Supporting Information for

Synthesis of block copolymers of polyester and polystyrene by means of cross-metathesis of cyclic unsaturated polyester and atom transfer radical polymerization

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1. Materials

All starting materials were purchased from commercial suppliers (TCI, Aldrich, Wako and Kanto). Pyridine was dehydrated by means of reflux over CaH_2 followed by distillation under reduced pressure, and stored in a schlenk flask under argon before used. Diisopropylamine was dehydrated by means of reflux over CaH_2 followed by distillation, and stored in an ampoule under argon before used. Sebacoyl dichloride was refluxed with thionyl chloride followed by distillation under reduced pressure, and stored in a schlenk flask under argon. Prepared *cis*- and *trans*-4-octene-1,8-diol were dried in vacuo over P_2O_5 overnight immediately before use. Styrene was flowed through a short column containing active neutral alumina to remove the stabilizer immediately before used. Other starting materials were used without further purification. Commercially available dehydrated tetrahydrofuran (THF, stabilizer-free; Kanto), dehydrated dichloromethane (Kanto) and dehydrated ethanol (Wako) were used as dry solvents.

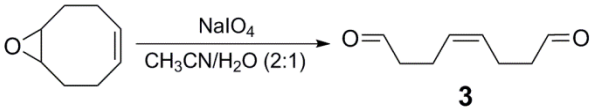
2. General

^1H and ^{13}C NMR spectra were obtained on JEOL ECA-500 and ECA-600 spectrometers. The internal standard for ^1H NMR spectra in $CDCl_3$ was tetramethylsilane (0.00 ppm), and the internal standard for ^{13}C NMR spectra in $CDCl_3$ was the midpoint of $CDCl_3$ (77.0 ppm). IR spectra were recorded on a JASCO FT/IR-410. The M_n and M_w/M_n values of polymers were measured on a Shodex GPC-101 gel permeation chromatography unit (eluent, THF 1.00 mL/min; calibration, polystyrene standards; column temperature, 40 °C) with two Shodex KF-804L columns, Shodex UV-41, Shodex RI-71S, and Wyatt Technology DAWN EOS multiangle light scattering (MALS, Ga-As laser, l ¼ 690 nm) detectors. The $M_{n(MALS)}$ value was also calculated by division of the M_w from MALS by the M_w/M_n ratio from GPC. Purification of polyester after cross metathesis was conducted with a Shimadzu LC-6AD preparative HPLC (eluent: THF, flow rate: 5.0 mL/min) equipped with Shimadzu SPD-10A, Shimadzu RID-10A, and two TOSOH TSKgel columns (2 × GMH_{HR}-H). Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Shimadzu/Kratos AXIMA-CFR plus in the reflectron mode by use of a laser (λ = 337 nm). Dithranol (1,8-dihydroxy-9[10*H*]-anthracenone) was used as the matrix for the MALDI-TOF mass measurements. Differential scanning calorimetry (DSC) analyses were performed on a Hitachi X-DSC7000 calorimeter from -90 °C to 140 °C at heating/cooling rate of 10 °C/min under a nitrogen atmosphere. High resolution mass spectroscopy (HRMS) analysis was performed by a JEOL AccuTOF CS JMS-T100CS mass spectrometer. The all reactions below were conducted under inert gas atmosphere. Column chromatography was performed on silica gel (Silica gel 60, 230–400 mesh; Merck) with a specified solvent. All glass apparatuses were dried prior to use.

3. Syntheses

3-1. Synthesis of monomers

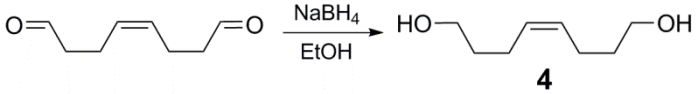
Synthesis of *cis*-4-octenedial (3)[1]



3

Sodium periodate (13.17 g, 61.57 mmol) was suspended in a mixed solvent of acetonitrile and water (2/1, v/v) (77 mL). A solution of 9-oxabicyclo[6.1.0]non-4-ene (2.549 g, 20.53 mmol) in the above mixed solvent (5 mL) was added into the suspension, and the mixture was stirred at room temperature for 2 days. The reaction mixture was then filtrated, and the filter cake was washed with diethyl ether. The filtrate was separated, and the aqueous layer was extracted with diethyl ether 3 times. The combined organic layers were washed with saturated aqueous NaCl twice, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as an orange-colored liquid (2.2881 g, 80%). The crude product was purified by means of column chromatography (SiO_2, hexane/ethyl acetate = 3/2) to afford **3** as a pale yellow liquid (1.930 g, 67%): R_f = 0.37 (hexane/ethyl acetate = 3/2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.82-9.74 (m, 2 H), 5.43-5.36 (m, 2 H), 2.54-2.51 (m, 4 H), 2.43-2.38 (m, 4 H).

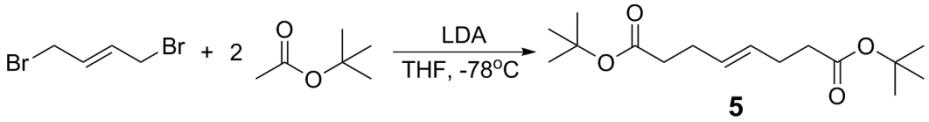
Synthesis of *cis*-4-octene-1,8-diol (4)[2]



4

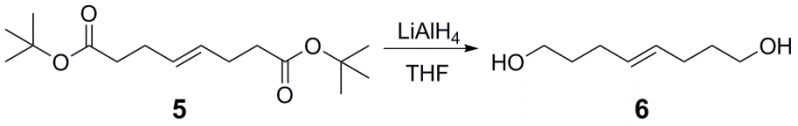
To a stirred solution of **3** (1.967 g, 14.03 mmol) in dehydrated ethanol (28.0 mL), sodium borohydride (purity: 90%) (1.31 g, 31.2 mmol) was added at 0 °C. The reaction mixture was stirred at 0 °C for 2 hours before further addition of sodium borohydride (0.594 g, 14.1 mmol) then stirred 30 minutes. The reaction was quenched by adding water (80 mL), and 2 M HCl (50 mL) was added to decompose excess sodium borohydride. The mixture was extracted with ethyl acetate 4 times. The combined organic layers were washed with saturated aqueous NaCl once, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as a pale yellow viscous liquid (1.7900 g, 88%). The crude product was purified by means of column chromatography (SiO_2, hexane/ethyl acetate = 1/10) to afford **4** as a pale yellow viscous liquid (1.4485 g, 72%): R_f = 0.36 (hexane/ethyl acetate = 1/10); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.45-5.37 (m, 2H), 3.46 (t, J = 6.3 Hz, 4H), 2.22-2.16 (m, 6H), 1.66-1.60 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 129.80, 61.74, 32.19, 23.22; IR (KBr crystal) 3326, 2926, 1656, 1544, 1439, 1050 cm^{-1}.

Synthesis of di-*tert*-butyl *trans*-4-octenedioate (5)[3]



The atmosphere in a round-bottomed flask was replaced with argon. Diisopropylamine (11.6 mL, 82.5 mmol) and dehydrated THF (155 mL) were added to the flask, and cooled to -78 °C. A solution of 1.6 M *n*-butyllithium in hexane (50.5 mL, 81 mmol) was added dropwise to the flask via a syringe at -78 °C. The mixture was stirred at -78 °C for 15 minutes before *tert*-butyl acetate (10.0 mL, 74.9 mmol) was added dropwise to the flask via a syringe at -78 °C, and the mixture was stirred at -78 °C for 30 minutes. A solution of *trans*-1,4-dibromo-2-butene (6.4148 g, 29.99 mmol) in dehydrated THF (25.0 mL) was added dropwise to the flask via a syringe at -78 °C for 20 minutes. The reaction mixture was stirred at -78 °C for 5 hours and then at room temperature for 16 hours before the reaction was quenched with saturated aqueous NH_4Cl (130 mL). Ethyl acetate (64 mL) was added to the mixture, and the separated aqueous layer was extracted with ethyl acetate (64 mL) 3 times. The combined organic layers were washed with saturated aqueous NH_4Cl and saturated aqueous NaCl (each 100 mL) sequentially, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as an orange-colored liquid (8.1348 g, 95%). The crude product was purified by means of column chromatography (SiO_2, hexane/ethyl acetate = 12/1) to afford **5** as a colorless solid (3.9782 g, 47%): R_f = 0.32 (hexane/ethyl acetate = 12/1); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.45 (t, *J* = 3.1 Hz, 2 H), 2.26 (s, 8 H), 1.44 (s, 18 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.46, 129.34, 80.07, 35.35, 28.08, 28.00; IR (KBr tablet) 3003, 2979, 2913, 1720, 1460, 1444, 1425, 1381, 1369, 1333, 1291, 1256, 1206, 1161, 1143, 1003, 972, 945, 849, 783, 761 cm^{-1}.

Synthesis of *trans*-4-octene-1,8-diol (6)[3]

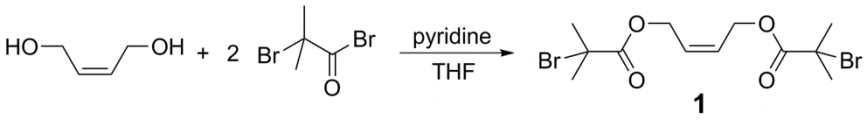


To a stirred solution of **5** (3.8397 g, 13.502 mmol) in dehydrated THF (80.0 mL), lithium aluminum hydride (2.0562 g, 54.18 mmol) was added slowly at 0 °C. The reaction mixture was stirred at room temperature for 4 hours before quenching with water (2.2 mL), 15% aqueous solution of NaOH (2.2 mL), and water (6.6 mL) sequentially. Diethyl ether (25 mL) was added into the mixture, and then the mixture was stirred for 30 minutes before it was filtrated through Celite® 545. The filtrate was washed with saturated aqueous NH_4Cl and saturated aqueous NaCl sequentially, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as a yellow liquid (1.8263 g, 94%). The crude product was purified by means of column chromatography (SiO_2, ethyl acetate) to

afford **6** as a colorless liquid (1.5817 g, 81%): R_f = 0.47 (ethyl acetate); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.50-5.44 (m, 2 H), 3.65 (t, *J* = 6.5 Hz, 4 H), 2.12-2.06 (m, 4 H), 1.64 (quint, *J* = 6.5 Hz, 4 H), 1.48 (br s, 2 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 130.18, 62.27, 32.25, 28.81; IR (KBr crystal) 3361, 2934, 1655, 1445, 1057, 968, 915 cm^{-1}.

