

Electronic Supplementary Information

Installation of adamantyl group in polystyrene-*block*-poly(methyl methacrylate) via Friedel–Crafts alkylation to modulate microphase-separated morphology and dimension

Takuya Isono,^{1,*} Ema Baba,² Shunma Tanaka,² Ken Miyagi,³ Takahiro Dazai,³ Feng Li,¹ Takuya Yamamoto,¹ Kenji Tajima,¹ Toshifumi Satoh^{1,*}

¹*Faculty of Engineering, Hokkaido University, Sapporo 060-8628, Japan.*

²*Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan.*

³*Lithography Process Materials Research Group, R&D Department, Tokyo Ohka Kogyo Co., Ltd., Kanagawa 253-0114, Japan.*

Experimental

Materials. Trifluoromethanesulfonic acid (triflic acid), 1-adamantanol (AD-OH), 2-methyl-2-adamantanol (MeAd-OH), and 3,5-dimethyl-1-adamantanol (Me₂Ad-OH) were purchased from Tokyo Chemical Industry Co., Ltd. (TCI, Tokyo, Japan) and used as received. 3,5,7-Trimethyladamantanol was purchased from AA Blocks and used as received. PS_{10k} and PMMA_{10k} homopolymers were purchased from Sigma and Polymer Laboratories, respectively, and used as received. Commercially available dry dichloromethane (Kanto Chemical Co., Inc., >99.5%, water content, <0.001%) was further purified using an MBRAUN MB-SPS Compact solvent purification system equipped with a MB-KOL-A column, which was then directly used for the reactions. The anionically synthesized polystyrene-*block*-poly(methyl methacrylate)s (PS-*b*-PMMA)s were provided in the forms of propylene glycol methyl ether acetate solutions by Tokyo Ohka Kogyo Co., Ltd., which were precipitated in methanol and dried under high vacuum prior to use. In this study, symmetric PS-*b*-PMMA with three different molecular weights were used: PS_{14k}-*b*-PMMA_{14k} (28 kg mol⁻¹, $\bar{D} = 1.02$; St/MMA = 51/49 (mol%/mol%)), PS_{10k}-*b*-PMMA_{10k} (20 kg mol⁻¹, $\bar{D} = 1.02$; St/MMA = 51/49 (mol%/mol%)), PS_{4.2k}-*b*-PMMA_{4.3k} (8.5 kg mol⁻¹, $\bar{D} = 1.03$ St/MMA = 49/51 (mol%/mol%)).

Instruments. An MBRAUN stainless steel glovebox equipped with a gas purification system (molecular sieves and copper catalyst) was operated under a dry argon atmosphere (H₂O, O₂ <0.1 ppm). The moisture and oxygen contents in the glovebox were monitored by an MB-MO-SE 1 moisture probe and an MB-OX-SE 1 oxygen probe, respectively. The solvent used for the reaction (CH₂Cl₂)

was purified using an MBRAUN solvent purification system (MB SPS COMPACT) consisting of an activated alumina column and an activated copper catalyst column. The number-average molecular weight ($M_{n,SEC}$) and dispersity (D) of the polymers were calculated on the basis of a polystyrene calibration. The size exclusion chromatography (SEC) was performed at 40 °C in THF (flow rate, 1.0 mL min⁻¹) using a Shodex GPC-101 gel permeation chromatography system (Shodex DU-2130 dual pump, Shodex RI-71 reflective index detector, and Shodex ERC-3125SN 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, 8 mm × 300 mm). The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded using a JEOL ECS400 spectrometer. The inverse-gated decoupling ¹³C NMR (100 MHz) spectra were recorded using a 25 wt% sample (in CDCl₃) at 30 °C with a following condition: pulse angle, 45°; acquisition time, 2.0 s; relaxation delay under NOE-eliminated condition, 7.0 s; and scan time, 5000. The weight loss temperature of the polymer samples was measured using a Hitachi High-Tech Science STA200RV under nitrogen atmosphere with the heating rate of 10 °C min⁻¹. The glass transition temperature of the polymer samples was measured from 0 up to 300 °C during the second heating by a Hitachi High-Tech Science DSC7000X differential scanning calorimeter under a nitrogen atmosphere with the heating rate of 10 °C min⁻¹ and cooling rate 20 °C min⁻¹. Small-angle X-ray scattering (SAXS) experiments for bulk samples were performed at the BL-6A beamline of the Photon Factory of High Energy Accelerator Research Organization (KEK, Tsukuba, Japan). The X-ray wavelength and exposure time were 1.50 Å (8.27 keV) and 60 s, respectively. A PILATUS3 1M

(Dectris Ltd., Switzerland) detector, with 981×1043 pixels at a pixel size of $172 \times 172 \mu\text{m}$ and a counter depth of 20 bits (1,048,576 counts), was used for data acquisition. The sample-to-detector distance was calibrated using the scattering patterns of silver behenate (Nagara Science Co., Ltd., Japan). The SAXS data were acquired under ambient conditions, and 1D profiles were obtained as plots of scattering intensity as functions of scattering vector (q), where $q = (4\pi/\lambda)\sin(\theta/2)$ (λ , wave length; θ , scattering angle). Bright-field TEM images of the thin-sliced bulk samples were obtained using a JEM-2100 electron microscope (JEOL) with an accelerating voltage of 80 kV. The thermally annealed bulk samples were embedded in a photocurable resin (Toagosei Co., Ltd., Alonix D-800). Then, thin slices of the samples with a thickness of 40-50 nm were obtained using a Leicca Ultracut S ultramicrotome equipped with a diamond knife (DiATOME, Ultra 35°) at room temperature, and a piece of the thin slice was transferred to copper grids. The thin slices were visualized by TEM after staining with RuO₄ vapor.

