)₈CH=CH(CH₂)₇CH₃), 5.2–5.0 (benzyl), 4.4–4.2 (-COOCH₂CH₂O-), 4.2–3.8 (-COOCH₂CH₂CH₂-), 3.8–3.4 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -CH₂OCH₃), 3.4–3.3 (-OCH₃), 2.6–2.2 (-CH₂CHCO-), 2.1–2.0 (-COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃), 2.0–1.5 (-CH₂CHCO-), 1.8–1.6 (-COOCH₂CH₂(CH₂)₁₅CH₃), -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.5–1.2 (-COOCH₂CH₂(CH₂)₁₅CH₃), -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.0–0.8 (-COO(CH₂)₁₇CH₃), -COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃).

P8, ODA/OLA random copolymer: AIBN (0.021 mmol, 3.4 mg) was added in a 30 mL glass tube. Then, toluene (1.3 mL), tetralin (0.050 mL), a 1670 mM toluene solution of ODA (0.62 mmol, 0.37 mL), and a 2100 mM toluene solution of OLA (0.63 mmol, 0.30 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 2 mL). The glass tube was placed in an oil bath kept at 80 °C. At predetermined intervals, the mixture was sampled with a syringe under dry argon; 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. ODA+OLA = 67%, 5 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl₃ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): *M_n* = 13600, *M_w*/*M_n* = 1.48. ¹H NMR [500 MHz, CDCl₃, 25 °C, δ = 7.26 (CHCl₃)]: δ 5.5–5.2 (-COO(CH₂)₈CH=CH(CH₂)₇CH₃), 4.2–3.8 (-COOCH₂CH₂CH₂-), 2.5–2.1 (-CH₂CHCO-), 2.1–1.9 (-COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃), 1.9–1.5 (-CH₂CHCO-), 1.8–1.5 (-COOCH₂CH₂(CH₂)₁₅CH₃), -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.5–1.1 (-COOCH₂CH₂(CH₂)₁₅CH₃), -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.0–0.8 (-COO(CH₂)₁₇CH₃), -COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃).

P9, PEGA/ODA-PEGA/OLA random block terpolymer: RuCp*Cl(PPh₃)₂ (0.019 mmol, 15 mg) was added in a 30 mL glass tube. Then, toluene (5.0 mL), tetralin (0.50 mL), a 400 mM toluene solution of *n*-Bu₃N (0.76 mmol, 1.9 mL), PEGA (7.5 mmol, 3.3 mL), a 1670 mM toluene solution of ODA (11 mmol, 6.8 mL), and a 140 mM toluene solution of BzMA-Br (0.18 mmol, 1.3 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 19 mL). The glass tube was placed in an oil bath kept at 80 °C. After 7h, 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. PEGA/ODA = 26%/27%. The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl₃ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature to give a PEGA/ODA random copolymer (**P9-1st**). SEC (THF, PMMA std.): *M*_n = 13100, *M*_w/*M*_n = 1.13. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.4–7.2 (aromatic), 5.1–5.0 (benzyl), 4.4–4.1 (-COOCH₂CH₂O-), 4.1–3.8 (-COOCH₂CH₂CH₂-), 3.8–3.4 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -CH₂OCH₃), 3.4–3.3 (-OCH₃), 2.5–2.1 (-CH₂CHCO-), 2.1–1.5 (-CH₂CHCO-), 1.7–1.5 (-COOCH₂CH₂(CH₂)₁₅CH₃), 1.4–1.1 (-COOCH₂CH₂(CH₂)₁₅CH₃), 0.9–0.8 (-COO(CH₂)₁₇CH₃).

Then, **P9-1st** (Br = 0.024 mmol, 354 mg) and RuCp*Cl(PPh₃)₂ (0.0025 mmol, 2.0 mg) were added in a 30 mL glass tube. Then, toluene (0.062 mL), tetralin (0.060 mL), a 400 mM toluene solution of *n*-Bu₃N (0.096 mmol, 0.24 mL), PEGA (1.4 mmol, 0.60 mL), and a 1830 mM toluene solution of OLA (2.0 mmol, 1.1 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 2.4 mL). The glass tube was placed in an oil bath kept at 80 °C. After 79 h, 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. PEGA/OLA = 23%/28%. The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in CHCl₃ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): *M*_n = 24500, *M*_w/*M*_n = 1.35. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.4–7.3 (aromatic), 5.1–5.0 (benzyl), 4.5–4.1 (-COOCH₂CH₂O-), 4.1–3.8 (-COOCH₂CH₂CH₂-), 3.8–3.4 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -CH₂OCH₃), 3.4–3.2 (-OCH₃), 2.5–2.1 (-CH₂CHCO-), 2.1–2.0 (-COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃), 2.0–1.5 (-CH₂CHCO-), 1.8–1.5 (-COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.5–1.0 (-COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 0.9–0.7 (-COO(CH₂)₁₇CH₃, -COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃).

