# Supplementary Information

## Design guide of amphiphilic crystalline random copolymers for sub-10 nm microphase separation

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## Contents

## Experimental Section

### Materials.

Poly(ethylene glycol) acrylate [PEG(OH)A: $CH_2$=$CHCO_2(CH_2CH_2O)_nH$, $M_n$ = 510, $n$ = 10.0 on average, Nichiyu], poly(propylene glycol) methacrylate [PPO(OH)MA: $CH_2$=$C(CH_3)CO_2(CH_2CH(CH_3)O)_nH$ $M_n$ = 375, $n$ = 5.0 on average, Nichiyu], and poly(ethylene glycol) methacrylate [PEG(OH)MA: $CH_2$=$C(CH_3)CO_2(CH_2CH_2O)_nH$, $M_n$ = 360, $n$ = 6.2 on average, Aldrich] [S1] were degassed by triple vacuum-argon purge cycles before use. Poly(ethylene glycol) methyl ether methacrylate [PEGMA: $CH_2$=$C(CH_3)CO_2(CH_2CH_2O)_nMe$, $M_n$ = 480, $n$ = 8.5 on average, Aldrich], octadecyl acrylate (ODA, TCI, purity >97%), and octadecyl methacrylate (ODMA, TCI, purity >97%) were purified by an inhibitor removal column (Aldrich) and degassed by triple vacuum-argon purge cycles before use. Benzyl 2-bromo-2-methylpropanoate (BzMA-Br) was synthesized as shown below.[S2] $RuCp^*Cl(PPh_3)_2$ (Cp*: pentamethylcyclopentadienyl, Aldrich, purity >97%) was used as received and handled in a glove box under moisture- and oxygen-free argon ($H_2O$ < 1 ppm; $O_2$ < 1 ppm). 2.2'-Azobis(isobutyronitrile) (AIBN, TCI, >98%) was used as received. Tetralin (1,2,3,4-tetrahydronaphthalene, TCI, purity >97%, an internal standard for $^1$H NMR analysis) was dried overnight over calcium chloride and distilled from calcium hydride under reduced pressure before use. $n$-$Bu_3N$ (TCI, purity >98%) and 1,4-dioxane (Wako, purity >99.5%) were 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.). Triethylamine (TCI, purity >99%) was purified by distillation before use. 2-Bromoisobutyryl bromide (TCI, purity >98%), benzylalcohol (Wako, purity >99%), dry $CH_2Cl_2$ (Wako, dehydrated), and THF (Wako, purity >99.5%, stabilizer: 2,6-di-$t$-butyl-4-methyl phenol) 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, Shodex GPC-104) in THF at 40 °C (flow rate: 0.3 mL/min). In the SEC system, three linear-type polystyrene gel columns (Shodex LF-404: exclusion limit = $2 \times 10^6$; particle size = 6 μm; pore size = 3000 Å; 0.46 cm i.d. × 25 cm) were connected to a DU-2000 pump, a RI-74 refractive index detector, and a UV-41 ultraviolet detector set at 250 nm (all from Shodex). The columns were calibrated against 16 standard poly(MMA) samples (Polymer Laboratories: $M_p$ = 625–1250000; $M_w/M_n$ = 1.02–1.30). To remove the residue of catalysts and unreacted monomers, polymer samples were purified before characterization by preparative SEC in $CHCl_3$ at 25 °C (flow rate: 10 mL/min) on Shodex K-5003 (exclusion limit = $7 \times 10^4$, particle size = 15 μm, 50 mm i.d. × 300 mm). A partly crosslinked polymer (**P6**) was further fractionated into two samples with different molecular weight by recycling

preparative SEC in $CHCl_3$ at 25 ºC on LaboACE (LC-5060, Japan Analytical Industry Co., Ltd.) with JAIGEL-2HR and JAIGEL-2.5HR (flow rate: 10 mL/min). $^1H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ and acetone-$d_6$ on a JEOL JNM-ECA500 spectrometer operating at 500 ($^1H$) and 125 ($^{13}C$) MHz. Absolute weight-average molecular weight ($M_w$) of the polymers in THF was determined by multiangle light scattering (MALS) equipped with SEC on a Dawn HELEOS II instrument (Wyatt Technology, semiconductor laser, $\lambda$ = 663 nm). The SEC was performed in THF at 40 ºC (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L) that were connected to a Jasco PU-4080 precision pump, a Jasco RI-4030 refractive index detector, and a Jasco UV-4075 UV/vis detector set at 270 nm.

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

Powder X-ray diffractometry (PXRD) was performed on a Rigaku SmartLab Diffractometer, using a Cu anode and a $K_\alpha$ monochromator ($\lambda$ = 0.154 nm). Small angle X-ray scattering (SAXS) measurements were performed at RIKEN beamline BL45XU of SPring-8, Japan. The X-ray wavelength, distance of sample to detector, and the detector used at BL45XU were 0.1 nm, 2500 mm, and PILATUS 3X 2M, respectively. The obtained 2-dimentional data were circularly averaged and corrected for background of cell and electronic noise of detector.

**Synthesis of Initiator**

**Benzyl 2-bromo-2-methylpropanoate (BzMA-Br)**: In 50 mL round-bottomed flask equipped with a three-way stopcock, benzyl alcohol (8.0 mmol, 0.83 mL), triethylamine (18 mmol, 2.5 mL), and dry $CH_2Cl_2$ (20 mL) were added at 25 °C under argon. Into the solution, 2-bromo-2-methylpropionyl bromide (12 mmol, 1.5 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 $Na_2CO_3$ aqueous solutions (50 mL) twice, dilute HCl aqueous solutions (50 mL) twice, water (100 mL) three times, and brine (100 mL) once. The organic layer was then dried on sodium sulfate for 1 h. 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 0.91 g (44 %). $^1$H NMR [500 MHz, $CDCl_3$, r.t., δ = 7.26 ppm ($CHCl_3$)]: δ 7.4-7.3 (m, 5H, aromatic), 5.2 (s, 2H, benzyl), 2.0 (s, 6H, methyl). $^{13}$C NMR [125 MHz, $CDCl_3$, r.t., δ = 77.16 ppm ($CDCl_3$)]: δ 171.6 (-O-*C*O-), 135.6, 128.7, 128.5, 128.0 (*C*$_6$H$_5$-), 67.7 (-O-*C*H$_2$-C$_6$H$_5$), 55.8 (-CO-*C*(CH$_3$)$_2$-Br), 30.9 ((*C*H$_3$)$_2$-CBr-CO-).

