Electronic Supplementary Information

Downsizing Feature of Microphase-Separated Structures via Intramolecular crosslinking of Block Copolymers

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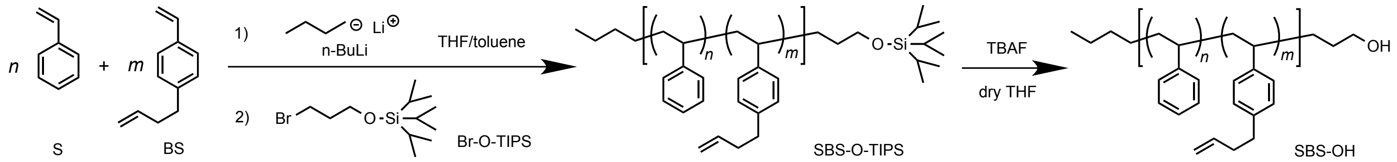
S1. Experimental

Materials. *sec*-Butyllithium (*sec*-BuLi; Kanto Chemical Co., Inc. (Kanto), 1.05 mol L^{-1} in *n*-hexane), *n*-butyllithium (*n*-BuLi; Kanto, 1.01 mol L^{-1} in *n*-hexane), tetrabutylammonium fluoride (TBAF; Tokyo Chemical Industry Co., Ltd. (TCI), 1.0 mol L^{-1} in THF), absolute benzene (Wako Pure Chemical Industries, Ltd., super dehydrated, >99.5%), benzoic acid (TCI, >99.0%), Grubbs 2nd generation catalyst (G2; Sigma-Aldrich Chemicals Co.), and ethyl vinyl ether (TCI, >98.0%) were purchased and used as received. Styrene (S; TCI, >99.0%) and 1,8-diazabicyclo[5.4.0]-7-undecene (DBU; TCI, >98.0%) were purchased and purified by distillation over CaH_2 under vacuum. *rac*-Lactide (LA; TCI, >98.0%) was purchased and purified by recrystallization twice from dry toluene. *p*-3-Butenyl styrene (BS)[1] and (3-bromopropoxy)triisopropylsilane (Br–OTIPS)[2] were prepared according to the reported methods, then further purified by distillation over CaH_2 under vacuum. Commercially available dry THF (Kanto, >99.5%, water content, <0.001%), dry toluene (Kanto, >99.5%, water content, <0.001%), and dry CH_2Cl_2 (Kanto, >99.5%, water content, <0.001%) were further purified by an MBRAUN MB SPS Compact solvent purification system equipped with a MB-KOL-A and a MB-KOL-M Type 1 columns (for dry THF), a MB-KOL-C and a MB-KOL-A columns (for dry toluene), or two MB-KOL-A columns (for dry CH_2Cl_2) which were then directly used for the polymerizations.

Instruments. The ring-opening polymerization of *rac*-LA was carried out in an MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) in a dry argon atmosphere (H_2O, O_2 <1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 moisture sensor and an MB-OX-SE 1 oxygen sensor, respectively. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained using a JEOL JNM-ESC400 instrument at room temperature. The size exclusion chromatography (SEC) measurements were performed at 40 °C in THF (flow rate, 1.0 mL min^{-1}) using a Jasco high-performance liquid chromatography system (PU-980 Intelligent HPLC Pump, CO-2065 Plus Intelligent Column Oven, RI-2031 Plus Intelligent RI Detector, and DG-2080-53 Degasser) equipped with a Shodex KF-G guard column (4.6 mm × 10 mm; particle size, 8 μm) and two Shodex KF-804L columns (linear; particle size, 7 μm; 8.0 mm × 300 mm; exclusion limit, 4×10^4). Preparative SEC purification was performed in $CHCl_3$ (3.5 mL min^{-1}) at 23 °C using JAI LC-9201 equipped with a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7×10^4) and a JAI RI-50s refractive index detector. The Fourier transform infrared spectroscopy (FT-IR) analysis was carried out using a PerkinElmer Frontier MIR spectrometer equipped with a single reflection diamond universal attenuated total reflection (ATR) accessory. Differential scanning calorimetry (DSC) experiments were performed using a Bruker AXS DSC 3100 under a nitrogen atmosphere. All polymers for DSC measurement were heated to 150 or 200 °C, cooled to 10 °C, and heated to 150 or 200 °C again at the heating and cooling rate of 10 °C min^{-1} and 20 °C min^{-1}, respectively.

Synthesis of ω-end hydroxy-functionalized statistical copolymer of S and BS (SBS_{5k}–OH).



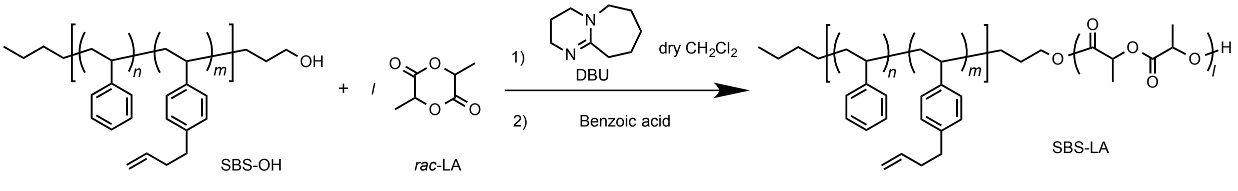
A typical procedure for the copolymerization of S and BS is as follows (method A). In the glovebox, dry toluene (47 mL) and dry THF (23 mL) were placed in a Schlenk flask. After sealing, the flask was taken out from the glovebox. *sec*-BuLi (100 μL, 105 μmol as a 1.05 mol L^{-1} stock solution in *n*-hexane) was added to the solvent under an Ar atmosphere to remove water completely. Then, the solvent was further purified by trap-to-trap distillation under high vacuum to transfer to another Schlenk flask for polymerization. After cooling to –78 °C, *n*-BuLi (900 μL, 909 μmol as a 1.01 mol L^{-1} stock solution in *n*-hexane) was added to the flask. In another flame-dried Schlenk flask, S (2.5 g, 24 mmol) and BS (1.6 g, 10 mmol) were mixed together under an Ar atmosphere. The mixture was added at once to the initiator solution using a syringe. After monomer addition, the mixture was stirred at −78 °C for 6 h. Br−O−TIPS (679 mg, 2.30 mmol) was added to the solution of living polymer anions at −78 °C, and the whole mixture was allowed to react for 0.5 h at −78 °C and an additional 1 h at room temperature. Afterwards, The solvent was removed from the polymerization mixture under reduced pressure. TBAF (6.89 mL, 6.89 mmol as a 1.0 mol L^{-1} stock solution in THF) and dry THF (20 mL) were added to the crude product at room temperature. After 15 h stirring, the reaction mixture was passed through a short silica-gel column, and the resulting residue was purified by repeated reprecipitation (at least twice) from the THF solution into MeOH to give SBS_{5k}–OH as a white solid. Yield: 3.76 g (86.4%). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40−6.19 (m, 10H × *n* + 8H × *m*, $-C_6H_{10}$, $-C_6H_8-$), 5.97−5.74 (m, 1H × *m*, $-CH{=}CH_2$), 5.15−4.90 (m, 2H × *m*, $-CH{=}CH_2$), 3.47−3.33 (m, 2H, $-CH_2OH$), 2.85−2.45 (m, 2H × *m*, $-C_6H_8CH_2-$), 2.46−2.14 (m, 2H × *m*, $-C_6H_8CH_2CH_2-$), 2.15−1.62 (m, 1H × (*n*+*m*), $-CH(C_6H_{10})-$, $-CH(C_6H_8-)-$), 1.74−0.69 (m, 2H × (*m*+*n*) + 9H, $-CH_2CH(C_6H_{10})-$, $-CH_2CH(C_6H_8-)-$, C_4H_9-). $M_{n,NMR}$ = 4,670 ($CDCl_3$), the mole fraction of the BS units = 0.28, $M_{n,SEC}$ = 4,610 (THF), $Đ$ = 1.09 (THF).

Synthesis of *ω*-end hydroxy-functionalized statistical copolymer of S and BS (SBS_{8k}−OH). Method A was used for the living anionic copolymerization of S (2.5 g, 24 mmol) and BS (1.6 g, 10 mmol) with *n*-BuLi (560 μL, 598 μmol as a 1.07 mol L^{-1} stock solution in *n*-hexane) and Br–O–TIPS (620 mg, 2.10 mmol) in mixture solvent of dry toluene (47 mL) and dry THF (23 mL) for 6 h followed by the deprotection with TBAF (6.30 mL, 6.30 mmol as a 1.0 mol L^{-1} stock solution in THF) in dry THF (20 mL) to give SBS_{8k}–OH. Yield: 3.25 g (76.3 %). $M_{n,NMR}$ = 7,940 ($CDCl_3$), f_{BS} = 0.31, $M_{n,SEC}$ = 4,730 (THF), $Đ$ = 1.04 (THF).

Synthesis of *ω*-end hydroxy-functionalized statistical copolymer of S and BS (SBS^*_{9k}−OH). Method A was used for the living anionic copolymerization of S (1.8 g, 17 mmol) and BS (2.7 g, 17 mmol) with *n*-BuLi (640 μL, 493 μmol as a 0.77 mol L^{-1} stock solution in *n*-hexane) and Br–O–TIPS (508 mg, 1.72 mmol) in mixture solvent of dry toluene (47 mL) and dry THF (23 mL) for 6 h followed by the deprotection with TBAF (5.17 mL, 5.17 mmol as a 1.0 mol L^{-1} stock solution in THF) in dry THF (20 mL) to give SBS^{*}_{9k}–OH. Yield: 4.33 g (93.5 %). $M_{n,NMR}$ = 9,460 ($CDCl_3$), f_{BS} = 0.49, $M_{n,SEC}$ = 8,250 (THF), $Đ$ = 1.04 (THF).

Synthesis of *ω*-end hydroxy-functionalized statistical copolymer of S and BS (SBS_{27k}–OH). Method A was used for the living anionic copolymerization of S (2.5 g, 24 mmol) and BS (1.6 g, 10 mmol) with *n*-BuLi (280 μL, 155 μmol as a 0.55 mol L^{-1} stock solution in *n*-hexane) and Br–O–TIPS (298 mg, 1.01 mmol) in mixture solvent of dry toluene (47 mL) and dry THF (23 mL) for 6 h followed by the deprotection with TBAF (3.03 mL, 3.03 mmol as a 1.0 mol L^{-1} stock solution in THF) in dry THF (20 mL) to give SBS_{27k}–OH. Yield: 4.11 g (99.5 %). $M_{n,NMR}$ = 27,000 ($CDCl_3$), f_{BS} = 0.29, $M_{n,SEC}$ = 19,600 (THF), $Đ$ = 1.02 (THF).

Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) (SBS_{5k}–LA_{7k}) via ring-opening polymerization of *rac*-LA using SBS_{5k}–OH as an initiator.