Synthesis details

Synthesis of Ad-PS-*b*-PMMA: General procedure for the Friedel-Crafts alkylation reaction is as follows (Method A): In an Ar-filled glovebox, PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and Ad-OH (112 mg, 0.735 mmol, 0.50 eq.) were placed in a Schlenk flask and dissolved in CH₂Cl₂ (10 mL). After sealing with a rubber septum, the Schlenk flask was taken out from the glovebox. Triflic acid solution (1.10 mmol, 0.75 eq. in 10 mL CH₂Cl₂) was added into the polymer

solution to start the reaction. The reaction mixture was stirred at room temperature for 1 h, after which the solution was poured into methanol to precipitate the polymer. The resulting precipitate was filtered and dried under vacuum to give Ad-PS_{10k}-*b*-PMMA_{10k} as a white powder (381 mg, 92.5 %).

Synthesis of MeAd-PS-*b*-PMMA: The Method A was used for the reaction of PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and MeAd-OH (122 mg, 0.735 mmol, 0.50 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (1.10 mmol, 0.75 eq. in 10 mL CH₂Cl₂), to give MeAd-PS_{10k}-*b*-PMMA_{10k} as a white powder (294 mg, 69.6%).

Synthesis of Me₂Ad-PS-*b*-PMMA: The Method A was used for the reaction of PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (132 mg, 0.735 mmol, 0.50 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (1.10 mmol, 0.75 eq. in 10 mL CH₂Cl₂), to give Me₂Ad-PS_{10k}-*b*-PMMA_{10k} as a white powder (390 mg, 90.1%). The extent of the reaction was calculated to be 0.41 based on the inverse-gated ¹³C NMR analysis, so that the sample code of this samples is Me₂Ad_{0.41}-PS_{10k}-*b*-PMMA_{10k}. The aliquot of the product was subjected to preparative SEC (in CHCl₃) to remove the high-molecular-weight byproduct, giving highly pure Me₂Ad_{0.41}-PS_{10k}-*b*-PMMA_{10k} ($M_{n,SEC} = 20,900 \text{ gmol}^{-1}$, $D = 1.02$).

A series of Me₂Ad-PS-*b*-PMMA with varied *f* and PS-*b*-PMMA molecular weight was

prepared by following the sample protocol with the modification of the amount of Me₂Ad-OH and triflic acid:

The Method A was used for the reaction of PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (26.5mg, 0.147 mmol, 0.10 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (19.5 μL, 0.220 mmol, 0.15 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.07}-PS_{10k}-*b*-PMMA_{10k} as a white powder ($M_{n,SEC} = 19,300 \text{ gmol}^{-1}$, $D = 1.02$. yield: 300.7 mg, 92.1 %).

The Method A was used for the reaction of PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (53.0 mg, 0.294 mmol, 0.20 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (39.0 μL, 0.440 mmol, 0.30 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.20}-PS_{10k}-*b*-PMMA_{10k} as a white powder ($M_{n,SEC} = 20,300 \text{ gmol}^{-1}$, $D = 1.03$. yield: 299.5 mg, 84.9 %).

The Method A was used for the reaction of PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (DMA-OH; 79.5 mg, 0.44 mmol, 0.30 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (58.5 μL, 0.661 mmol, 0.45 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.29}-PS_{10k}-*b*-PMMA_{10k} as a white powder ($M_{n,SEC} = 21,600 \text{ gmol}^{-1}$, $D = 1.07$. yield: 330.6 mg, 87.1 %).

The Method A was used for the reaction of PS_{10k}-*b*-PMMA_{10k} (300 mg, 1.47 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (108.9 mg, 0.588 mmol, 0.40 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (78.0 μL, 0.881 mmol, 0.60 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.38}-PS_{10k}-*b*-PMMA_{10k} as a white powder ($M_{n,SEC} = 24,200 \text{ gmol}^{-1}$, $D = 1.35$. yield: 337.5 mg, 83.1 %).

The Method A was used for the reaction of PS_{14k}-*b*-PMMA_{14k} ($M_{n,SEC} = 26,100 \text{ gmol}^{-1}$, $D =$

1.02, 300 mg, 1.45 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (26.2 mg, 0.145 mmol, 0.10 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (19.3 μL, 0.218 mmol, 0.15 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.08}-PS_{14k}-*b*-PMMA_{14k} as a white powder ($M_{n,SEC} = 26,600 \text{ gmol}^{-1}$, $D = 1.02$. yield: 282.4 mg, 86.6 %)

The Method A was used for the reaction of PS_{14k}-*b*-PMMA_{14k} (300 mg, 1.45 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (52.5 mg, 0.291 mmol, 0.20 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (38.6 μL, 0.436 mmol, 0.30 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.14}-PS_{14k}-*b*-PMMA_{14k} as a white powder ($M_{n,SEC} = 28,000 \text{ gmol}^{-1}$, $D = 1.03$. yield: 315.5 mg, 89.5 %)

The Method A was used for the reaction of PS_{14k}-*b*-PMMA_{14k} (300 mg, 1.45 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (78.7 mg, 0.436 mmol, 0.30 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (57.9 μL, 0.655 mmol, 0.45 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.28}-PS_{14k}-*b*-PMMA_{14k} as a white powder ($M_{n,SEC} = 30,300 \text{ gmol}^{-1}$, $D = 1.09$. yield: 350.0 mg, 92.4 %)

The Method A was used for the reaction of PS_{4.2k}-*b*-PMMA_{4.3k} ($M_{n,SEC} = 9,000 \text{ gmol}^{-1}$, $D = 1.03$, 300 mg, 1.41 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (25.4 mg, 0.141 mmol, 0.10 eq.) in CH₂Cl₂ (10 mL) with triflic acid solution (18.7 μL, 0.211 mmol, 0.15 eq. in 10 mL CH₂Cl₂), to give Me₂Ad_{0.09}-PS_{4.2k}-*b*-PMMA_{4.3k} as a white powder ($M_{n,SEC} = 9,300 \text{ gmol}^{-1}$, $D = 1.03$. yield: 277.0 mg, 85.1 %)

