

Supplementary Information

Single-chain crosslinked polymers via the transesterification of folded polymers: from efficient synthesis to crystallinity control

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Contents

Experimental Section	S2
Supporting Data	
Figure S1. Living radical copolymerization of ODMA, HEMA, and MA	S8
Table S1. Synthesis of polymer precursors	S8
Figure S2. Guinier plots of the SAXS profiles of P2 in octane or THF	S9
Figure S3. Transesterification of model ester compounds with benzyl alcohol	S10
Figure S4. Transesterification of PMA and PMMA with benzyl alcohol	S11
Figure S5. Transesterification of P6 with various catalysts in octane	S12
Figure S6. Transesterification of P6 with Ti(O <i>i</i> -Pr) ₄ in octane	S13
Figure S7. Transesterification of P9 , P10 , and P11 with Sc(OTf) ₃ in octane	S14
Figure S8. Effects of solvent and concentration on transesterification of P2	S15
Figure S9. Transesterification of P1 – P4 with Sc(OTf) ₃ in octane	S16
Figure S10. Guinier plots of the SANS profiles of P3 , P5 , and crosslinked products	S17
Figure S11. Synthesis of crosslinked P2 with different crosslinking density	S18
Table S2. Characterization of crosslinked P2 with different crosslinking density	S19
Figure S12. DSC measurements of P1 – P4 and crosslinked products	S19

Experimental Section

Materials.

Methyl methacrylate (MMA, TCI, purity >99.8%), methyl acrylate (MA, TCI, purity >99%), and tetralin (1,2,3,4-tetrahydronaphthalene, TCI, purity >98%, an internal standard for ¹H NMR analysis) were dried overnight with calcium chloride and distilled from calcium hydride under reduced pressure before use. Octadecyl methacrylate (ODMA, TCI, purity >95%), dodecyl methacrylate (DMA, TCI, purity >97%) and 2-hydroxyethyl methacrylate (HEMA, TCI, purity >95%) were purified by column chromatography with inhibitor remover (Aldrich) and degassed by triple vacuum-argon purge cycles before use. Ethyl α -bromophenylacetate (EBPA, Wako, purity >94%), tributylamine (*n*-Bu₃N, TCI, purity >98%), and 1,4-dioxane (Wako, purity >99.5%) were degassed by triple vacuum-argon purge cycles before use. RuCp*Cl(PPh₃)₂ (Aldrich, purity >97%), Sc(OTf)₃ (TCI, purity >98%), Hf(OTf)₄ (TCI, purity >90%), La(OTf)₃ (TCI, purity >98%), Y(OTf)₃ (Aldrich, purity >99.9%), and FeCl₃ (Aldrich, purity >97%) were used as received and handled in a glove box under moisture- and oxygen-free argon (H₂O <1 ppm; O₂ <1 ppm). Ti(O*i*-Pr)₄ (Aldrich, purity >97%) 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 System, Nikko Hansen & Co., Ltd.). Octane (Wako, purity >98%), anisole (Wako, purity >99%), benzyl alcohol (Wako, purity >99%), methyl isobutyrate (MI, TCI, purity >99%) and methyl pivalate (MPi, TCI, purity >98%) 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 = 2×10^6 ; particle size = 6 μ m; pore size = 3000 Å; 0.46 cm i.d. \times 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 residues of catalysts and unreacted monomers, polymer samples were purified before characterization by precipitation into methanol or preparative SEC in CHCl₃ at 25 °C (flow rate: 10 mL/min) on Shodex K-5003 (exclusion limit = 7×10^4 , particle size = 15 μ m, 5 cm i.d. \times 30 cm). ¹H NMR spectra were recorded in CDCl₃ or CD₂Cl₂ at 25 °C on a JEOL JNM-ECA500 spectrometer operating at 500.16 MHz.

Absolute weight-average molecular weight (M_w) of the polymers in THF was determined by

multiangle laser light scattering (MALLS) equipped with SEC on a Dawn HELEOS II instrument (Wyatt Technology, semiconductor laser, $\lambda = 663$ nm). The SEC system was performed in THF at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L) that were connected to a Jasco PU-2080 precision pump, a Jasco RI-1530 refractive index detector, and a Jasco UV-1570 UV/vis detector set at 270 nm. Intrinsic viscosity measurement of the polymers in THF was performed on a Viscotek TDAmix SEC system (Malvern) equipped with two linear-type polystyrene gel columns (Shodex KF-805L). Dynamic light scattering (DLS) was measured on Otsuka Photol ELSZ-0 equipped with a semi-conductor laser ($\lambda = 658$ nm) at 25 °C. The measuring angle was 165°.

Differential scanning calorimetry (DSC) was performed for polymer samples (ca. 1-3 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 °C/min and -10 °C/min, respectively, between -80 °C and 150 °C. The first cooling or second heating scans were employed as data in this work.

Powder X-ray diffraction (PXRD) was performed on a Rigaku SmartLab diffractometer, using a Cu anode and a K_{α} 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, sample to detector distance, and the detector used at BL45XU were 0.1 nm, 2500 nm, and PILATUS 3X 2M, respectively. The obtained 2-dimensional data were circularly averaged and corrected for background of cell and electronic noise of detector.

Small angle neutron scattering (SANS) measurements were performed on a BL15 TAIKAN in the Material and Life Science Experimental Facility (MLF) of the Japan Proton Accelerator Research Complex (J-PARC, Tokai, Japan). We utilized the data from the small-angle detector bank. Temperature was controlled with a circulating bath (Ministat 125, Huber Co.). The sample solutions were contained in quartz cells (Starna Scientific Co.) with a 1 mm path length and low neutron absorption ability. The exposure time was around ~0.5 h. For data corrections, air, the empty cell, and THF- d_8 filled in the cell were measured. All SANS data were normalized to an absolute intensity by the scattering of a glassy carbon standard after data corrections such as air and cell scattering. The scattering intensities from the cell and the solvent were subtracted with the measured transmission and the volume fraction of the solvent.

Polymer Synthesis.

The synthesis of **P1** – **P11** was carried out by syringe technique under argon in glass tubes equipped with a three-way stopcock.

P1 (ODMA/HEMA/MA copolymer): Into a 30 mL glass tube, RuCp*Cl(PPh₃)₂ (0.0080 mmol, 6.4 mg) was weighed, and toluene (0.54 mL), 1,4-dioxane (1.03 mL), tetralin (0.10 mL), a 400 mM toluene solution of *n*-Bu₃N (0.20 mL, *n*-Bu₃N = 0.080 mmol), ODMA (16 mmol, 6.27 mL), HEMA (4.4 mmol, 0.53 mL), MA (11.6 mmol, 1.04 mL), and a 280 mM toluene solution of EBPA (0.29 mL, EBPA = 0.080 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 10 mL). The glass tube was immersed in an oil bath kept at 80 °C for 24 h and then cooled to –78 °C to terminate the reaction. The monomer conversion was determined by ¹H NMR measurement of the terminated reaction solution in CDCl₃ at 25 °C with tetralin as an internal standard: ODMA/HEMA/MA = 71%/83%/44%. The reaction solution was evaporated to dryness to give the crude polymer. To remove catalyst residues and unreacted monomers, the product was purified by precipitation into methanol to give **P1**. SEC (THF, PMMA std.): *M*_n = 64200; *M*_w/*M*_n = 1.14. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.3-7.2 (aromatic protons), 4.2-4.0, (-COOCH₂CH₂OH), 4.0-3.8 (-COOCH₂(CH₂)₁₆CH₃), 3.8-3.7 (-COOCH₂CH₂OH), 3.7–3.5 (-OCH₃), 2.5–1.2 (-CH₂CH(COO)-, -CH₂CH(COO)-, -CH₂C(CH₃)-), 1.7–1.6 (-COOCH₂CH₂(CH₂)₁₅CH₃), 1.4–1.2 (-COOCH₂CH₂(CH₂)₁₅CH₃), 1.2–0.8 (-CH₂C(CH₃)-), 0.9–0.8 (-COOCH₂(CH₂)₁₆CH₃). *dn/dc* = 0.080 (THF). **P2** – **P5** were similarly prepared.