A typical procedure for the polymerization of *rac*-LA is as follows (method B). SBS_{5k}–OH was freeze-dried from its absolute benzene solution three times prior to the polymerization. In the glovebox, SBS_{5k}–OH ($M_{n,NMR}$ = 4,670, 1.04 g, 223 μmol) and *rac*-LA (1.50 g, 10.4 mmol) were dissolved in dry CH_2Cl_2 (20.8 mL). DBU (15.5 μL, 104 μmol) was then added to the CH_2Cl_2 solution to initiate the polymerization. After 18 min, the polymerization was quenched by the addition of benzoic acid. The mixture was purified by reprecipitation from the CH_2Cl_2 solution into MeOH to give $SBS_{5k}–LA_{7k}$ as a white solid (2.21 g, 90.6%). The product was further purified by preparative SEC prior to the intramolecular crosslinking reaction and each measurement. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40−6.19 (m, 10H × n + 8H × m, $-C_6H_{10}$, $-C_6H_8-$), 5.97−5.74 (m, 1H × m, $-CH{=}CH_2$), 5.42−5.05 (m, 1H × ($2l$-1), $-OCOCH(CH_3)-$), 5.15−4.90 (m, 2H × m, $-CH{=}CH_2$), 4.43−4.31 (m, 1H, $-CH(CH_3)OH$), 4.00−3.76 (m, 2H, $-CH_2O-$), 2.85−2.45 (m, 2H × m, $-C_6H_8CH_2-$), 2.46−2.14 (m, 2H × m, $-C_6H_8CH_2CH_2-$), 2.15−1.62 (m, 1H × (n+m), $-CH(C_6H_{10})-$, $-CH(C_6H_8-)-$), 1.77−0.69 (m, 3H × $2l$ + 2H × (m+n) + 9H, $-CH_2CH(C_6H_{10})-$, $-CH_2CH(C_6H_8-)-$, C_4H_9-). Conversion = 93%, $M_{n,NMR}$ = 11,000 ($CDCl_3$), the weight fraction of SBS = 0.42, $M_{n,SEC}$ = 13,900 (THF), $Đ$ = 1.04 (THF).

Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) ($SBS_{8k}–LA_{5k}$) via ring-opening polymerization of *rac*-LA using SBS_{8k}−OH as an initiator. Method B was used for the ring-opening polymerization of *rac*-LA (532 mg, 36.9 μmol) with SBS_{8k}–OH ($M_{n,NMR}$ = 7,940, 736 mg, 92.2 μmol) and DBU (5.5 μL, 36.8 μmol) in dry CH_2Cl_2 (7.4 mL) for 10 min to give $SBS_{5k}–LA_{6k}$ as a white solid (1.11 g, 87.5%)). The product was further purified by preparative SEC prior to the intramolecular crosslinking reaction and each measurement. Conversion = 81%, $M_{n,NMR}$ = 12,600 ($CDCl_3$), F_{SBS} = 0.63, $M_{n,SEC}$ = 12,500 (THF), $Đ$ = 1.03 (THF).

Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) ($SBS_{8k}–LA_{8k}$) via

ring-opening polymerization of *rac*-LA using SBS_{8k}–OH as an initiator. Method B was used for the ring-opening polymerization of *rac*-LA (1.26 g, 8.71 mmol) with SBS_{8k}–OH ($M_{n,NMR}$ = 7,940, 1.25 g, 157 μmol) and DBU (13.0 μL, 87.1 μmol) in dry CH_2Cl_2 (17.4 mL) for 35 min to give SBS_{8k}–LA_{8k} as a white solid. Yield: 2.36 g, 87.5%). Conversion = 96%, $M_{n,NMR}$ = 16,200 ($CDCl_3$), F_{SBS} = 0.49, $M_{n,SEC}$ = 16,500 (THF), $Đ$ = 1.03 (THF).

Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) (SBS^{*}_{9k}–LA_{6k}) via ring-opening polymerization of *rac*-LA using SBS^{*}_{9k}–OH as an initiator. Method B was used for the ring-opening polymerization of *rac*-LA (439 mg, 3.05 mmol) with SBS^{*}_{9k}–OH ($M_{n,NMR}$ = 9,460, 604 mg, 67.6 μmol) and DBU (5.0 μL, 33.5 μmol) in dry CH_2Cl_2 (6.1 mL) for 13 min to give SBS^{*}_{9k}–LA_{6k} as a white solid (930 mg, 89.2%)). The product was further purified by preparative SEC prior to the intramolecular crosslinking reaction and each measurement. Conversion = 89%, $M_{n,NMR}$ = 15,900 ($CDCl_3$), F_{SBS} = 0.60, $M_{n,SEC}$ = 16,800 (THF), $Đ$ = 1.03 (THF).

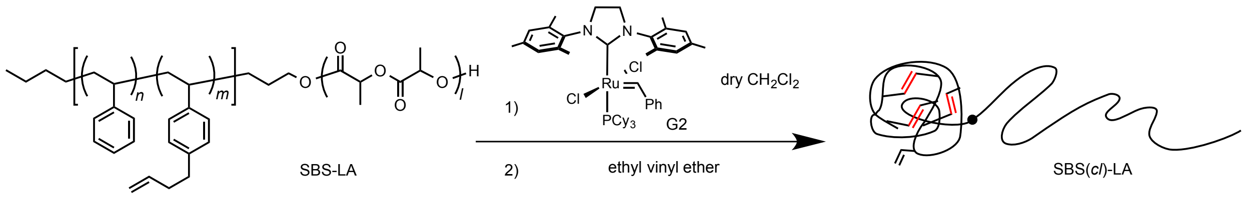
Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) (SBS^{*}_{9k}–LA_{11k}) via ring-opening polymerization of *rac*-LA using SBS^{*}_{9k}–OH as an initiator. Method B was used for the ring-opening polymerization of *rac*-LA (1.46 g, 10.1 mmol) with SBS^{*}_{9k}–OH ($M_{n,NMR}$ = 9,460, 999 mg, 112 μmol) and DBU (15.0 μL, 100 μmol) in dry CH_2Cl_2 (6.1 mL) for 20.2 min to give SBS^{*}_{9k}–LA_{11k} as a white solid (2.06 g, 83.8%)). The product was further purified by preparative SEC prior to the intramolecular crosslinking reaction and each measurement. Conversion = 85%, $M_{n,NMR}$ = 20,900

($CDCl_3$), F_{LA} = 0.45, $M_{n,SEC}$ = 23,300 (THF), $Đ$ = 1.03 (THF).

Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) (SBS_{27k}–LA_{13k}) via ring-opening polymerization of *rac*-LA using SBS_{27k}–OH as an initiator. Method B was used for the ring-opening polymerization of *rac*-LA (729 mg, 5.06 mmol) with SBS_{27k}–OH ($M_{n,NMR}$ = 27,000, 1.00 g, 37.0 μmol) and DBU (7.6 μL, 50.6 μmol) in dry CH_2Cl_2 (10.0 mL) for 35 min to give SBS_{27k}–LA_{13k} as a white solid (1.37 g, 79.2%)). The product was further purified by preparative SEC prior to the intramolecular crosslinking reaction and each measurement. Conversion = 75%, $M_{n,NMR}$ = 40,400 ($CDCl_3$), F_{SBS} = 0.67, $M_{n,SEC}$ = 16,500 (THF), $Đ$ = 1.03 (THF).

Synthesis of block copolymer consisting of SBS and poly(*rac*-LA) (SBS_{27k}–LA_{28k}) via ring-opening polymerization of *rac*-LA using SBS_{27k}–OH as an initiator. Method B was used for the ring-opening polymerization of *rac*-LA (1.37 g, 9.52 mmol) with SBS_{27k}–OH ($M_{n,NMR}$ = 27,000, 1.00 g, 37.0 μmol) and DBU (14.1 μL, 94.7 μmol) in dry CH_2Cl_2 (18.9 mL) for 45 min to give SBS_{27k}–LA_{13k} as a white solid (1.96 g, 82.5%)). The product was further purified by preparative SEC prior to the intramolecular crosslinking reaction and each measurement. Conversion = 81%, $M_{n,NMR}$ = 54,900 ($CDCl_3$), F_{SBS} = 0.49, $M_{n,SEC}$ = 54,400 (THF), $Đ$ = 1.03 (THF).

Intramolecular crosslinking of SBS_{5k}–LA_{7k} via olefin metathesis reaction.



A typical procedure for the intramolecular crosslinking is as follows (method C). SBS_{5k}–LA_{7k} ($M_{n,NMR}$ = 11,000, 403 mg, 471 μmol olefin-containing units) was dissolved in dry CH_2Cl_2 (1340 mL). After degassing by N_2 bubbling, G2 (4.0 mg, 4.7 μmol) was added to the mixture. After stirring for 3 h under an N_2 atmosphere at 30 °C, the reaction was quenched by the addition of ethyl vinyl ether. The solvent was removed by evaporation, then the residue was purified by reprecipitation from the CH_2Cl_2 solution into MeOH to givecrosslinked–linear diblock copolymer (SBS_{5k}(*cl*)–LA_{6k}) as a white solid (373 mg, 92.6%). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 12,300 (THF), $Đ$ = 1.03 (THF), the conversion of the terminal olefins = 93%.

Intramolecular crosslinking of SBS_{8k}–LA_{5k} via olefin metathesis reaction. Method C was used for the intramolecular crosslinking of SBS_{8k}–LA_{5k} ($M_{n,NMR}$ = 12,600, 400 mg, 614 μmol olefin-containing units) with G2 (5.3 mg, 6.2 μmol) in dry CH_2Cl_2 (1340 mL) for 3 h to give SBS_{8k}(*cl*)–LA_{5k} as a white solid (377 mg, 94.2 %)). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 11,200 (THF), $Đ$ = 1.03 (THF), conv.$_{olefin}$ = 88%.

Intramolecular crosslinking of SBS_{8k}–LA_{8k} via olefin metathesis reaction. Method C was used for the intramolecular crosslinking of SBS_{8k}–LA_{8k} ($M_{n,NMR}$ = 16,200, 309 mg, 410 μmol olefin-containing units) with G2 (3.5 mg, 4.1 μmol) in dry CH_2Cl_2 (1030 mL) for 3 h to give $SBS_{8k}(cl)–LA_{5k}$ as a white solid (260 mg, 84.1 %)). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 15,300 (THF), $Đ$ = 1.03 (THF), conv.$_{olefin}$ = 79%.

Intramolecular crosslinking of $SBS^*_{9k}–LA_{6k}$ via olefin metathesis reaction. Method C was used for the intramolecular crosslinking of $SBS^*_{9k}–LA_{6k}$ ($M_{n,NMR}$ = 15,900, 341 mg, 510 μmol olefin-containing units) with G2 (4.3 mg, 5.1 μmol) in dry CH_2Cl_2 (1030 mL) for 3 h to give $SBS^*_{9k}(cl)–LA_{6k}$ as a white solid (260 mg, 76.2 %)). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 13,900 (THF), $Đ$ = 1.03 (THF), conv.$_{olefin}$ = 86%.

Intramolecular crosslinking of $SBS^*_{9k}–LA_{11k}$ via olefin metathesis reaction. Method C was used for the intramolecular crosslinking of $SBS^*_{9k}–LA_{11k}$ ($M_{n,NMR}$ = 20,900, 362 mg, 612 μmol olefin-containing units) with G2 (5.2 mg, 6.1 μmol) in dry CH_2Cl_2 (1200 mL) for 3 h to give $SBS^*_{9k}(cl)–LA_{11k}$ as a white solid (262 mg, 72.4 %)). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 20,600 (THF), $Đ$ = 1.03 (THF), conv.$_{olefin}$ = 89%.