The Method A was used for the reaction of PS_{4.2k}-*b*-PMMA_{4.3k} (300 mg, 1.41 mmol of styrene units, 1.00 eq.) and Me₂Ad-OH (76.3 mg, 0.423 mmol, 0.30 eq.) in CH₂Cl₂ (10 mL) with triflic acid

solution (56.2 μL , 0.635 mmol, 0.45 eq. in 10 mL CH_2Cl_2), to give $\text{Me}_2\text{Ad}_{0.41}\text{-PS}_{4.2\text{k}}\text{-}b\text{-PMMA}_{4.3\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 10,200 \text{ gmol}^{-1}$, $D = 1.05$. yield: 331.5 mg, 88.1 %).

The Method A was used for the reaction of $\text{PS}_{4.2\text{k}}\text{-}b\text{-PMMA}_{4.3\text{k}}$ (300 mg, 1.41 mmol of styrene units, 1.00 eq.) and $\text{Me}_2\text{Ad-OH}$ (152.7 mg, 0.847 mmol, 0.60 eq.) in CH_2Cl_2 (10 mL) with triflic acid solution (112.4 μL , 1.27 mmol, 0.90 eq. in 10 mL CH_2Cl_2), to give $\text{Me}_2\text{Ad}_{0.59}\text{-PS}_{4.2\text{k}}\text{-}b\text{-PMMA}_{4.3\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 13,430 \text{ gmol}^{-1}$, $D = 1.36$. yield: 391.6 mg, 86.5 %).

Synthesis of $\text{Me}_3\text{Ad-PS-}b\text{-PMMA}$: $\text{Me}_3\text{Ad-OH}$ was used instead of $\text{Me}_2\text{Ad-OH}$ to synthesize the modified $\text{PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ with high f value.

The Method A was used for the reaction of $\text{PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ (150 mg, 0.735 mmol of styrene units, 1.00 eq.) and $\text{Me}_3\text{Ad-OH}$ (71.5 mg, 0.368 mmol, 0.50 eq.) in CH_2Cl_2 (5 mL) with triflic acid solution (48.8 μL , 0.553 mmol, 0.75 eq. in 5 mL CH_2Cl_2), to give $\text{Me}_3\text{Ad}_{0.35}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 22,200 \text{ gmol}^{-1}$, $D = 1.02$. yield: 216 mg, 97.7 %).

The Method A was used for the reaction of $\text{PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ (150 mg, 0.735 mmol of styrene units, 1.00 eq.) and $\text{Me}_3\text{Ad-OH}$ (85.8 mg, 0.441 mmol, 0.60 eq.) in CH_2Cl_2 (5 mL) with triflic acid solution (58.5 μL , 0.663 mmol, 0.90 eq. in 5 mL CH_2Cl_2), to give $\text{Me}_3\text{Ad}_{0.63}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 24,000 \text{ gmol}^{-1}$, $D = 1.06$. yield: 228 mg, 96.5 %).

The Method A was used for the reaction of $\text{PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ (150 mg, 0.735 mmol of styrene units, 1.00 eq.) and $\text{Me}_3\text{Ad-OH}$ (114.4 mg, 0.588 mmol, 0.80 eq.) in CH_2Cl_2 (5 mL) with triflic acid

solution (78.0 μL , 0.884 mmol, 1.20 eq. in 5 mL CH_2Cl_2), to give $\text{Me}_3\text{Ad}_{0.86}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 25,400 \text{ g mol}^{-1}$, $D = 1.06$. yield: 224 mg, 84.6 %).

Synthesis of $\text{Me}_2\text{Ad-PS}_{10\text{k}}$. $\text{PS}_{10\text{k}}$ ($M_{n,\text{SEC}} = 9,100 \text{ g mol}^{-1}$, $D = 1.03$) was used instead of $\text{PS-}b\text{-PMMA}$ to synthesized $\text{Me}_2\text{Ad-PS}_{10\text{k}}$ for the etching tests.

The Method A was used for the reaction of $\text{PS}_{10\text{k}}$ (76.5 mg, 0.735 mmol of styrene units, 1.00 eq.) and $\text{Me}_2\text{Ad-OH}$ (26.5 mg, 0.147 mmol, 0.20 eq.) in CH_2Cl_2 (5 mL) with triflic acid solution (19.5 μL , 0.221 mmol, 0.30 eq. in 5 mL CH_2Cl_2), to give $\text{Me}_2\text{Ad}_{0.18}\text{-PS}_{10\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 10,200 \text{ g mol}^{-1}$, $D = 1.06$. yield: 87 mg, 87.0 %).

The Method A was used for the reaction of $\text{PS}_{10\text{k}}$ (76.5 mg, 0.735 mmol of styrene units, 1.00 eq.) and $\text{Me}_2\text{Ad-OH}$ (66.3 mg, 0.368 mmol, 0.50 eq.) in CH_2Cl_2 (5 mL) with triflic acid solution (48.8 μL , 0.553 mmol, 0.75 eq. in 5 mL CH_2Cl_2), to give $\text{Me}_2\text{Ad}_{0.62}\text{-PS}_{10\text{k}}$ as a white powder ($M_{n,\text{SEC}} = 13,400 \text{ g mol}^{-1}$, $D = 1.29$. yield: 115 mg, 85.0 %).

Etching Test

Thin films of $\text{Me}_2\text{Ad-PS}_{10\text{k}}$, $\text{PS}_{10\text{k}}$, and $\text{PMMA}_{10\text{k}}$ were prepared by spin-coating the THF polymer solutions onto a silicon wafer (500 rpm, 60 s). The refractometry confirmed the film thickness of around 230 nm. These thin films ($n = 3$ for each condition) were subjected to O_2 reactive ion etching ($\text{O}_2\text{-RIE}$) for 15, 30, 60, and 120 sec using a Samco RIE-10NRV with the RIE power of 50 W and O_2

flow rate of 50 sccm under 1.5 Pa. The etching depth was determined by comparing the film thickness before and after the O₂-RIE.

