

Organocatalytic controlled/living ring-opening polymerization of 1,3,5-triphenyl-1,3,5-tri-*p*-tolylcyclotrisiloxane for the precise synthesis of fusible, soluble, functionalized, and solid poly[phenyl(*p*-tolyl)siloxane]s

Keita Fuchise,* Kazuhiko Sato, and Masayasu Igarashi*

Interdisciplinary Research Center for Catalytic Chemistry (IRC3), National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

E-mail: k-fuchise@aist.go.jp (K. F.) and masayasu-igarashi@aist.go.jp (M. I.)

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Experimental Section

Materials.

Hexamethylcyclotrisiloxane (D3, Tokyo Chemical Industry (TCI), 98%), phenyltrichlorosilane (PhSiCl₃, Shin-Etsu Chemical), 4-bromotoluene (TCI, >99.0%), magnesium (Mg, turnings, for Grignard reaction, >99.5%, FUJIFILM Wako), triphenylsilanol (Ph₃SiOH, TCI, >98.0%), trimethylsilanol (Me₃SiOH, Sigma-Aldrich, 97.5%), *tert*-butylimino-tri(pyrrolidino)phosphorane (*t*Bu-P₁(pyrr), Aldrich, ≥97.0%), benzoic acid (Kanto, >99.5%), pyridine (FUJIFILM Wako, dehydrated, >99.5%), chlorodimethylsilane (HMe₂SiCl, Aldrich, 98%), chlorodimethyl(vinyl)silane (Me₂ViSiCl, TCI, >97.0%), allyl(chloro)dimethylsilane (AllylSiMe₂Cl, Sigma-Aldrich, 97%), chloro(bromomethyl)dimethylsilane (BrCH₂SiMe₂Cl, TCI, >95.0%), lithium trimethylsilylanolate (Me₃SiOLi, Sigma-Aldrich, 95%), sodium hydrogen carbonate (NaHCO₃, FUJIFILM Wako, 99.6–100.3%), sodium sulfate (Na₂SO₄, FUJIFILM Wako, >99.0%), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, ≥98%), silver trifluoroacetate (TFAAg, FUJIFILM Wako, >97.0%), sodium trifluoroacetate (TFANa, FUJIFILM Wako, >97.0%), hexane (FUJIFILM Wako, >97.0%), ‘dry’ diethyl ether (Et₂O, FUJIFILM Wako, super dehydrated, >99.5%), acetonitrile (MeCN, FUJIFILM Wako, >99.5%), ‘dry’ CH₂Cl₂ (FUJIFILM Wako, super dehydrated, water content < 0.001%), ‘dry’ toluene (FUJIFILM Wako, super dehydrated, water content < 0.001%), and ‘dry’ THF (FUJIFILM Wako, dehydrated –Super Plus–, water content < 0.001%) were used as received.

1-Hydroxy-1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxane (MeD4OH),^{S1} 1,3-trimethylene-2-*n*-propylguanidine (TMnPG),^{S2} (diethylamino)ethynyldimethylsilane,^{S3} dichlorophenyl(*p*-tolyl)silane,^{S4} and chlorodimethyl(1-naphthyl)silane (NaphSiMe₂Cl)^{S5} were synthesized as previously reported.

Measurements

NMR

¹H (600 MHz), ¹³C{¹H} (150 MHz), and ²⁹Si{¹H} (119 MHz) NMR spectra were recorded using a BRUKER Biospin AVANCE III HD 600 NMR spectrometer with a CryoProbe. Chemical shifts are reported in δ (ppm) and are referenced to tetramethylsilane (0.00 ppm) for ¹H, ¹³C, and ²⁹Si.

Size-exclusion chromatography (SEC)

Size-exclusion chromatography (SEC) was performed at 45 °C using a Waters ACQUITY Advanced Polymer Chromatography (APC) System consisting of a p-Isocratic Solvent Manager (Model AIS), Sample Manager pFTN (Model ASM), Column Manager-S (Model AZC), PDA TS Detector (Model ADT), and Refractive Index (RI) Detector (Model URI) equipped with a Waters APCTM XT45 column (linear: 4.6 mm × 150 mm; pore size: 4.5 nm; bead size: 1.7 μm; exclusion limit: 5000), a Waters APCTM XT200 column (linear: 4.6 mm × 150 mm; pore size: 20.0 nm; bead size: 2.5 μm; exclusion limit: 70 000), and a Waters APCTM XT450 column (linear: 4.6 mm × 150 mm; pore size: 45.0 nm; bead size: 2.5 μm; exclusion limit: 400 000) in toluene at a flow rate of 0.70 mL min⁻¹. The number-average molar mass ($M_{n,SEC}$) and molar-mass dispersity (D_M) were determined based on a calibration curve prepared using polystyrene (PS) samples from a TSKgel[®] standard polystyrene oligomer kit (Tosoh) with weight-average molecular mass (M_w) and (D_M) values of 19.0×10⁵ g mol⁻¹ (1.04), 9.64×10⁴ g mol⁻¹ (1.01), 3.79×10⁴ g mol⁻¹ (1.01), 1.74×10⁴ g mol⁻¹ (1.01), 1.02×10⁴ g mol⁻¹ (1.02), 5.06×10³ g mol⁻¹ (1.02), 2.63×10³ g mol⁻¹ (1.05), 1.01×10³ g mol⁻¹ (1.16), and 5.9×10² g mol⁻¹ (1.19), along with PS samples from