¹H NMR [500 MHz, CDCl₃, 25 °C, δ = 7.26 (CHCl₃)]: δ 5.5–5.2 (-COO(CH₂)₈CH=CH(CH₂)₇CH₃), 5.1–5.0 (benzyl), 4.4–4.1 (-COOCH₂CH₂O-), 4.1–3.9 (-COOCH₂CH₂CH₂-), 3.9–3.4 (-COOCH₂CH₂O-, -OCH₂CH₂O-, -CH₂OCH₃), 3.4–3.3 (-OCH₃), 2.5–2.1 (-CH₂CHCO-), 2.1–2.0 (-COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃), 2.0–1.5 (-CH₂CHCO-), 1.7–1.5 (-

COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃, 1.5–1.1 (-
COOCH₂CH₂(CH₂)₁₅CH₃, -COOCH₂CH₂(CH₂)₅CH₂CH=CHCH₂(CH₂)₆CH₃), 1.0–0.8 (-
COO(CH₂)₁₇CH₃, -COO(CH₂)₇CH₂CH=CHCH₂(CH₂)₆CH₃). **P10** were similarly synthesized.

Preparation of Solid Polymer Samples for DSC, XRD, and SAXS Measurements

Solid samples of **P1** – **P10** were prepared as follows: CH₂Cl₂ solutions of their polymers (50 mg/mL) were evaporated to dryness in vials at 25 °C. The resulting solid polymers were further dried under vacuum overnight and then utilized as samples for DSC, XRD, and SAXS measurements.