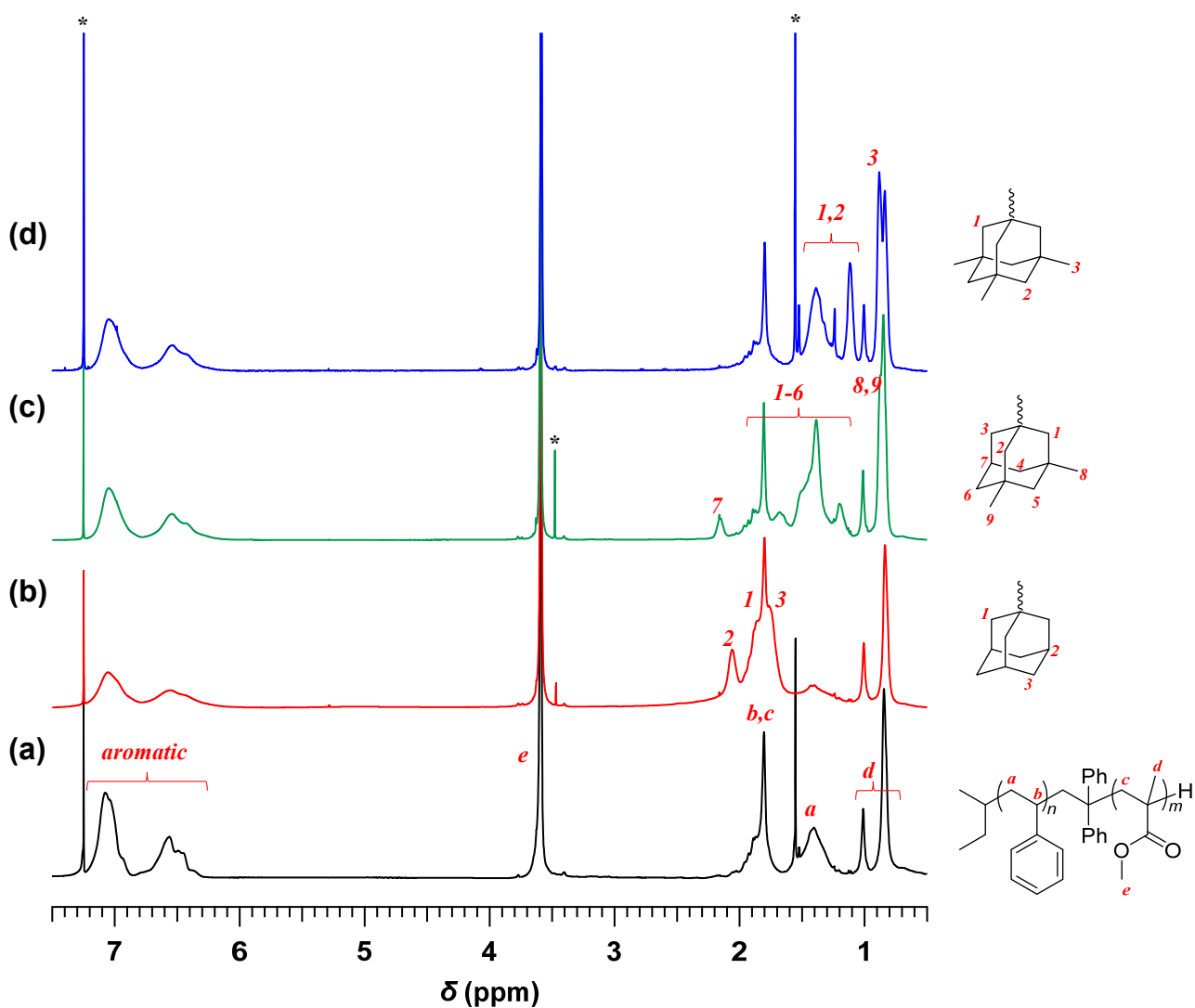


Figure S1. ^1H NMR spectra of (a) $\text{PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$, (b) $\text{Ad-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$, (c) $\text{Me}_2\text{Ad}_{0.41}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$, and (d) $\text{Me}_3\text{Ad}_{0.35}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ in CDCl_3 (400 MHz). The asterisks represent residual solvents.