Intramolecular crosslinking of $SBS_{27k}–LA_{13k}$ via olefin metathesis reaction. Method C was used for the intramolecular crosslinking of $SBS_{27k}–LA_{13k}$ ($M_{n,NMR}$ = 40,400, 130 mg, 212 μmol olefin-containing units) with G2 (1.8 mg, 2.1 μmol) in dry CH_2Cl_2 (430 mL) for 3 h to give $SBS_{27k}(cl)–LA_{13k}$ as a white solid (100 mg, 76.9 %)). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 28,900 (THF), $Đ$ = 1.03 (THF), conv.$_{olefin}$ = 88%.

Intramolecular crosslinking of SBS_{27k}–LA_{28k} via olefin metathesis reaction. Method C was used for the intramolecular crosslinking of SBS_{27k}–LA_{28k} ($M_{n,NMR}$ = 54,900, 253 mg, 307 μmol olefin-containing units) with G2 (2.9 mg, 3.4 μmol) in dry CH_2Cl_2 (840 mL) for 3 h to give SBS_{27k}(*cl*)–LA_{28k} as a white solid (158 mg, 62.5 %)). The product was further purified by preparative SEC prior to each measurement. $M_{n,SEC}$ = 45,400 (THF), $Đ$ = 1.04 (THF), $conv._{olefin}$ = 87%.

Small-angle X-ray scattering (SAXS). The morphologies and *d* values of samples in the bulk state were investigated using SAXS. The experiments were performed on the BL-6A beamline at the Photon Factory in the High Energy Accelerator Research Organization (KEK, Tsukuba, Japan) using X-ray beams with λ = 1.5 Å. The two-dimensional scattering patterns were collected by a PILATUS3 1M detector (Dectris Ltd.), where the sample-to-detector distance was set to 1.0 or 1.5 m. The scattering angle (θ) was calibrated using silver behenate (Nagara Science Co., Ltd.) as the standard and subsequently converted to the scattering vector (q) using Bragg's equation ($q = (4\pi/\lambda)\sin(\theta/2)$). The *d* values of the samples were calculated according to $d = 2\pi/q^*$, where q^* is the principal scattering peak position. The sample powder were annealed at 150 or 180 °C for 1 h under vacuum and then put into a glass capillary (Hilgenberg, Mark-tube, lindemann glass, 2.0 mm diameter).

Transmission electron microscopy (TEM). Bright-field TEM images of the thinly sliced bulk samples were obtained using a JEM-3200FS electron microscope (JEOL) with an accelerating voltage of 100 kV. Bulk film samples prepared by drop-cast from the toluene solutions were annealed at 150 °C for

1 h under vacuum and then embedded in a photocurable resin (Toagosei Co., Ltd., Alonix D-800). Sample slices with a thickness of 35−50 nm were obtained using a Leicca Ultracut S ultramicrotome equipped with a diamond knife (DiATOME, Ultra 35°) at room temperature, and a piece of slice was transferred to copper grids.

Atomic force microscopy (AFM). The AFM phase images were realized using a Molecular Imaging PicoPlus atomic force microscope operating in the tapping mode with a silicon cantilever (Nanoworld AG, NANOSENSORS^{TM} PPP-NCH) having a resonant frequency and a force constant of 190 kHz and 48 N m^{-1}, respectively. The thin films for AFM experiments were prepared by spin-coating (2000 rpm for 1 min) the polymer solution in toluene (1.0 wt%) onto a Si substrate with a native oxide layer. The obtained thin film samples were annealed in the vapor of THF to induce the microphase separation. In a closed glass desiccator (ca. 3.0 L), the samples were positioned above the surface of THF (30 mL) placed in a reservoir for 4 h at 20 °C. The thin films were then taken out from the desiccator and allowed to dry at 20 °C. The film thickness was measured by ellipsometry (JASCO M-500S).

S2. Figures and Table

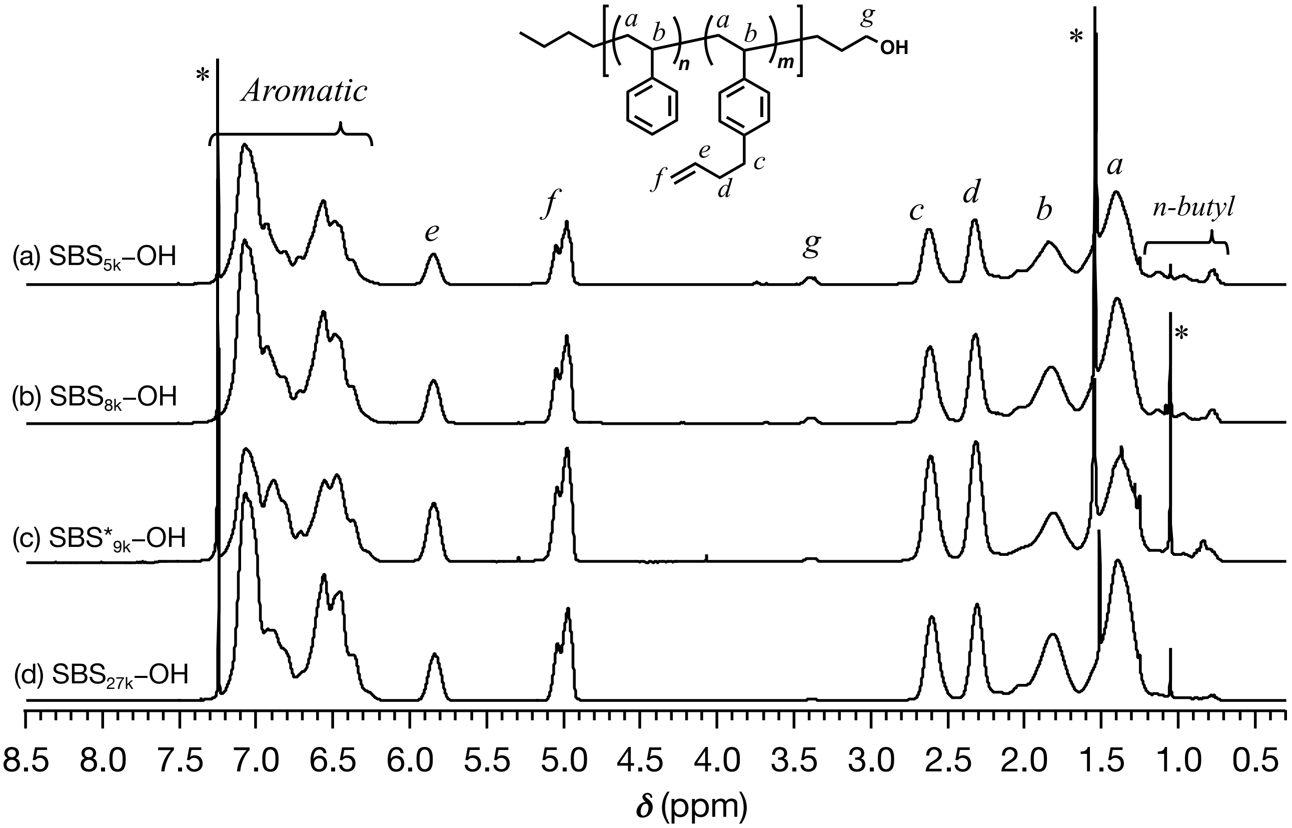


Figure S1. ^{1}H NMR spectra of (a) SBS_{5k}–OH, (b) SBS_{8k}–OH, (c) SBS^*_{9k}–OH, and (d) SBS_{27k}–OH in $CDCl_3$ (400 MHz).

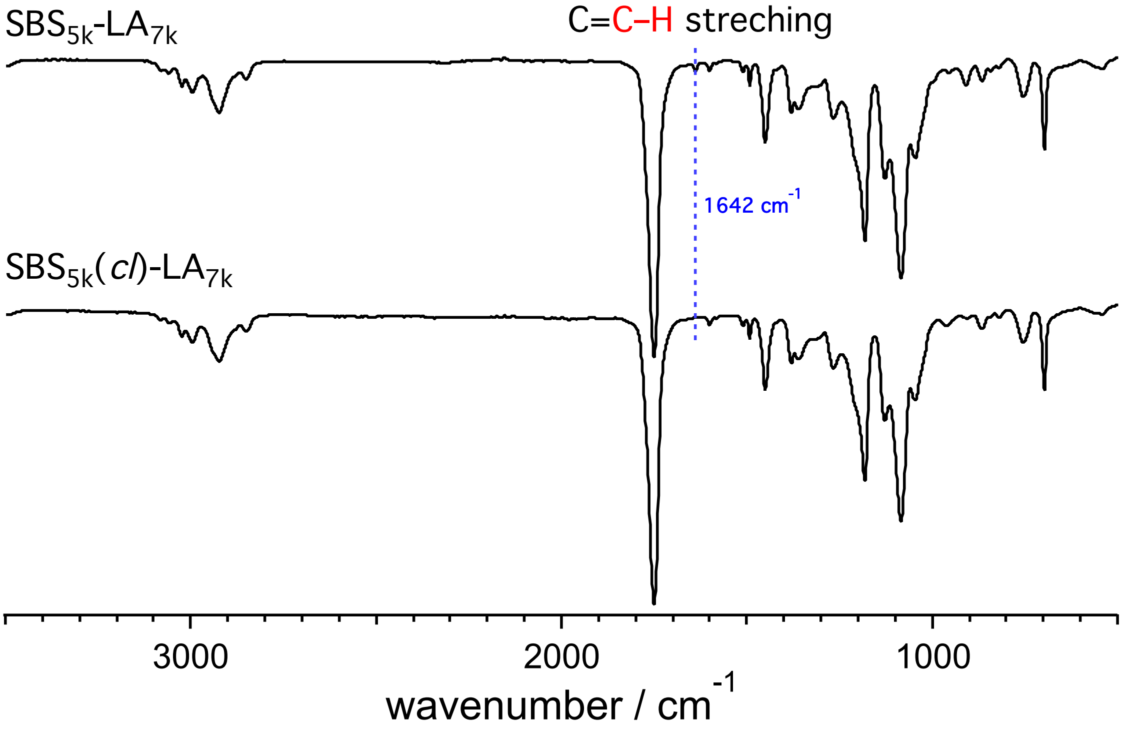


Figure S2. IR spectra of SBS_{5k}–LA_{7k} (upper) and SBS_{5k}(*cl*)–LA_{7k} (lower).