Chemco Co. with M_w (D_M) values of $17.0 \times 10^5 \text{ g mol}^{-1}$ (1.06), $4.75 \times 10^4 \text{ g mol}^{-1}$ (1.06), $9.00 \times 10^3 \text{ g mol}^{-1}$ (1.04), and $4.00 \times 10^3 \text{ g mol}^{-1}$ (1.03).

High-resolution mass spectrometry (HR-MS)

High-resolution electrospray ionization (ESI) mass spectra were obtained using a Bruker micrOTOF II.

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS)

MALDI-TOF MS of the obtained polymers was performed using a Bruker autoflex™ speed TOF/TOF system with a Smartbeam laser (Bruker Daltonics). Spectra were acquired in the positive linear mode by accumulating 2500 to 5000 laser shots at a 19 kV acceleration voltage. External calibration was performed using Tosoh TSKgel® standard Polystyrene TS-502 ($M_w = 2.63 \text{ kg mol}^{-1}$, $D_M = 1.05$) and TS-521 ($M_w = 5.06 \text{ kg mol}^{-1}$, $D_M = 1.02$). In a typical measurement, a solution of the external standard was prepared by mixing TS-502 (12.5 μL , 10 mg mL^{-1} in THF), TS-521 (12.5 μL , 10 mg mL^{-1} in THF), the matrix (DCTB, 50 mg mL^{-1} , 20 μL), and the cationization agent (TFAAg, 2.2 mg mL^{-1} , 45 μL). Solution of the samples were prepared by mixing polysiloxane (30 mg mL^{-1} in THF, 10 μL), the matrix (DCTB, 50 mg mL^{-1} , 20 μL), and the cationization agent (TFANa or TFAAg, 2.2 mg mL^{-1} , 45 μL). Approximately 10 μL of the obtained mixture was spotted on a ground steel target plate and dried prior to measurements.

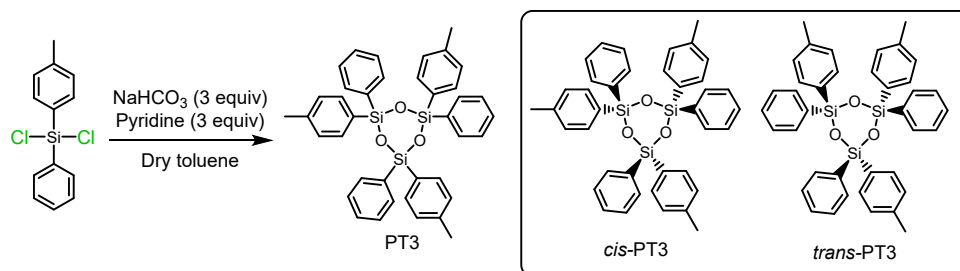
Thermogravimetric analyses (TGA)

TGA measurements of the synthesized polysiloxanes were conducted using a HITACHI STA7200RV. The samples (~5 mg) were placed in aluminum pans for each measurement. The samples were heated from 25 °C to 540 °C at a heating rate of 10 °C min^{-1} under a nitrogen flow of 200 mL min^{-1} .

Differential scanning calorimetry (DSC)

DSC measurements were conducted using a Hitachi Hitech-Science DSC 7020. The samples (~5 mg) were placed in aluminum pans with a lid for each measurement. The samples were heated to 180–250 °C, cooled to –150 °C, heated again to 180–250 °C, and cooled again to 30 °C under a nitrogen flow of 50 mL min^{-1} . The heating and cooling rates were 10 °C min^{-1} .