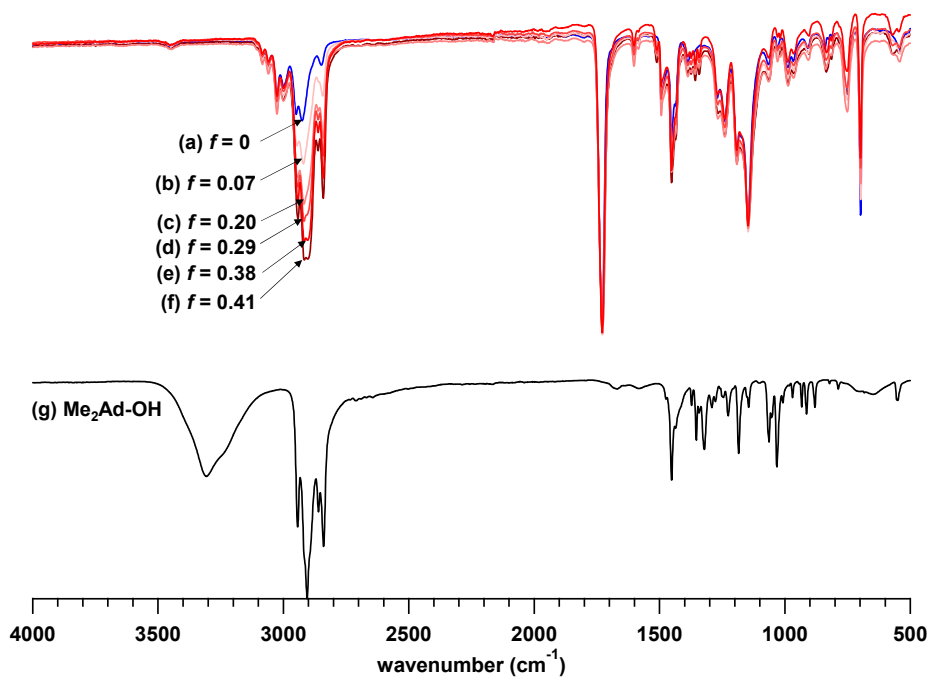


Figure S2. FT-IR spectra of $\text{Me}_2\text{Ad-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ with different f and $\text{Me}_2\text{Ad-OH}$.

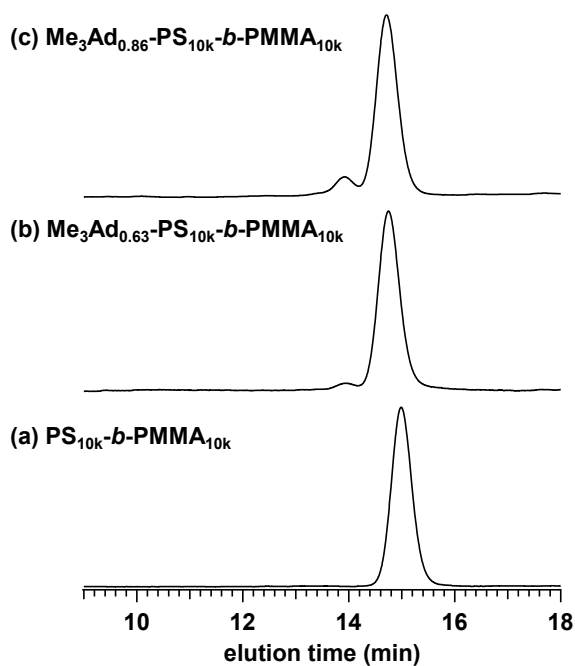


Figure S3. SEC traces of $\text{Me}_3\text{Ad-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ s and the corresponding $\text{PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ (eluent, THF; flow rate, 1.0 mL min^{-1}).

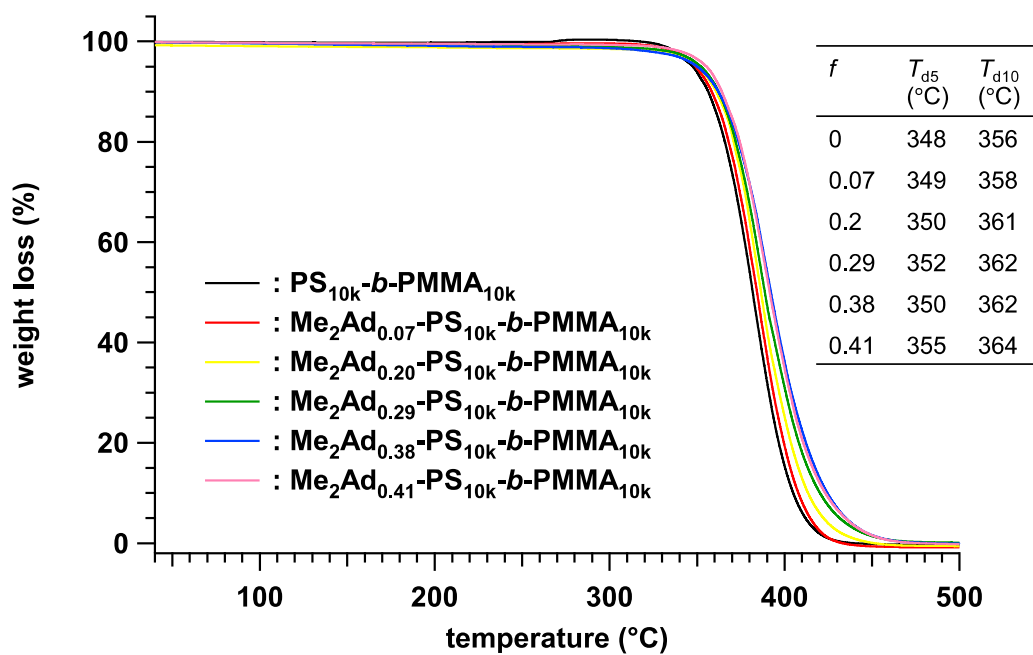


Figure S4. TGA profiles of $\text{Me}_2\text{Ad-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ with different f .