P6 (DMA/HEMA/MA copolymer): Into a 30 mL glass tube, RuCp*Cl(PPh₃)₂ (0.020 mmol, 15.9 mg) was weighed, and toluene (2.67 mL), 1,4-dioxane (4.03 mL), tetralin (0.20 mL), a 400 mM toluene solution of *n*-Bu₃N (0.50 mL, *n*-Bu₃N = 0.20 mmol), DMA (30 mmol, 8.79 mL), HEMA (7.5 mmol, 0.91 mL), MA (22.5 mmol, 2.03 mL), and a 230 mM toluene solution of EBPA (0.87 mL, EBPA = 0.20 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 20 mL). The glass tube was immersed in an oil bath kept at 80 °C for 60 h and then cooled to –78 °C to terminate the reaction. The monomer conversion was determined by ¹H NMR measurement of the terminated reaction solution in CDCl₃ at r.t. with tetralin as an internal standard: DMA/HEMA/MA = 64%/77%/38%. The reaction solution was evaporated to dryness to give the crude polymer. The product was precipitated into methanol to give **P6**. SEC (THF, PMMA std.): *M*_n = 43600; *M*_w/*M*_n = 1.16. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.3-7.2 (aromatic protons), 4.2-4.0, (-COOCH₂CH₂OH), 4.0-3.8 (-COOCH₂(CH₂)₁₀CH₃), 3.8 (-COOCH₂CH₂OH), 3.7–3.5 (-OCH₃), 2.5–1.2 (-CH₂CH(COO)-, -CH₂CH(COO)-, -CH₂C(CH₃)-), 1.7–1.6 (-COOCH₂CH₂(CH₂)₉CH₃), 1.4–1.2 (-COOCH₂CH₂(CH₂)₉CH₃), 1.2–0.8 (-CH₂C(CH₃)-), 0.9–0.8 (-COOCH₂(CH₂)₁₀CH₃). *dn/dc* = 0.081 (THF).

P7 (MMA/HEMA/MA copolymer): Into a 30 mL glass tube, RuCp*Cl(PPh₃)₂ (0.012 mmol, 9.6 mg) was weighed, and toluene (0.38 mL), 1,4-dioxane (1.12 mL), tetralin (0.060 mL), a 400 mM toluene solution of *n*-Bu₃N (0.30 mL, *n*-Bu₃N = 0.12 mmol), MMA (19.2 mmol, 2.05 mL), HEMA (4.8 mmol, 0.58 mL), MA (12 mmol, 1.08 mL), and a 280 mM toluene solution of EBPA (0.43 mL, EBPA = 0.12 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 6 mL). The glass tube was immersed in an oil bath kept at 80 °C for 48 h and then cooled to -78 °C to terminate the reaction. The monomer conversion was determined by ¹H NMR measurement of the terminated reaction solution in CDCl₃ at r.t. with tetralin as an internal standard: MMA/HEMA/MA = 74%/83%/47%. The reaction solution was evaporated to dryness to give the crude polymer. The product was fractionated by preparative SEC to give **P7**. SEC (THF, PMMA std.): *M_n* = 28800; *M_w*/*M_n* = 1.19. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.3-7.2 (aromatic protons), 4.2-4.0, (-COOCH₂CH₂OH), 3.8 (-COOCH₂CH₂OH), 3.7-3.5 (-OCH₃), 2.5-1.2 (-CH₂CH(COO)-, -CH₂CH(COO)-, -CH₂C(CH₃)-), 1.2-0.8 (-CH₂C(CH₃)-). *dn/dc* = 0.085 (THF).

P8 (HEMA/MA copolymer): Into a 30 mL glass tube, RuCp*Cl(PPh₃)₂ (0.010 mmol, 8.0 mg) was weighed, and 1,4-dioxane (0.60 mL), tetralin (0.010 mL), a 400 mM toluene solution of *n*-Bu₃N (0.25 mL, *n*-Bu₃N = 0.10 mmol), HEMA (3.0 mmol, 0.36 mL), MA (27 mmol, 2.43 mL), and a 284 mM toluene solution of EBPA (0.35 mL, EBPA = 0.10 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 4 mL). The glass tube was immersed in an oil bath kept at 80 °C for 48 h and then cooled to -78 °C to terminate the reaction. The monomer conversion was determined by ¹H NMR measurement of the terminated reaction solution in CDCl₃ at r.t. with tetralin as an internal standard: HEMA/MA = 78%/40%. The reaction solution was evaporated to dryness to give the crude polymer. The product was fractionated by preparative SEC to give **P8**. SEC (THF, PMMA std.): *M_n* = 17000; *M_w*/*M_n* = 1.11. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, δ = 5.32 (CDHCl₂)]: δ 7.3-7.2 (aromatic protons), 4.2-4.0, (-COOCH₂CH₂OH), 3.8-3.7 (-COOCH₂CH₂OH), 3.7-3.5 (-OCH₃), 2.5-1.2 (-CH₂CH(COO)-, -CH₂CH(COO)-, -CH₂C(CH₃)-), 1.2-0.8 (-CH₂C(CH₃)-). *dn/dc* = 0.079 (THF).

P9 (ODMA/MA copolymer): Into a 30 mL glass tube, RuCp*Cl(PPh₃)₂ (0.0018 mmol, 1.43 mg) was weighed, and toluene (0.30 mL), tetralin (0.020 mL), a 400 mM toluene solution of *n*-Bu₃N (0.050 mL, *n*-Bu₃N = 0.018 mmol), ODMA (3.6 mmol, 1.41 mL), MA (1.8 mmol, 0.16 mL), and a 284 mM toluene solution of EBPA (0.060 mL, EBPA = 0.018 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 2 mL). The glass tube was immersed in an oil bath kept at 80 °C for 22 h and then cooled to -78 °C to terminate the reaction. The monomer conversion was determined by ¹H NMR measurement of the terminated reaction solution in CDCl₃ at r.t. with tetralin as an internal standard: ODMA/MA = 73%/44%. The reaction solution was

evaporated to dryness to give the crude polymer. The product was fractionated by preparative SEC to give **P9**. SEC (THF, PMMA std.): $M_n = 49700$; $M_w/M_n = 1.11$. $^1\text{H NMR}$ [500 MHz, CD_2Cl_2 , 25 °C, $\delta = 5.32$ (CDHCl_2)]: δ 7.3-7.2 (aromatic protons), 4.1-3.8 ($-\text{COOCH}_2(\text{CH}_2)_{16}\text{CH}_3$), 3.7-3.5 ($-\text{OCH}_3$), 2.4-1.2 ($-\text{CH}_2\text{CH}(\text{COO})-$), $-\text{CH}_2\text{CH}(\text{COO})-$, $-\text{CH}_2\text{C}(\text{CH}_3)-$, 1.7-1.6 ($-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$), 1.4-1.2 ($-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$), 1.2-0.8 ($-\text{CH}_2\text{C}(\text{CH}_3)-$), 0.9-0.8 ($-\text{COOCH}_2(\text{CH}_2)_{16}\text{CH}_3$).

P10 (ODMA/HEMA copolymer): Into a 30 mL glass tube, $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ (0.0188 mmol, 14.9 mg) was weighed, and toluene (1.74 mL), 1,4-dioxane (2.88 mL), tetralin (0.25 mL), a 400 mM toluene solution of *n*- Bu_3N (0.47 mL, *n*- $\text{Bu}_3\text{N} = 0.188$ mmol), ODMA (45 mmol, 17.6 mL), HEMA (11.3 mmol, 1.36 mL), and a 280 mM toluene solution of EBPA (0.67 mL, EBPA = 0.188 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 25 mL). The glass tube was immersed in an oil bath kept at 80 °C for 26 h and then cooled to -78 °C to terminate the reaction. The monomer conversion was determined by $^1\text{H NMR}$ measurement of the terminated reaction solution in CDCl_3 at r.t. with tetralin as an internal standard: ODMA/HEMA = 24%/41%. The reaction solution was evaporated to dryness to give the crude polymer. The product was precipitated into methanol to give **P10**. SEC (THF, PMMA std.): $M_n = 30600$; $M_w/M_n = 1.18$. $^1\text{H NMR}$ [500 MHz, CD_2Cl_2 , 25 °C, $\delta = 5.32$ (CDHCl_2)]: δ 7.3-7.2 (aromatic protons), 4.2-4.0, ($-\text{COOCH}_2\text{CH}_2\text{OH}$), 4.0-3.8 ($-\text{COOCH}_2(\text{CH}_2)_{16}\text{CH}_3$), 3.8-3.7 ($-\text{COOCH}_2\text{CH}_2\text{OH}$), 2.2-1.6 ($-\text{CH}_2\text{C}(\text{CH}_3)-$), 1.7-1.6 ($-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$), 1.4-1.2 ($-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$), 1.2-0.8 ($-\text{CH}_2\text{C}(\text{CH}_3)-$), 0.9-0.8 ($-\text{COOCH}_2(\text{CH}_2)_{16}\text{CH}_3$).