Synthesis of 1,3,5-triphenyl-1,3,5-tri-*p*-tolylcyclotrisiloxane (PT3)^{S6}

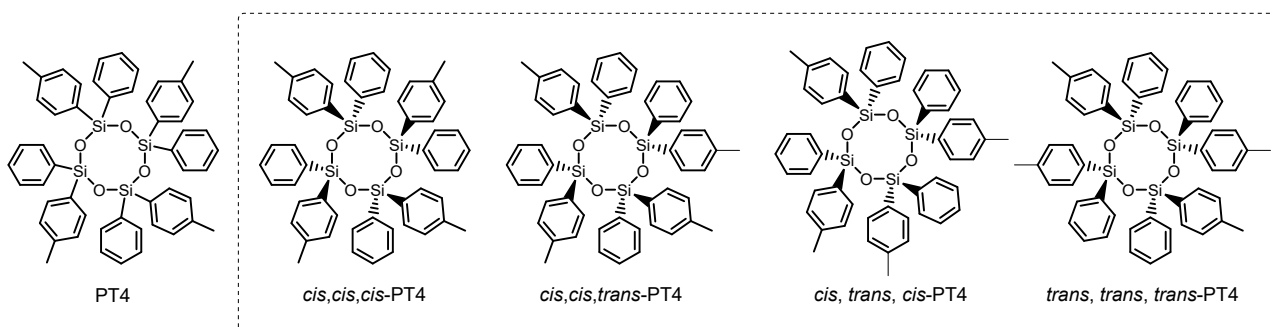


NaHCO₃ (4.75 g, 56.6 mmol) was gradually added to a solution of dichloro(phenyl)-*p*-tolylsilane (15.1 g, 56.6 mmol) and pyridine (4.46 mL, 56.6 mmol) in dry toluene (57 mL) at ambient temperature (22–25 °C) under an argon atmosphere. The reaction mixture was stirred for 3 days. Then, the reaction mixture was diluted with

toluene and filtered through a filter paper. The filtrate was washed with water three times. The separated organic phase was dried over Na_2SO_4 , filtered through a filter paper, and the filtrate was concentrated under reduced pressure. The obtained white solid was washed with hexane/diethyl ether = 9/1 (v/v) to dissolve and remove higher oligomers of (phenyl)-*p*-tolylsiloxanes, which mainly consisted of 1,3,5,7-tetramethyl-1,3,5,7-tetra-*p*-tolylcyclotetrasiloxane (PT4). The remaining solid was dried *in vacuo* to obtain PT3 as a white solid; yield: 3.89 g (4.58 mmol, 32.3%). The obtained PT3 was a mixture of *cis*- and *trans* isomers (*cis/trans* = 1/3 (*n/n*)).

^1H NMR (600 MHz, CDCl_3): δ . 7.62–7.55 (m, 6H, *oo*-position of the phenyl group), 7.53–7.45 (m, 6H, *oo*-position of the tolyl group), 7.42–7.35 (m, 3H, *p*-position of the phenyl group), 7.31–7.24 (m, 6H, *m*-position of the phenyl group), 7.14–7.08 (m, 6H, *m*-position of the tolyl group), 2.33₈, 2.33₄, 2.32₉ (three s peaks, 9H, $-\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 140.31 (tolyl 4-position), 134.44 (tolyl 2,6-positions), 134.31 (phenyl 1-position), 134.37 (phenyl 2,6-positions), 130.59 (tolyl 1-position), 130.22 (phenyl 4-position), 128.55 (tolyl 3,5-positions), 127.68 (phenyl 3,5-positions), 21.63 ($-\text{CH}_3$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (119 MHz, CDCl_3): δ -33.71 (*cis*- and *trans*-PT3). HRMS (ESI in 2-propanol) calcd. for $[\text{C}_{39}\text{H}_{36}\text{O}_3\text{Si}_3\text{Na}]^+ [\text{M}+\text{Na}]^+$ 659.1864, found 659.1864.

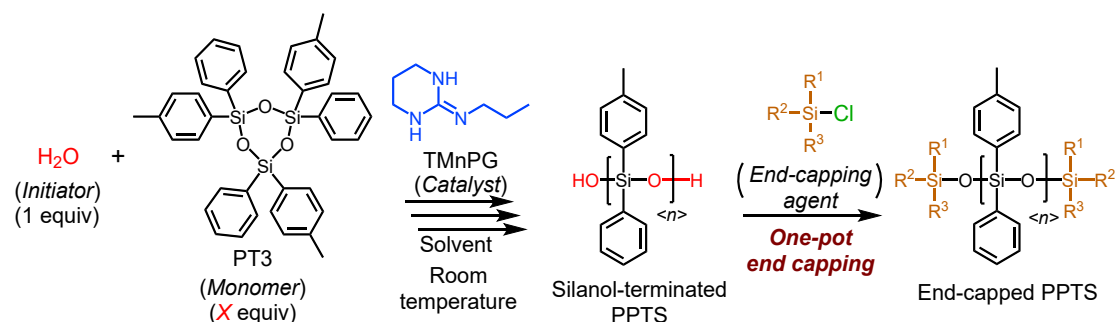
Isolation of 1,3,5,7-tetraphenyl-1,3,5,7-tetra-*p*-tolylcyclotrisiloxane (PT4)



PT4 was isolated from the crude reaction mixture in the synthesis of PT3. The crude product was a mixture of PT3, PT4, and other oligomers of phenyl(*p*-tolyl)siloxane. The extract of the crude reaction mixture in Et_2O /hexane = 1/9 (v/v) contained PT4 and a small amounts of PT3 and other oligomers. This fraction was further extracted with hexane. The fraction insoluble in hexane was a white solid, which was almost pure PT4 containing a slight amount of PT3.