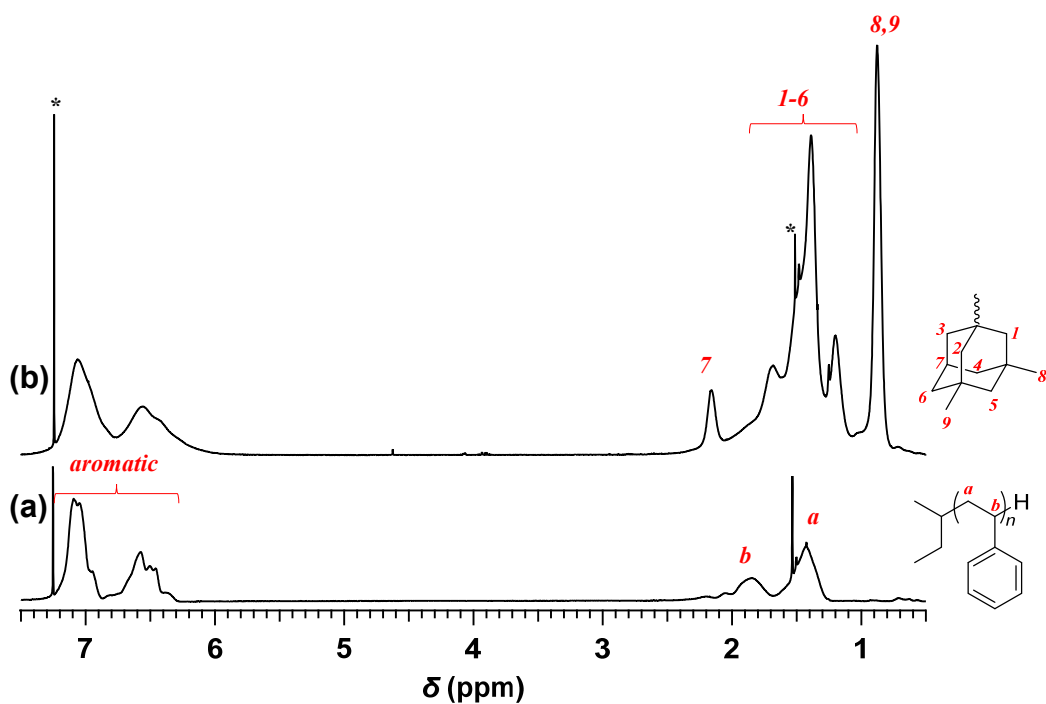


Figure S5. ^1H NMR spectra of (a) $\text{PS}_{10\text{k}}$ and (b) $\text{Me}_2\text{Ad}_{0.62}\text{-PS}_{10\text{k}}$ in CDCl_3 (400 MHz). The asterisks represent residual solvents.

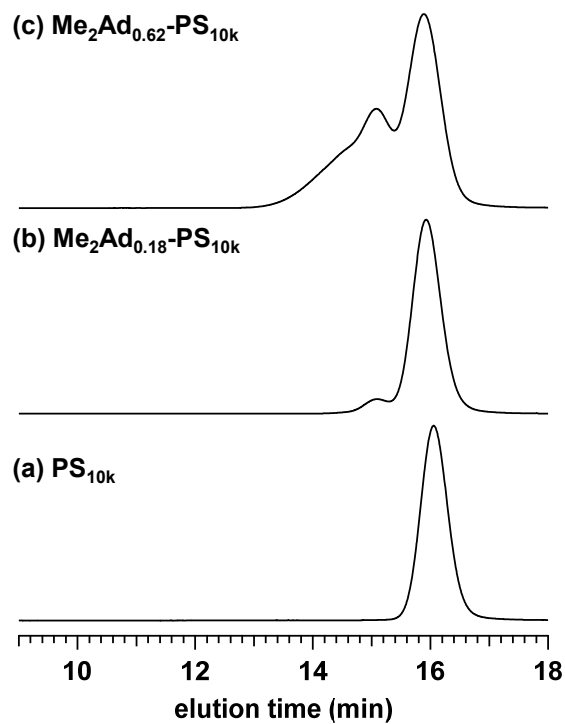


Figure S6. SEC traces of (a) PS_{10k}, (b) Me₂Ad_{0.18}-PS_{10k}, and (c) Me₂Ad_{0.62}-PS_{10k} (eluent, THF; flow rate, 1.0 mL min⁻¹).

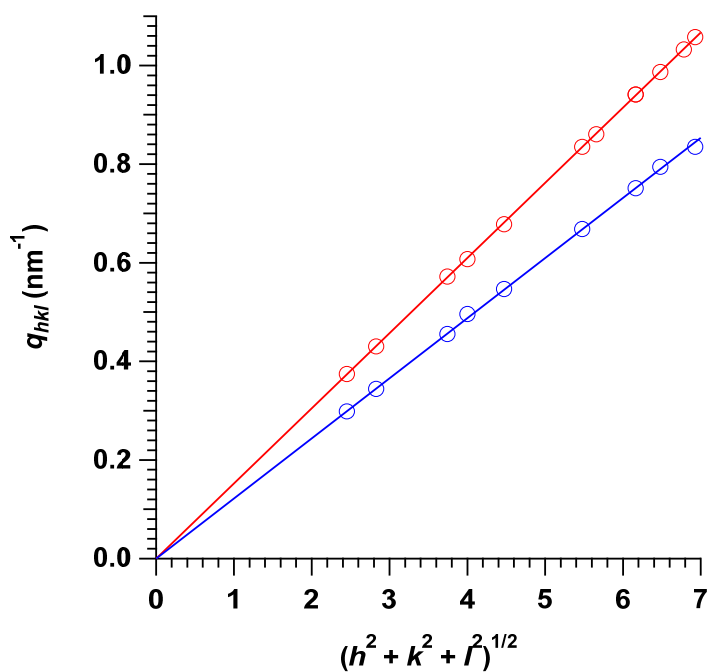


Figure S7. SAXS analysis for GYR-forming Me₂Ad_{0.29}-PS_{10k}-*b*-PMMA_{10k} and Me₂Ad_{0.28}-PS_{14k}-*b*-PMMA_{14k}. q_{hkl} versus $(h^2 + k^2 + l^2)^{1/2}$ plot based on the SAXS pattern validated the peak assignment.