**Synthesis of Random Copolymers**

The synthesis of amphiphilic random copolymers (**P1** - **P12**) was carried out by syringe technique under argon in baked glass tubes equipped with a three-way stopcock. Typical procedures were given:

PEGOHA/ODA random copolymer (**P3**): RuCp*Cl(PPh$_3$)$_2$ (0.0070 mmol, 5.6 mg) was charged in a 30 mL glass tube. Then, toluene (2.1 mL), tetralin (0.10 mL), a 400 mM toluene solution of *n*-Bu$_3$N (0.14 mmol, 0.35 mL), a 640 mM toluene solution of PEGOHA (1.4 mmol, 2.2 mL), a 1245 mM toluene solution of ODA (2.1 mmol, 1.7 mL), and a 123 mM toluene solution of BzMA-Br (0.57 mL, 0.070 mmol) were added sequentially into the tube at 25 °C under argon (the total volume: 7.0 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PEGOHA/ODA = 68%/61%, 28 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in $CHCl_3$ 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; $M_w/M_n$ = 1.13. $^1$H NMR [500 MHz, $CD_2Cl_2$, 25 °C, δ = 5.2 ($CDHCl_2$)]: δ 7.4–7.3 (aromatic), 4.4–4.1 (-COOC$\underline{H}_2$CH$_2$O-), 4.1-3.8 (-COOC$\underline{H}_2$CH$_2$CH$_2$-), 3.7–3.6 (-COOCH$_2$C$\underline{H}_2$O-), 3.6–3.4 (-OC$\underline{H}_2$C$\underline{H}_2$O-), 2.8 (-O$\underline{H}$), 2.6–2.2 (-CH$_2$C$\underline{H}$CO-), 2.0–1.5 (-C$\underline{H}_2$CHCO-, -COOCH$_2$C$\underline{H}_2$(CH$_2$)$_{15}$CH$_3$), 1.4–1.1 (-COOCH$_2$CH$_2$(C$\underline{H}_2$)$_{15}$CH$_3$), 0.9–0.8 (-COO(CH$_2$)$_{17}$C$\underline{H}_3$). **P1**, **P2**, **P4**, **P5**, and **P6** were synthesized similarly.

PEGOHA/ODA random copolymer (**P7**): AIBN (0.045 mmol, 7.4 mg) was charged in a 30 mL glass tube. Then, 1,4-dioxane (3.3 mL), tetralin (0.10 mL), 640 mM toluene solution of PEGOHMA

(1.2 mmol, 1.9 mL), and 2490 mM 1,4-dioxane solution of ODA (1.8 mmol, 0.72 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 6.0 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PEGOHA/ODA = 96%/96%, 7.5 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in $CHCl_3$ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): $M_n$ = 13900; $M_w/M_n$ = 2.40. $^1$H NMR [500 MHz, $CDCl_3$, 25 °C, δ = 7.26 ($CHCl_3$)]: δ 4.4–4.1 (-$COOC\underline{H}_2CH_2O$-), 4.1-3.8 (-$COOC\underline{H}_2CH_2CH_2$-), 3.7–3.6 (-$COOCH_2C\underline{H}_2O$-), 3.6–3.4 (-$OC\underline{H}_2C\underline{H}_2O$-), 2.8 (-O<u>H</u>), 2.6–2.2 (-$CH_2C\underline{H}CO$-), 2.0–1.5 (-$C\underline{H}_2CHCO$-, -$COOCH_2C\underline{H}_2(CH_2)_{15}CH_3$), 1.4–1.1 (-$COOCH_2CH_2(C\underline{H}_2)_{15}CH_3$), 0.9–0.8 (-$COO(CH_2)_{17}C\underline{H}_3$).

PEGOHMA/ODA random copolymer (**P8**): $RuCp^*Cl(PPh_3)_2$ (0.0080 mmol, 7.5 mg) was charged in a 30 mL glass tube. Then, toluene (1.6 mL), tetralin (0.090 mL), a 400 mM toluene solution of *n*-$Bu_3N$ (0.19 mmol, 0.47 mL), a 1960 mM toluene solution of PEGOHMA (3.7 mmol, 1.9 mL), a 1440 mM toluene solution of ODA (5.6 mmol, 3.9 mL), and a 67.5 mM toluene solution of BzMA-Br (0.090 mmol, 1.4 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 9.4 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PEGOHMA/ODA = 91%/55%, 24 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in $CHCl_3$ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): $M_n$ = 34100; $M_w/M_n$ = 2.22. $^1$H NMR [500 MHz, acetone-$d_6$, 25 °C, δ = 2.05 ($CD_2HCOCD_3$)]: δ 7.4–7.3 (aromatic), 4.4–3.8 (-$COOC\underline{H}_2CH_2O$-, -$COOC\underline{H}_2CH_2CH_2$-), 3.7–3.6 (-$COOCH_2C\underline{H}_2O$-), 3.6–3.4 (-$OC\underline{H}_2C\underline{H}_2O$-), 3.2–4.0 (-O<u>H</u>), 2.6–2.2 (-$CH_2C\underline{H}CO$-), 2.0–1.5 (-$C\underline{H}_2CHCO$-, -$C\underline{H}_2CCH_3CO$-, -$COOCH_2C\underline{H}_2(CH_2)_{15}CH_3$), 1.4–1.1 (-$COOCH_2CH_2(C\underline{H}_2)_{15}CH_3$), 1.1-0.9 (-$CH_2CC\underline{H}_3CO$-), 0.9–0.8 (-$COO(CH_2)_{17}C\underline{H}_3$)

PEGOHA/ODMA random copolymer (**P9**): AIBN (0.060mmol, 9.8 mg) was charged in a 30 mL glass tube. Then, 1,4-dioxane (4.2 mL), tetralin (0.10 mL), 640 mM toluene solution of PEGOHMA (1.6 mmol, 2.5 mL), and 1910 mM 1,4-dioxane solution of ODMA (2.4 mmol, 1.2 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 8.0 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PEGOHA/ODMA = 93%/99%, 7.5 h). The quenched reaction mixture was evaporated to dryness. The crude product

was purified by preparative SEC in $CHCl_3$ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): $M_n$ = 20200; $M_w/M_n$ = 6.54. $^1$H NMR [500 MHz, $CDCl_3$, 25 °C, δ = 7.26 ($CHCl_3$)]: δ 4.4–3.8 (-COOC$\underline{H}_2$CH$_2$O-, -COOC$\underline{H}_2$CH$_2$CH$_2$-), 3.7–3.6 (-COOCH$_2$C$\underline{H}_2$O-), 3.6–3.4 (-OCH$_2$CH$_2$O-), 2.8 (-O$\underline{H}$), 2.6–2.2 (-CH$_2$C$\underline{H}$CO-), 2.0–1.5 (-C$\underline{H}_2$CHCO-, -C$\underline{H}_2$CCH$_3$CO-, -COOCH$_2$C$\underline{H}_2$(CH$_2$)$_{15}$CH$_3$), 1.1-0.9 (-CH$_2$CC$\underline{H}_3$CO-), 1.4–1.1 (-COOCH$_2$CH$_2$(C$\underline{H}_2$)$_{15}$CH$_3$), 0.9–0.8 (-COO(CH$_2$)$_{17}$C$\underline{H}_3$).