3-2. Synthesis of ExRs

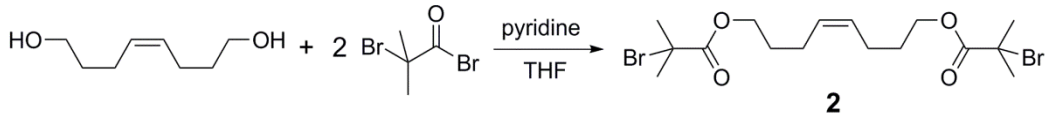
Synthesis of (*Z*)-but-2-ene-1,4-diyl bis(2-bromo-2-methylpropanoate) (1)[4]



1

To a stirred solution of *cis*-2-butene-1,4-diol (1.41 g, 16.0 mmol) and pyridine (3.00 mL, 37.1 mmol) in dehydrated THF (93 mL), a solution of 2-bromoisobutyryl bromide (8.13 g, 36.1 mmol) in dehydrated THF (78 mL) was added dropwise at 0 ºC. The reaction mixture was stirred at 0 ºC for 2 hours followed by room temperature for 16 hours. The mixture was filtrated and concentrated under reduced pressure. The residue was diluted with ethyl acetate (160 mL), washed with water (160 mL) 4 times, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as a pale yellow liquid (6.517g, 105%). The crude product was purified by means of column chromatography (SiO_2, hexane/ethyl acetate = 7/1) to afford **1** as a colorless liquid (5.074 g, 82%): R_f = 0.38 (hexane/ethyl acetate = 7/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86-5.80 (m, 2 H), 4.81 (dd, *J* = 1.1 and 4.0 Hz, 4 H), 1.94 (s, 12 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.33, 127.90, 61.45, 55.48, 30.69; IR (KBr crystal) 3451, 3005, 2977, 2932, 2361, 2343, 1736, 1464, 1389, 1371, 1343, 1272, 1155, 1108, 1011, 971, 912, 823, 763, 642 cm^{-1}.

Synthesis of (*Z*)-oct-4-ene-1,8-diyl bis(2-bromo-2-methylpropanoate) (2)[4]



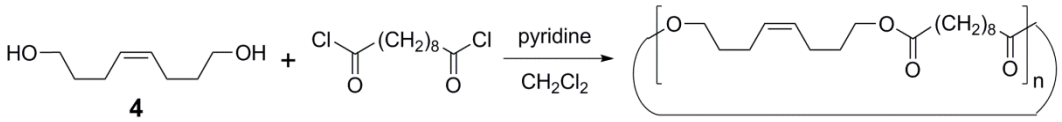
2

To a stirred solution of *cis*-4-butene-1,8-diol (0.291 g, 2.02 mmol) and pyridine (0.380 mL, 4.70 mmol) in dehydrated THF (10 mL), a solution of 2-bromoisobutyryl bromide (1.02 g, 4.44 mmol) in dehydrated THF (10 mL) was added dropwise at 0 ºC. The reaction mixture was stirred at 0 ºC for 2 hours followed by room temperature for 18 hours. The mixture was filtrated and concentrated under reduced pressure. The residue was diluted with ethyl acetate (20 mL), washed with water 4 times, dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as a pale yellow liquid (0.850 g, 95%). The crude product was purified by means of column chromatography (SiO_2, hexane/ethyl acetate = 10/1) to afford **2** as a colorless liquid (0.688 g, 77%): R_f = 0.29 (hexane/ethyl

acetate = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.46-5.40 (m, 2 H), 4.19 (t, J = 6.6 Hz, 4 H), 2.21-2.13 (m, 4 H), 1.94 (s, 12 H), 1.75 (quint, J = 6.6 Hz, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.67, 129.40, 65.36, 55.91, 30.78, 28.30, 23.45; IR (KBr crystal) 3450, 2930, 2278, 1737, 1580, 1462, 1390, 1371, 1274, 1162, 1109, 1023, 644 cm^{-1}; HR-MS (ESI) m/z for $C_{16}H_{26}Br_2O_4$ [**M**+Na]$^+$, calcd. 465.18, found: 465.01.

3-3. Synthesis of cyclic polyesters (PEss)

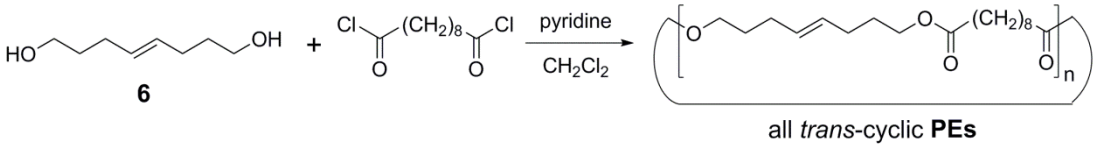
Polycondensation of 4 and sebacoyl dichloride



all *cis*-cyclic **PEs**

A round-bottomed flask was flame-dried and replaced with argon. A solution of **4** (0.2886 g, 2.001 mmol) and dry pyridine (0.340 mL, 4.20 mmol) in dry dichloromethane (10.00 mL) was added to the flask via a syringe, and the mixture was cooled to 0 °C. To the stirred reaction mixture, a solution of sebacoyl dichloride (0.4928 g, 2.061 mmol) in dry dichloromethane (10.00 mL) was added dropwise via a syringe at 0 °C. The reaction mixture was stirred at room temperature for 2 days, and then the reaction was quenched with 1 mL of methanol. The mixture was washed with 1 M HCl twice, saturated aqueous solution of $NaHCO_3$ twice, and saturated aqueous solution of NaCl once sequentially. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to afford a crude product as a pale yellow viscous liquid (0.5910 g, 95%). The crude product was dissolved in dichloromethane and precipitated into methanol. The supernatant liquid was removed by decantation. The precipitated viscous liquid was collected by dissolving in dichloromethane and concentrated in vacuo to afford all *cis*-cyclic PEs as a slightly yellow viscous liquid (0.3597 g, 58%): M_n = 10900, M_w/M_n = 3.82.

Polycondensation of 6 and sebacoyl dichloride



all *trans*-cyclic **PEs**

A round-bottomed flask was flame-dried and replaced with argon. A solution of **6** (0.2882 g, 1.998 mmol) and dry pyridine (0.340 mL, 4.20 mmol) in dry dichloromethane (10.00 mL) was added to the flask via a syringe, and the mixture was cooled to 0 °C. To the stirred reaction mixture, a solution of sebacoyl dichloride (0.4924 g, 2.059 mmol) in dry dichloromethane (10.00 mL) was added dropwise via a syringe at 0 °C. The reaction mixture was stirred at room temperature for 3 days, and then the reaction was quenched with 1 mL of methanol. The mixture was washed with 1 M HCl twice,

saturated aqueous solution of $NaHCO_3$ once, and water twice sequentially. The organic layer was dried over anhydrous $MgSO_4$, and concentrated in vacuo to afford a crude product as a slightly yellowish white solid (0.6147 g, 99%). The crude product was dissolved in dichloromethane and precipitated into methanol. The precipitate was filtrated, dissolved in dichloromethane and dried in vacuo to afford all *trans*-cyclic PEs as a white translucent solid (0.4776 g, 77%): M_n = 21200, M_w/M_n = 3.16.

4. Supporting figures and tables

4-1. Synthesis of macro-ExR having PSt

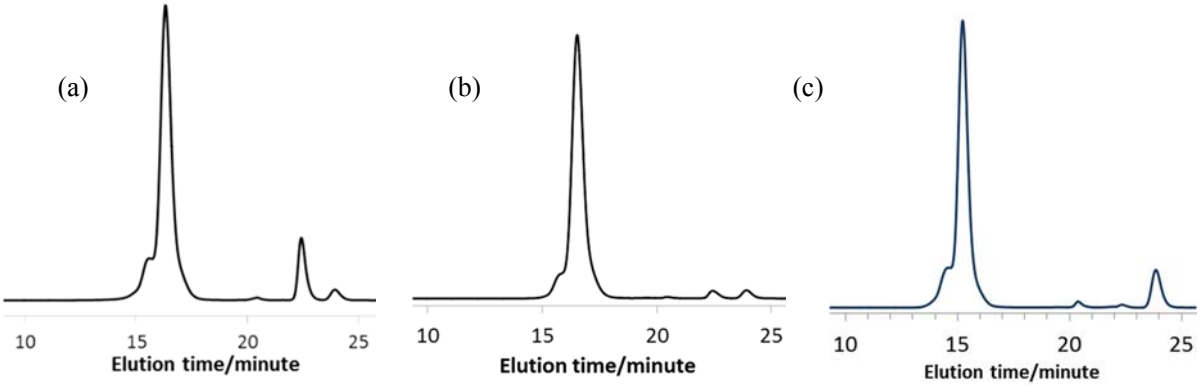


Figure S1. GPC elution curve of (a) **PSt-1** (M_n = 6880, M_w/M_n = 1.15) obtained by ATRP of St with **1** (Table 1, entry 1), (b) **PSt-2a** (M_n = 5880, M_w/M_n = 1.08) obtained by ATRP of St with **2** (entry 2), and (c) **PSt-2b** (M_n = 14300, M_w/M_n = 1.13) obtained by ATRP of St with **2** (Table 1, entry 3).

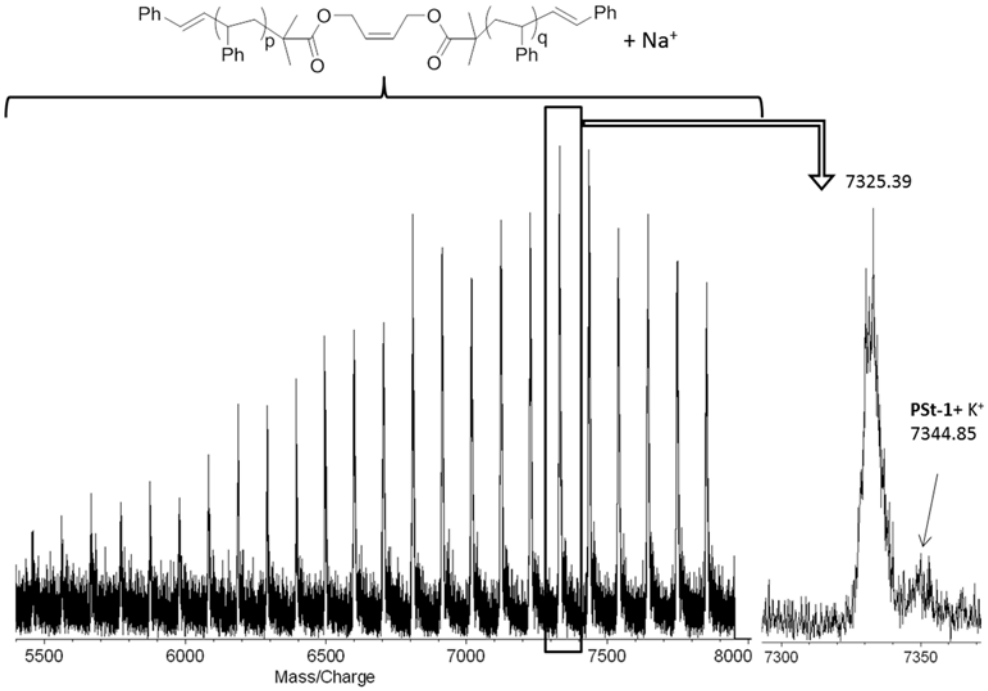


Figure S2. MALDI-TOF mass spectrum of **PSt-1** (Table 1, entry 1).