P11 (ODMA/HEMA/MMA copolymer): Into a 30 mL glass tube, $\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2$ (0.0018 mmol, 1.43 mg) was weighed, and toluene (0.11 mL), 1,4-dioxane (0.22 mL), tetralin (0.020 mL), a 400 mM toluene solution of *n*- Bu_3N (0.050 mL, *n*- $\text{Bu}_3\text{N} = 0.018$ mmol), ODMA (3.35 mmol, 1.31 mL), HEMA (8.5 mmol, 0.10 mL), MMA (1.2 mmol, 0.13 mL), and a 284 mM toluene solution of EBPA (0.060 mL, EBPA = 0.018 mmol) were added sequentially in that order at 25 °C under argon (the total volume: 2 mL). The glass tube was immersed in an oil bath kept at 80 °C for 48 h and then cooled to -78 °C to terminate the reaction. The monomer conversion was determined by $^1\text{H NMR}$ measurement of the terminated reaction solution in CDCl_3 at r.t. with tetralin as an internal standard: ODMA/HEMA/MMA = 37%/55%/45%. The reaction solution was evaporated to dryness to give the crude polymer. The product was fractionated by preparative SEC to give **P11**. SEC (THF, PMMA std.): $M_n = 38800$; $M_w/M_n = 1.10$. $^1\text{H NMR}$ [500 MHz, CD_2Cl_2 , 25 °C, $\delta = 5.32$ (CDHCl_2)]: δ 7.3-7.2 (aromatic protons), 4.2-4.0, ($-\text{COOCH}_2\text{CH}_2\text{OH}$), 4.0-3.8 ($-\text{COOCH}_2(\text{CH}_2)_{16}\text{CH}_3$), 3.8 ($-\text{COOCH}_2\text{CH}_2\text{OH}$), 3.6-3.5 ($-\text{OCH}_3$), 2.2-1.6 ($-\text{CH}_2\text{C}(\text{CH}_3)-$), 1.7-1.6 ($-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$), 1.4-1.2 ($-\text{COOCH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$), 1.2-0.8 ($-\text{CH}_2\text{C}(\text{CH}_3)-$), 0.9-0.8 ($-\text{COOCH}_2(\text{CH}_2)_{16}\text{CH}_3$).

Transesterification.

Transesterification was carried out by syringe technique under argon in glass tubes equipped with a three-way stopcock.

Transesterification of Methyl Isobutyrate and Methyl Pivalate. A typical procedure for the transesterification of methyl isobutyrate was given: Into a 30 mL glass tube, Sc(OTf)₃ (0.020 mmol, 9.8 mg) was weighed, and toluene (0.76 mL), benzyl alcohol (0.76 mL), tetralin (0.02 mL), and methyl isobutyrate (4.0 mmol, 0.46 mL) were added sequentially in that order at 25 °C under argon (the total volume: 2 mL). The glass tube was immersed in an oil bath kept at 80 °C. The solution was sampled at predetermined intervals. The sampled solutions were cooled to -78 °C to terminate the reaction. The conversion was determined by ¹H NMR measurement of the terminated solutions in CDCl₃ at r.t. with tetralin as an internal standard (61%, 48 h, Figure S3).

Synthesis of Single-Chain Polymer Nanoparticles via Transesterification. A typical procedure for the intramolecular transesterification of **P1** with Sc(OTf)₃ was given: Into a 50 mL round-bottomed flask, a 10 wt% dichloromethane solution of **P1** ($M_n = 64200$, $M_w/M_n = 1.14$, 1.0 mL, polymer = 0.0016 mmol, 100 mg) was added and the solution was evaporated to remove the solvent. Into this, Sc(OTf)₃ (0.010 mmol, 4.9 mg) was weighed and octane (10 mL) was added at 25 °C under argon (the total volume: 10 mL). The flask was immersed in an oil bath kept at 120 °C for 48 h and cooled to -78 °C to terminate the reaction. The quenched solution was evaporated to dryness to give the crude product. The product was fractionated by preparative SEC to remove the catalyst residue. SEC (THF, PMMA std.): $M_n = 39800$; $M_w/M_n = 1.15$. ¹H NMR [500 MHz, CD₂Cl₂, 25 °C, $\delta = 5.32$ (CDHCl₂)]: δ 7.3-7.2 (aromatic protons), 4.2-3.8 (-COOCH₂(CH₂)₁₆CH₃), 3.7-3.5 (-OCH₃), 2.5-1.2 (-CH₂CH(COO)-, -CH₂CH(COO)-, -CH₂C(CH₃)-), 1.7-1.6 (-COOCH₂CH₂(CH₂)₁₅CH₃), 1.4-1.2 (-COOCH₂CH₂(CH₂)₁₅CH₃), 1.2-0.8 (-CH₂C(CH₃)-), 0.9-0.8 (-COOCH₂(CH₂)₁₆CH₃). $dn/dc = 0.080$ (THF).

Supporting Data

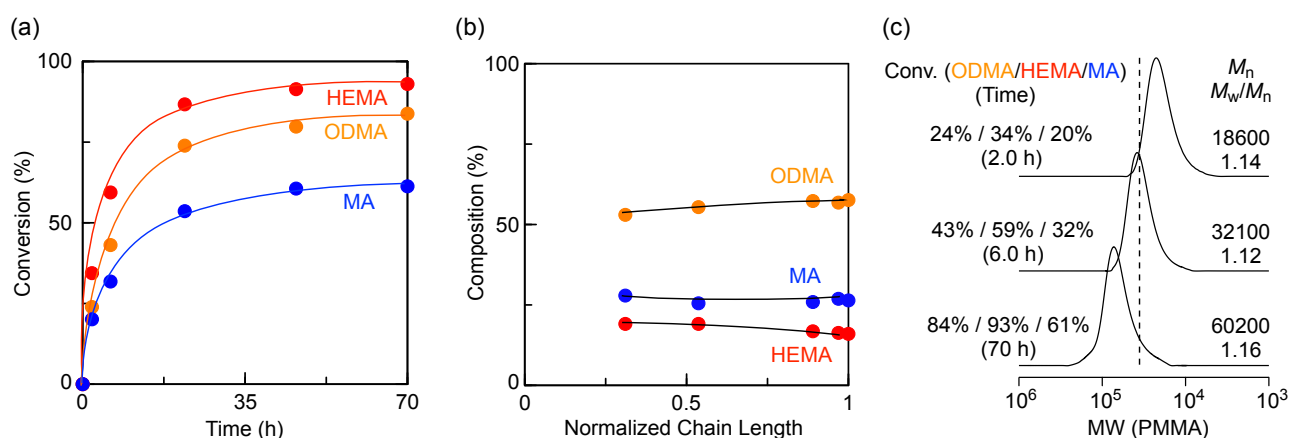


Figure S1. Ru-catalyzed living radical copolymerization of ODMA, HEMA, and MA with EBPA for a ODMA/HEMA/MA random copolymer: $[\text{ODMA}]_0/[\text{HEMA}]_0/[\text{MA}]_0/[\text{EBPA}]_0/[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0/[\textit{n}\text{-Bu}_3\text{N}]_0 = 1600/400/1000/10/1/10$ mM in toluene/1,4-dioxane (1/1, v/v) at 80 °C. (a) Time-conversion plot, (b) cumulative monomer composition (F_{cum}) of the resulting copolymer as a function of normalized chain length, and (c) SEC curves of the products.

Table S1. Synthesis of Control Precursor Polymers^a

Entry	Monomer	Time (h)	Conv. ^b (%)	M_n^c (SEC)	M_w/M_n^c (SEC)	DP ^d
P9	ODMA/MA	22	73/44	49700	1.11	160/45
P10	ODMA/HEMA	26	24/41	30600	1.18	75/30
P11	ODMA/HEMA/MMA	48	37/55/45	38800	1.10	90/35/35

^a Polymer Precursors were synthesized by Ru-catalyzed living radical (co)polymerization. **P9**: $[\text{ODMA}]_0/[\text{MA}]_0/[\text{EBPA}]_0/[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0/[\textit{n}\text{-Bu}_3\text{N}]_0 = 1800/900/9/0.9/9$ mM in toluene at 80 °C. **P10**: $[\text{ODMA}]_0/[\text{HEMA}]_0/[\text{EBPA}]_0/[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0/[\textit{n}\text{-Bu}_3\text{N}]_0 = 1800/450/7.5/0.75/7.5$ mM in toluene/1,4-dioxane (1/1, v/v) at 80 °C. **P11**: $[\text{ODMA}]_0/[\text{HEMA}]_0/[\text{MMA}]_0/[\text{EBPA}]_0/[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]_0/[\textit{n}\text{-Bu}_3\text{N}]_0 = 1675/425/600/9/0.9/9$ mM in toluene/1,4-dioxane (1/1, v/v) at 80 °C.

^b Conversion determined by ¹H NMR with tetralin as an internal standard.

^c Determined by SEC in THF (**P1** – **P6**, **P8** – **P15**) or DMF (**P7**) with PMMA standard calibration.

^d Degree of polymerization (DP) of the copolymers determined by ¹H NMR.