PEGOHMA/ODMA random copolymer (**P10**): AIBN (0.053mmol, 8.6 mg) was charged in a 30 mL glass tube. Then, 1,4-dioxane (5.1 mL), tetralin (0.10 mL), 1960 mM toluene solution of PEGOHMA (1.4 mmol, 0.72 mL), and 1910 mM 1,4-dioxane solution of ODMA (2.1 mmol, 1.1 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 7.0 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PEGOHMA/ODMA = 93%/92%, 8 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in $CHCl_3$ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): $M_n$ = 25700; $M_w/M_n$ = 1.98. $^1$H NMR [500 MHz, $CDCl_3$, 25 °C, δ = 7.26 ($CHCl_3$)]: δ4.4–4.1 (-COOC$\underline{H}_2$CH$_2$O-), 4.1-3.8 (-COOC$\underline{H}_2$CH$_2$CH$_2$-), 3.7–3.6 (-COOCH$_2$C$\underline{H}_2$O-), 3.6–3.4 (-OC$\underline{H}_2$C$\underline{H}_2$O-), 2.0–1.5 (-C$\underline{H}_2$CCH$_3$CO-, -COOCH$_2$C$\underline{H}_2$(CH$_2$)$_{15}$CH$_3$), 1.1-0.9 (-CH$_2$CC$\underline{H}_3$CO-), 1.4–1.1 (-COOCH$_2$CH$_2$(C$\underline{H}_2$)$_{15}$CH$_3$), 0.9–0.8 (-COO(CH$_2$)$_{17}$C$\underline{H}_3$).

PEGMA/ODA random copolymer (**P11**): RuCp*Cl(PPh$_3$)$_2$ (0.0080 mmol, 6.8 mg) was charged in a 30 mL glass tube. Then, toluene (2.5 mL), tetralin (0.11 mL), a 400 mM toluene solution of *n*-Bu$_3$N (0.17 mmol, 0.43mL), PEGMA (2.6 mmol, 1.1 mL), a 1930 mM toluene solution of ODA (6.0 mmol, 3.1 mL), and a 68 mM toluene solution of BzMA-Br (0.085 mmol, 1.3 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 8.5 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PEGMA/ODA = 68%/60%, 24 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in $CHCl_3$ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): $M_n$ = 22000; $M_w/M_n$ = 1.16. $^1$H NMR [500 MHz, acetone-$d_6$, 25 °C, δ = 2.05 ($CD_2HCOCD_3$)]: δ 7.4–7.3 (aromatic), 4.4–3.8 (-COOC$\underline{H}_2$CH$_2$O-, -COOC$\underline{H}_2$CH$_2$CH$_2$-), 3.7–3.6 (-COOCH$_2$C$\underline{H}_2$O-), 3.6–3.5 (-OC$\underline{H}_2$C$\underline{H}_2$O-), 3.5–3.4 (-C$\underline{H}_2$OCH$_3$), 3.3 (-OC$\underline{H}_3$), 2.6–2.2 (-CH$_2$C$\underline{H}$CO-), 2.0–1.5 (-C$\underline{H}_2$CHCO-, -C$\underline{H}_2$CCH$_3$CO-, -COOCH$_2$C$\underline{H}_2$(CH$_2$)$_{15}$CH$_3$), 1.4–1.1 (-COOCH$_2$CH$_2$(C$\underline{H}_2$)$_{15}$CH$_3$, -CH$_2$CC$\underline{H}_3$CO-), 0.9–0.8 (-COO(CH$_2$)$_{17}$C$\underline{H}_3$).

PPOOHMA/ODA random copolymer (**P12**): RuCp*Cl($PPh_3$)$_2$ (0.0090 mmol, 6.9 mg) was charged in a 30 mL glass tube. Then, toluene (1.3 mL), tetralin (0.080 mL), a 400 mM toluene solution of *n*-$Bu_3N$ (0.17 mmol, 0.43 mL), a 1820 mM toluene solution of PPO(OH)MA (3.5 mmol, 1.9 mL), a 1440 mM toluene solution of ODA (5.2 mmol, 3.6 mL), and a 68 mM toluene solution of BzMA-Br (0.090 mmol, 1.3 mL) were added sequentially into the tube at 25 °C under argon (the total volume: 8.7 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 $^1$H NMR in $CDCl_3$ with tetralin as an internal standard (Conv. PPO(OH)MA/ODA = 89%/62%, 9 h). The quenched reaction mixture was evaporated to dryness. The crude product was purified by preparative SEC in $CHCl_3$ as an eluent to remove catalyst residue and unreacted monomers. The product was dried under vacuum at room temperature. SEC (THF, PMMA std.): $M_n$ = 22500; $M_w/M_n$ = 1.40. $^1$H NMR [500 MHz, acetone-$d_6$, 25 °C, δ = 2.05 ($CD_2HCOCD_3$)]: δ 7.4–7.3 (aromatic), 4.8 (-$CH_2CHCH_3O\underline{H}$) 4.0–3.8 (-$COOC\underline{H}_2CH_2O$-, -$COOC\underline{H}_2CH_2CH_2$-), 3.6–3.5 (-$COOCH_2C\underline{H}CH_3O$-), 3.5-3.1 (-$OC\underline{H}_2C\underline{H}CH_3O$-), 2.0–1.5 (-$C\underline{H}_2CHCO$-, -$C\underline{H}_2CCH_3CO$-, -$COOCH_2C\underline{H}_2(CH_2)_{15}CH_3$), 1.6 (-$COOCH_2C\underline{H}_2$-), 1.4–1.1 (-$COOCH_2CH_2(C\underline{H}_2)_{15}CH_3$, -$CH_2CC\underline{H}_3CO$-), 0.9–0.8 (-$COO(CH_2)_{17}C\underline{H}_3$).