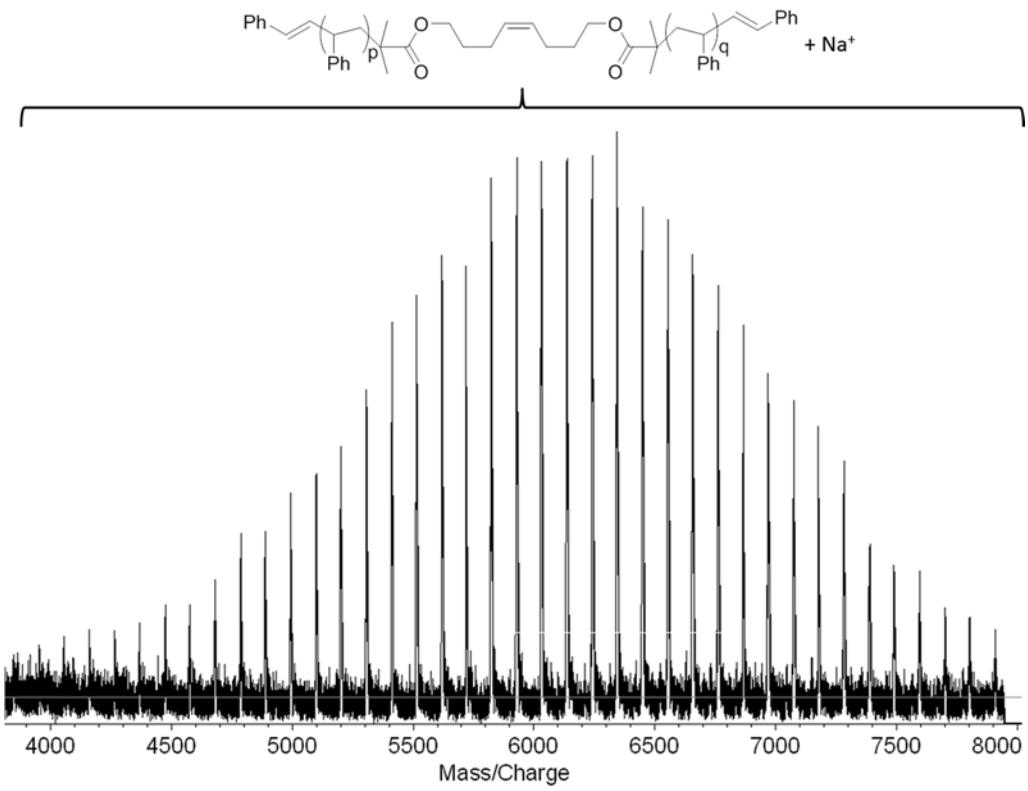


Figure S3. MALDI-TOF mass spectrum of **PSt-2a** (entry 2).

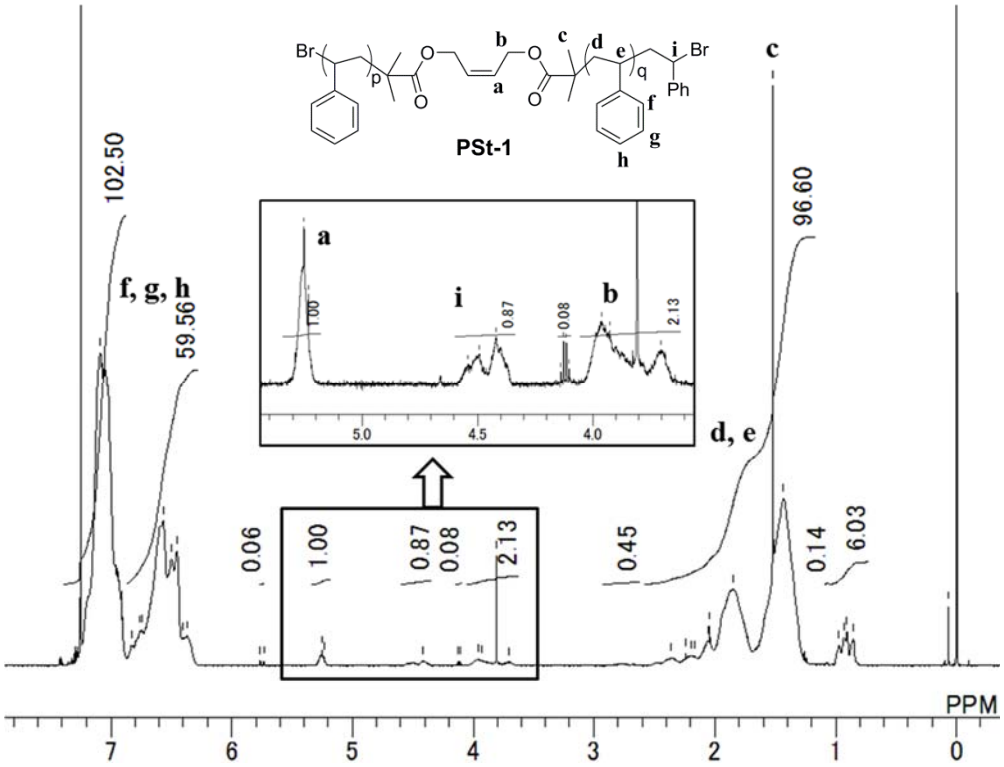


Figure S4. ^{1}H NMR spectrum of **PSt-1** (Table 1, entry 1) in $CDCl_3$ at 25 ^{o}C.

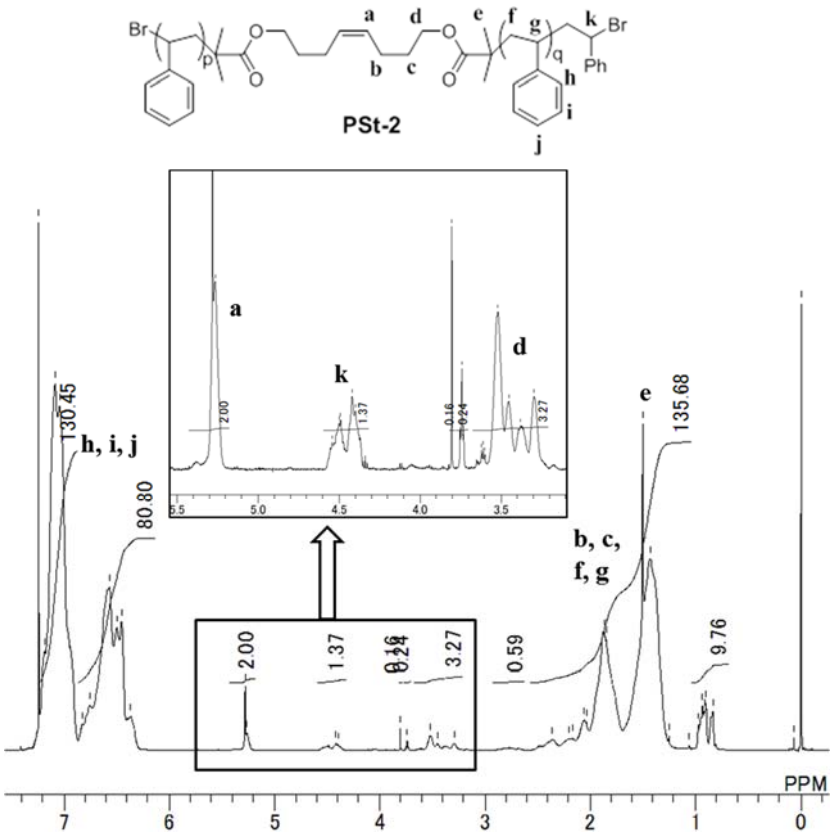


Figure S5. ^{1}H NMR spectrum of **PSt-2a** (entry 2) in $CDCl_3$ at 25 ^{o}C.

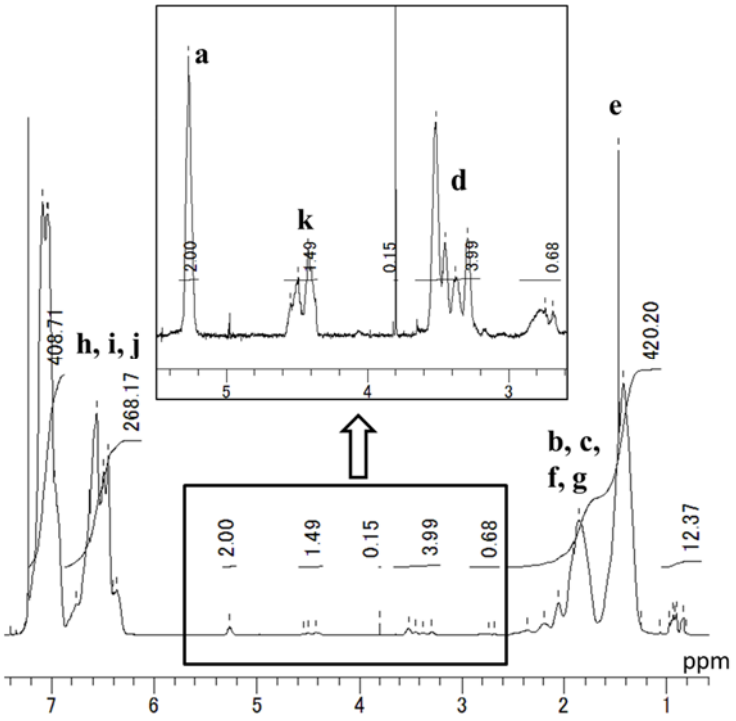


Figure S6. ^{1}H NMR spectrum of **PSt-2b** (entry 3) in $CDCl_3$ at 25 ^{o}C.

4-2. Cross-metathesis of cyclic PEs with macro-ExR

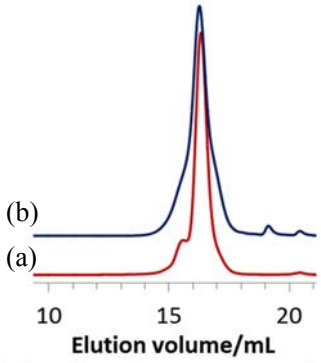


Figure S7. GPC elution curves of (a) **PSt-1** (M_n = 6880, M_w/M_n = 1.15) and (b) **BC-1a** (M_n = 6800, M_w/M_n = 1.20), obtained by cross metathesis of *cis*-cyclic PEs with **PSt-1** (Table 2, entry 1).