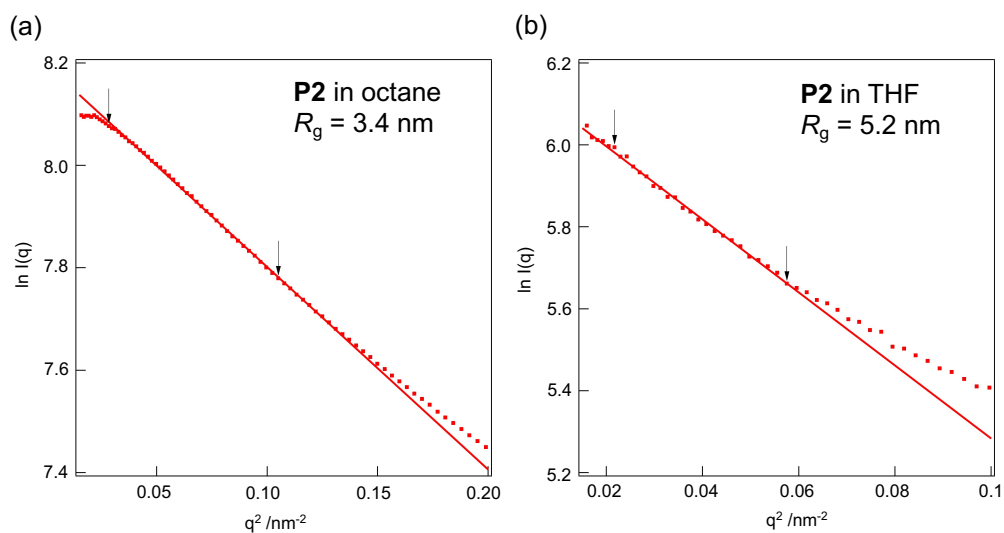


Figure S2. Guinier plots obtained from the SAXS profiles of **P2** in (a) octane or (b) THF at 25 °C (see Figure 1b): $[\mathbf{P2}] = 1 \text{ mg/mL}$.

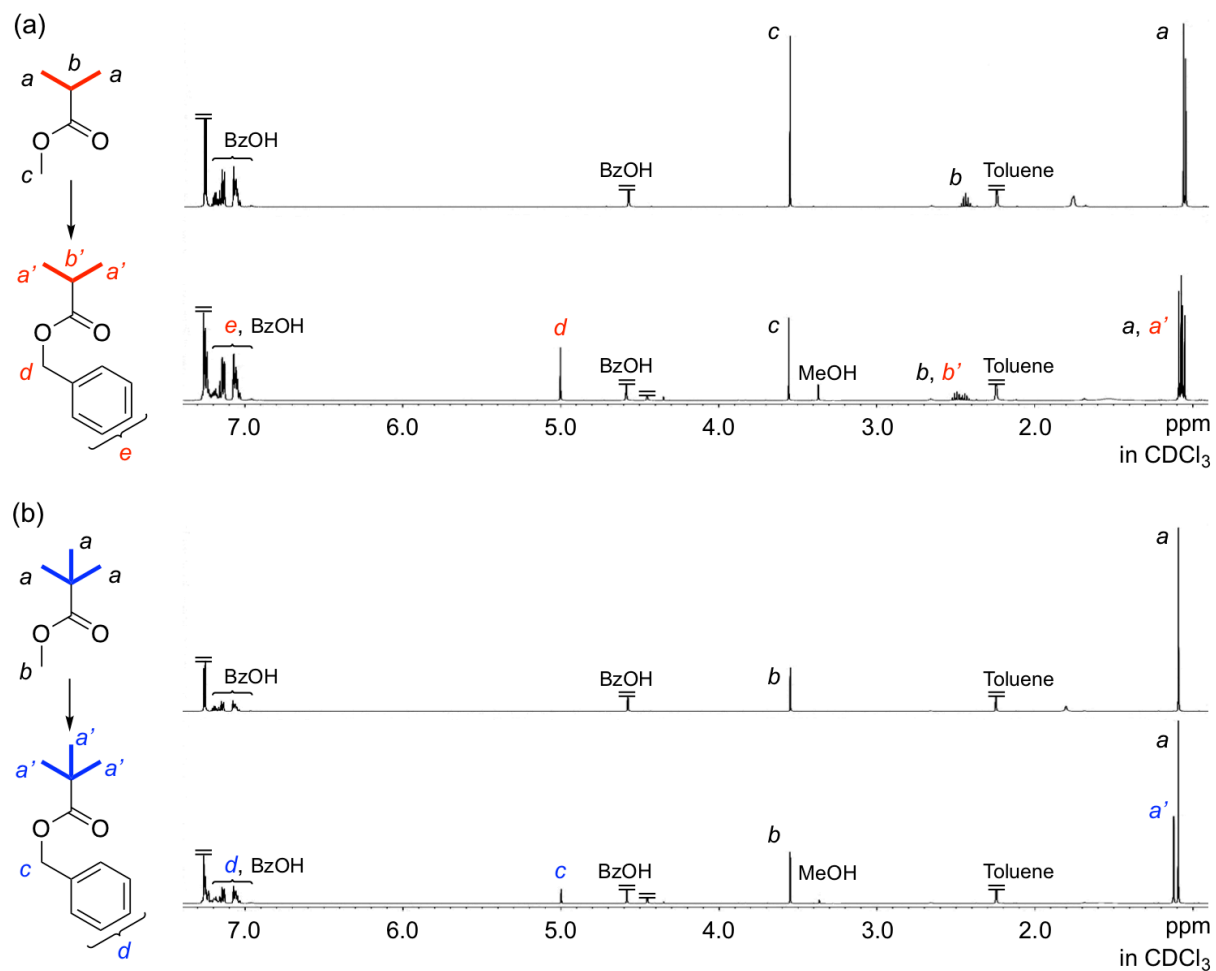


Figure S3. ¹H NMR spectra (in CDCl₃ at 25 °C) of the crude products obtained from the transesterification of (a) methyl isobutyrate or (b) methyl pivalate: [substrate]₀/[Sc(OTf)₃]₀ = 2000/10 mM in toluene/benzyl alcohol (BzOH) (1/1, v/v) at 80 °C for 48 h ([BzOH]₀ = 3500 – 3700 mM).