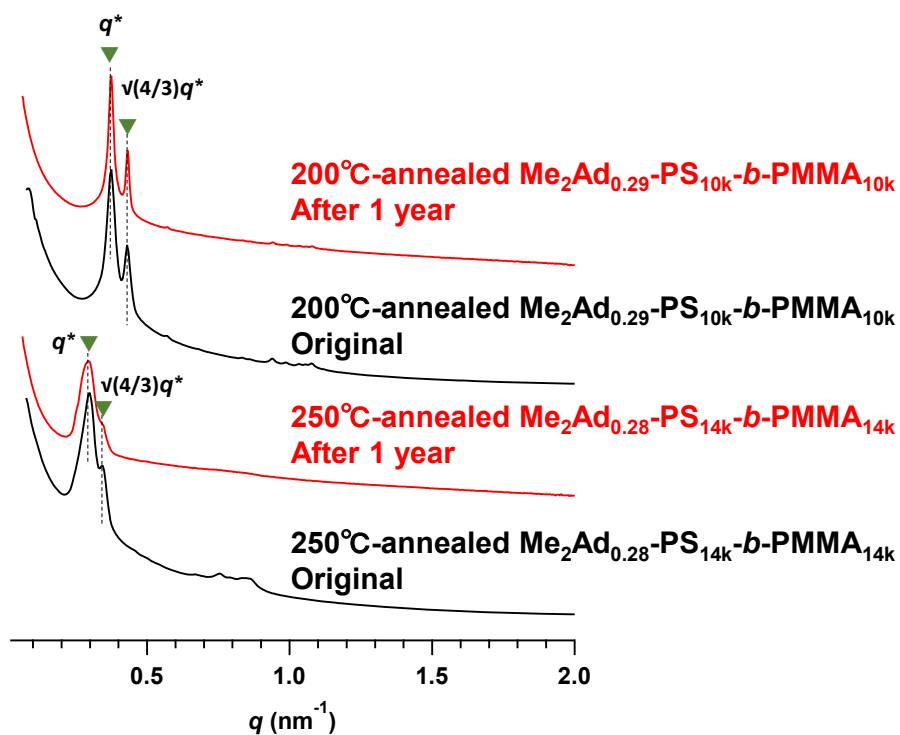


Figure S8. SAXS profiles of GYR-forming $\text{Me}_2\text{Ad}_{0.29}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$ (upper red curve) and $\text{Me}_2\text{Ad}_{0.28}\text{-PS}_{14\text{k}}\text{-}b\text{-PMMA}_{14\text{k}}$ (lower red curve) after leaving for one year at ambient condition. The SAXS profiles of the corresponding samples just after the thermal treatment are also shown as the black curves.

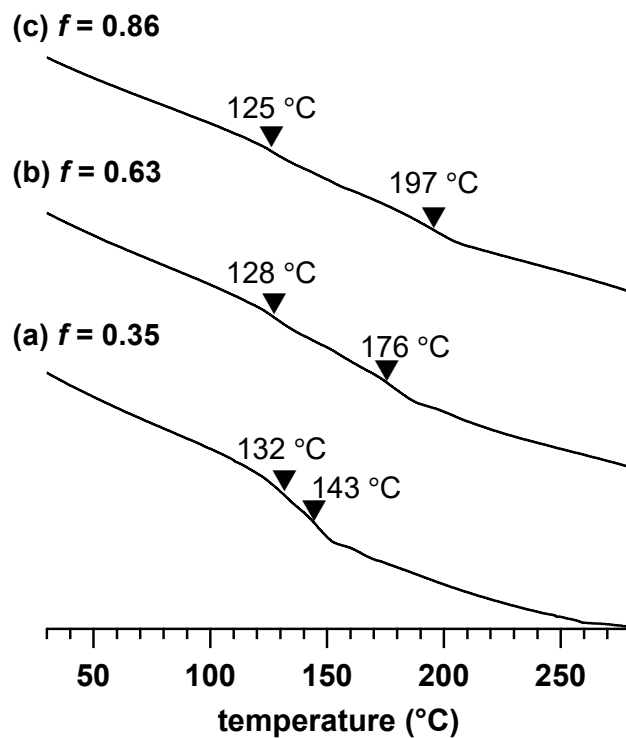


Figure S9. Second heating DSC traces of (a) $\text{Me}_3\text{Ad}_{0.35}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$, (b) $\text{Me}_3\text{Ad}_{0.63}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$, and (c) $\text{Me}_3\text{Ad}_{0.86}\text{-PS}_{10\text{k}}\text{-}b\text{-PMMA}_{10\text{k}}$.

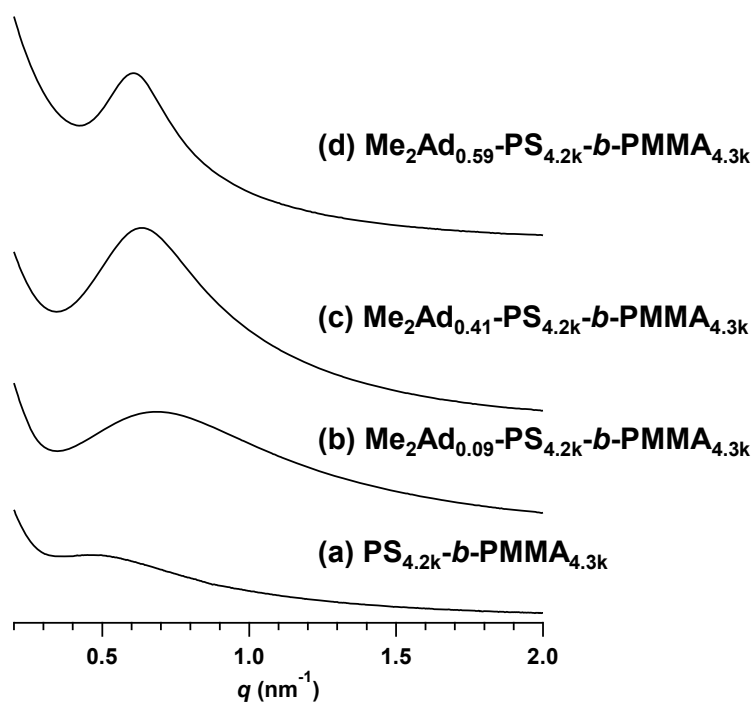


Figure S10. SAXS profiles of the thermally-annealed $\text{Me}_2\text{Ad-PS}_{4.2\text{k}}\text{-}b\text{-PMMA}_{4.3\text{k}}$. All the samples were annealed at 150 °C for 24 h.