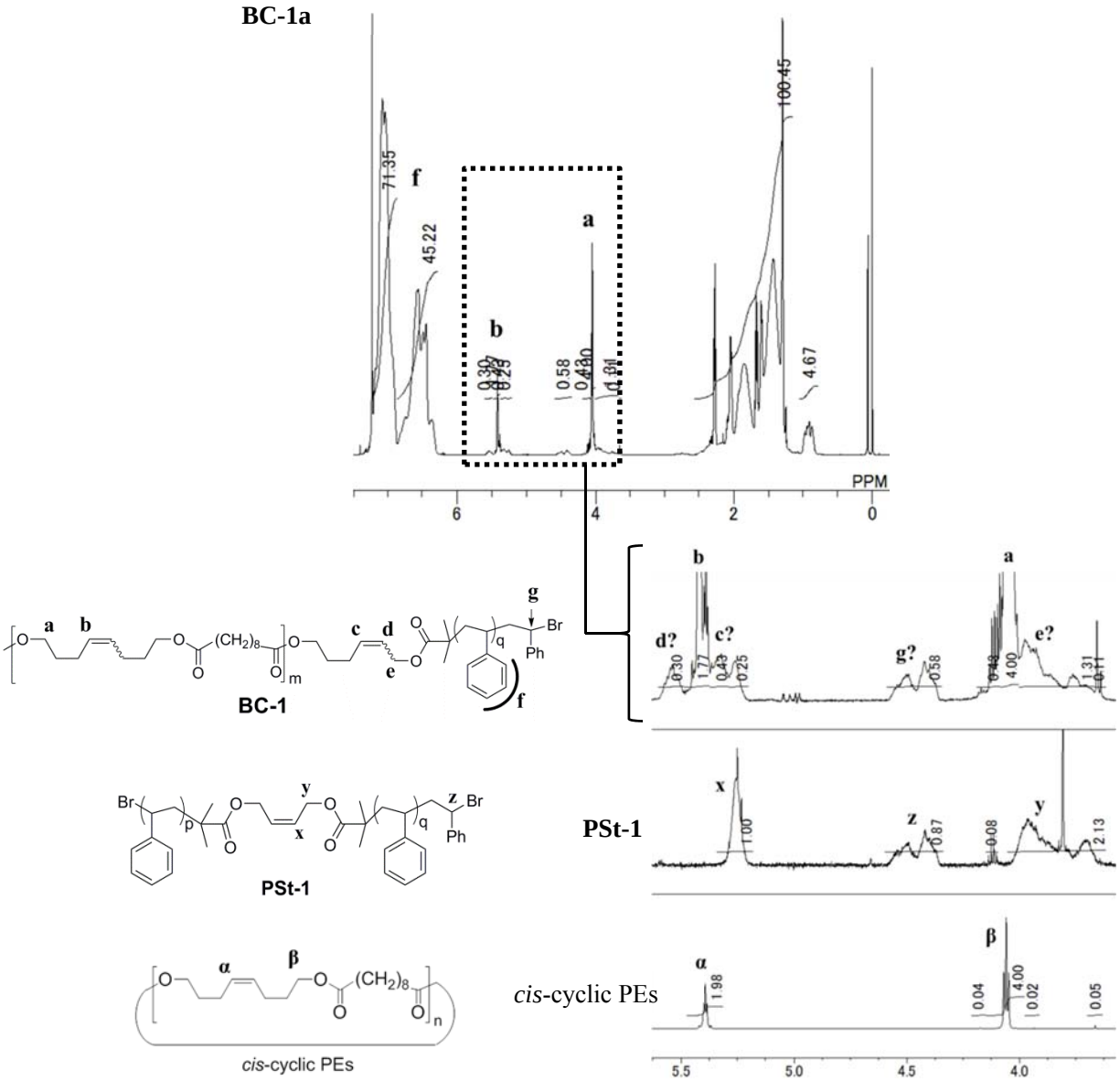


Figure S8. ^{1}H NMR spectra of **BC-1a**, obtained by cross metathesis of *cis*-cyclic PEs with **PSt-1** (Table 2, entry 1), measured in $CDCl_3$ at 25 °C.

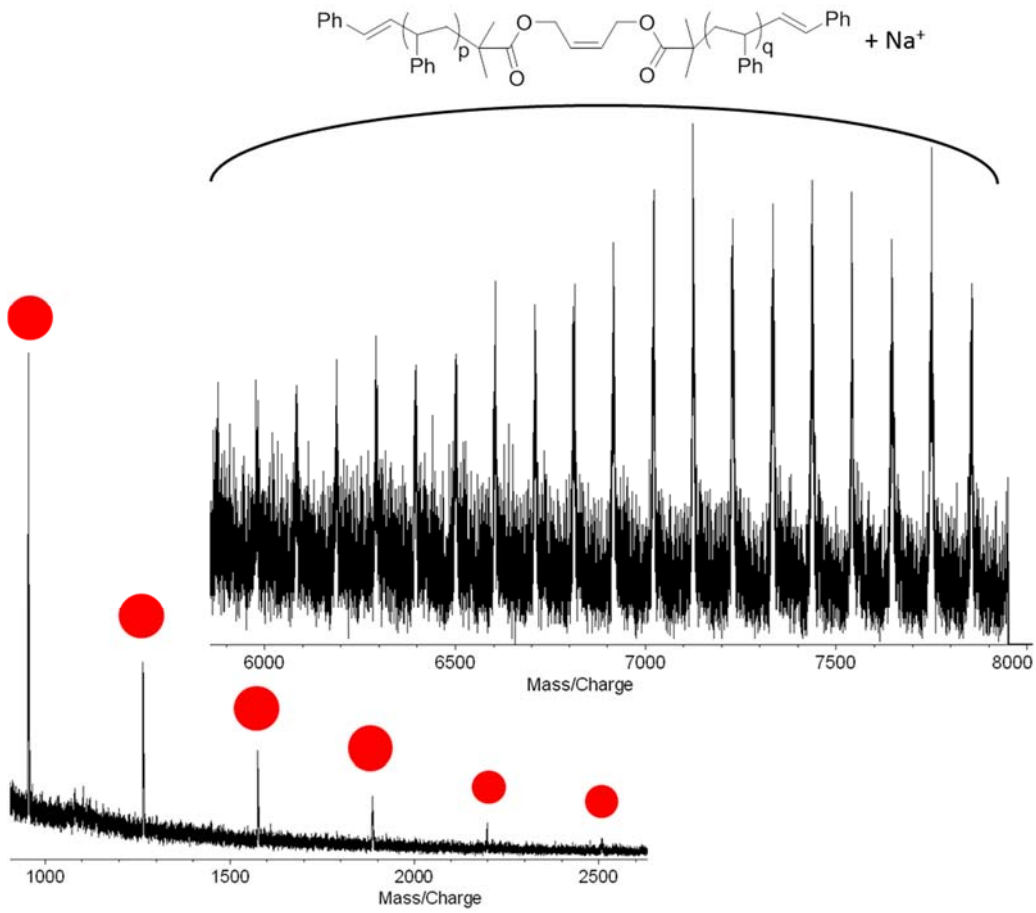


Figure S9. MALDI-TOF mass spectrum of **BC-1a** obtained by cross metathesis of *cis*-cyclic PEs with 20 mol% of **PSt-1** (Table 2, entry 1).

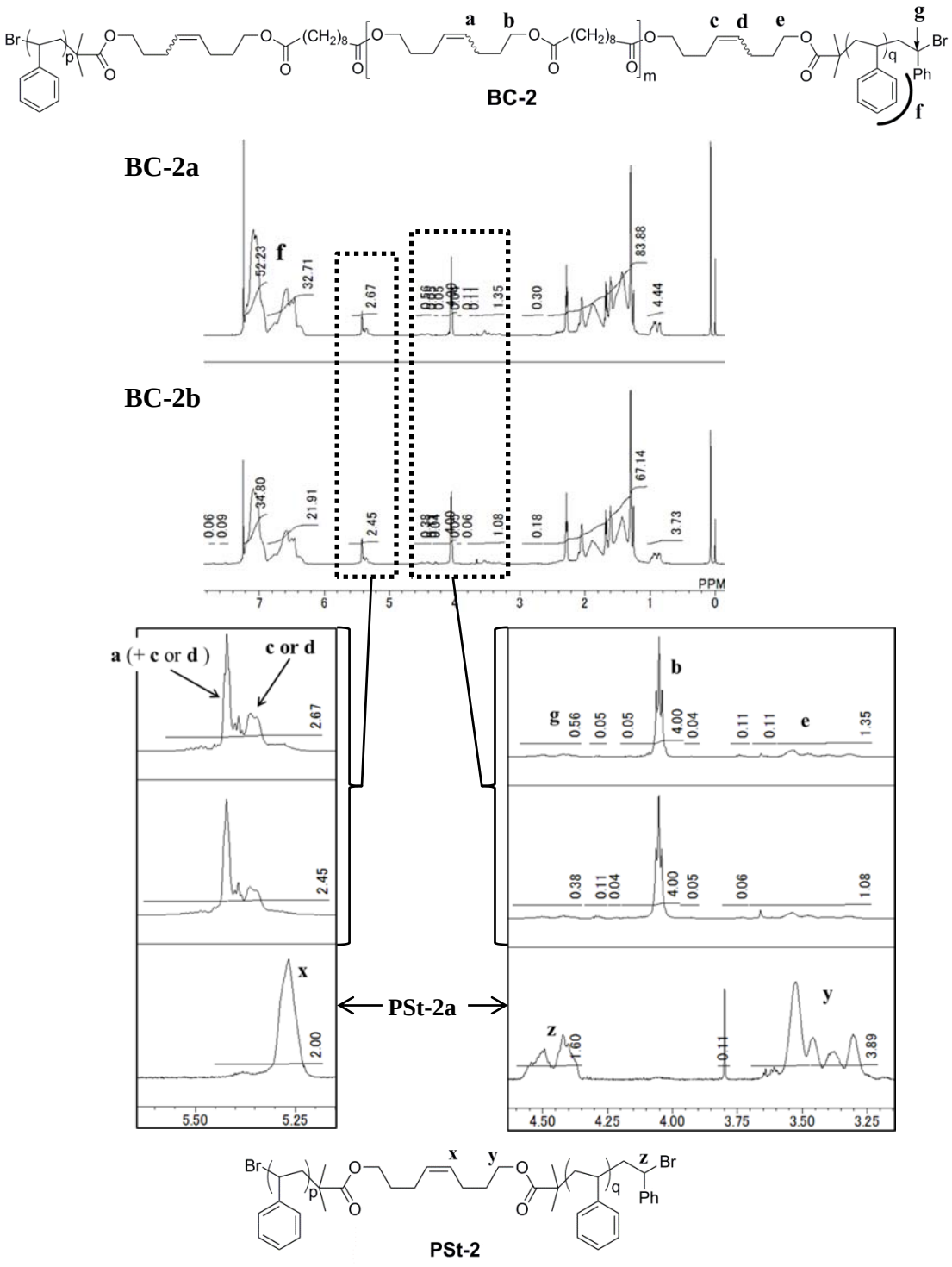


Figure S10. ^{1}H NMR spectra of **BC-2a** (top) and **BC-2b** (bottom), obtained by cross metathesis of *cis*-cyclic PEs with **PSt-2a** (Table 2, entries 2-3), measured in $CDCl_3$ at 25 ^{o}C.