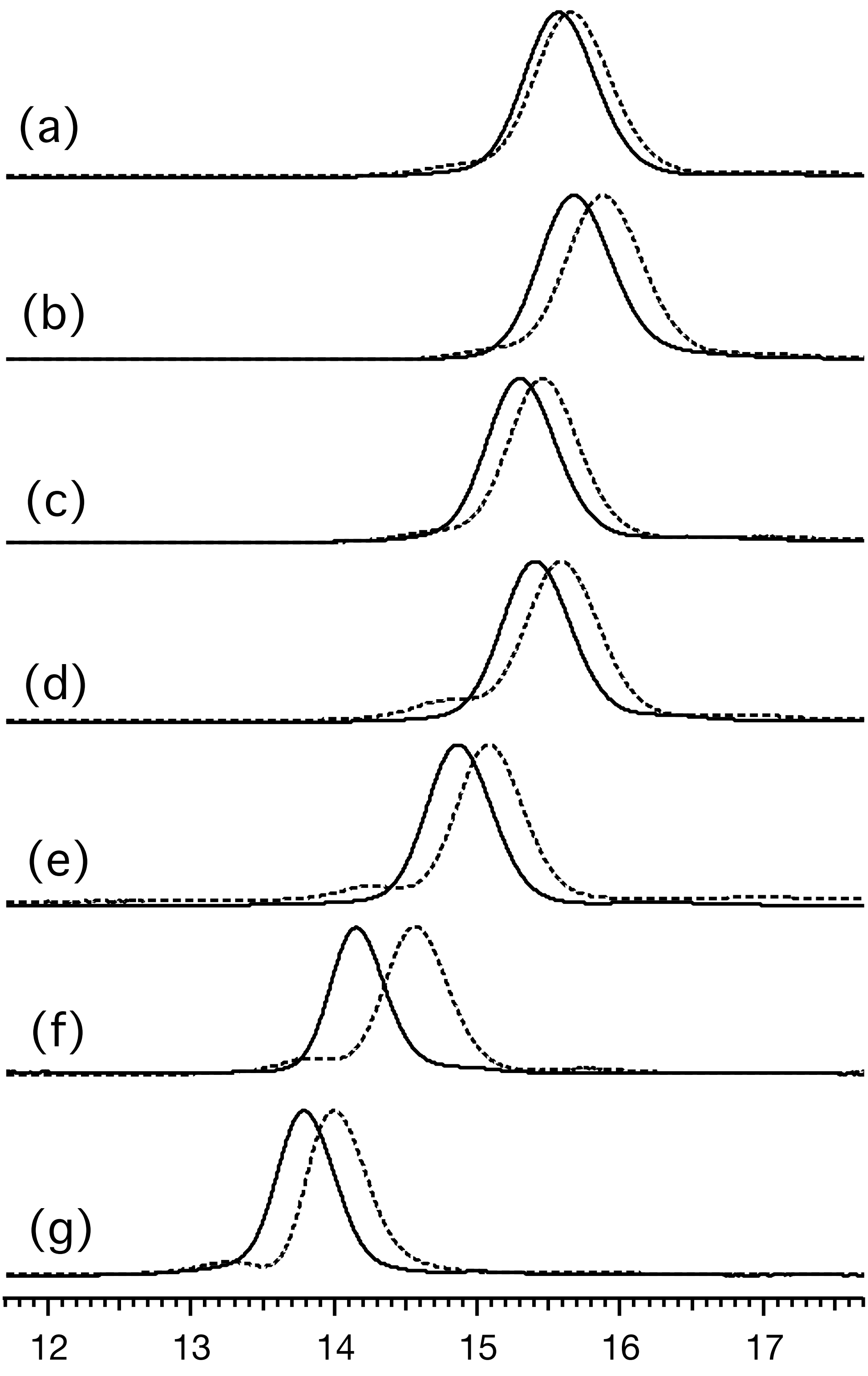


Figure S3. SEC traces of (a) SBS_{5k}–LA_{7k} and SBS_{5k}(*cl*)–LA_{7k}, (b) SBS_{8k}–LA_{5k} and SBS_{8k}(*cl*)–LA_{5k}, (c) SBS_{8k}–LA_{8k} and SBS_{8k}(*cl*)–LA_{8k}, (d) SBS^{*}_{9k}–LA_{6k} and SBS^{*}_{9k}(*cl*)–LA_{6k}, (e) SBS^{*}_{9k}–LA_{11k} and SBS^{*}_{9k}(*cl*)–LA_{11k}, (f) SBS_{27k}–LA_{13k} and SBS_{27k}(*cl*)–LA_{13k}, and (g) SBS_{27k}–LA_{28k} and SBS_{27k}(*cl*)–LA_{28k} (eluent, THF; flow rate, 1.0 mL min^{-1}). SBS–LAs and the corresponding SBS(*cl*)–LAs are presented using solid and dashed lines, respectively. SEC traces for SBS(*cl*)–LAs were obtained before preparative SEC purification.

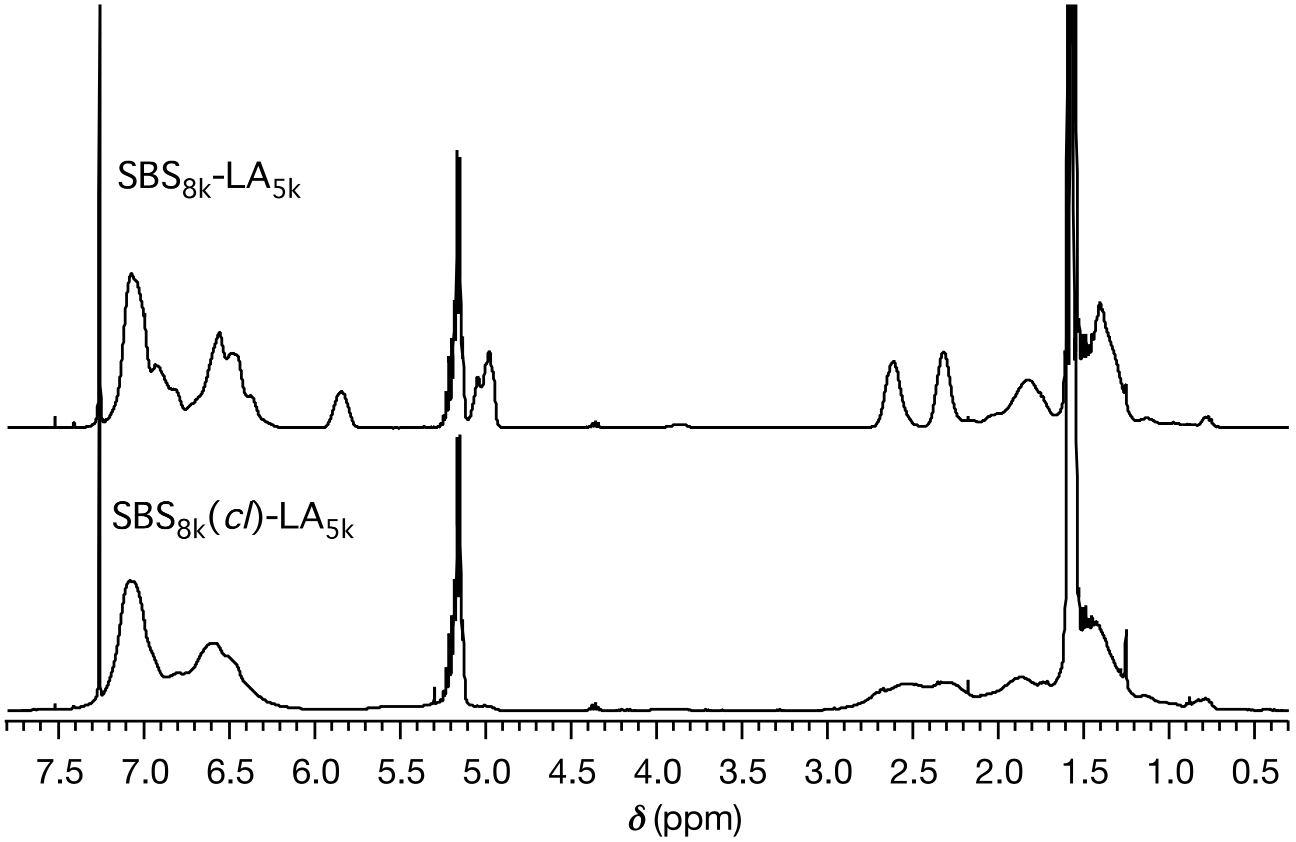


Figure S4. ^{1}H NMR spectra of SBS$_{8k}$–LA$_{5k}$ (upper) and SBS$_{8k}$(*cl*)–LA$_{5k}$ (lower) in CDCl$_3$ (400 MHz).

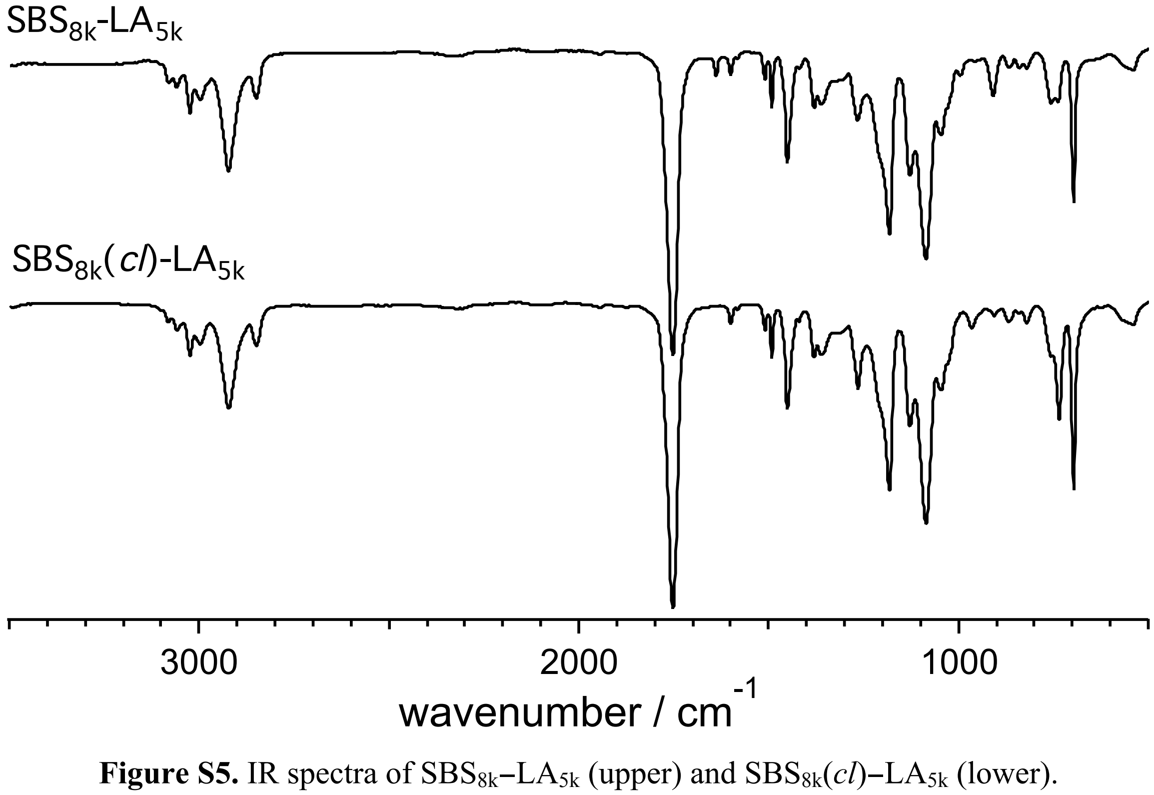


Figure S5. IR spectra of SBS$_{8k}$–LA$_{5k}$ (upper) and SBS$_{8k}$(*cl*)–LA$_{5k}$ (lower).