^1H NMR (600 MHz, CDCl_3): δ . 7.47–7.41 (m, 6H, *o*-position of the phenyl group), 7.37–7.32 (m, 6H, *o*-position of the tolyl group), 7.33–7.28 (m, 3H, *p*-position of the phenyl group), 7.18–7.11 (m, 6H, *m*-position of the phenyl group), 7.01–6.95 (m, 6H, *m*-position of the tolyl group), 2.34–2.292 (2.31₉, 2.31₅, 2.31₂, 2.30₈, 2.30₁) (multiple s peaks, 9H, $-\text{CH}_3$). $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CDCl_3): δ 139.79+139.76 (tolyl 4-position), 134.87 (phenyl 1-position), 134.44 (phenyl 2,6-positions), 134.38+134.36+134.34 (tolyl 2,6-positions), 131.08 (tolyl 1-position), 129.79+129.75 (phenyl 4-position), 128.35+128.32 (tolyl 3,5-positions), 127.49+127.47 (phenyl 3,5-positions), 21.58 ($-\text{CH}_3$). δ -42.85 (*cis,cis,cis*-, *cis,cis,trans*-, *cis,trans,cis*-, and *trans,trans,trans*-PT4 are overlapping). HRMS (ESI in 2-propanol) calcd. for $[\text{C}_{52}\text{H}_{48}\text{NO}_4\text{Si}_4\text{Na}]^+ [\text{M}+\text{Na}]^+$ 871.2522 found 871.2526.

Polymerization of PT3

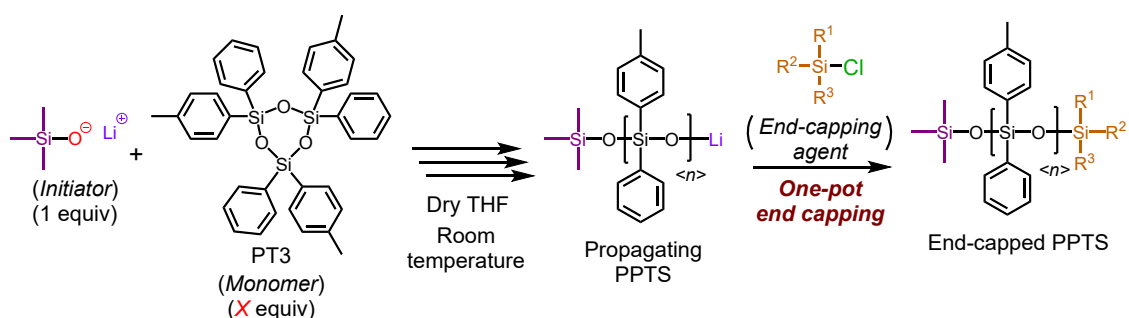


A typical polymerization of PT3 was conducted as follows. PT3 (120 mg, 188 μmol), dry THF (706 μL), and a THF solution of H_2O (1/99 (v/v), 33.9 μL , 18.8 μmol) were added to a vial with a screw cap under an argon atmosphere. A toluene solution of TMnPG (100 mg mL^{-1} , 10.6 μL , 7.54 μmol) was added to initiate the polymerization at ambient temperature ($\sim 25^\circ\text{C}$). After 21 h of stirring, pyridine (10.0 μL , 124 μmol , 6.6 equiv) as a hydrochloric acid scavenger and ViSiMe_2Cl (10.2 μL , 73.9 μmol , 3.9 equiv) as an end-capping agent were added to the mixture. The end-capping reaction was continued for 20 h at ambient temperature. The reaction mixture was dropped directly into MeCN (4 mL) to reprecipitate the generated PPTS. The precipitate was further washed with MeCN (4 mL) three times. The residue was dried *in vacuo* to obtain α,ω -bis[dimethyl(vinyl)silyl]-terminated PPTS (46.7 mg, 37.5%, $M_{n,\text{NMR}} = 6.58 \text{ kg mol}^{-1}$, $\langle X_n \rangle = 30.1$, $D_M = 1.11_2$) as a white solid. The ^1H NMR spectrum of the products is shown in Fig. S3.

The polymerizations using other solvents and other end-capping agents (Table 1) were conducted using similar procedures.

The polymerizations initiated by silanols (Table 2 and 3) were conducted with similar procedures using silanols, such as MeD_4OH , Ph_3SiOH , Me_3SiOH , and $\text{PDMS}-(\text{OH})_2$ instead of the THF solution of H_2O and various chlorosilanes as end-capping agents.

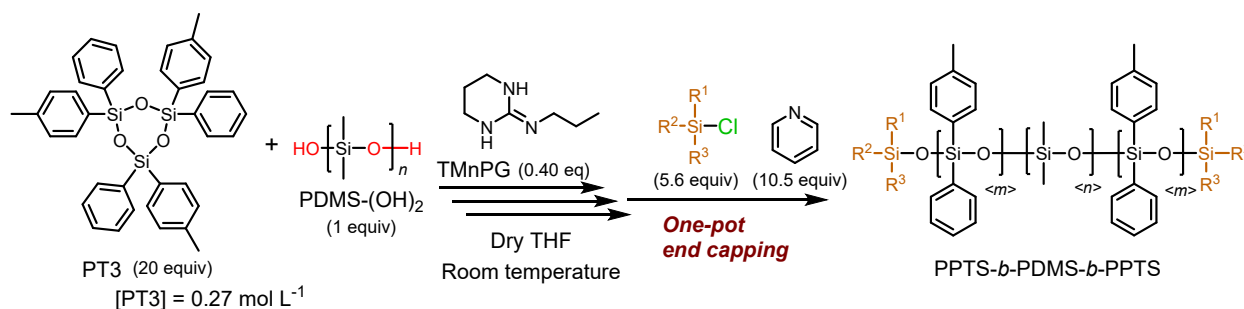
Polymerization of PT3 initiated by lithium trimethylsilylanolate (Me_3SiOLi) (Table 2, entry 4)