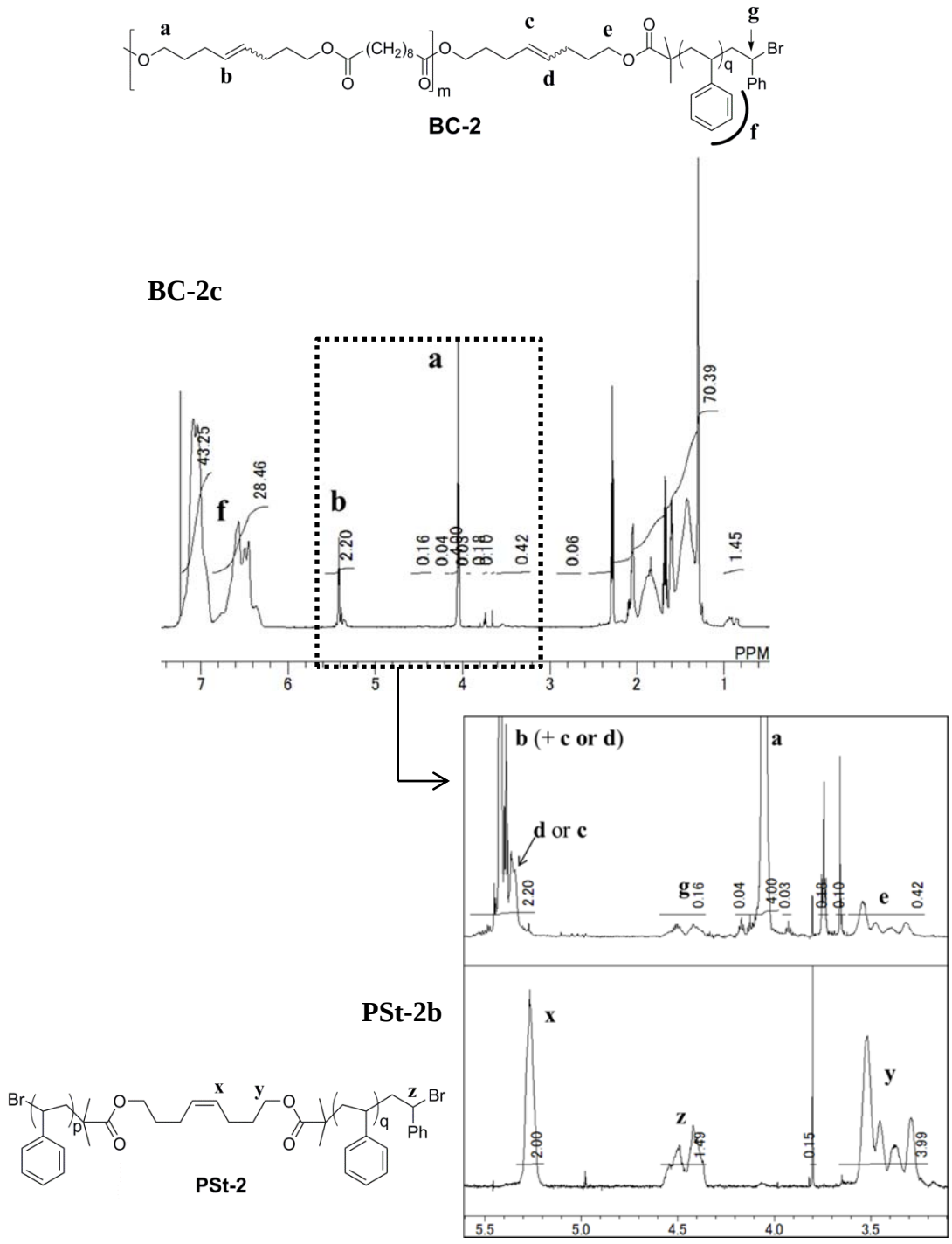


Figure S11. ^{1}H NMR spectrum of **BC-2c**, obtained by cross metathesis of *trans*-cyclic PEs with **PSt-2b** (Table 2, entry 4), measured in $CDCl_3$ at 25 ºC.

4-3. Synthesis of PEs macroinitiator

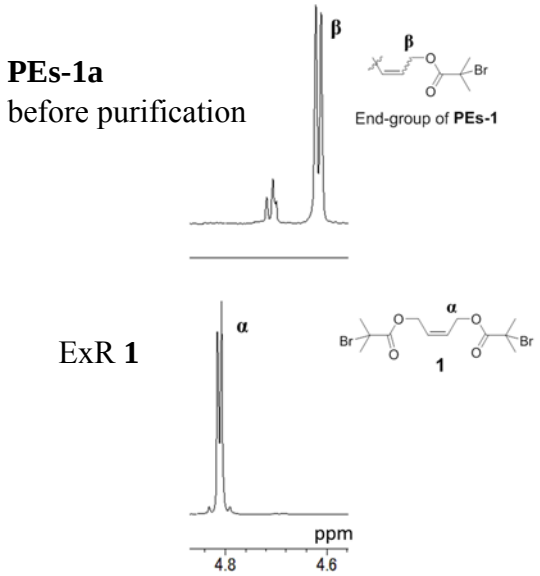


Figure S12. ^{1}H NMR spectra of **PEs-1a** before purification, obtained by cross metathesis of *cis*-cyclic PEs with 20 mol% of **1** (top) and ExR **1** (bottom), measured in $CDCl_3$ at 25 °C.

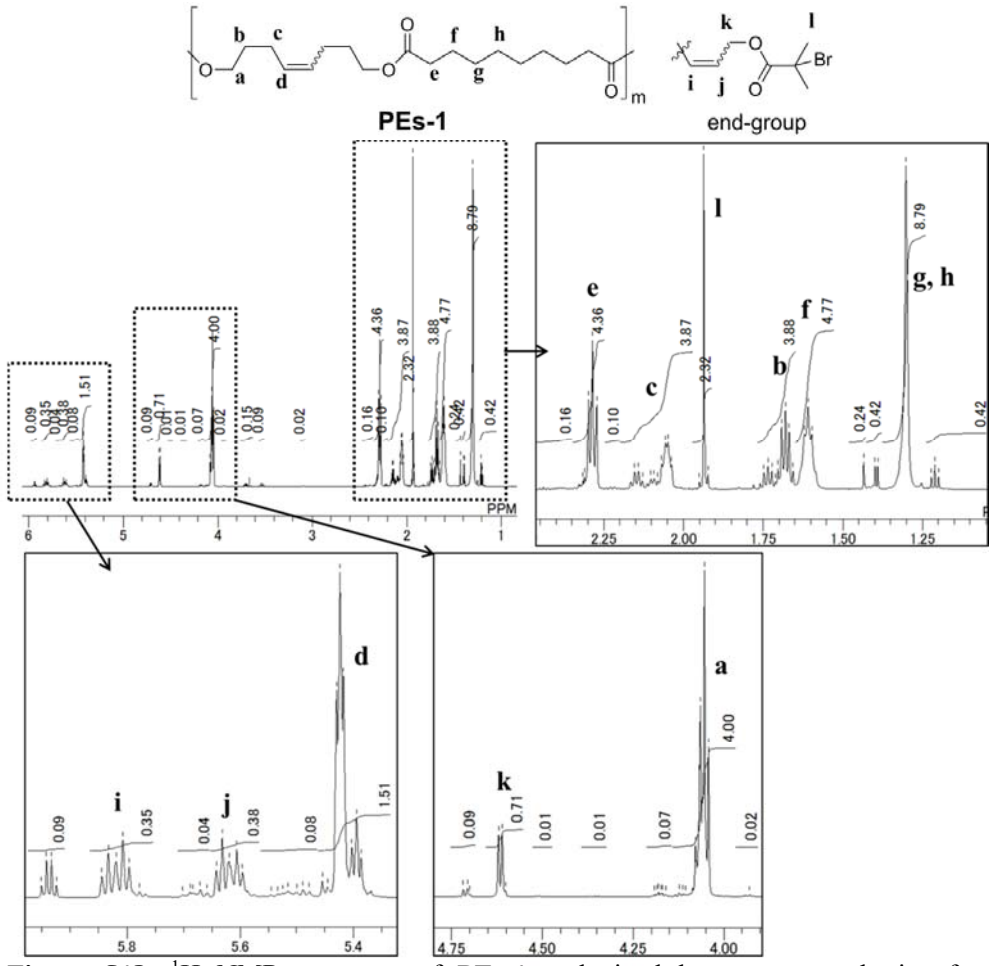


Figure S13. ^{1}H NMR spectrum of **PEs-1a**, obtained by cross metathesis of *cis*-cyclic PEs with 20 mol% of **1** (Table 3, entry 1), measured in $CDCl_3$ at 25 °C.

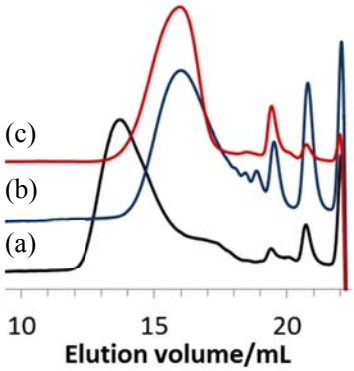


Figure S14. GPC elution curves of (a) *trans*-cyclic PEs (M_n = 21200, M_w/M_n = 3.16), (b) **PEs-1b** obtained by cross-metathesis with 5 mol % of **1** before purification (M_n = 6270, M_w/M_n = 1.91), and (c) **PEs-1b** after precipitation (M_n = 12300, M_w/M_n = 1.43) (Table 3, entry 2).

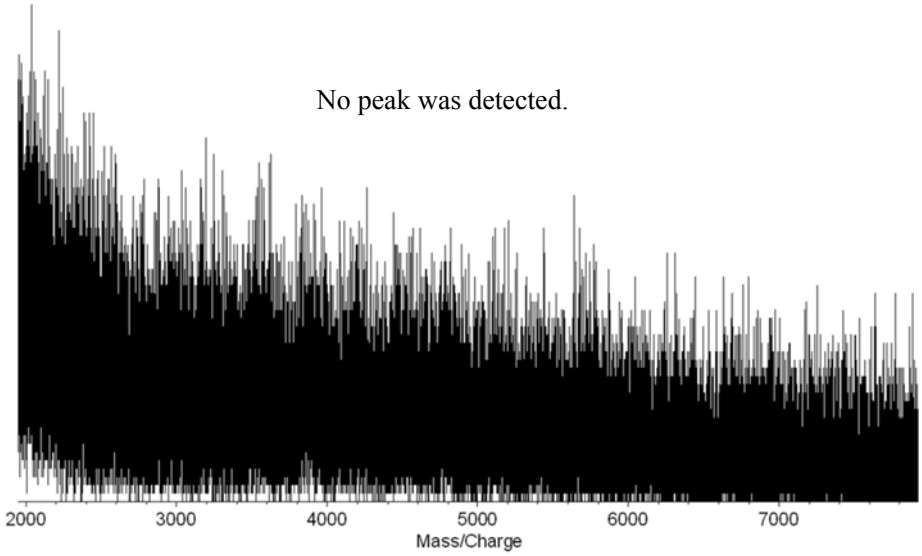


Figure S15. MALDI-TOF mass spectrum of **PEs-1b** obtained by cross-metathesis with 5 mol % of **1** (Table 3, entry 2).

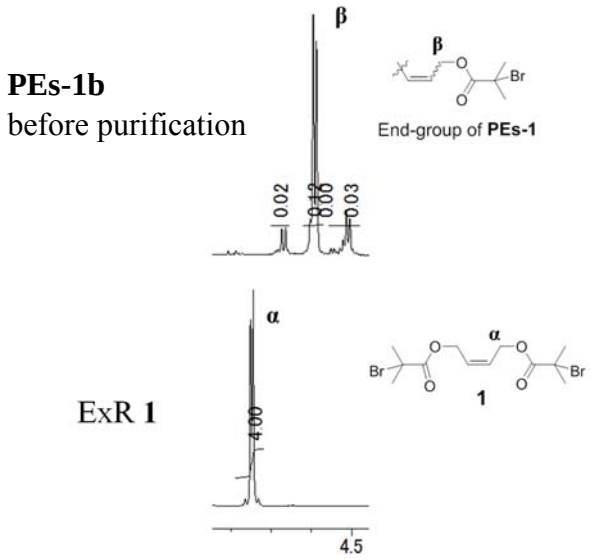


Figure S16. ^{1}H NMR spectra of **PEs-1b** before purification, obtained by cross metathesis of *trans*-cyclic PEs with 5 mol% of **1** (top) and ExR **1** (bottom), measured in $CDCl_3$ at 25 ^{o}C.