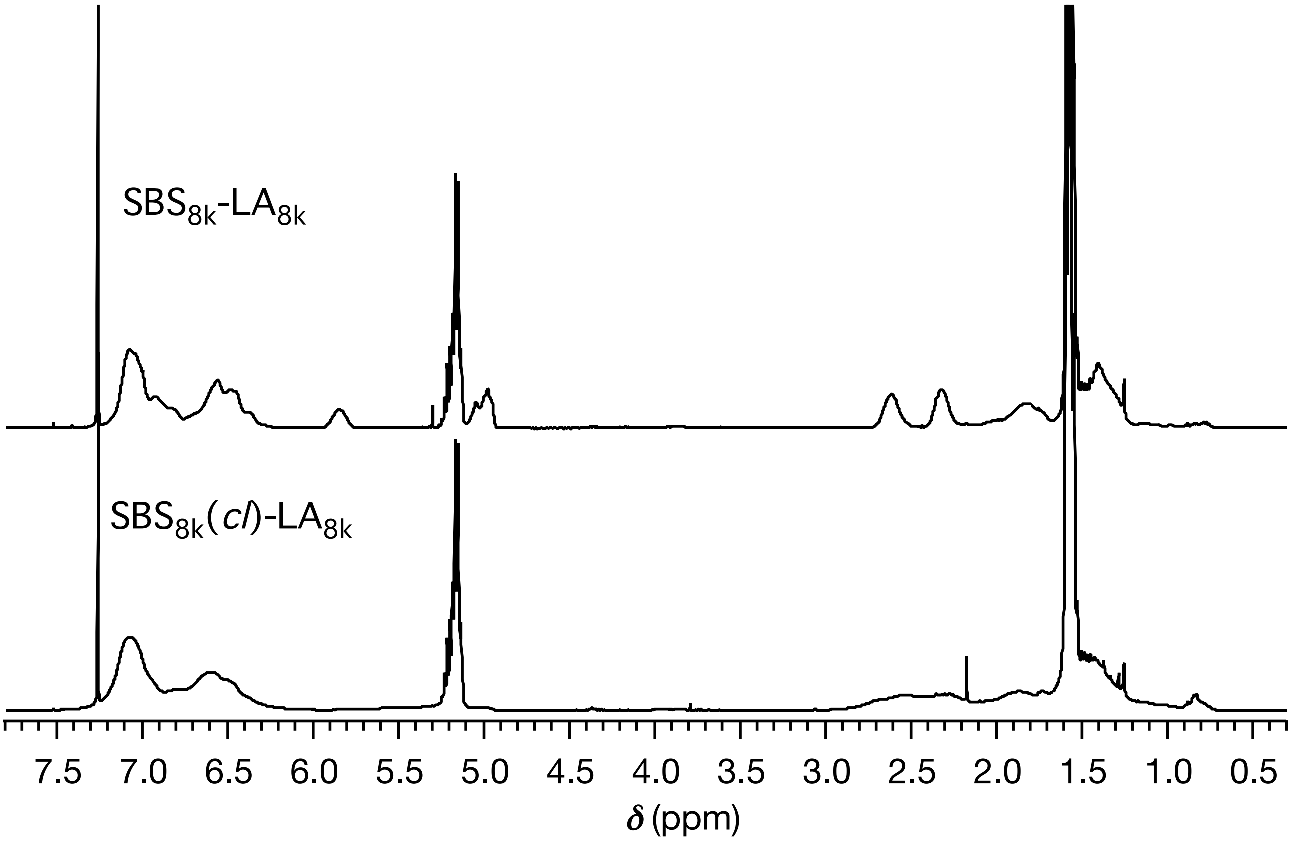


Figure S6. ^{1}H NMR spectra of $\mathrm{SBS_{8k}}$–$\mathrm{LA_{8k}}$ (upper) and $\mathrm{SBS_{8k}}$(*cl*)–$\mathrm{LA_{8k}}$ (lower) in $\mathrm{CDCl_3}$ (400 MHz).

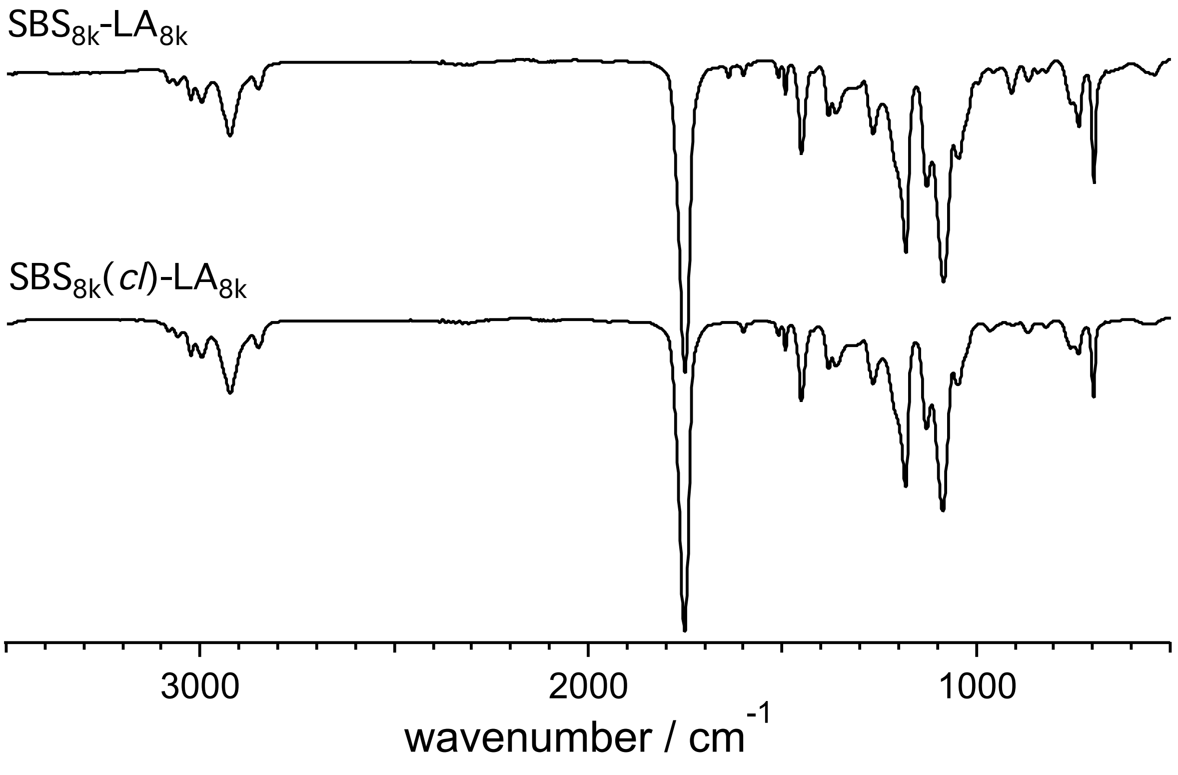


Figure S7. IR spectra of $\mathrm{SBS_{8k}}$–$\mathrm{LA_{8k}}$ (upper) and $\mathrm{SBS_{8k}}$(*cl*)–$\mathrm{LA_{8k}}$ (lower).

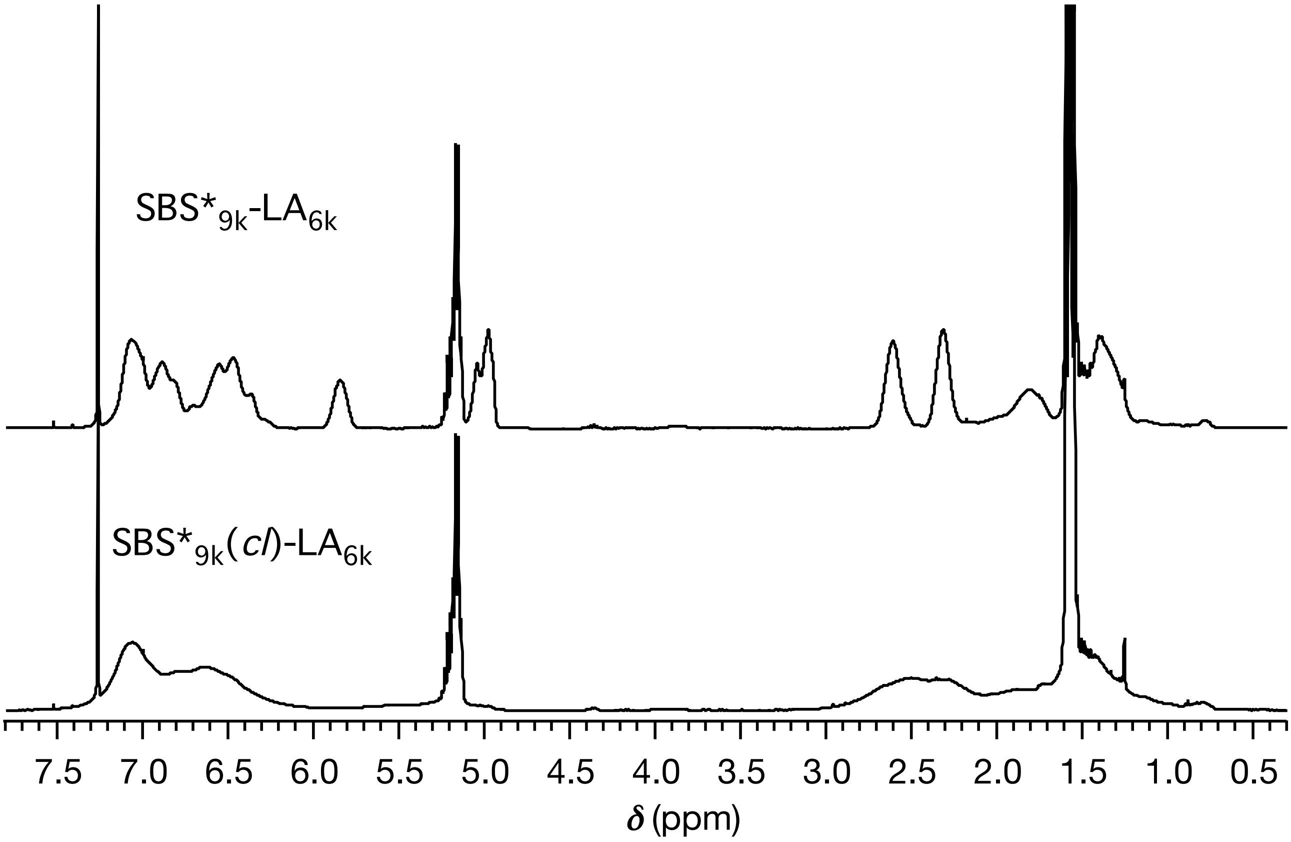


Figure S8. ^{1}H NMR spectra of SBS$^*_{9k}$–LA$_{6k}$ (upper) and SBS$^*_{9k}$(cl)–LA$_{6k}$ (lower) in $CDCl_3$ (400 MHz).