PT3 (120 mg, 188 μmol) and dry THF (572 μL) were added to a vial with a screw cap under an argon atmosphere. A THF solution of Me_3SiOLi (13.6 mg mL^{-1} , 133 μL , 18.8 μmol) was added to initiate the polymerization at ambient temperature ($22\text{--}25^\circ\text{C}$). After 21 days (504 h) of stirring, pyridine (10.0 μL , 124 μmol , 6.6 equiv) as a hydrochloric acid scavenger and ViSiMe_2Cl (10.2 μL , 73.9 μmol , 3.9 equiv) as an end-capping agent were added to the mixture. The end-capping reaction was continued for 20 h at ambient temperature. The product was analyzed without further purification.

Synthesis of block copolymers of PPTS and PDMS (Table 3)

Polymerization of PT3 using PDMS-(OH)₂ as a macroinitiator (Table 3, entries 1 and 2)

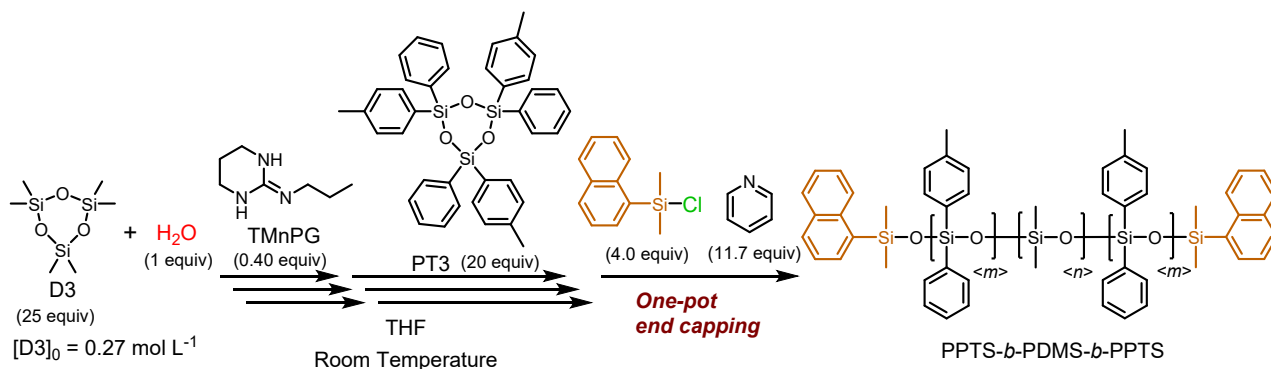


A toluene solution of TMnPG (100 mg mL⁻¹, 6.7 μL, 4.7 μmol, 0.40 equiv) was added to a solution of PT3 (151 mg, 236 μmol, 20 equiv) and PDMS-(OH)₂ (68.9 mg, 11.8 μmol, $M_{n,NMR} = 5.79$ kg mol⁻¹, $\langle X_{n,D} \rangle = 77.9$, 1.0 equiv) in dry THF (741 μL) in a glass vial under an argon atmosphere to initiate the polymerization at ambient temperature (24–26 °C). During the polymerization, an aliquot of the reaction mixture (~70 μL) was taken and mixed with a small amount of benzoic acid. The aliquot was analyzed using ¹H NMR to determine the conversion of the monomer and using SEC to analyze the molar-mass distribution of the crude product. After 16.3 h, dry pyridine (10.0 μL, 124 μmol, 10.5 equiv) was added as a hydrochloric acid scavenger, and AllylSiMe₂Cl (10.0 μL, 8.9 mg, 66 μmol, 5.6 equiv) was added to end-cap the propagating polymers. The end-capping reaction was continued for more than 12 h at room temperature to ensure quantitative end-capping. The reaction mixture was dropped directly into MeCN (4 mL) to reprecipitate the generated PPTS. The precipitate was further washed with MeCN (4 mL) three times. The residue was dried *in vacuo* to obtain α,ω-bis[allyldimethylsilyl]-terminated PPTS-*b*-PDMS-*b*-PPTS (131.4 mg, 58.5% yield, $M_{n,NMR} = 16.9$ kg mol⁻¹, $\langle X_{n,D}/X_{n,PT} \rangle = 77.9/51.2$, $D_M = 1.15_4$) as a white solid.

The polymerization shown in Table 3, entry 2 was conducted using PDMS-(OH)₂ (125 mg, 11.8 μmol, $M_{n,NMR} = 10.6$ kg mol⁻¹, $\langle X_{n,D} \rangle = 142.9$) and NaphSiMe₂Cl in a similar manner.