Supporting Data

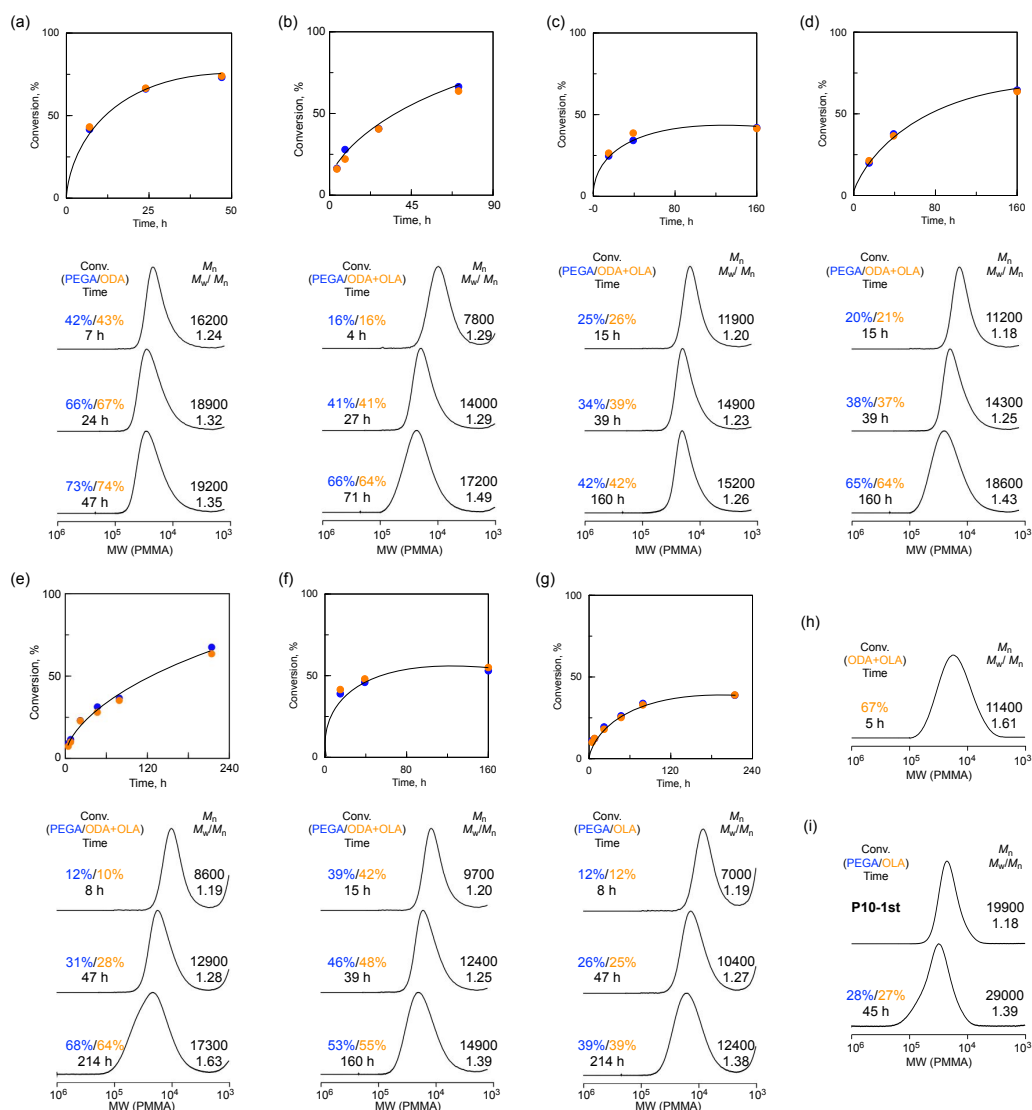


Figure S1. Ru-catalyzed living radical copolymerization of PEGA, ODA and OLA with a bromide initiator (upper: time-conversion plots, lower: SEC curves of sampled crude products): $[PEGA]_0/[ODA]_0/[OLA]_0/[BzMA-Br]_0/[RuCp^*Cl(PPh_3)_2]_0/[n-Bu_3N]_0 =$ (a) 400/600/0/10/1/20, (b) 400/550/50/10/1/40, (c) 400/480/120/10/1/40, (d) 400/420/180/10/1/40, (e) 400/300/300/10/1/20, (f) 400/180/420/10/1/40, (g) 400/0/600/10/1/20 mM in toluene at 80 °C. (h) Free radical copolymerization of ODA and OLA: $[ODA]_0/[OLA]_0/[AIBN]_0 = 300/300/10$ mM in toluene at 80 °C. (i) Ru-catalyzed living radical copolymerization of PEGA, OLA with a PEGA/ODA macro initiator: $[PEGA]_0/[OLA]_0/[P10-1st]_0/[RuCp^*Cl(PPh_3)_2]_0/[n-Bu_3N]_0 = 560/840/10/1/20$ mM in toluene at 80 °C. M_n and M_w/M_n values are determined by SEC analyses of the crude products. The final products (a - h) were purified by preparative SEC and used as **P1 – P8**, respectively. Thus, M_n and M_w/M_n of the final crude products are different from those of **P1 – P8**.