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

Solid polymer samples of **P1** – **P12** were prepared as follows: $CH_2Cl_2$ solutions of **P1** – **P12** (50 ~ 100 mg/mL) were dried in vials by flowing Ar or $N_2$ gas at 25 °C. The resulting solid polymers were further dried under vacuum overnight and then utilized in DSC, XRD, and SAXS measurements.

## Supporting Data

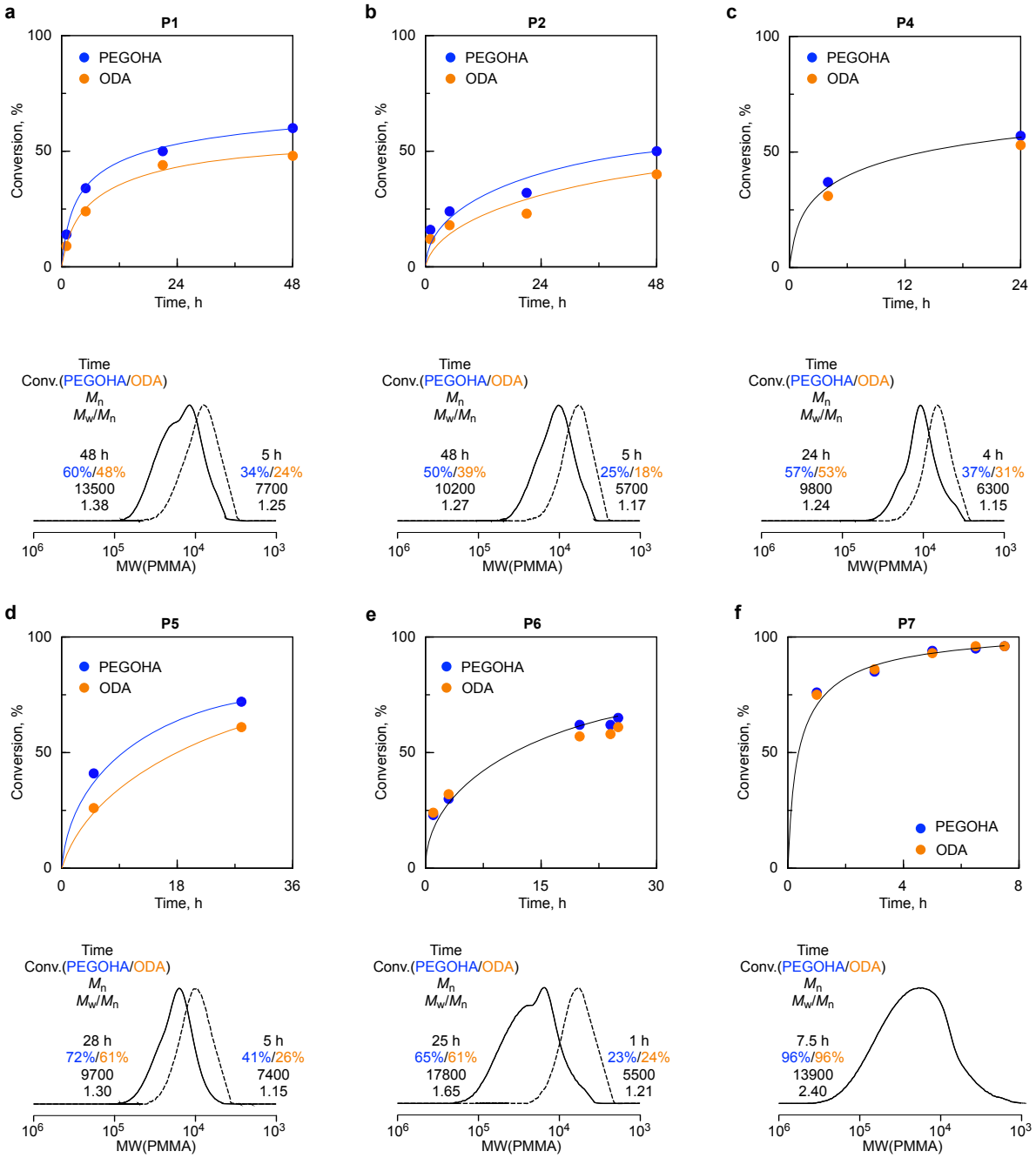


**Figure S1**. Ru-catalyzed living or free radical copolymerization of PEGOHA and ODA for (a) **P1**, (b) **P2**, (c) **P4**, (d) **P5**, (e) **P6**, and (f) **P7** (upper: time-conversion plots, lower: SEC curves of crude products). (a-e) $[PEGOHA]_0/[ODA]_0/[BzMA\text{-}Br]_0/[RuCp^*Cl(PPh_3)_2]_0/[n\text{-}Bu_3N]_0$ = (a) 400/100/10/1/20, (b) 250/250/10/1/20, (c) 150/350/10/1/20, and (d) 100/400/10/1/20, (e) 350/350/10/1/20 mM in toluene at 80 °C. (f) $[PEGOHA]_0/[ODA]_0/[AIBN]_0$ = 200/300/7.5 mM in toluene at 80 °C. The final crude products (a - f) were purified by preparative SEC to give (a) **P1**, (b) **P2**, (c) **P4**, (d) **P5**, (e) **P6**, and (f) **P7** respectively.

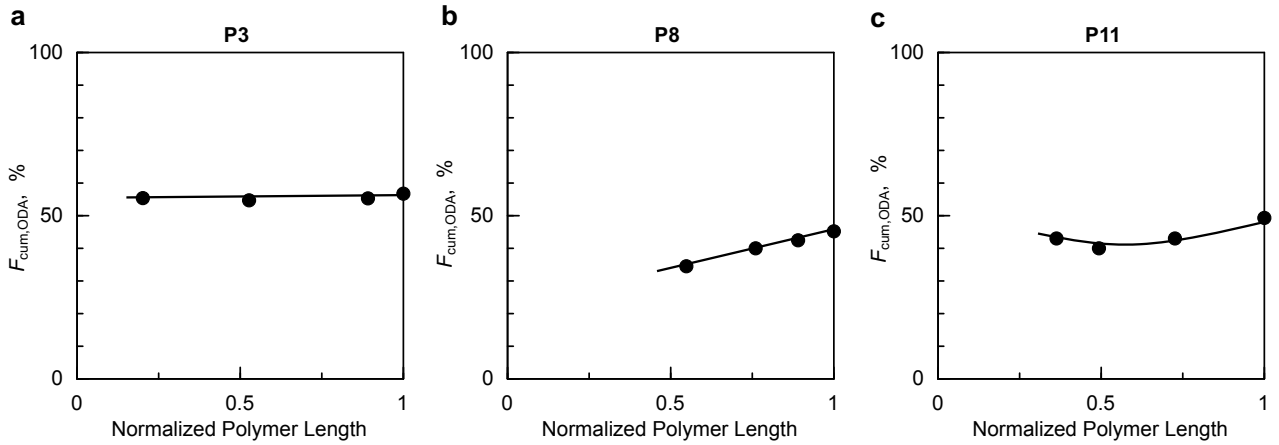


**Figure S2.** Cumulative content of ODA ($F_{cum,\%}$) in (a) **P3**, (b) **P8**, and (c) **P11** against a normalized polymer length.