The ¹H NMR spectra of the products are shown in Fig. S10 and S11.

Two-stage copolymerizations of D3 and PT3 (Table 3, entry 3)



A THF solution of TMnPG (100 mg mL⁻¹, 8.0 μL, 5.7 μmol, 0.40 equiv) was added to a solution of D3 (78.8 mg, 354 μmol, 25 equiv) and a THF solution of H₂O (1/99 (v/v), 25.5 μL, 14.2 μmol, 1.0 equiv) in dry THF (1.19 mL) in a glass vial under an argon atmosphere to initiate the polymerization at room temperature (24–26 °C). During the polymerization, an aliquot of the reaction mixture (~40 μL) was taken and mixed with a small amount of benzoic acid. The aliquot was analyzed using ¹H NMR to determine the conversion of the monomer and using SEC to analyze the molar-mass distribution of the crude product. During the first stage of the polymerization, 25 wt% of the reaction mixture was removed to check the progress of the polymerization. After 63.3 h, PT3 (135 mg, 212 μmol, 20 equiv) in dry THF (589 mg, 663 μL) was added to the reaction mixture. The second stage of the polymerization was continued for 29.9 h. Dry pyridine (10.0 μL, 124 μmol, 11.7 equiv) was added as a hydrochloric acid scavenger, and NaphSiMe₂Cl (9.4 mg, 42 μmol, 4.0 equiv) was added to end-cap the propagating polymers. The end-capping reaction was allowed to proceed for 15 h at room temperature to ensure quantitative end-capping. The reaction mixture was then directly reprecipitated into MeCN (4 mL). The precipitate was further washed with MeCN (4 mL) three times. The residue was dried *in vacuo* to obtain α,ω-bis[dimethyl(1-naphthyl)silyl]-terminated triblock PPTS-*b*-PDMS-*b*-PPTS (120 mg, 60.5% yield, $M_{n,NMR} = 15.7$ kg mol⁻¹ (outer block: $\langle X_{n,D}/X_{n,PT} \rangle_{outer} = 25.3_5/1.1_5$; inner block: $\langle X_{n,D} \rangle_{inner} = 64.7$), $D_M = 1.10_4$) as a white solid. The ¹H NMR spectrum of the product is shown in Fig. S11 (the sampling was conducted four times in this polymerization).

Determination of the number-average degree of polymerization ($\langle X_n \rangle$) and $M_{n,NMR}$ of the polysiloxane using 1H NMR spectroscopy

The M_n ($M_{n,NMR}$) values of the synthesized polysiloxanes were determined using 1H NMR spectroscopy.

The index 'Y' of $\langle X_{n,Y} \rangle$ is defined as:

PT = phenyl(*p*-tolyl)siloxane units;

D = dimethylsiloxane units;

The integral values of peak x in the 1H NMR spectra are written as I_x .

For symmetrically terminated PPTS (Table 1): The peaks in Fig. 2 and S1–5 were used for the calculation.

$$\langle X_{n,PT} \rangle = (I_{a-e} / 3) / (I_f / 12)$$

$$M_{n,NMR} = 212.32 \langle X_{n,PT} \rangle + M_{terminal}$$

(α,ω -bis[allyldimethylsilyl] groups: $M_{terminal} = 214.46$, α,ω -bis[dimethyl(vinyl)silyl] groups: $M_{terminal} = 186.40$, α,ω -bis(dimethylsilyl) groups: $M_{terminal} = 134.33$, α,ω -bis[(bromomethyl)dimethylsilyl] groups: $M_{terminal} = 320.17$, α,ω -bis[dimethyl(ethynyl)silyl] groups: $M_{terminal} = 182.37$)

For PPTS-(OH)₂ (Table 1): The peaks in Fig. S1 were used for the calculation.

$$\langle X_{n,PT} \rangle = (I_{a-e} / 3) / (I_{c-e} / 18)$$

$$M_{n,NMR} = 212.32 \langle X_{n,PT} \rangle + 18.016$$

For asymmetrically terminated PPTS (Table 2): The peaks in Fig. S6–S8 were used for the calculation.

(α -(1,1,3,3,5,5,7,7,7-nonamethyltetrasiloxyl)- ω -hydrodimethylsilyl-terminated PPTS, $M_{terminal} = 370.81$, Fig. S6)

$$\langle X_{n,PT} \rangle = (I_{a-e} / 3) / ((I_f / 6 + (I_g / 6 + I_h / 6 + I_i / 9)) / 5)$$

$$M_{n,NMR} = 212.32 \langle X_{n,PT} \rangle + M_{terminal}$$

(α -triphenylsilyl- ω -hydrodimethylsilyl-terminated PPTS, $M_{terminal} = 334.57$, Fig. S7)

$$\langle X_{n,PT} \rangle = (I_{a-e} / 3) / ((I_d + I_d') / 6)$$

$$M_{n,NMR} = 212.32 \langle X_{n,PT} \rangle + M_{terminal}$$

(α -trimethylsilyl- ω -hydrodimethylsilyl-terminated PPTS, $M_{terminal} = 148.35$, Fig. S8)

$$\langle X_{n,PT} \rangle = 2 (I_{a-e} / I_e)$$

$$M_{n,NMR} = 212.32 \langle X_{n,PT} \rangle + M_{terminal}$$

For PPTS-*b*-PDMS-*b*-PPTS with α,ω -bis(allyldimethylsilyl) groups (Table 3, entry 1): The peaks in Fig. S9–S11 were used for the calculation.