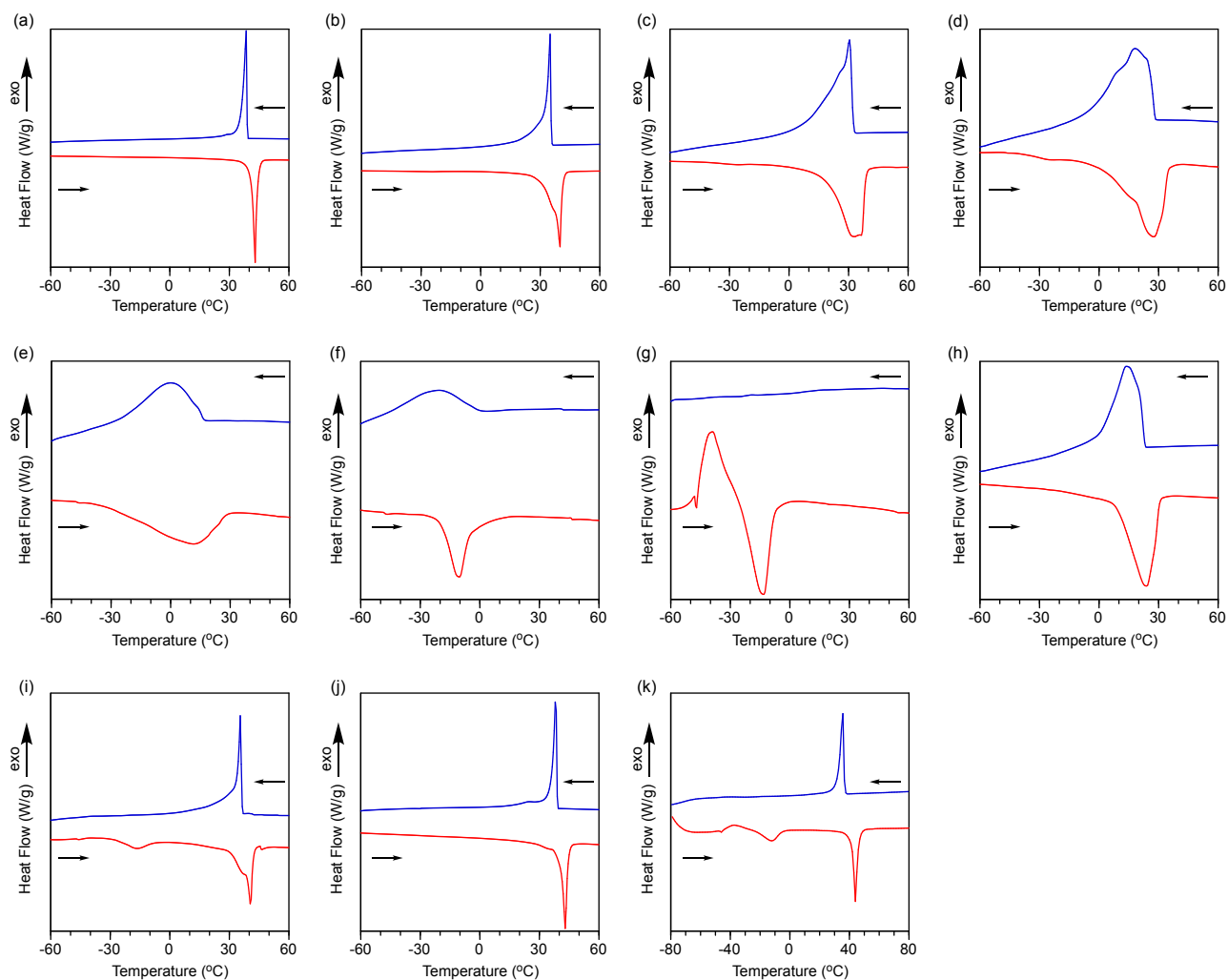


Figure S2. DSC curves recorded for the first cooling scans (blue) and second heating scans (red) of (a) **P1**, (b) **P2**, (c) **P3**, (d) **P4**, (e) **P5**, (f) **P6**, (g) **P7**, (h) **P8**, (i) **P9**, (j) **P10**, and (k) the binary mixture of **P1** and **P7** (1/1, wt/wt) between $-80\text{ }^{\circ}\text{C}$ and $150\text{ }^{\circ}\text{C}$. The cooling and heating rates were performed at -10 and $10\text{ }^{\circ}\text{C}/\text{min}$, respectively.

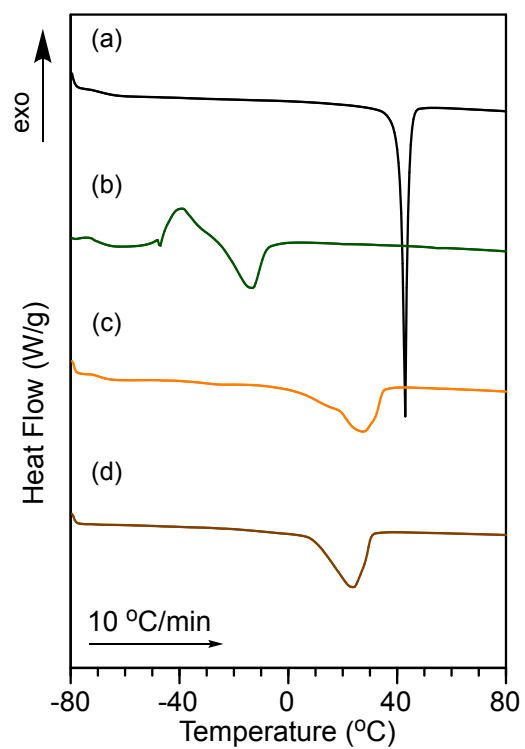


Figure S3. DSC curves recorded for the second heating scans of (a) **P1**, (b) **P7**, (c) **P4**, and (d) **P8** from -80 °C to 150 °C with the heating rate of 10 °C/min.

References

(S1) Hattori, G.; Takenaka, M.; Sawamoto, M.; Terashima, T. *J. Am. Chem. Soc.* **2018**, *140*, 8376-8379.