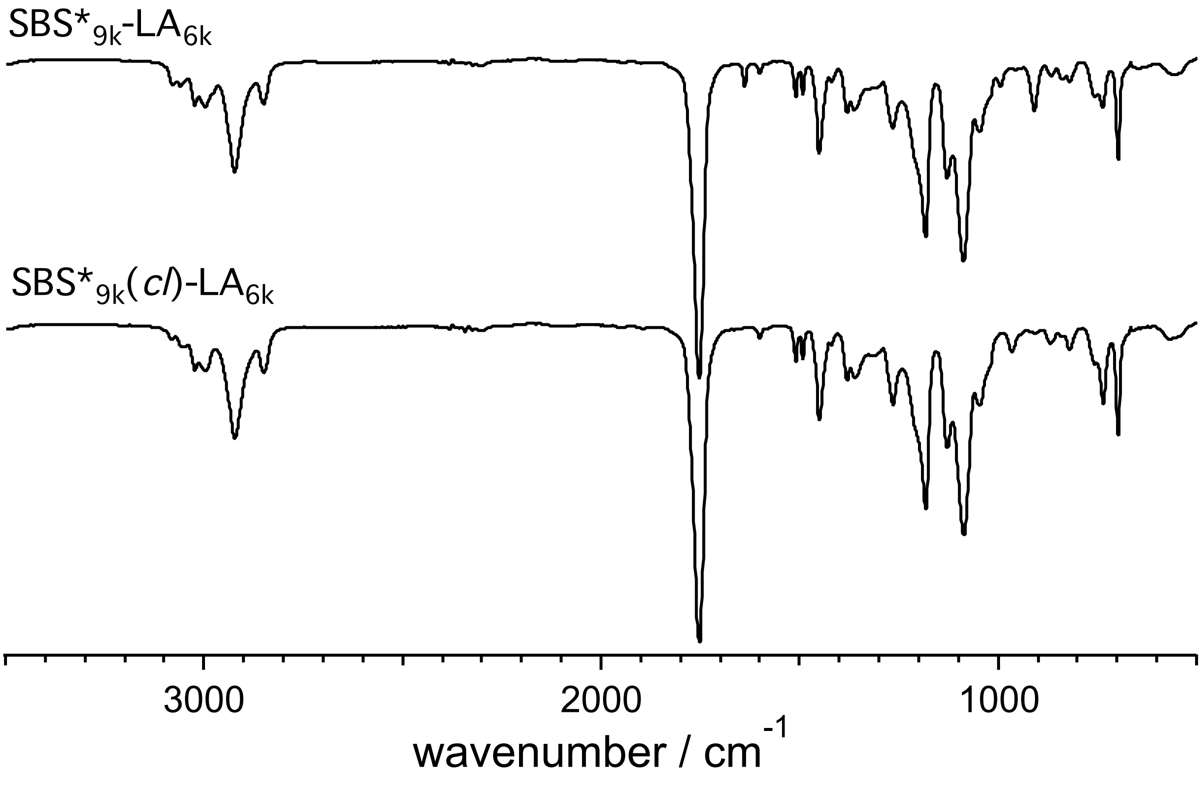


Figure S9. IR spectra of SBS$^*_{9k}$–LA$_{6k}$ (upper) and SBS$^*_{9k}$(cl)–LA$_{6k}$ (lower).

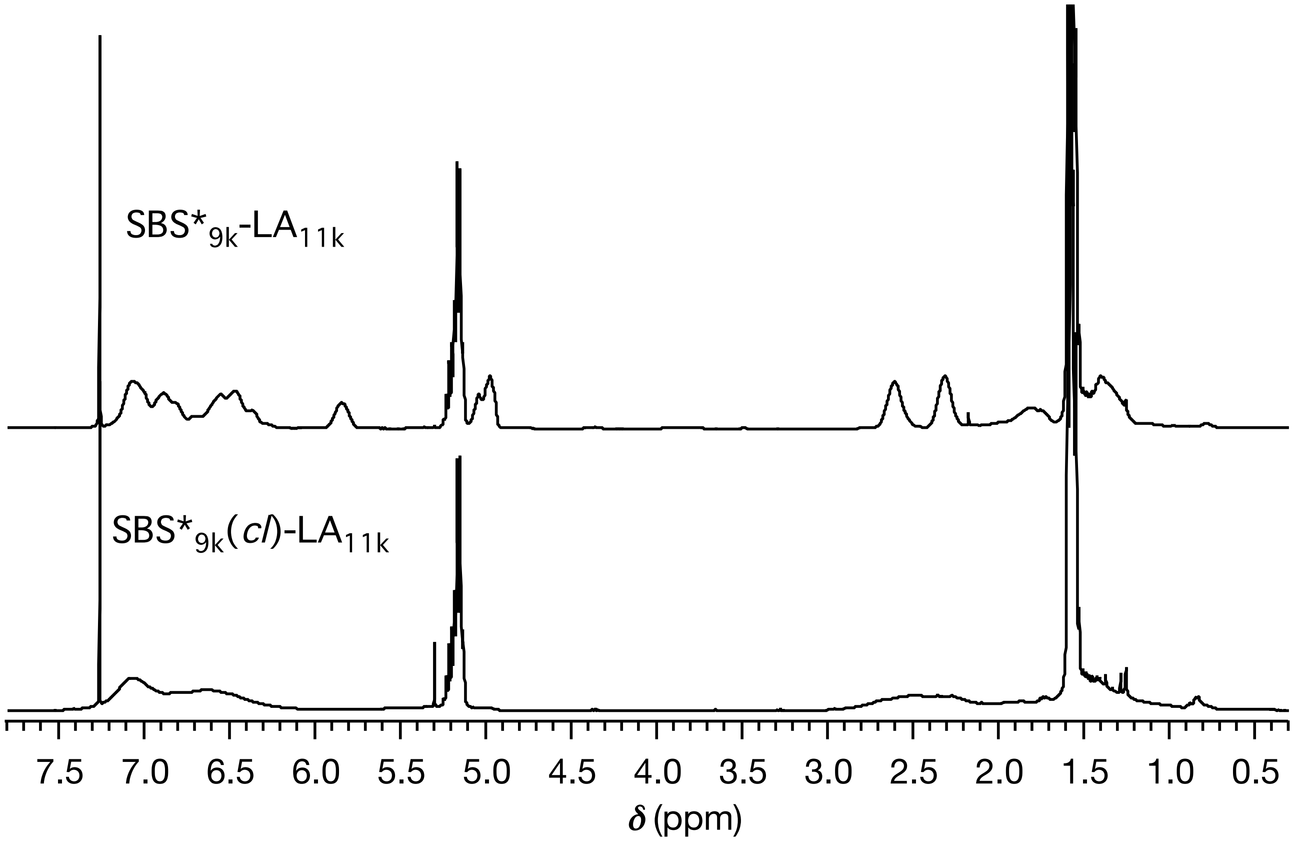


Figure S10. ^{1}H NMR spectra of SBS$^*_{9k}$–LA$_{11k}$ (upper) and SBS$^*_{9k}$(cl)–LA$_{11k}$ (lower) in CDCl$_3$ (400 MHz).

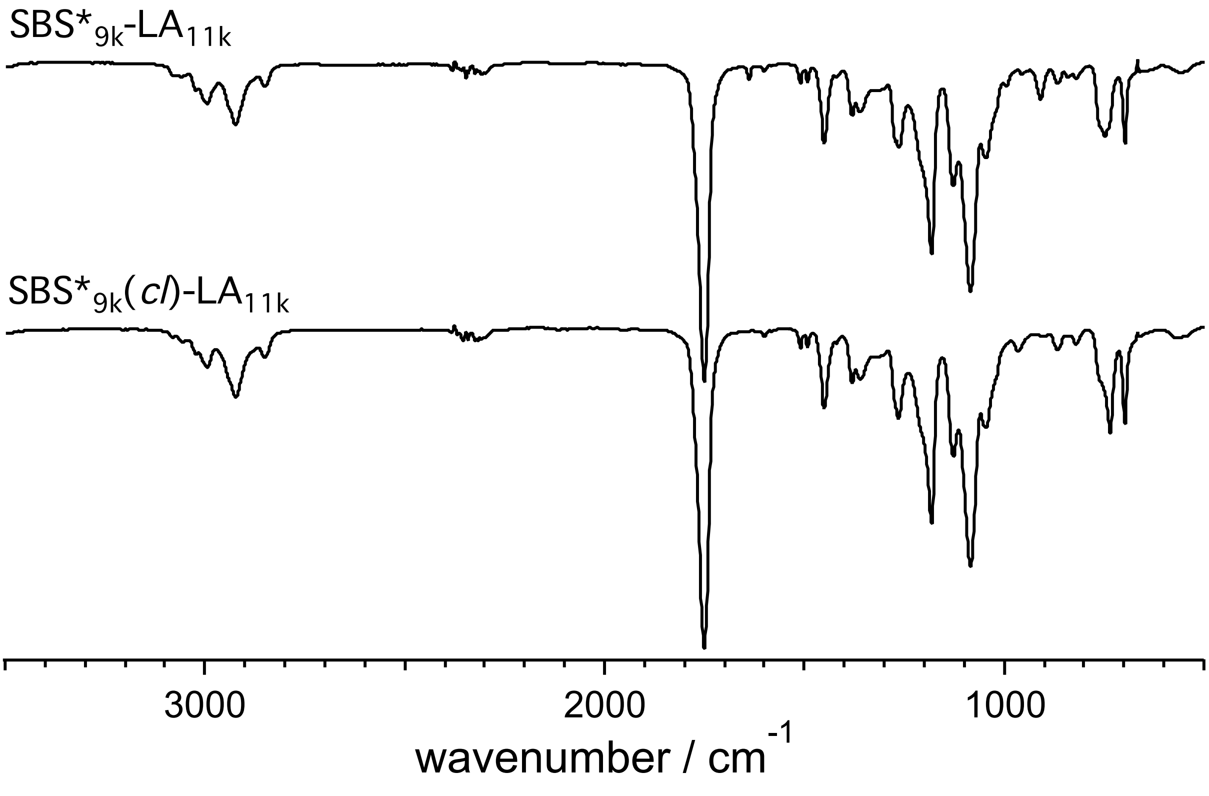


Figure S11. IR spectra of SBS$^*_{9k}$–LA$_{11k}$ (upper) and SBS$^*_{9k}$(cl)–LA$_{11k}$ (lower).