$$\langle X_{n,PT} \rangle = \{(I_{a-e} + I_{k-n}) / 3\} / (I_f / 12)$$

$$\langle X_{n,D} \rangle = (I_{o+t}/6) / (I_f/12)$$

$$M_{n,NMR} = 74.154 \langle X_{n,D} \rangle + 212.32 \langle X_{n,PT} \rangle + M_{\text{terminal}} =$$

(α,ω -bis(allyldimethylsilyl) groups: $M_{\text{terminal}} = 214.46$, α,ω -bis(dimethyl(1-naphthyl)silyl) groups: $M_{\text{terminal}} = 386.64$)

¹H NMR spectra and molar-mass distributions of the products

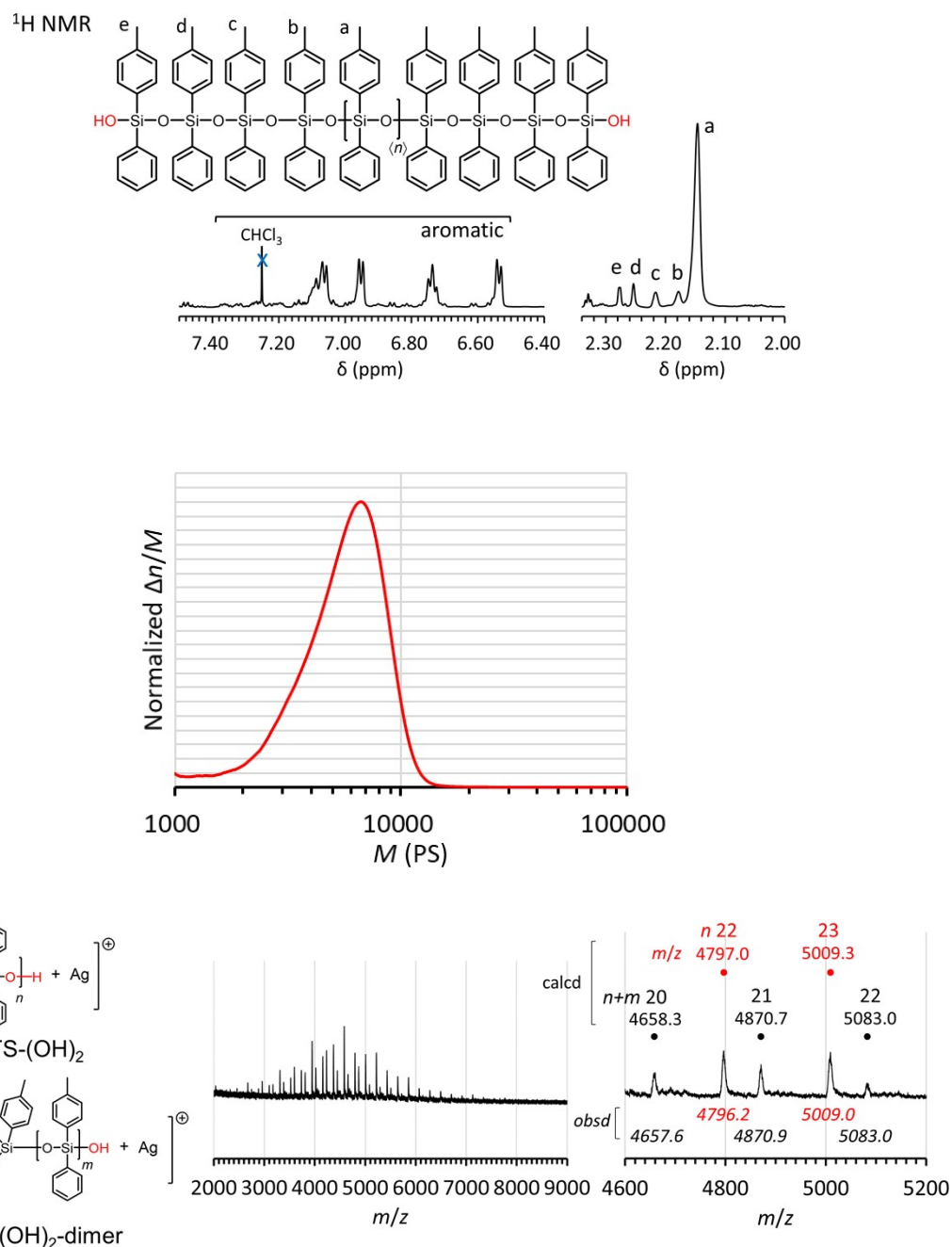


Fig. S1. ¹H NMR spectrum (600 MHz, in CDCl₃), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α,ω -bissilanol-terminated PPTS (PPTS-(OH)₂, $M_{n,NMR} = 8.49 \text{ kg mol}^{-1}$, $\langle X_{n,PT} \rangle = 39.9$, $D_M = 1.12_7$). (Integral values, $I_{c-e} = 18.0$, $I_{a-e} = 119.8373$)

The MALDI-TOF MS spectrum showed two series of molecular ion peaks assigned to PPTS-(OH)₂ and its dimer possibly generated by the elimination of 2 benzene molecules. The latter was generated on the ionization of the sample.