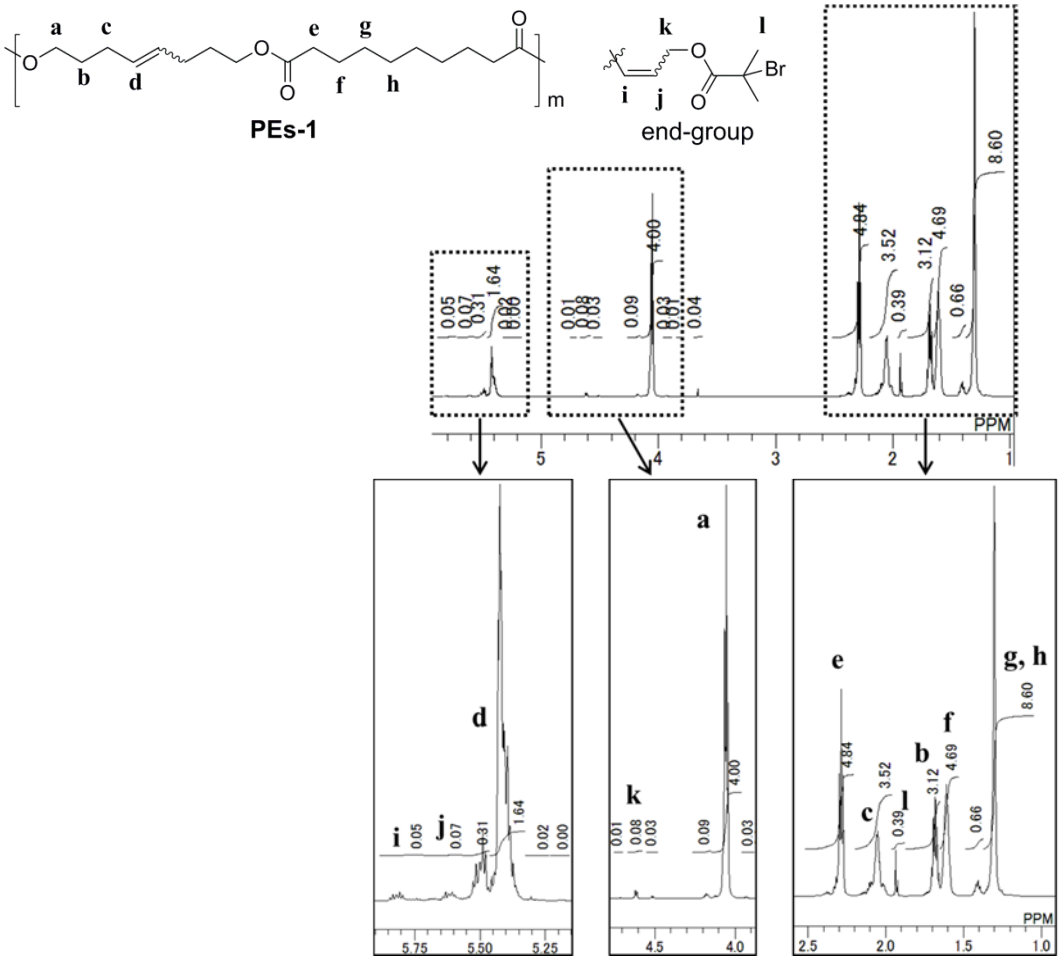


Figure S17. ^{1}H NMR spectrum of **PEs-1b**, obtained by cross metathesis of *trans*-cyclic PEs with 5 mol% of **1** (Table 3, entry 2), measured in $CDCl_3$ at 25 ^{o}C.

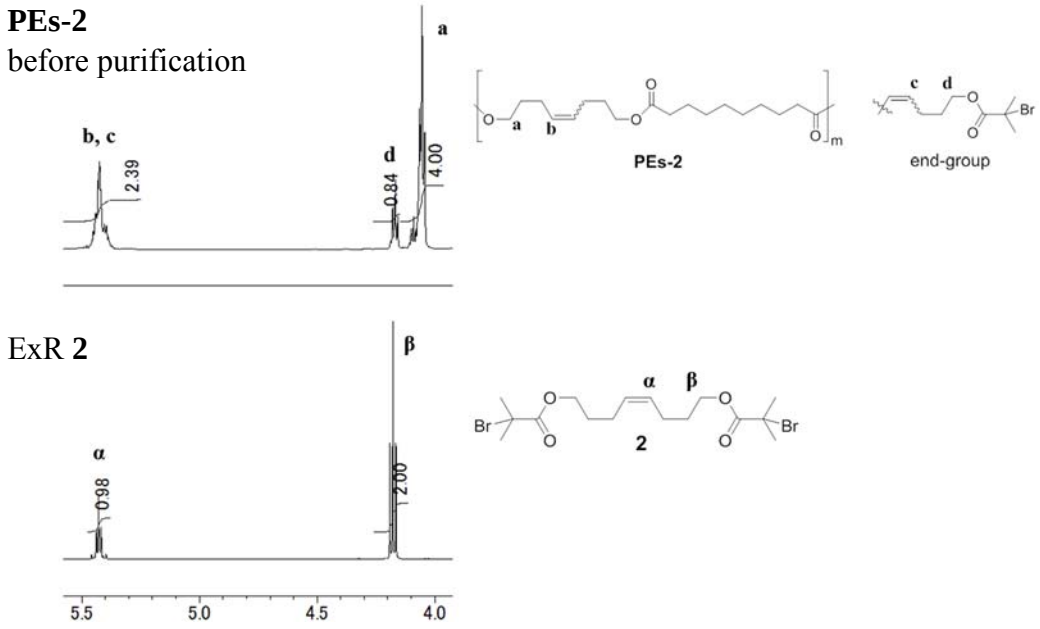


Figure S18. ^{1}H NMR spectra of **PEs-2** before purification, obtained by cross metathesis of *cis*-cyclic PEs with 20 mol% of **2** (top) and ExR **2** (bottom), measured in $CDCl_3$ at 25 °C.

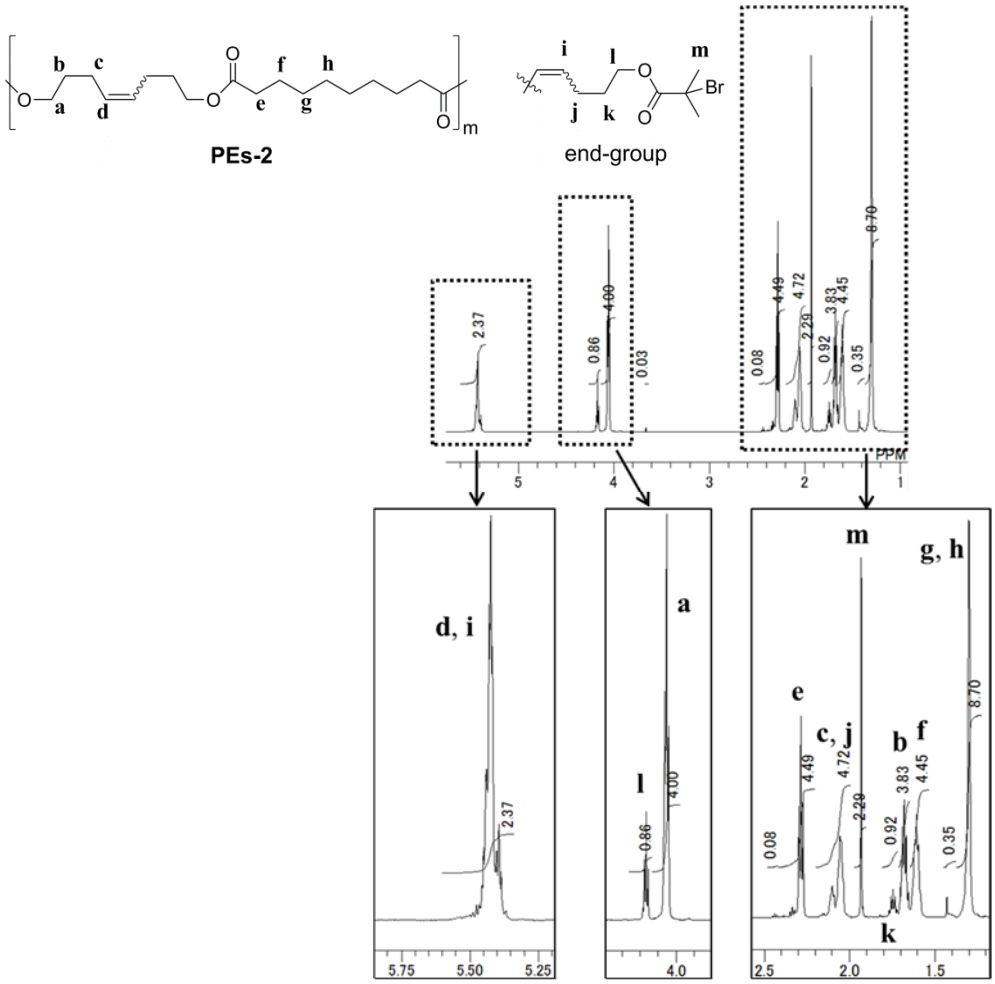


Figure S19. ^{1}H NMR spectrum of **PEs-2**, obtained by cross metathesis of *cis*-cyclic PEs with 20 mol% of **2** (Table 3, entry 3), measured in $CDCl_3$ at 25 °C.

4-4. ATRP of St from the end groups of PEs

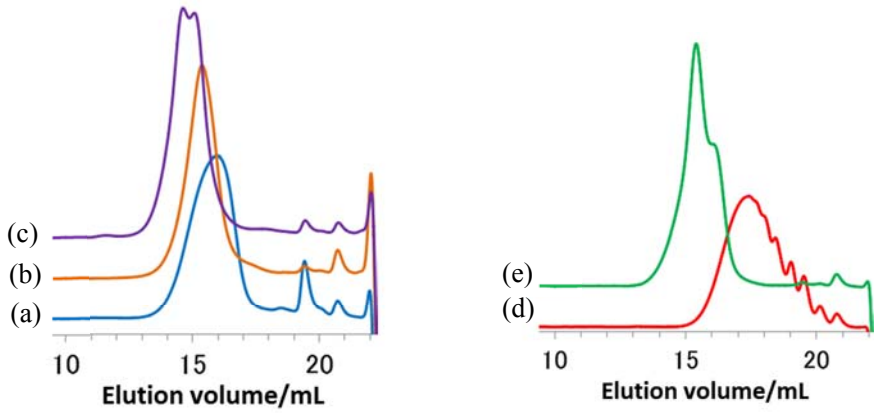


Figure S20. GPC elution curves of (a) macroinitiator **PEs-1b** (M_n = 12300, M_w/M_n = 1.43), (b) **BC-1c** (M_n = 14700, M_w/M_n = 1.49), and (c) **BC-1d** (M_n = 24000, M_w/M_n = 1.42) obtained by ATRP of St with **PEs-1b** (Table 4, entries 2-3); (d) macroinitiator **PEs-2** (M_n = 2920, M_w/M_n = 1.72) and (e) **BC-2d** (M_n = 15100, M_w/M_n = 1.30) obtained by ATRP of St with **PEs-2** (entry 4).