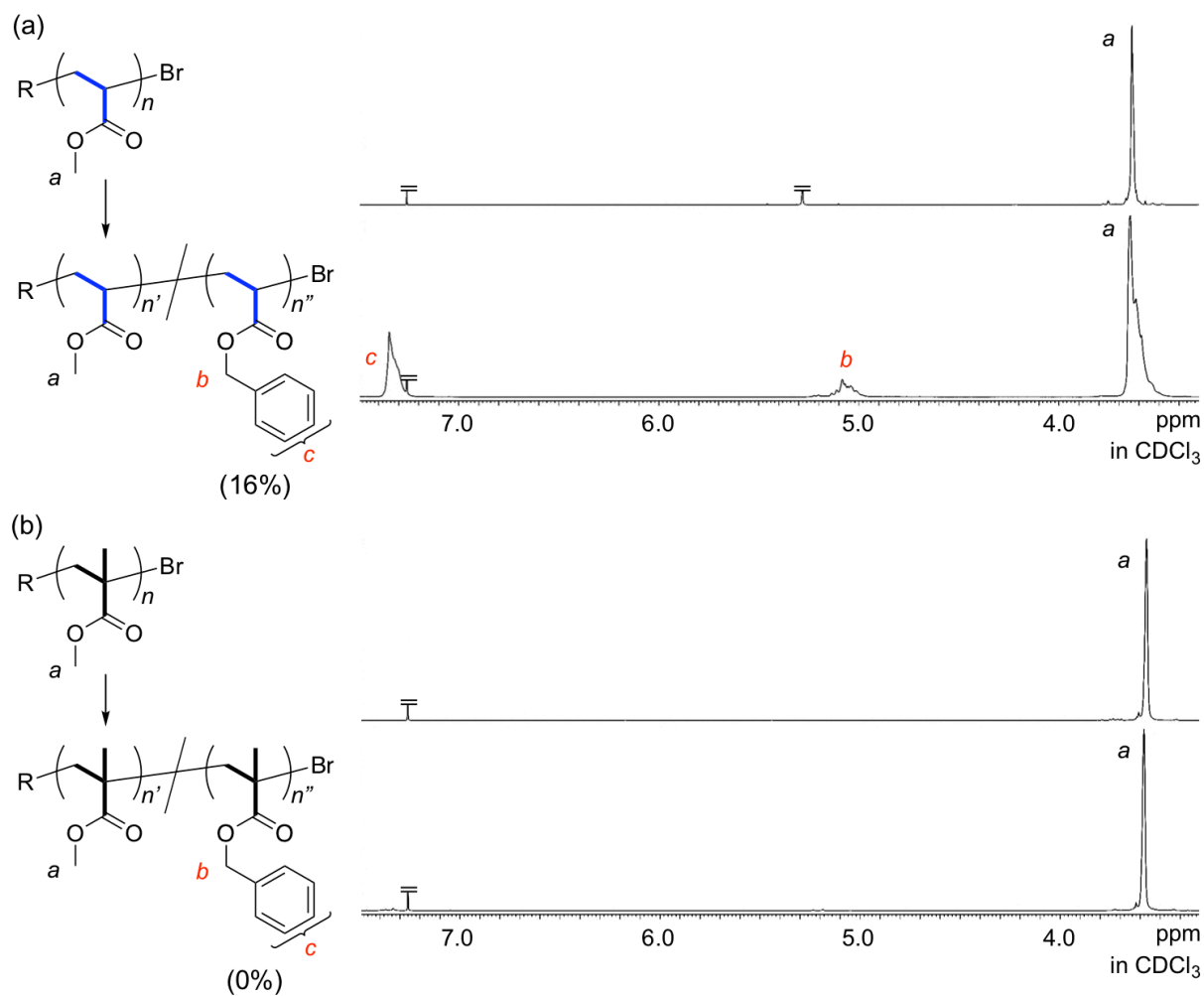


Figure S4. ^1H NMR spectra (in CDCl_3 at $25\text{ }^\circ\text{C}$) of the purified products obtained from the transesterification of (a) PMA ($M_n = 6200$, $M_w/M_n = 1.08$) or (b) PMMA ($M_n = 7600$, $M_w/M_n = 1.21$): $[\text{polymer}]_0 / [\text{Sc}(\text{OTf})_3]_0 = 10/2.5\text{ mM}$ with MS 4A (0.33 g/mL) in anisole/benzyl alcohol (BzOH) (1/1, v/v) at $120\text{ }^\circ\text{C}$ for 48 h ($[\text{BzOH}]_0 = 4800\text{ mM}$).

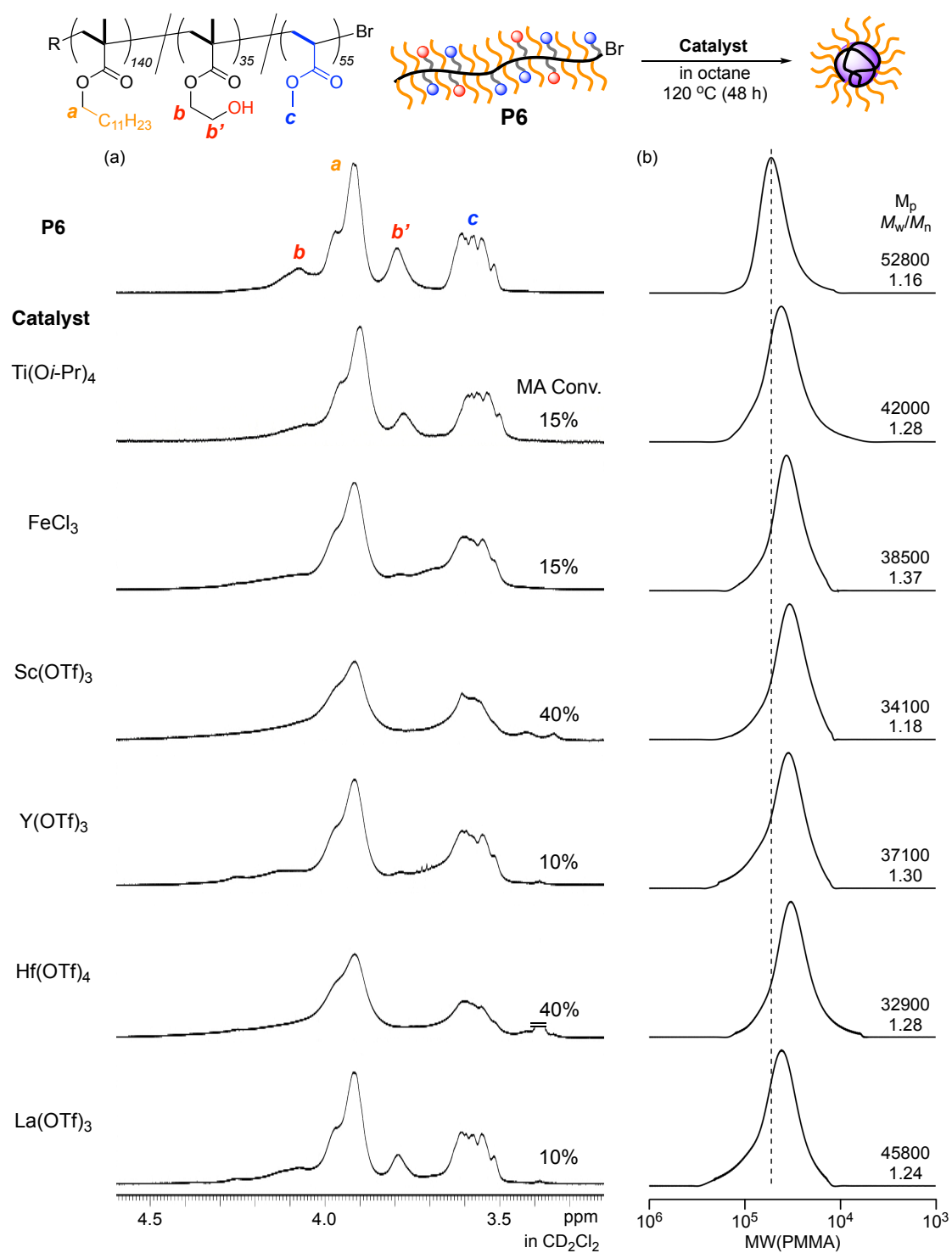


Figure S5. (a) ^1H NMR spectra (in CD_2Cl_2 at $25\text{ }^\circ\text{C}$) and (b) SEC curves of the products obtained from the crosslinking of **P6** with various catalysts: $[\text{P6}]_0 = 0.23\text{ mM}$ (10 mg/mL), $[\text{catalyst}]_0 = 1.0\text{ mM}$ in octane at $120\text{ }^\circ\text{C}$ for 48 h.

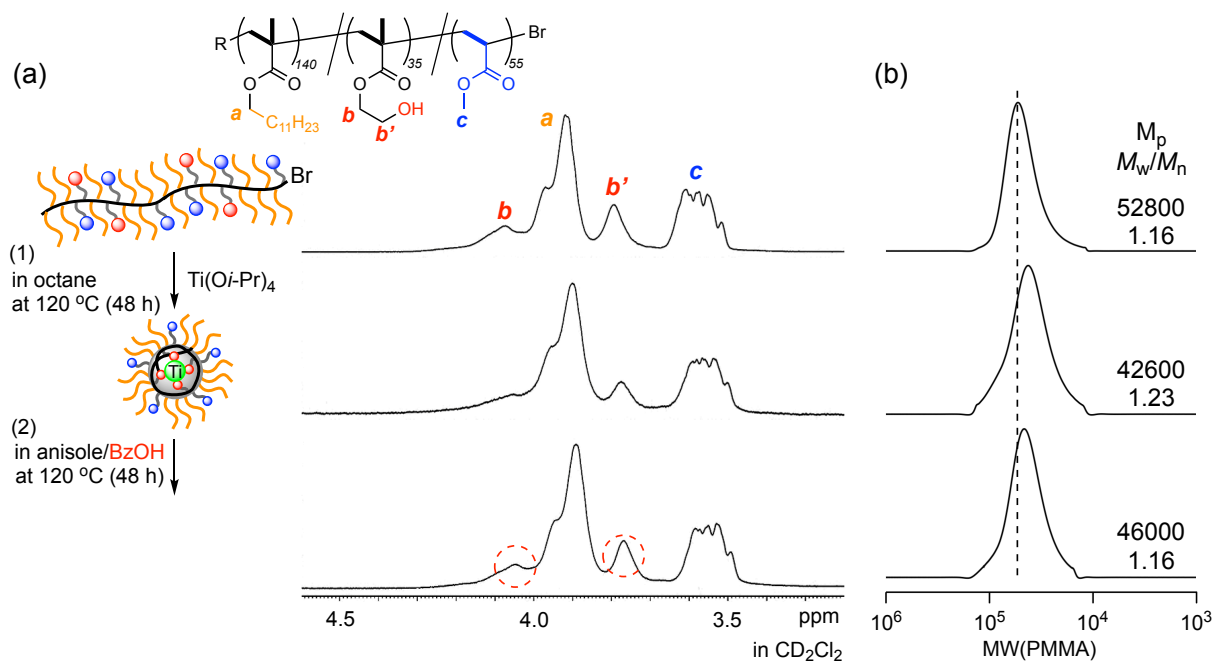


Figure S6. (a) ¹H NMR spectra (in CD₂Cl₂ at 25 °C) and (b) SEC curves of the product obtained from the crosslinking of **P6** with Ti(Oi-Pr)₄ (1) and the reaction of the crosslinked product with BzOH (2). (1) [**P6**]₀ = 0.23 mM (10 mg/mL), [Ti(Oi-Pr)₄]₀ = 1.0 mM in octane at 120 °C for 48 h. (2) [the crosslinked product]₀ = 10 mg/mL in anisole/BzOH (1/1, v/v) at 120 °C for 48 h.