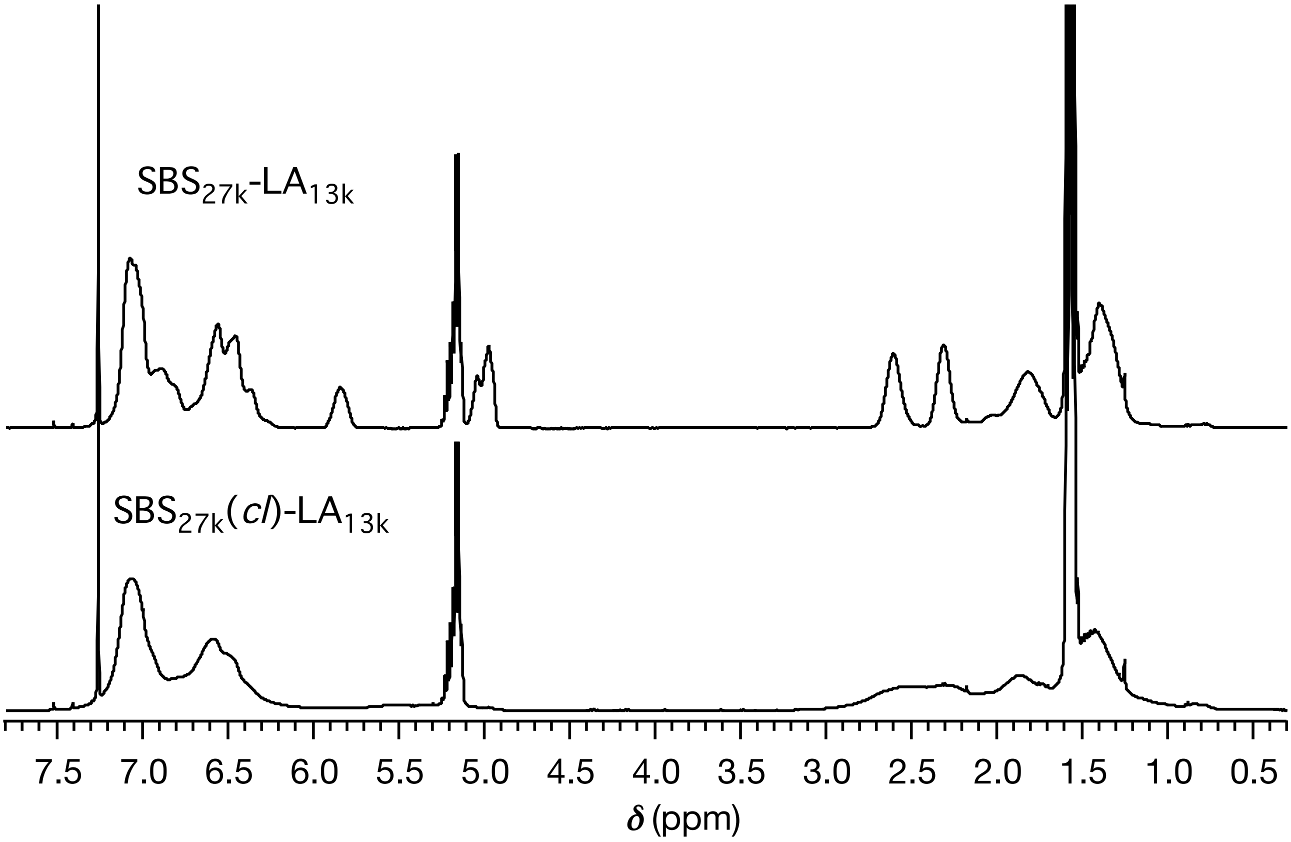


Figure S12. ^{1}H NMR spectra of SBS_{27k}–LA_{13k} (upper) and SBS_{27k}(*cl*)–LA_{13k} (lower) in $CDCl_3$ (400 MHz).

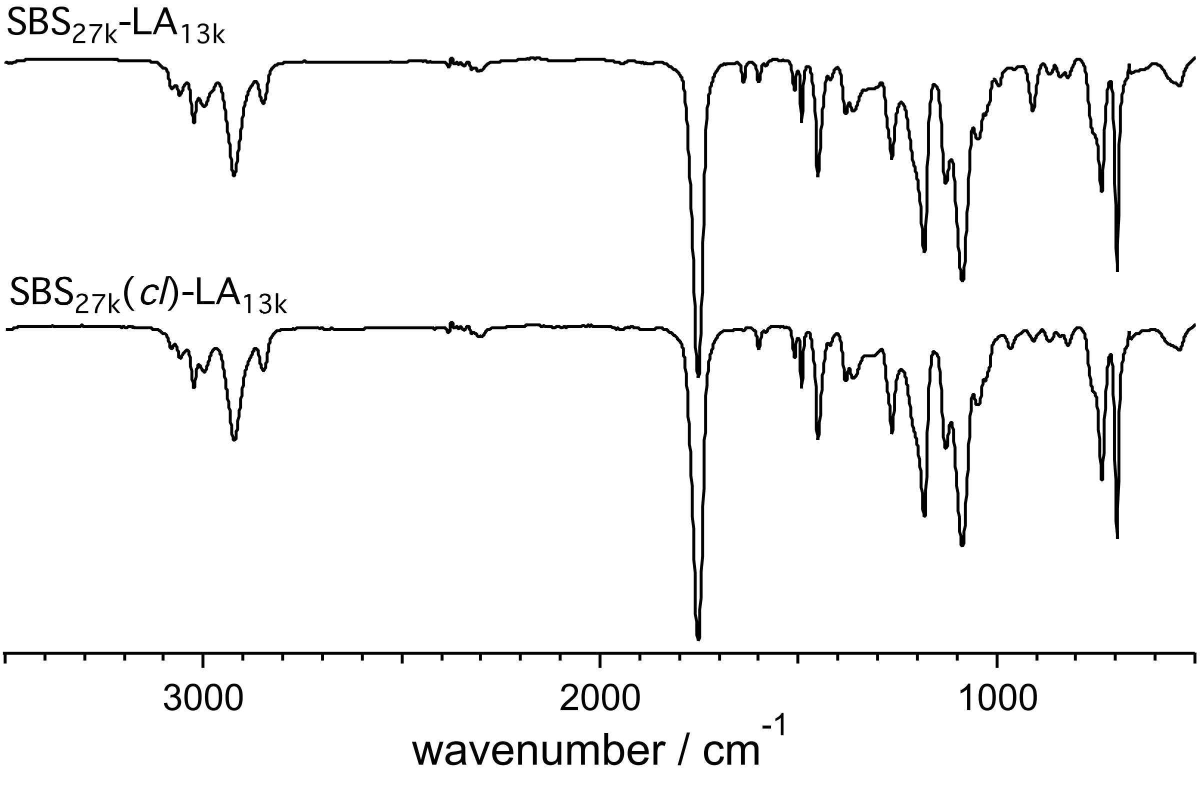


Figure S13. IR spectra of SBS_{27k}–LA_{13k} (upper) and SBS_{27k}(*cl*)–LA_{13k} (lower).

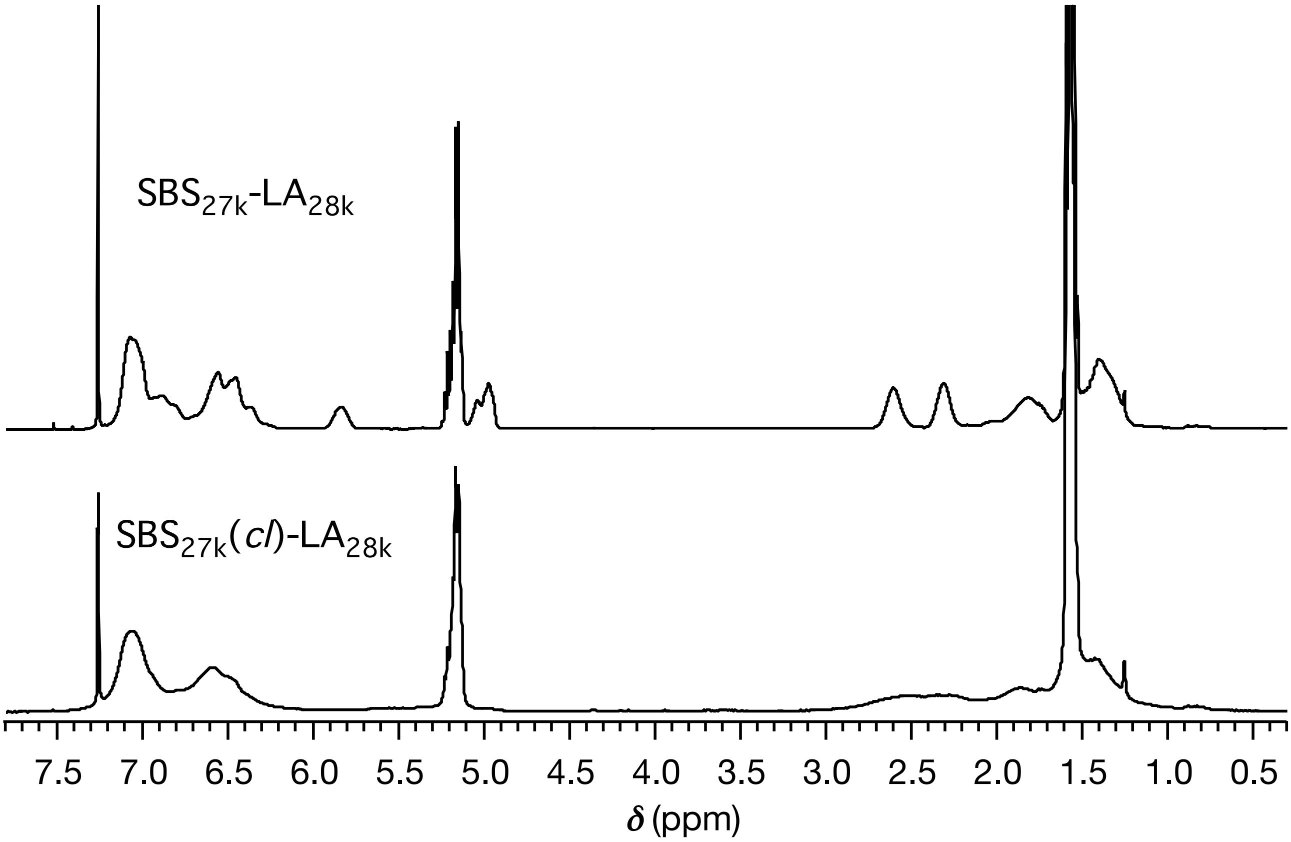


Figure S14. ^{1}H NMR spectra of SBS_{27k}–LA_{28k} (upper) and SBS_{27k}(*cl*)–LA_{28k} (lower) in $CDCl_3$ (400 MHz).

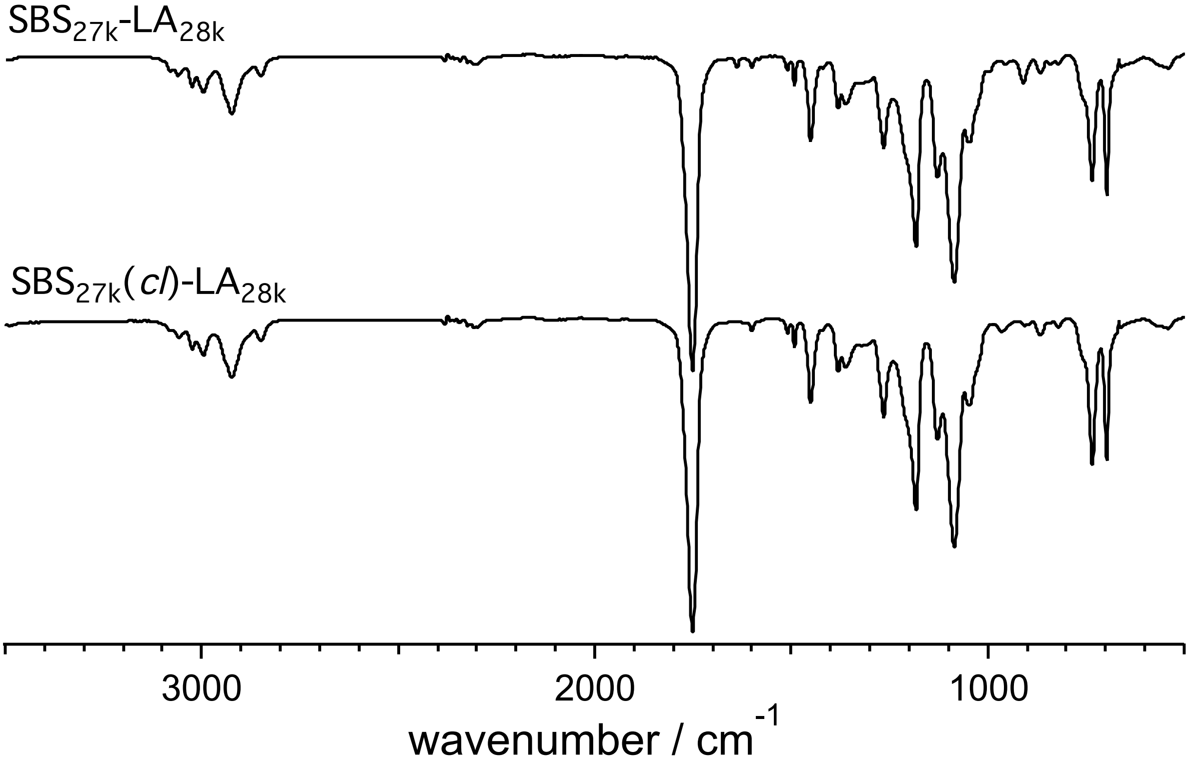


Figure S15. IR spectra of SBS_{27k}–LA_{28k} (upper) and SBS_{27k}(*cl*)–LA_{28k} (lower).