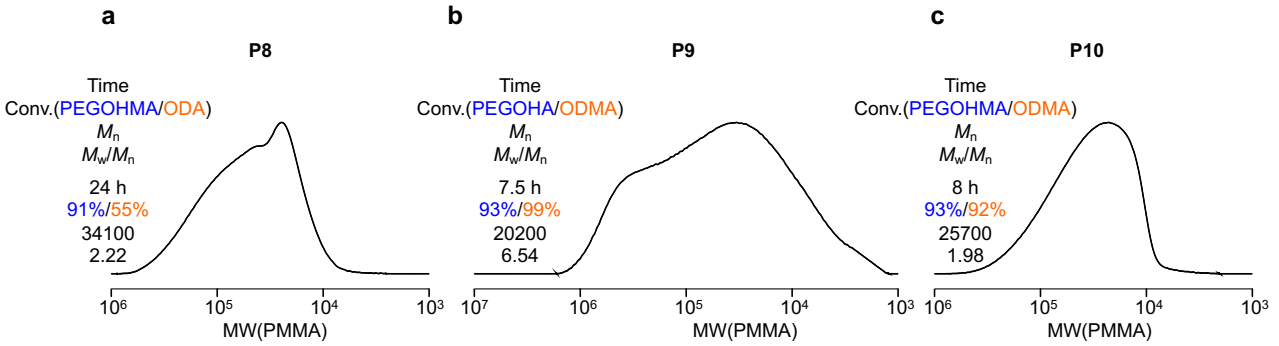


**Figure S3**. SEC curves of final products (a: **P8**, b: **P9**, c: **P10**) obtained from (a) Ru-catalyzed living radical copolymerization of PEGOHMA and ODA, (b) free radical copolymerization of PEGOHA and ODMA, and (c) free radical copolymerization of PEGOHMA and ODMA. **P8**: $[PEGOHMA]_0/[ODA]_0/[BzMA\text{-}Br]_0/[RuCp^*Cl(PPh_3)_2]_0/[n\text{-}Bu_3N]_0$ = 400/600/10/1/20 mM in 1,4-dioxane at 80 °C. **P9**: $[PEGOHA]_0/[ODMA]_0/[AIBN]_0$ = 200/300/7.5 mM in toluene/1,4-dioxane (3/7) at 80 °C. **P10**: $[PEGOHMA]_0/[ODMA]_0/[AIBN]_0$ = 200/300/7.5 mM in toluene/1,4-dioxane (1/9) at 80 °C.