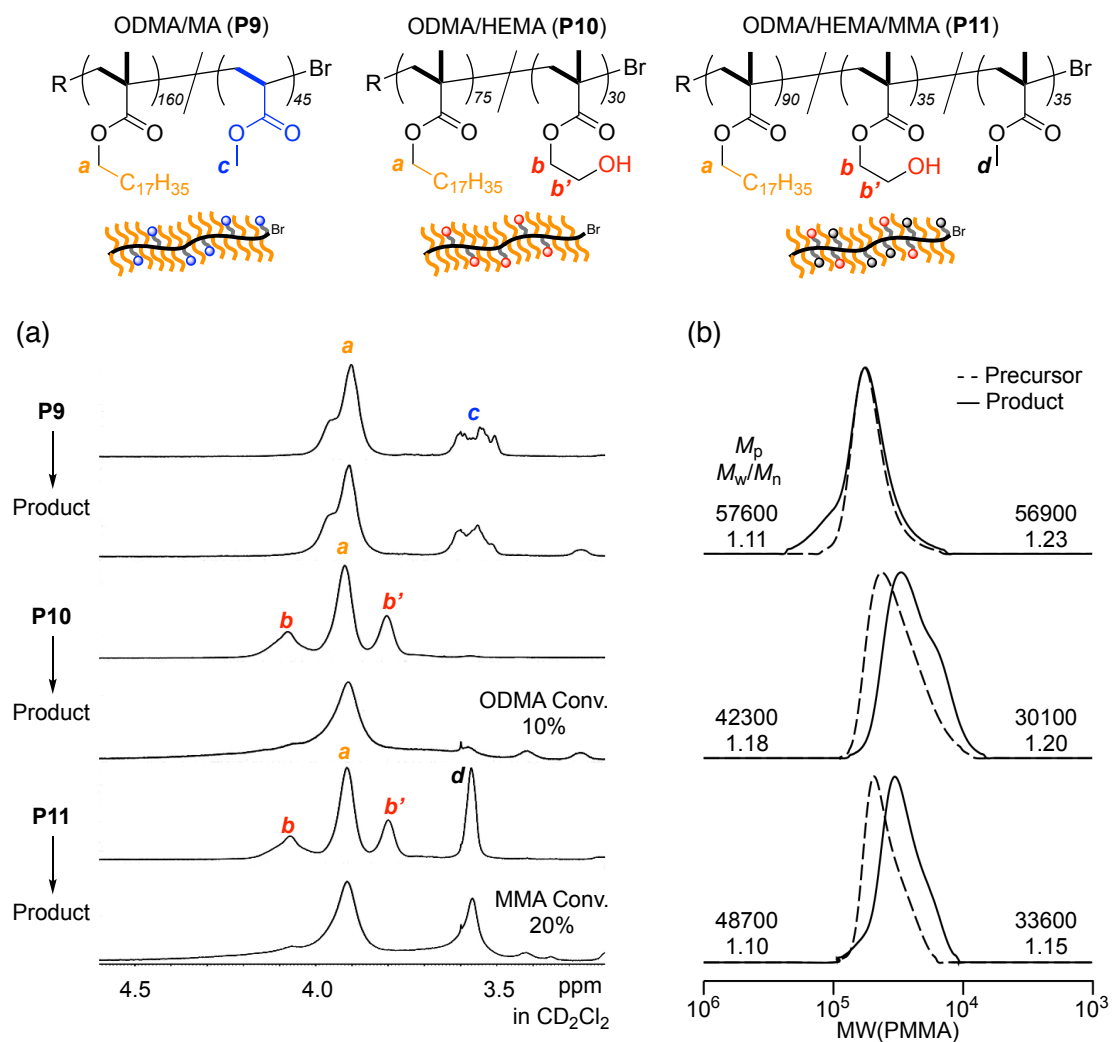


Figure S7. (a) ¹H NMR spectra (in CD₂Cl₂ at 25 °C) and (b) SEC curves of the products obtained from the reaction of ODMA/MA (**P9**), ODMA/HEMA (**P10**), and ODMA/HEMA/MMA (**P11**) copolymers with Sc(OTf)₃: [polymer]₀ = 10 mg/mL [0.20 (**P9**), 0.33 (**P10**), 0.26 (**P11**) mM] and [Sc(OTf)₃]₀ = 1.0 mM in octane at 120 °C for 48 h.

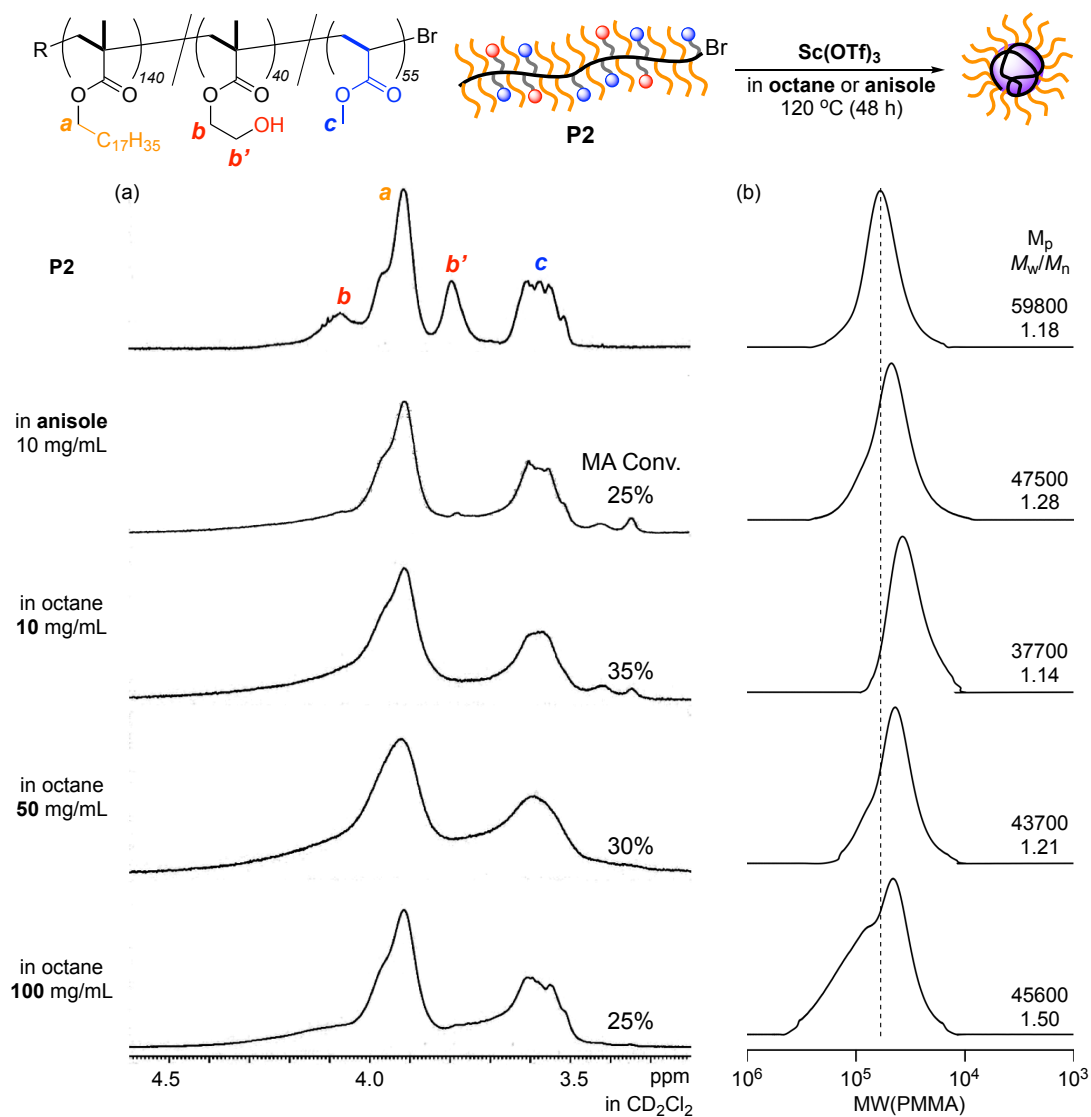


Figure S8. (a) ^1H NMR spectra and (b) SEC curves of the products obtained from the transesterification of **P2** with $\text{Sc}(\text{OTf})_3$: $[\text{P2}]_0 = 0.19 - 1.88$ mM (10 – 100 mg/mL), $[\text{Sc}(\text{OTf})_3]_0 = 1.0$ mM in octane or anisole at 120 °C for 48 h.