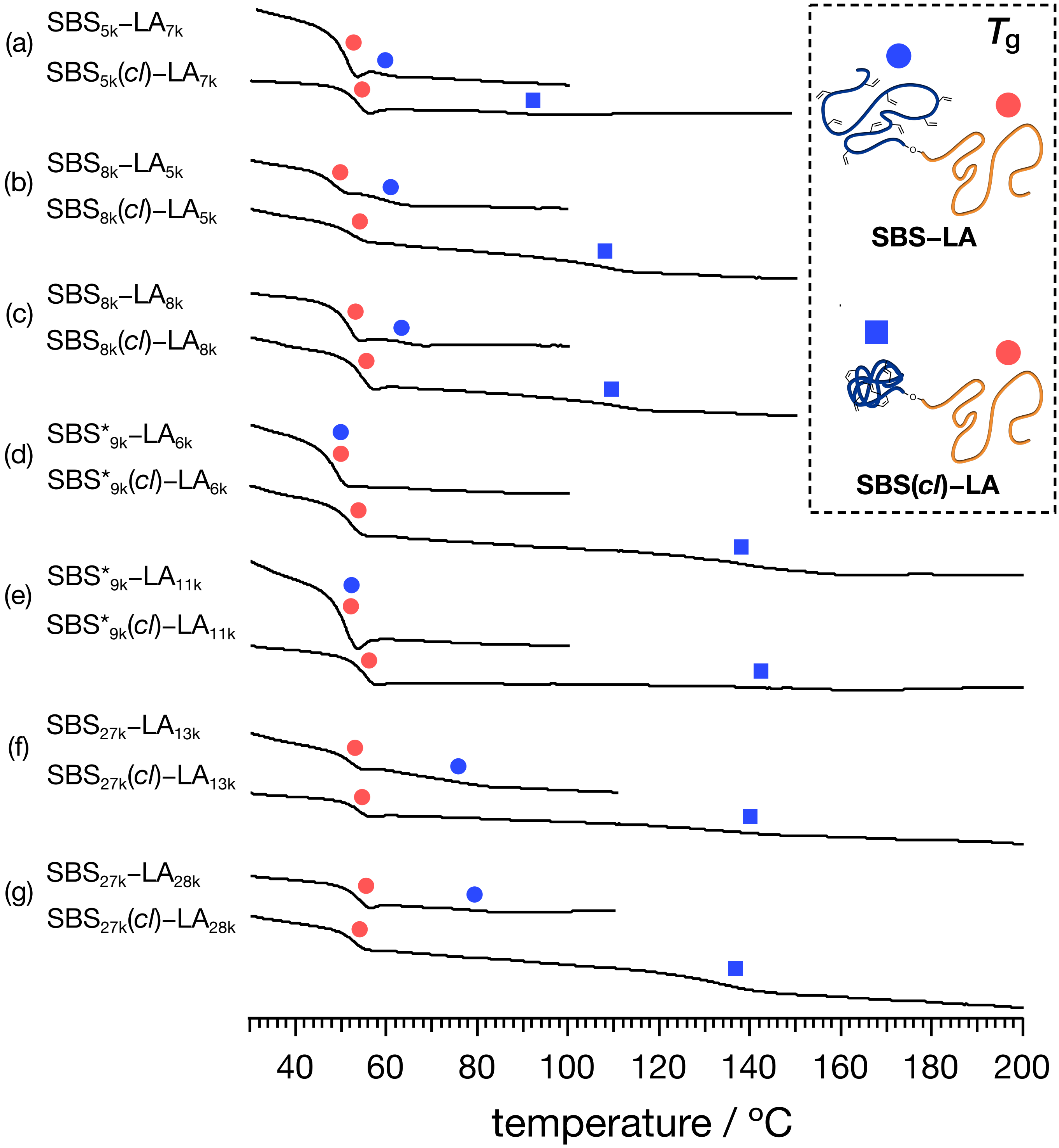


Figure S16. DSC curves during the 2nd heating process of (a) SBS$_{5k}$–LA$_{7k}$ and SBS$_{5k}$(*cl*)–LA$_{7k}$, (b) SBS$_{8k}$–LA$_{5k}$ and SBS$_{8k}$(*cl*)–LA$_{5k}$, (c) SBS$_{8k}$–LA$_{8k}$ and SBS$_{8k}$(*cl*)–LA$_{8k}$, (d) SBS$^{*}_{9k}$–LA$_{6k}$ and SBS$^{*}_{9k}$(*cl*)–LA$_{6k}$, (e) SBS$^{*}_{9k}$–LA$_{11k}$ and SBS$^{*}_{9k}$(*cl*)–LA$_{11k}$, (f) SBS$_{27k}$–LA$_{13k}$ and SBS$_{27k}$(*cl*)–LA$_{13k}$, and (g) SBS$_{27k}$–LA$_{28k}$ and SBS$_{27k}$(*cl*)–LA$_{28k}$. The red circle, blue circle, and blue square denote the T_g of LA, SBS, and SBS(*cl*) blocks, respectively.

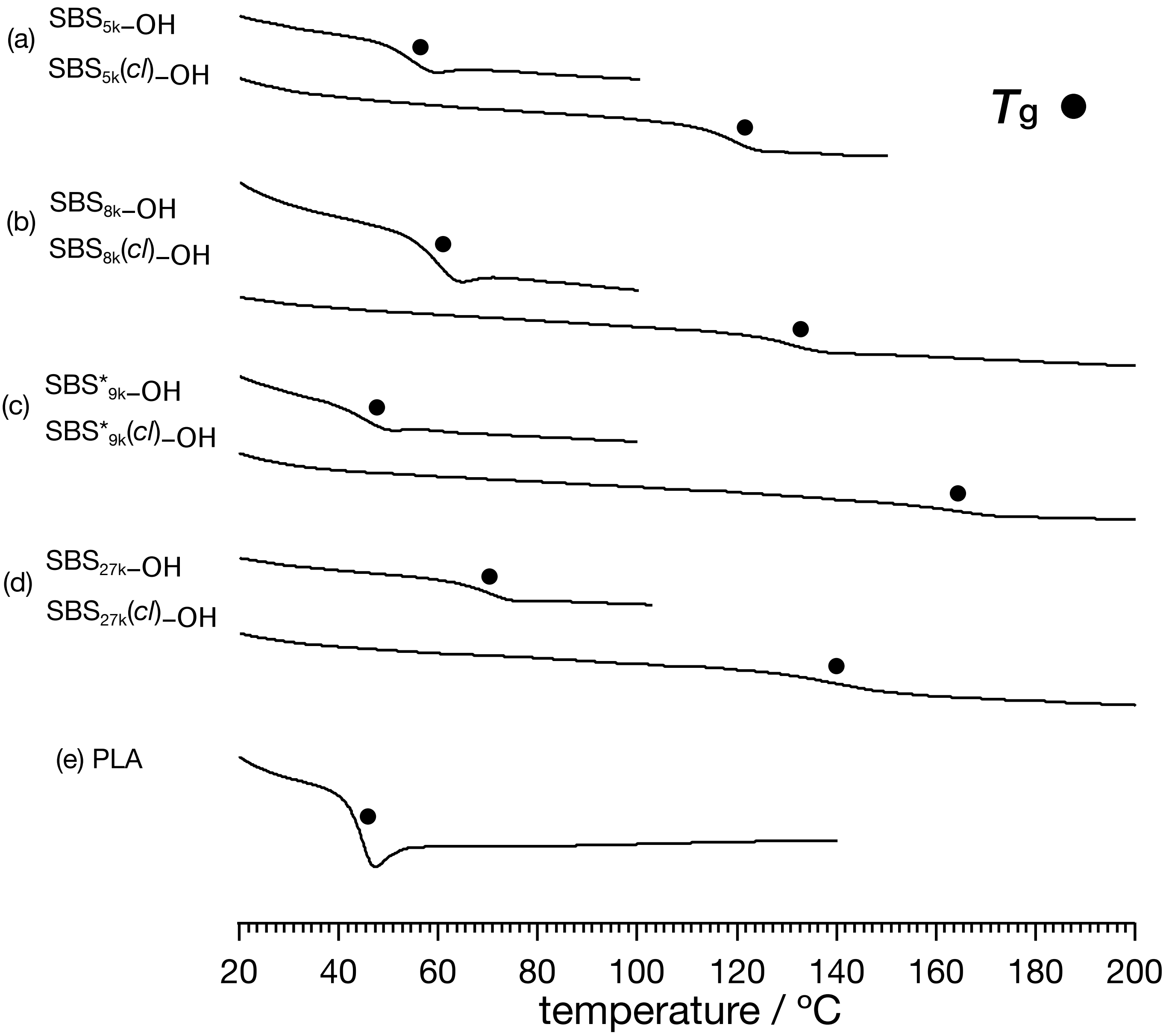


Figure S17. DSC curves during the 2nd heating process of (a) SBS_{5k}–OH and SBS_{5k}(*cl*)–OH, (b) SBS_{8k}–OH and SBS_{8k}(*cl*)–OH, (c) SBS^{*}_{9k}–OH and SBS^{*}_{9k}(*cl*)–OH, (d) SBS_{27k}–OH and SBS_{27k}(*cl*)–OH, and (g) PLA. The black circle denotes the T_g of each polymer.

Table S1 Characterization data for SBS–OHs, SBS(*cl*)–OHs, and PLA

sample name	conv.$_{\text{olefin}}$ (%)^a	$M_{\text{n,SEC}}$^{b}	$M_{\text{p,SEC}}$^{b}	$Đ^b$	$\langle G\rangle^c$	T_g (°C)^d
SBS_{5k}–OH		4,730	5,360	1.08		55
SBS_{5k}(*cl*)–OH	92	4,050	4,250	1.10	0.79	119
SBS_{8k}–OH		6,910	7,290	1.04		60
SBS_{8k}(*cl*)–OH	87	5,300	5,480	1.05	0.75	130
SBS^{*}_{9k}–OH		8,250	8,510	1.04		46
SBS^{*}_{9k}(*cl*)–OH	83	5,740	5,700	1.05	0.70	167
SBS_{27k}–OH		19,600	20,100	1.02		71
SBS_{27k}(*cl*)–OH	91	11,700	11,600	1.04	0.58	142
PLA		10,700		1.04		45

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC in THF using polystyrene standards. [c] Calculated by $M_{\text{p,SEC}}$(SBS(*cl*)–OH)/$M_{\text{p,SEC}}$(SBS–OH). [d] Determined by DSC at the heating rate of 10 °C min^{-1}.

References

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