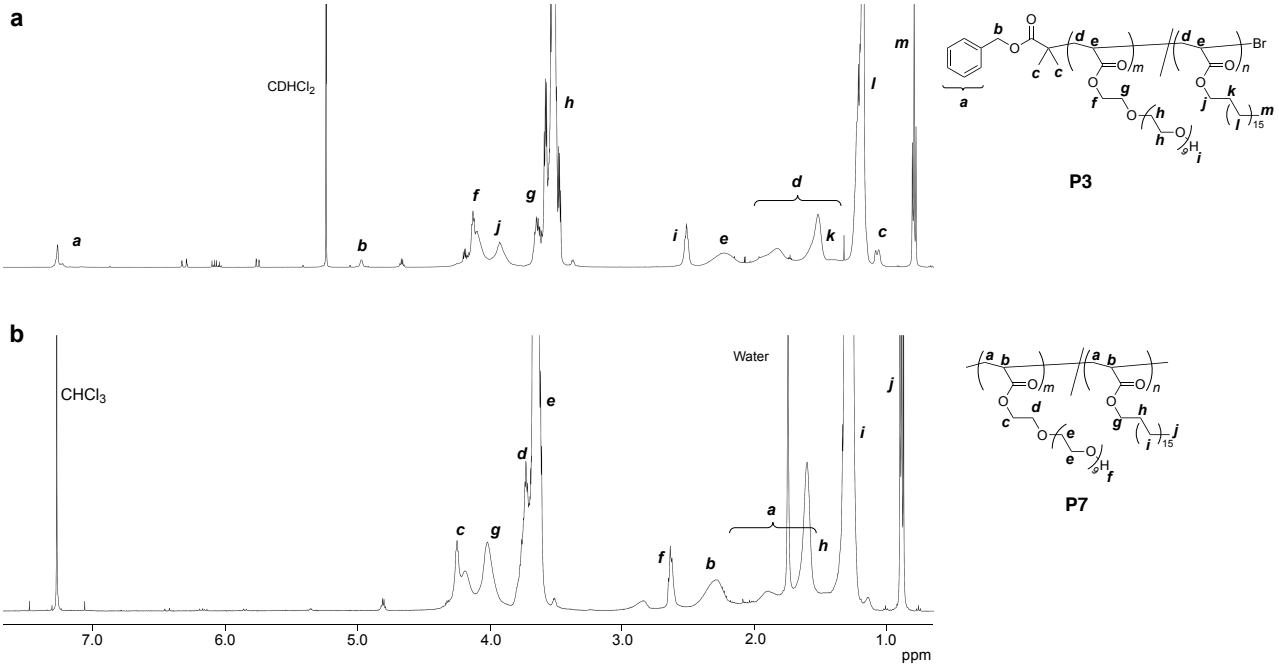


**Figure S4.** $^1$H NMR spectra of (a) **P3** in $CD_2Cl_2$ and (b) **P7** in $CDCl_3$ at 25 °C.

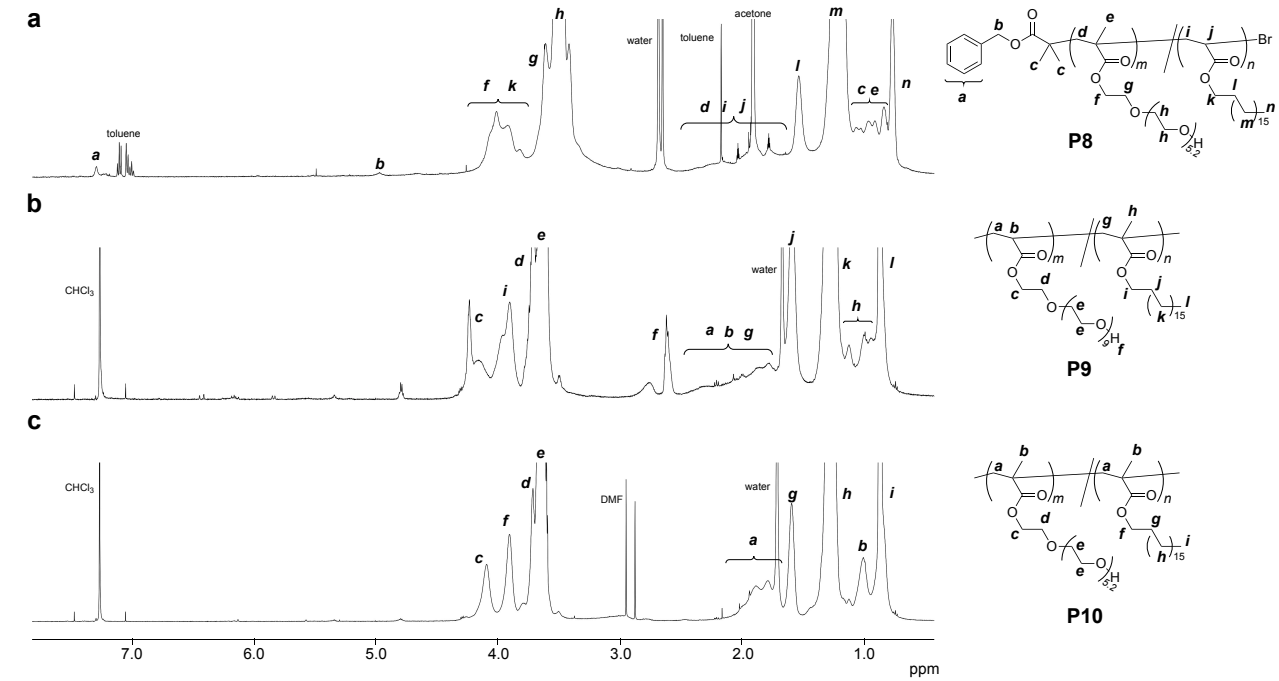


**Figure S5.** $^1$H NMR spectra of (a) **P8** in acetone-$d_6$, (b) **P9** in $CDCl_3$, and (c) **P10** in $CDCl_3$ at 25 °C.