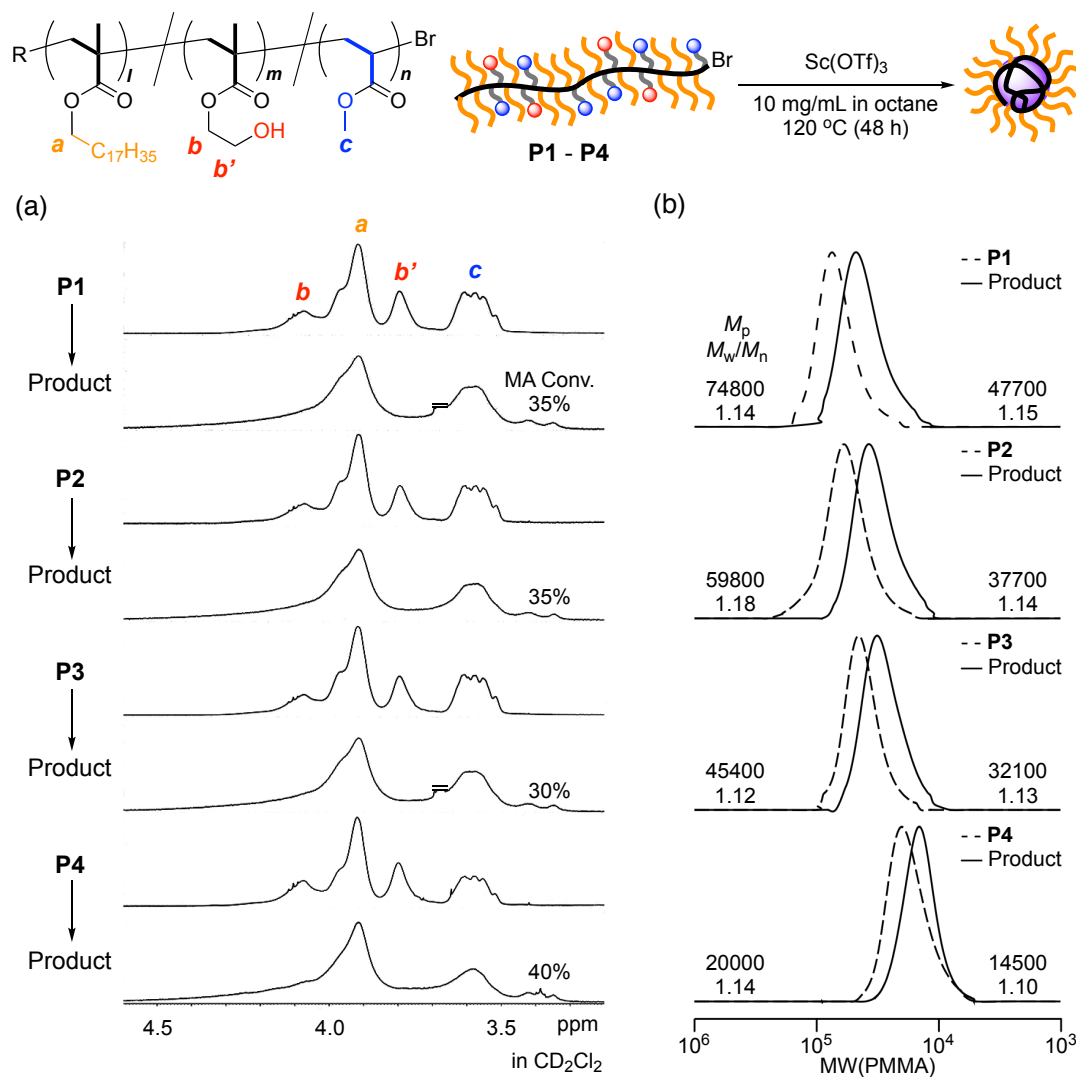


Figure S9. ^1H NMR spectra (a - d) and SEC curves (e - h) of the products obtained from the intramolecular transesterification of ODMA/HEMA/MA copolymers (a, e: **P1**, b, f: **P2**, c, g: **P3**, d, h: **P4**) with $\text{Sc}(\text{OTf})_3$: $[\text{polymer}]_0 = 10 \text{ mg/mL}$ (P1: 0.16, P2: 0.19, P3: 0.25, P4: 0.60 mM), $[\text{Sc}(\text{OTf})_3]_0 = 1.0 \text{ mM}$ in octane at $120 \text{ }^\circ\text{C}$ for 48 h.

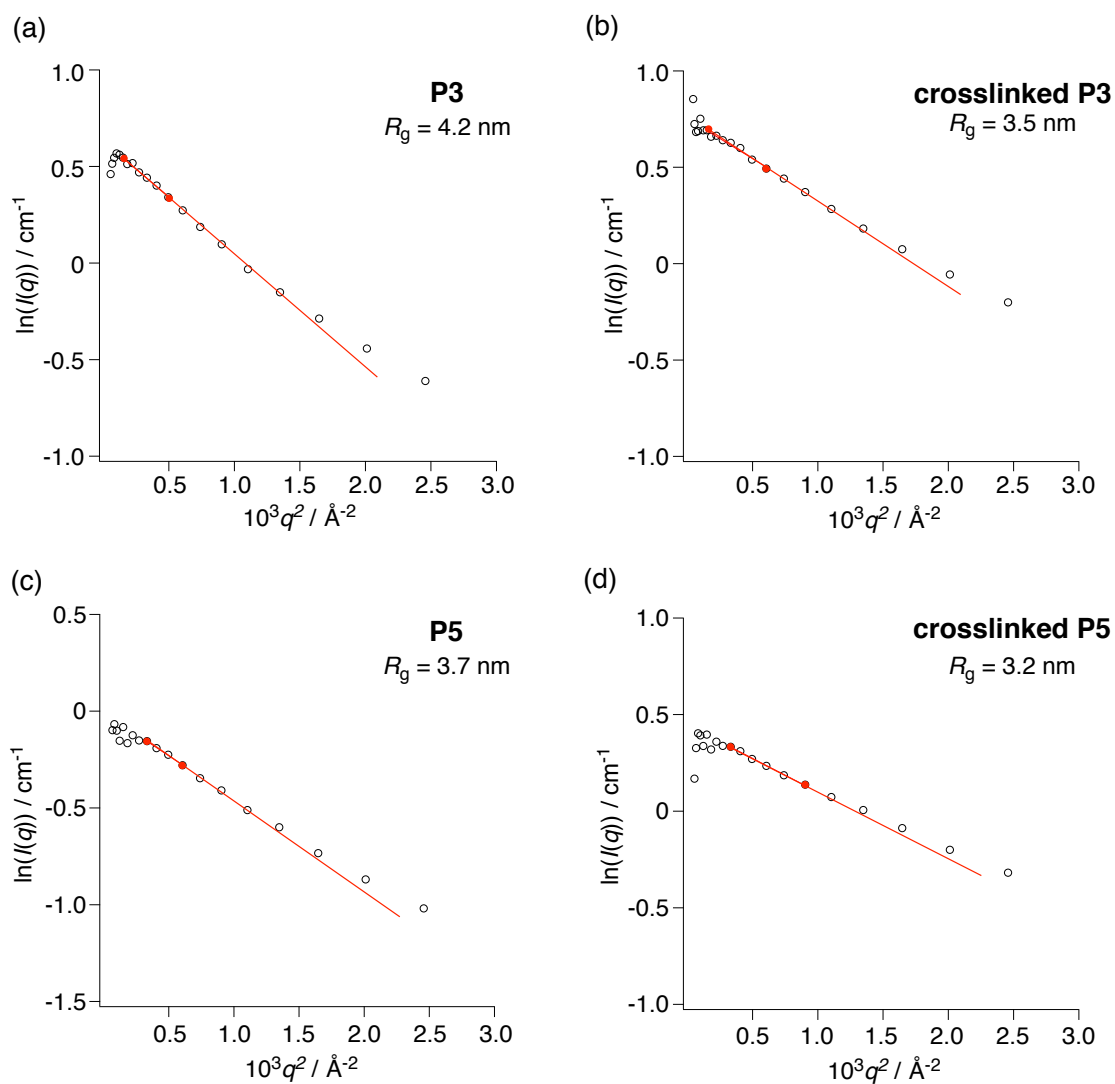


Figure S10. Guinier plots obtained from the SAXS profiles (Figure 6) of (a) **P3**, (b) crosslinked **P3**, (c) **P5**, and (d) crosslinked **P5** in THF- d_8 at 25 °C: [polymer] = 10 mg/mL.