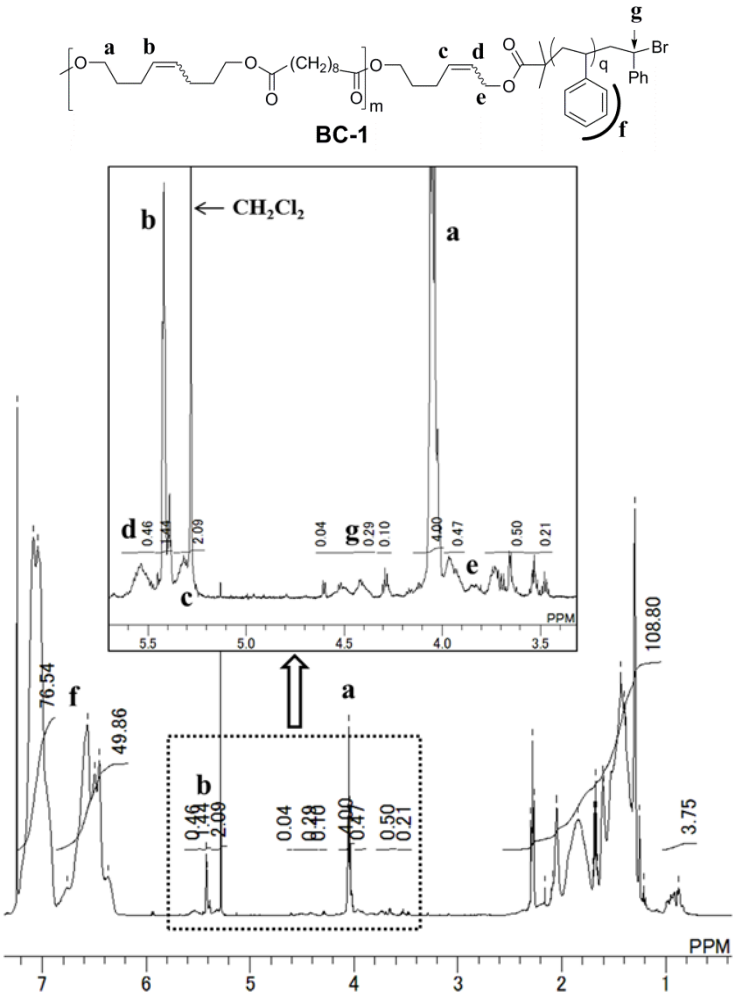


Figure S21. ^{1}H NMR spectrum of **BC-1b**, obtained by ATRP of St with **PEs-1a**, measured in $CDCl_3$ at 25 °C (Table 4, entry 1).

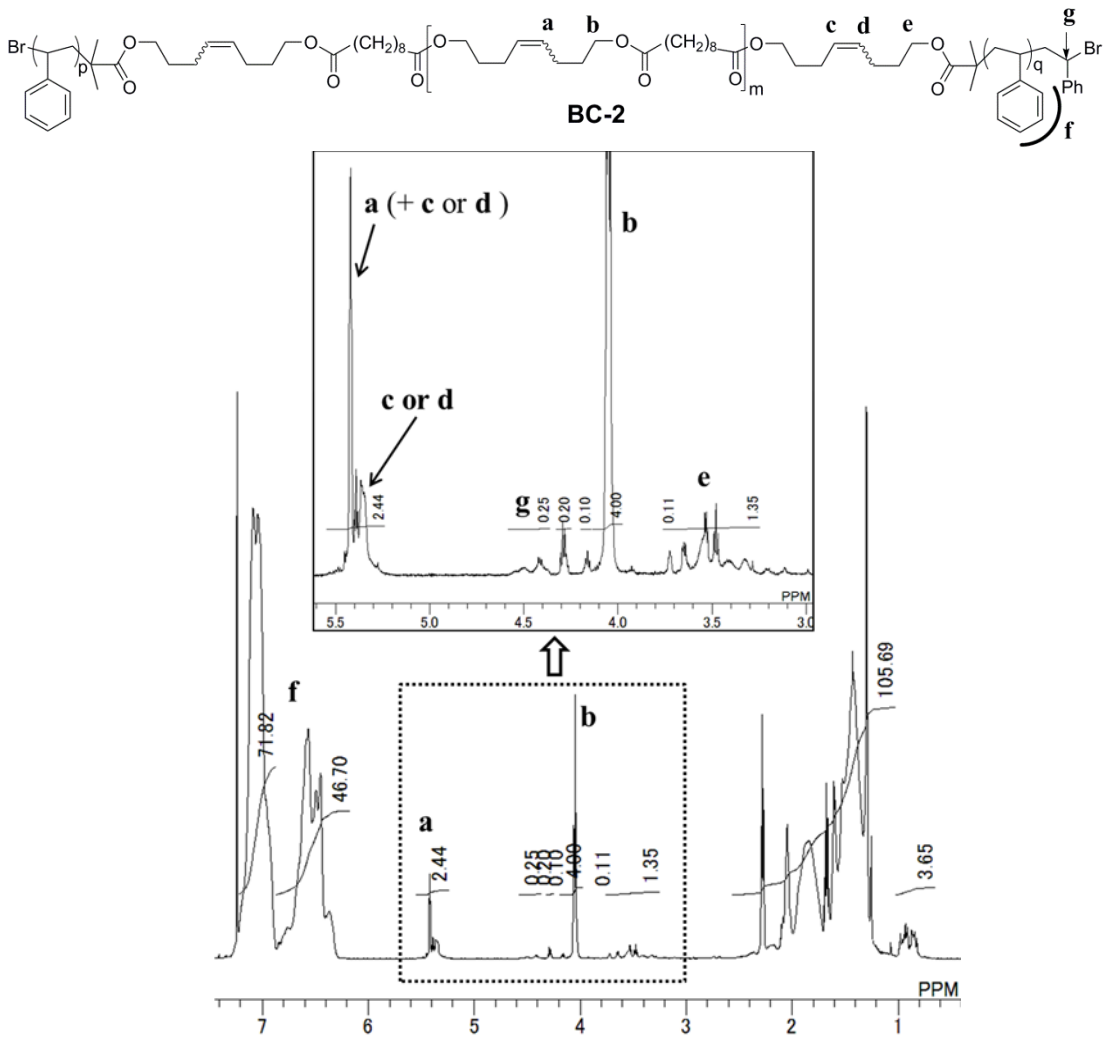


Figure S22. ^{1}H NMR spectrum of **BC-2d**, obtained by ATRP of St with **PEs-2**, measured in $CDCl_3$ at 25 ^{o}C (Table 4, entry 4).

4-4. Hydrogenation of block copolymers

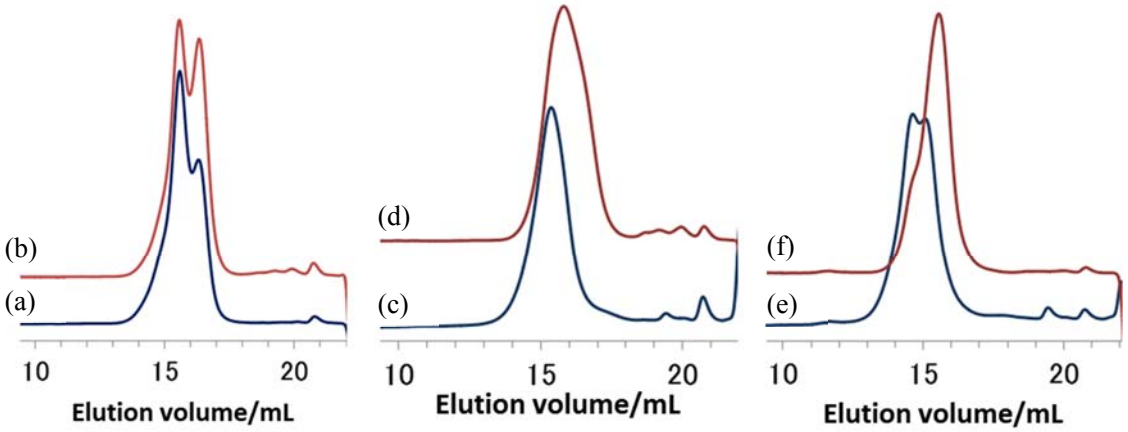


Figure S23. GPC elution curves of (a) **BC-1b**, (b) **BC-1b-H**, (c) **BC-1c**, (d) **BC-1c-H**, (e) **BC-1d**, and (f) **BC-1d-H**.

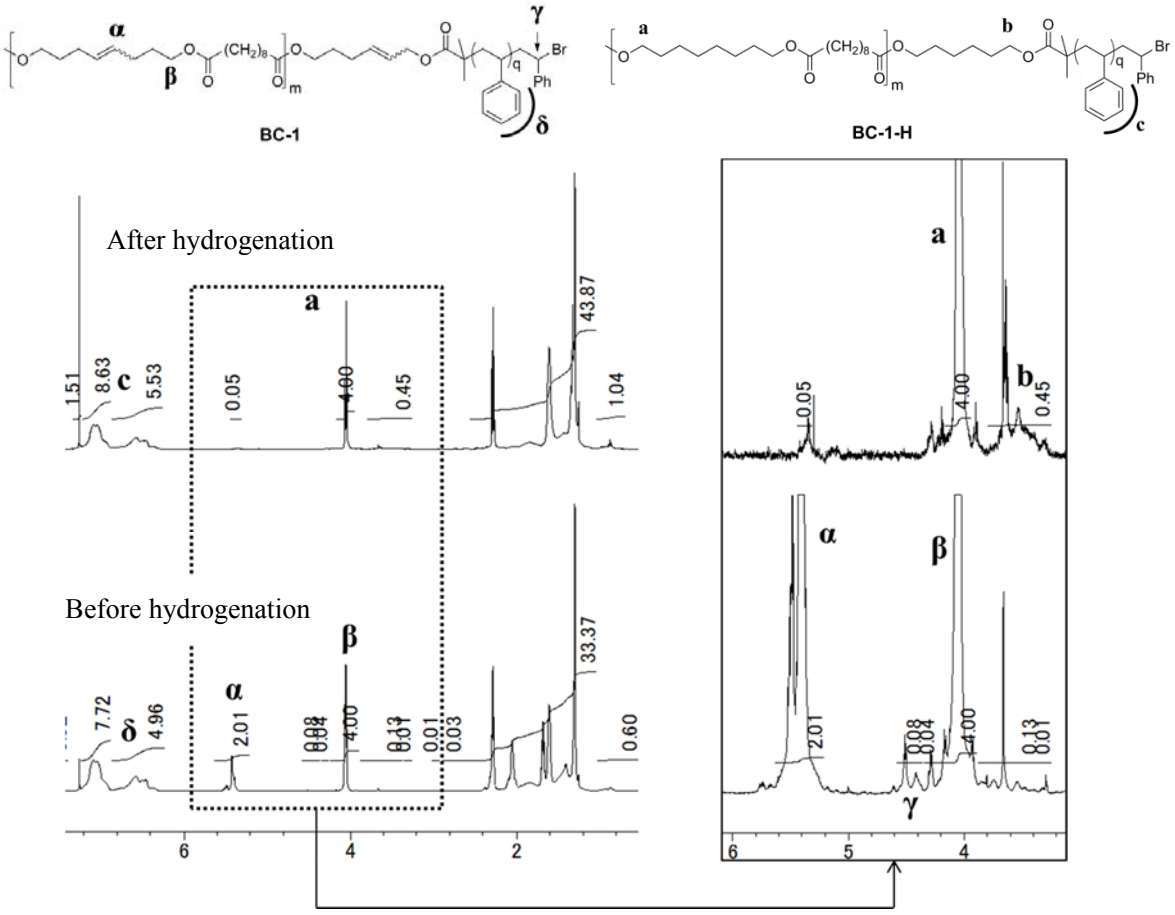


Figure S24. ^{1}H NMR spectra of **BC-1c** (bottom) and **BC-1c-H** (top), obtained by hydrogenation of **BC-1c**, measured in $CDCl_3$ at 25 °C.