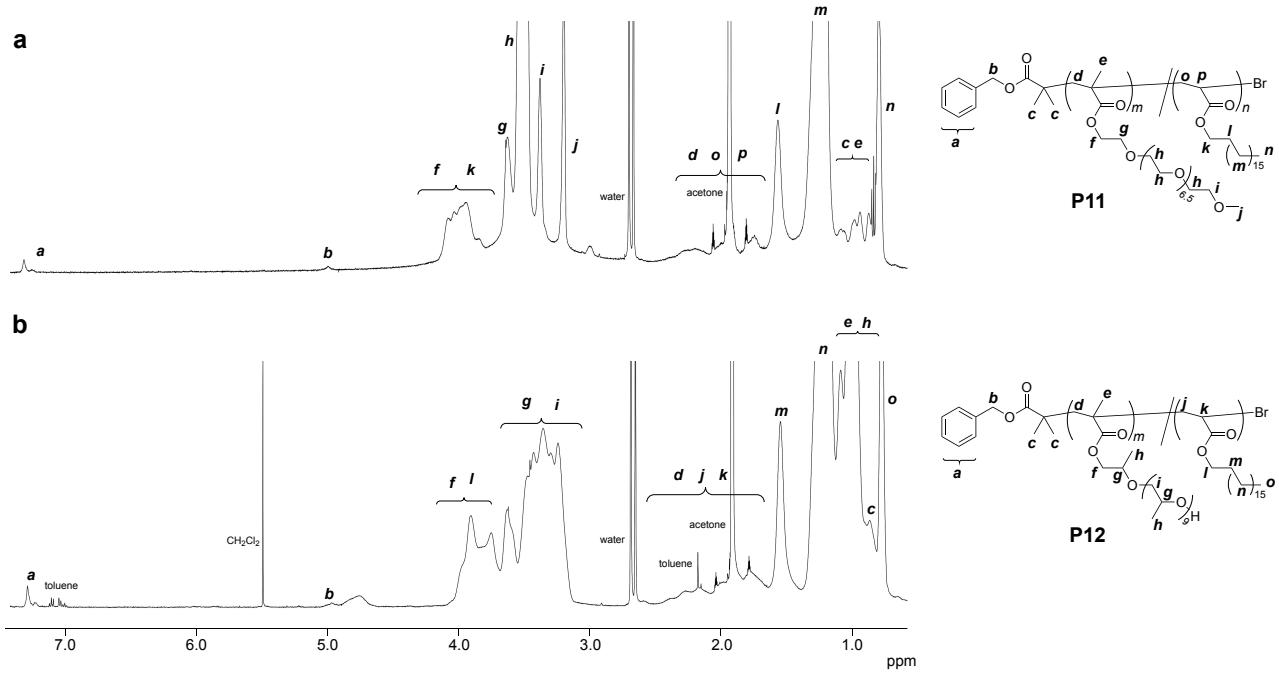


**Figure S6.** $^1$H NMR spectra of (a) **P11** and (b) **P12** in acetone-$d_6$ at 25 °C.

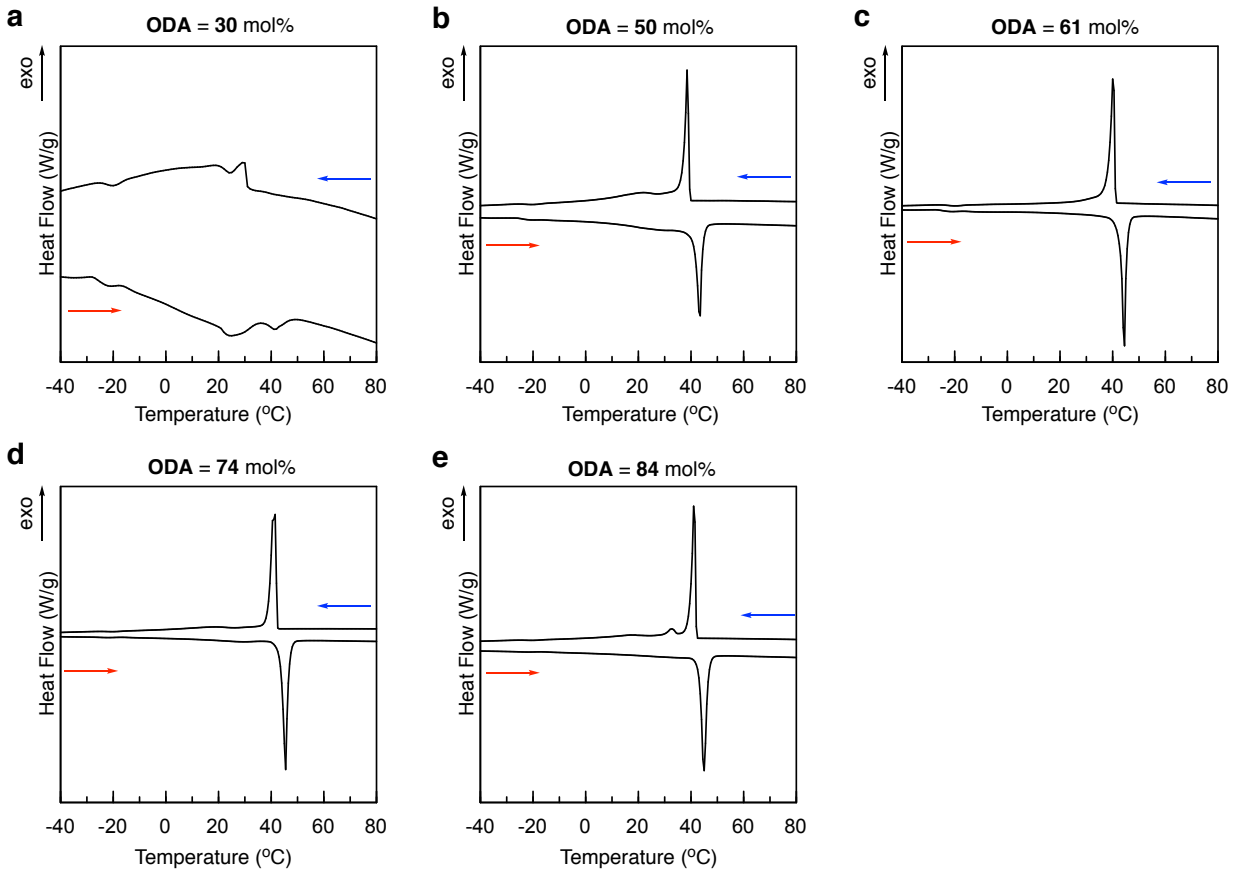


**Figure S7.** DSC curves of PEGOHA/ODA random copolymers (a: **P1**, b: **P2**, c: **P3**, d: **P4**, e: **P5**, ODA = 30 – 84 mol%). The heating and cooling rates were performed at 10 and -10 °C/min, respectively.

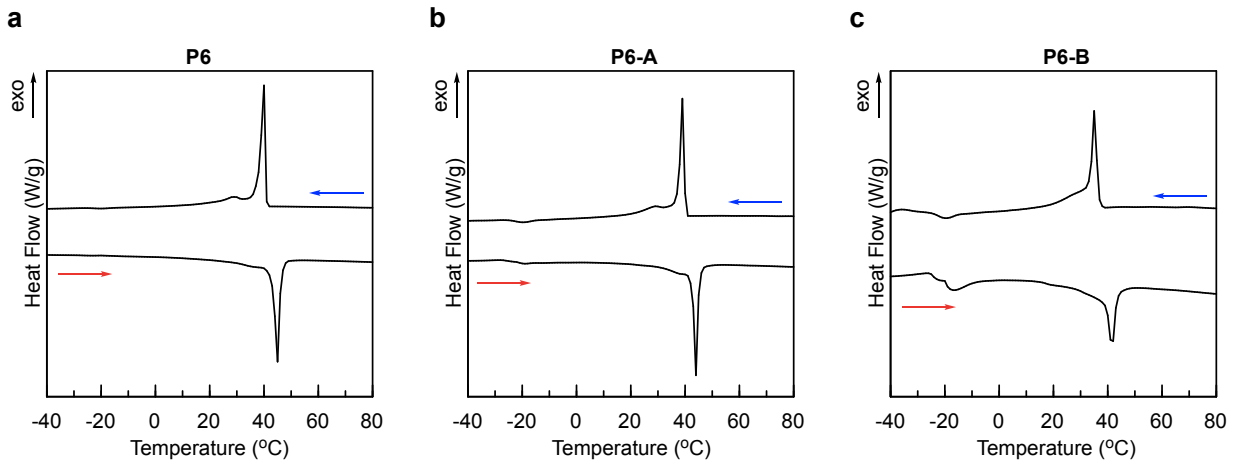


**Figure S8.** DSC curves of PEGOHA/ODA random copolymers (a: **P6**; b: **P6-A**; c: **P6-B**). The heating and cooling rates were performed at 10 and -10 °C/min, respectively.