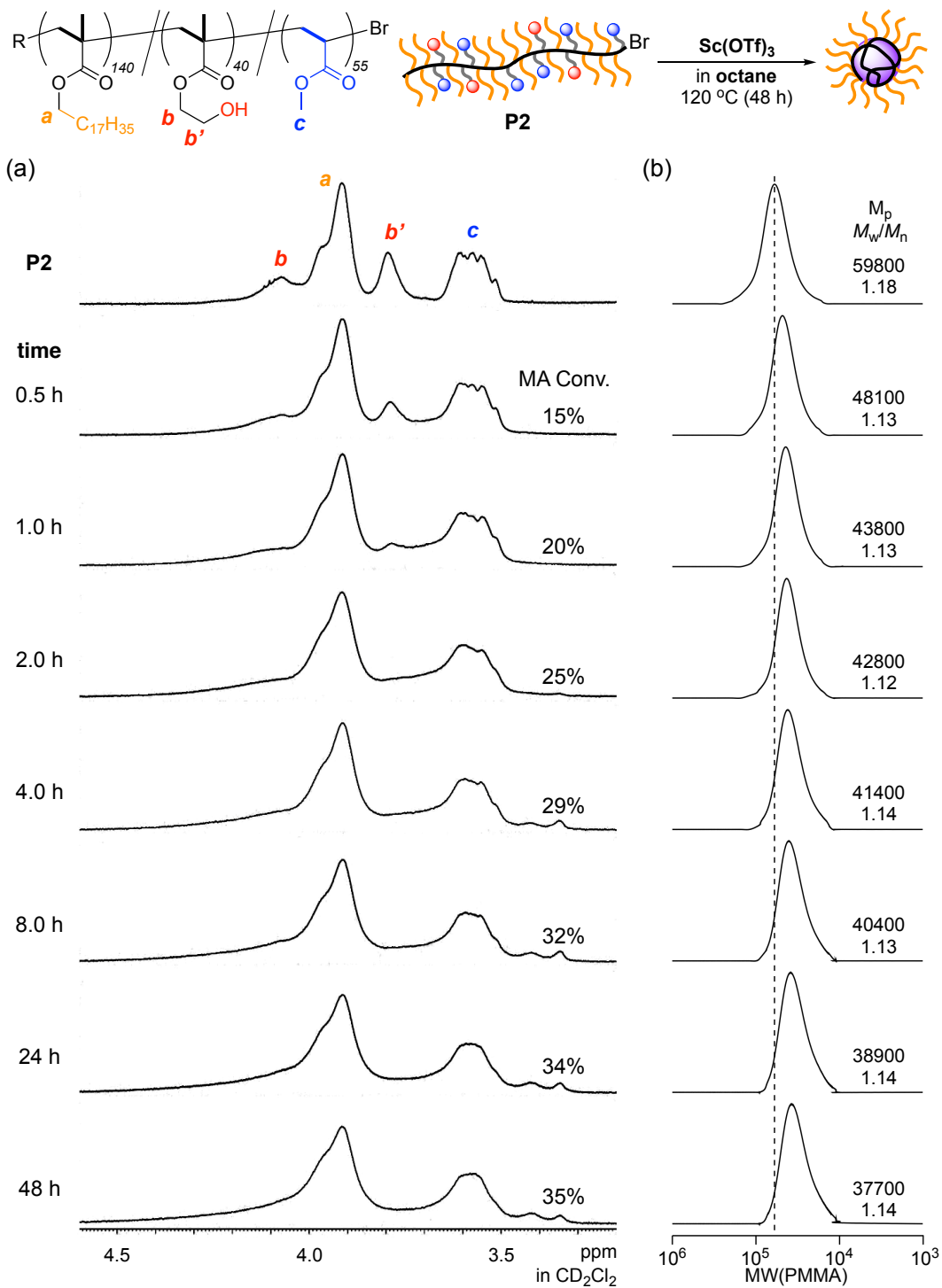


Figure S11. ¹H NMR spectra (a) and SEC curves (b) of the products obtained from the transesterification of ODMA/HEMA/MA copolymer (P2) with Sc(OTf)₃: [polymer]₀ = 10 mg/mL (0.19 mM) and [Sc(OTf)₃]₀ = 1.0 mM in octane at 120 °C for 0.5, 1.0, 2.0, 4.0, 8.0, 24, 48 h.

Table S2. Synthesis and Characterization of Crosslinked P2^a

Entry	Time (h)	M_n^b (SEC)	M_w/M_n^b (SEC)	$M_p/M_{p,precursor}^b$ (SEC)	M_w^c (MALLS)	MA Conv. ^d (%)	T_m^e (°C)	ΔH_m^e (J/g)	T_c^e (°C)	ΔH_c^e (J/g)
1	0.5	43800	1.13	0.80	64900	15	23.3	23.2	11.9	23.3
2	1.0	40000	1.13	0.73	65100	20	33.3	43.9	20.1	44.2
3	2.0	38300	1.12	0.72	63600	25	26.3	24.4	13.2	24.4
4	4.0	35600	1.14	0.69	68500	29	30.1	34.1	16.5	33.7
5	8.0	34000	1.13	0.68	66000	32	30.4	34.6	16.8	34.9
6	24	32100	1.14	0.65	70400	34	33.8	38.7	20.0	38.7
7	48	31000	1.14	0.63	73000	35	26.8	25.4	13.8	25.4

^a Conditions: [P2]₀ = 10 mg/mL, [Sc(OTf)₃]₀ = 1.0 mM in octane at 120 °C.

^b Determined by SEC in THF with PMMA standard calibration.

^c Absolute weight-average molecular weight determined by SEC-MALLS in THF.

^d MA conversion determined by ¹H NMR.

^e Melting and crystallization temperature (T_m , T_c) and the enthalpy of melting and crystallization (ΔH_m , ΔH_c) were determined by differential scanning calorimetry (DSC). The heating and cooling rate were performed at 10 °C/min and -10 °C/min, respectively, between -80 °C and 150 °C.

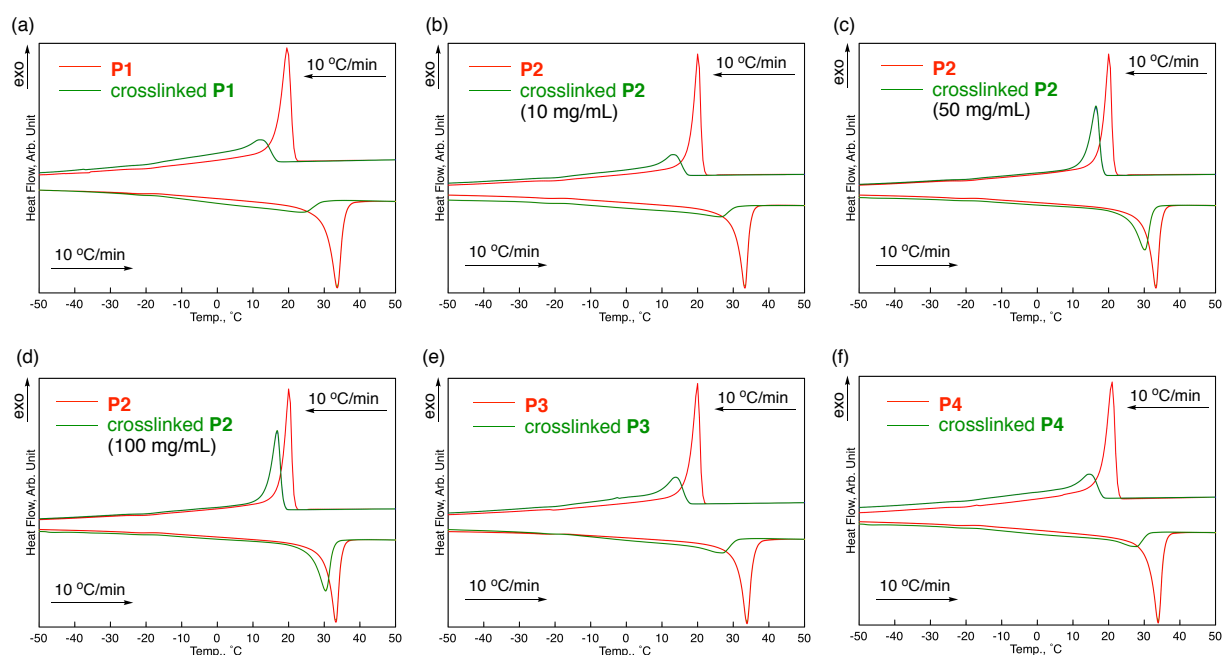


Figure S12. DSC thermograms of (a) P1 and crosslinked P1, (b-d) P2 and crosslinked P2 (b: 10 mg/mL, c: 50 mg/mL, d: 100 mg/mL), (e) P3 and crosslinked P3, and (f) P4 and crosslinked P4 (P1 – P4: red, their crosslinked products: green). Heating and cooling rate: 10 °C/min and -10 °C/min, respectively. Temperature range: -80 – 150 °C.