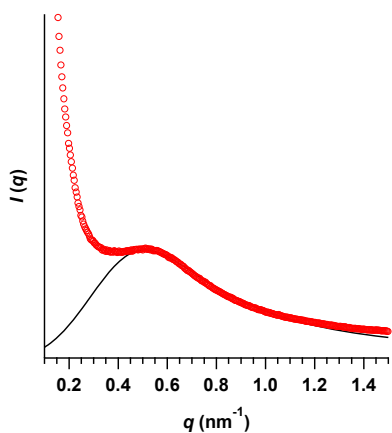
Estimation of χ parameter.

The χ parameters were estimated by fitting the SAXS scattering curves in the disordered state of Me₂Ad-PS_{4.2k}-*b*-PMMA_{4.3k} (measured at 200 °C) with the equations according to the Leibler's mean-field theory. For the reference, we also implemented the same analysis on PS_{10k}-*b*-PMMA_{10k}. The equations used for the fitting are reported elsewhere.^{S1} The parameters for fitting the SAXS profiles are given in **Table S1**, where the f , N , b , v , λ , and K are volume fraction, number-average degree of polymerization normalized with a reference volume of 118 Å³, statistical segment length, molar volume, molecular weight dispersity, and contrast factor, respectively. We input the f , N , v , and λ for the PS and PMMA blocks and b for PMMA listed in **Table S1** as the fixed parameters, while the b for the PS block, K , and χ were used as the adjustable parameters. The fitting results are listed in Figure S11.

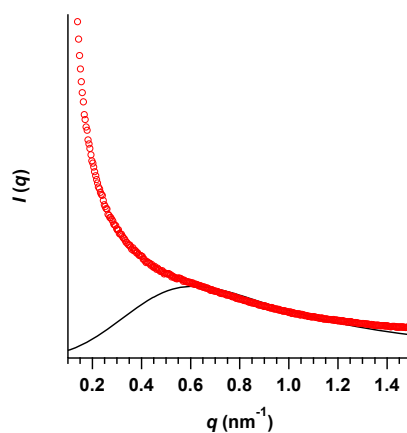
Table S1. Parameters used for the fitting shown in Figure S11

		f	N	b (nm)	v (cm ³ mol ⁻¹)	λ	K	χ
PS _{10k} - b - PMMA _{10k}	PS	0.53	80.7	0.785	99.2	1.02	9.91x10 ⁻⁵	0.032
	PMMA	0.47	62.4	0.750	87.1	1.02		
Me ₂ Ad _{0.09} - PS _{4.2k} - b - PMMA _{4.3k}	Me ₂ Ad-PS	0.56	33.9	1.14	99.2	1.03	1.33x10 ⁻⁴	0.064
	PMMA	0.44	26.9	0.750	87.1	1.03		
Me ₂ Ad _{0.41} - PS _{4.2k} - b - PMMA _{4.3k}	Me ₂ Ad-PS	0.64	33.9	1.21	99.2	1.03	8.99x10 ⁻⁵	0.17
	PMMA	0.36	26.9	0.750	87.1	1.03		
Me ₂ Ad _{0.59} - PS _{4.2k} - b - PMMA _{4.3k}	Me ₂ Ad-PS	0.68	33.9	1.41	99.2	1.03	5.43x10 ⁻⁵	0.21
	PMMA	0.32	26.9	0.750	87.1	1.03		

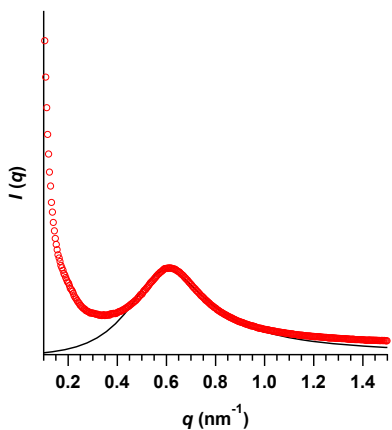
(a) PS_{10k}-*b*-PMMA_{10k}



(b) Me₂Ad_{0.09}-PS_{4.2k}-*b*-PMMA_{4.3k}



(c) Me₂Ad_{0.41}-PS_{4.2k}-*b*-PMMA_{4.3k}



(d) Me₂Ad_{0.59}-PS_{4.2k}-*b*-PMMA_{4.3k}

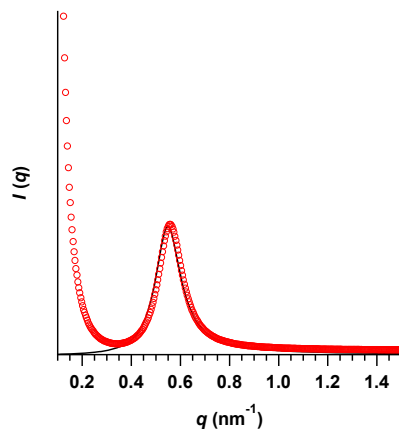


Figure S11. SAXS profiles of (a) PS_{10k}-*b*-PMMA_{10k}, (b) Me₂Ad_{0.09}-PS_{4.2k}-*b*-PMMA_{4.3k}, (c) Me₂Ad_{0.41}-PS_{4.2k}-*b*-PMMA_{4.3k}, and Me₂Ad_{0.59}-PS_{4.2k}-*b*-PMMA_{4.3k} acquired at 200 °C. The best-fit results are shown as the black curves.

Reference

- S1. Cushen, J. D.; Bates, C. M.; Rausch, E. L.; Dean, L. M.; Zhou, S. X.; Willson, C. G.; Ellison, C. J. *Macromolecules* **2012**, *45*, 8722–8728.