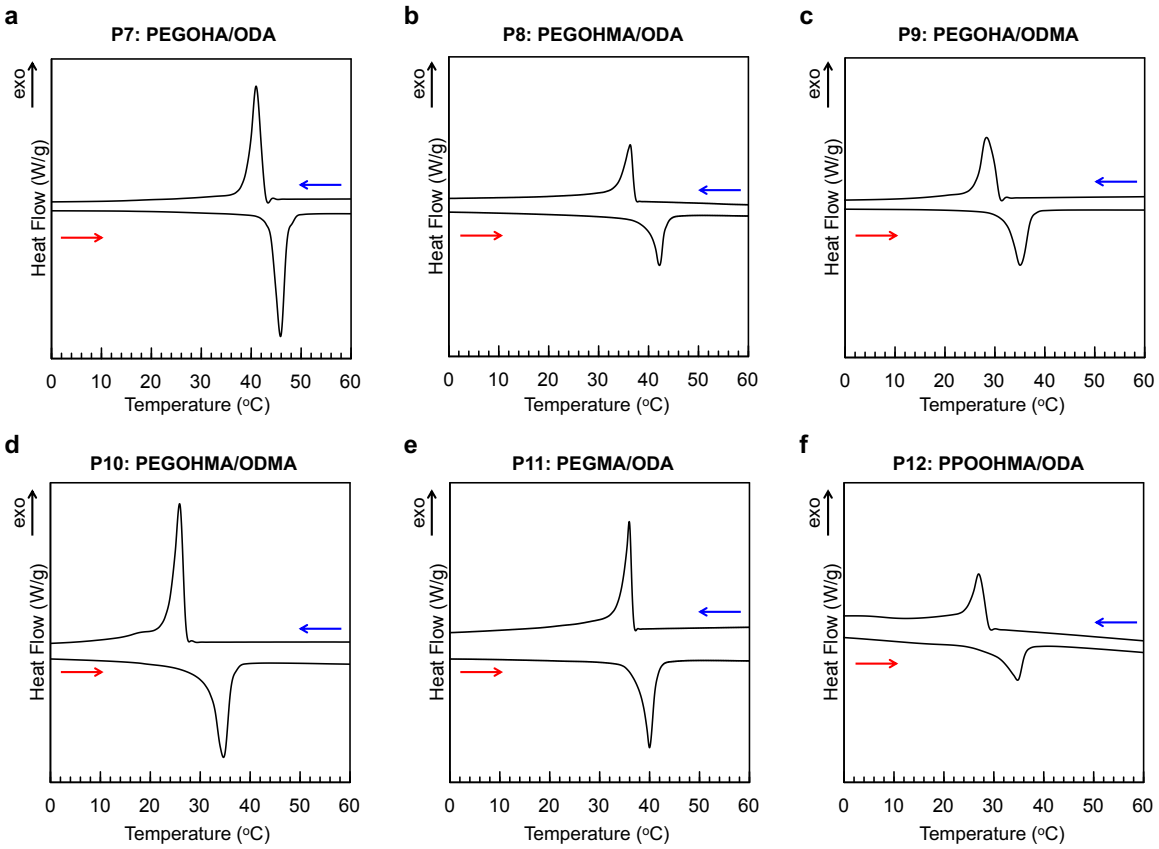


**Figure S9.** DSC curves of (a) **P7**, (b) **P8**, (c) **P9**, (d) **P10**, (e) **P11**, and (f) **P12**. The heating and cooling rates were performed at 10 and -10 °C/min, respectively.

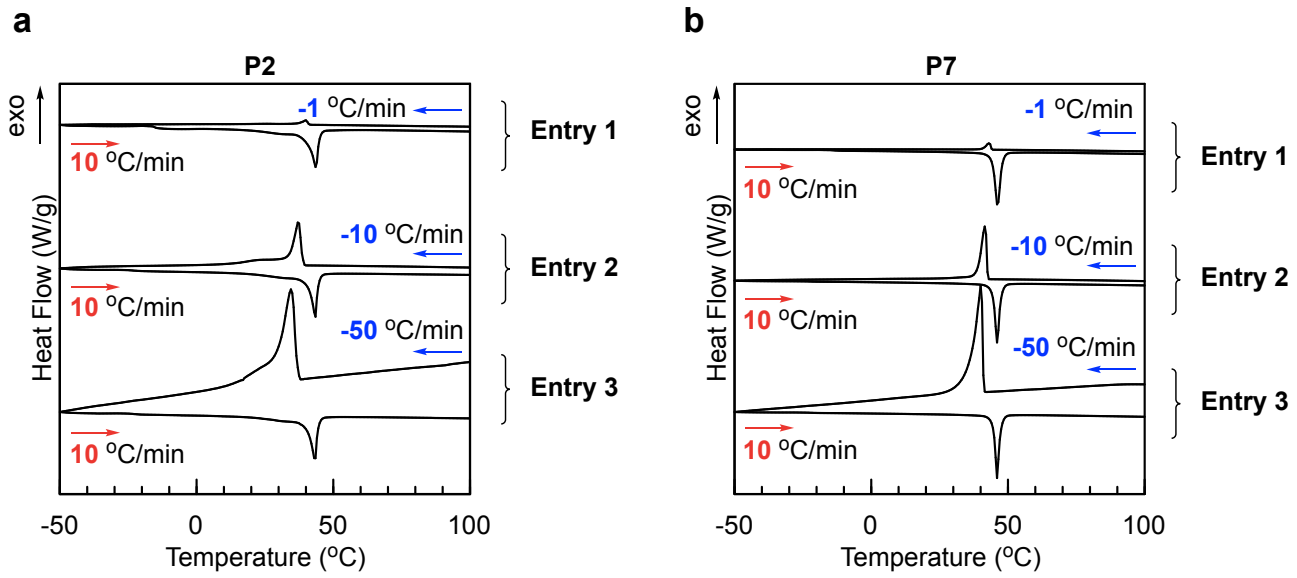


**Figure S10**. Effects of the cooling rates on the crystallization and melting behavior of (a) **P2** and (b) **P7**. DSC curves recorded for the first cooling scans and the subsequent heating scans of (a) **P2** and (b) **P7** between -80 °C and 150 °C. The cooling rates were varied to -1, -10, and -50 °C/min, while the heating rate was kept to 10 °C/min.

**Table S1. Crystallization and Melting Behavior of P2 and P7** [a]

| polymer | entry (Figure S10) | cooling rate (°C/min) | heating rate (°C/min) | $T_c$ (°C) | $\Delta H_c$ (J/g) | $T_m$ (°C) | $\Delta H_m$ (J/g) |
|---|---|---|---|---|---|---|---|
| | 1 | 1 | 10 | 39.9 | 30.9 | 43.6 | 31.9 |
| **P2** | 2 | 10 | 10 | 37.2 | 34.6 | 43.5 | 32.2 |
| | 3 | 50 | 10 | 34.5 | 31.6 | 43.3 | 32.2 |
| | 1 | 1 | 10 | 43.1 | 58.0 | 46.2 | 56.1 |
| **P7** | 2 | 10 | 10 | 41.7 | 53.8 | 46.0 | 54.0 |
| | 3 | 50 | 10 | 40.2 | 52.3 | 46.0 | 52.8 |

[a] **P2** and **P7** were analyzed by DSC at the temperature range between -80 °C and 150 °C (Figure S10). The cooling and heating rates were performed at 10 °C/min and -10 °C/min, respectively. Crystallization temperature ($T_c$) and the enthalpy of crystallization ($\Delta H_c$) of the octadecyl groups were obtained from the first cooling scans of the samples from 150 °C. Melting temperature ($T_m$) and the enthalpy of melting ($\Delta H_m$) of the octadecyl groups were obtained from the subsequent second heating scans of the samples from -80 °C.

**References**

(S1) M. M. Ali and H. D. H. Stöver, *Macromolecules*, 2004, **37**, 5219-5227.

(S2) G. Hattori, M. Takenaka, M. Sawamoto and T. Terashima, *J. Am. Chem. Soc.*, 2018, **140**, 8376-8379.