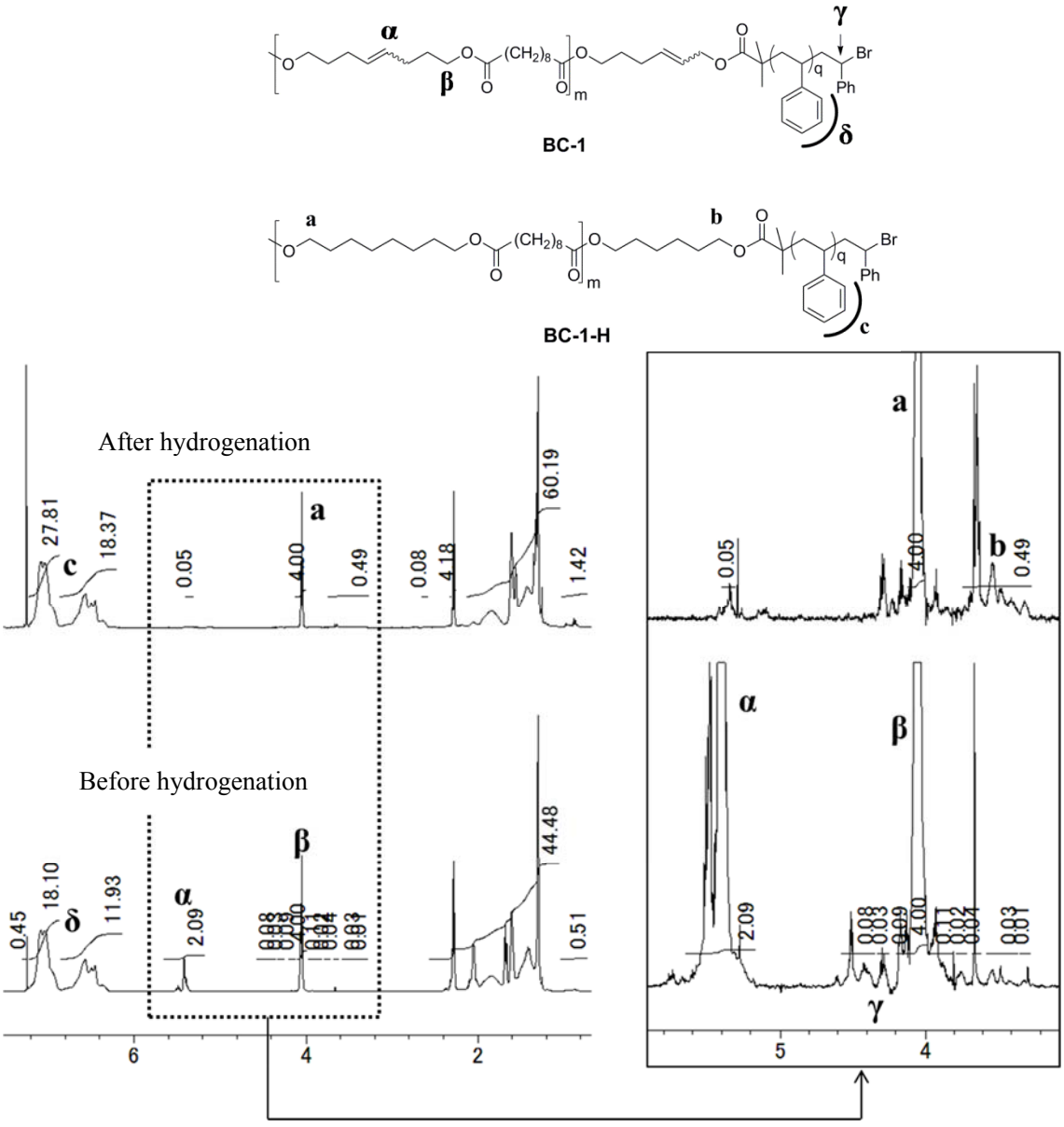


Figure S25. ^{1}H NMR spectra of **BC-1d** (bottom), and **BC-1d-H** (top), obtained by hydrogenation of **BC-1d**, measured in $CDCl_3$ at 25 ^{o}C.

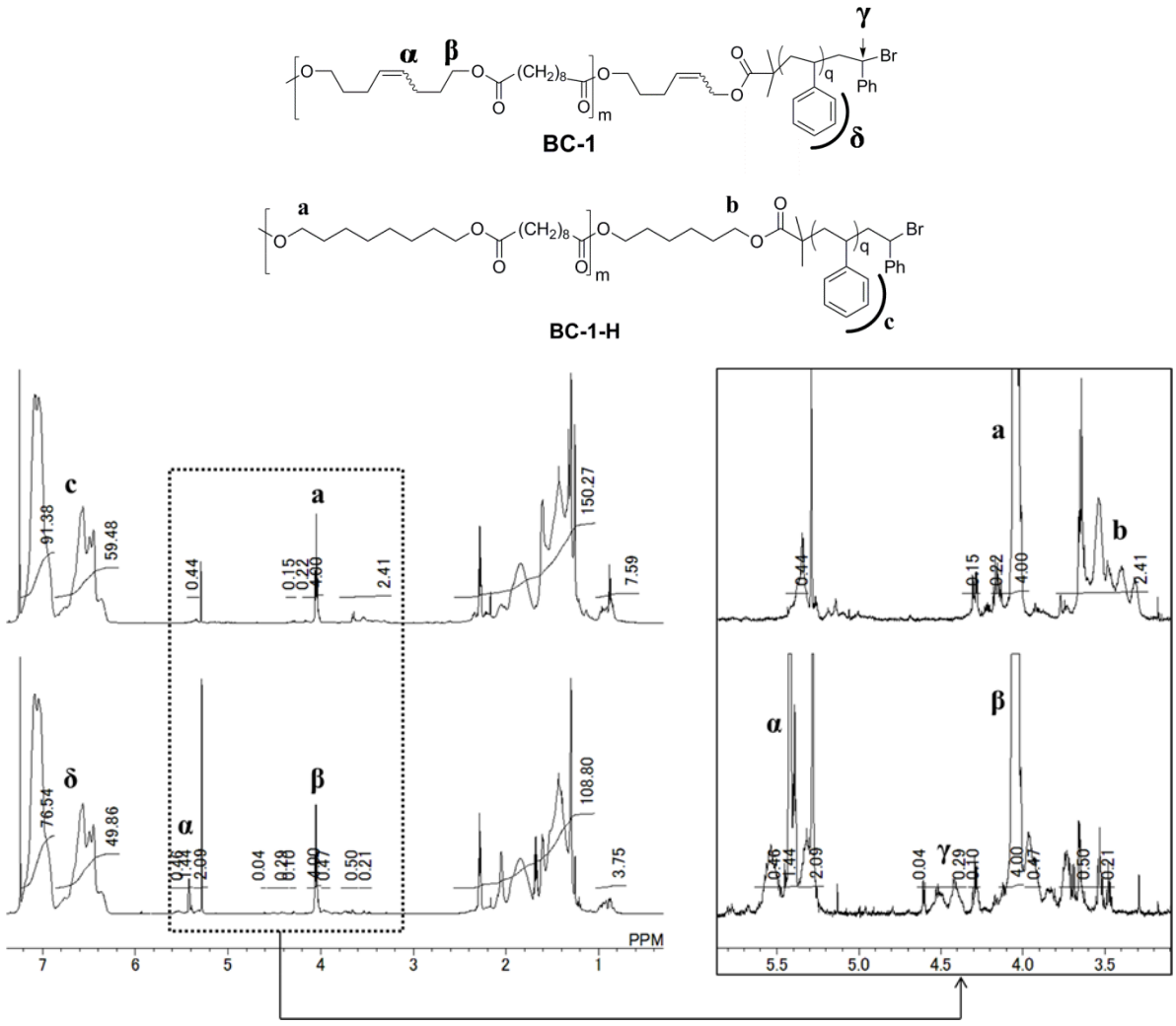


Figure S26. ^{1}H NMR spectra of **BC-1b** (bottom), and **BC-1b-H** (top) obtained by hydrogenation of **BC-1b**, measured in $CDCl_3$ at 25 °C.

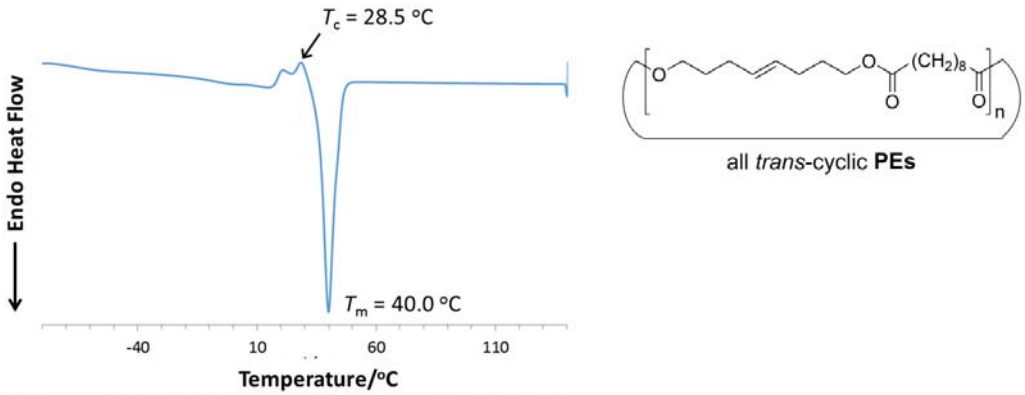


Figure S27. DSC curve of *trans*-cyclic **PEs** (M_n = 13300, M_w/M_n = 2.49) at heating/cooling rate of 10 °C/min under a nitrogen atmosphere.

References

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