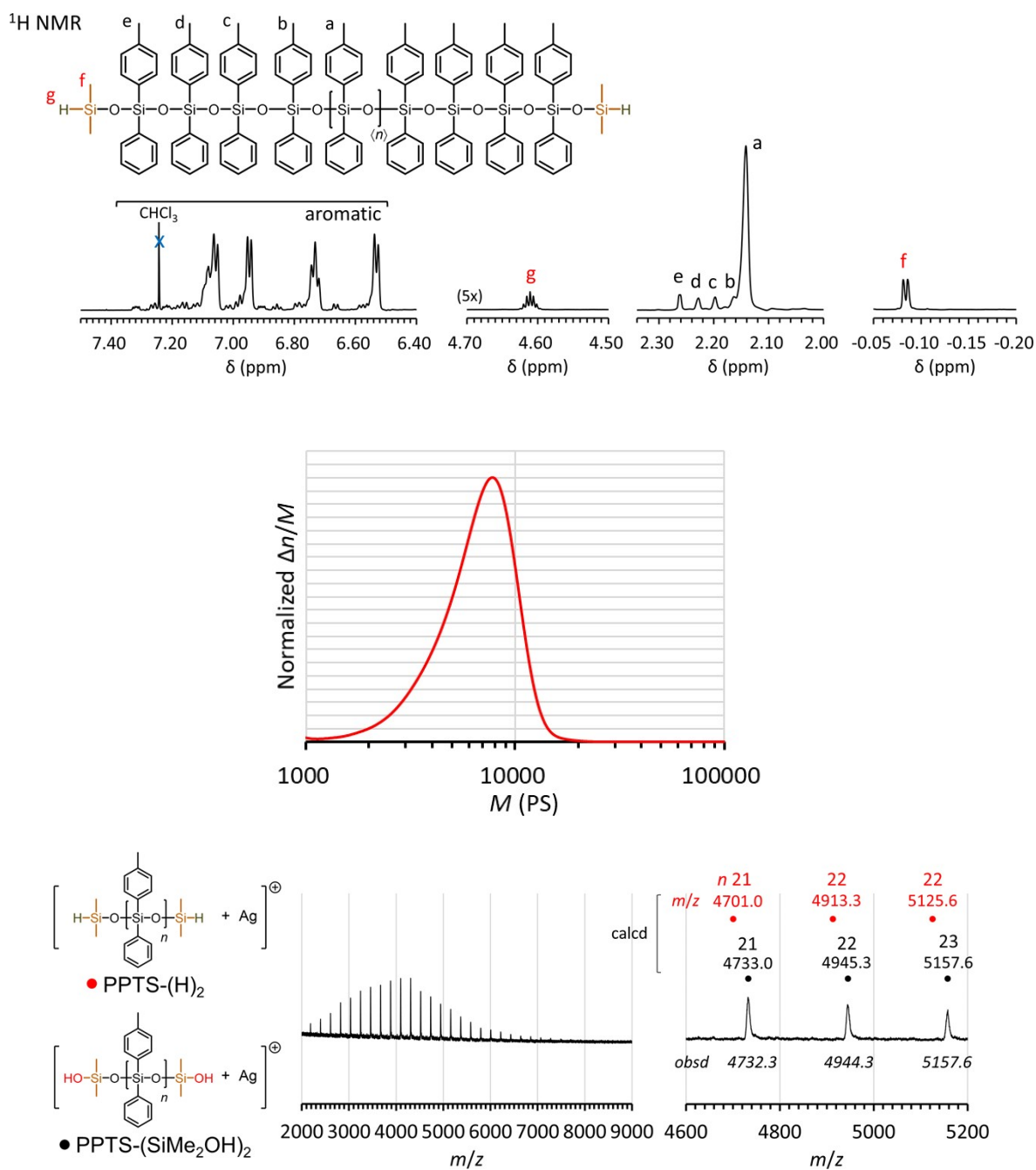


Fig. S2. $^1\text{H NMR}$ spectrum (600 MHz, in CDCl_3), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α,ω -bis[hydrodimethylsilyl]-terminated PPTS (PPTS-(H)₂, $M_{n,\text{NMR}} = 11.0 \text{ kg mol}^{-1}$, $\langle X_{n,\text{PT}} \rangle = 51.2$, $D_M = 1.13_g$). (Integral values, $I_f = 12.0$, $I_{a-e} = 153.5673$)

In the MALDI-TOF MS spectrum, PPTS-(H)₂ was observed as that of which Si-H bonds were converted to Si-OH bonds on the ionization.

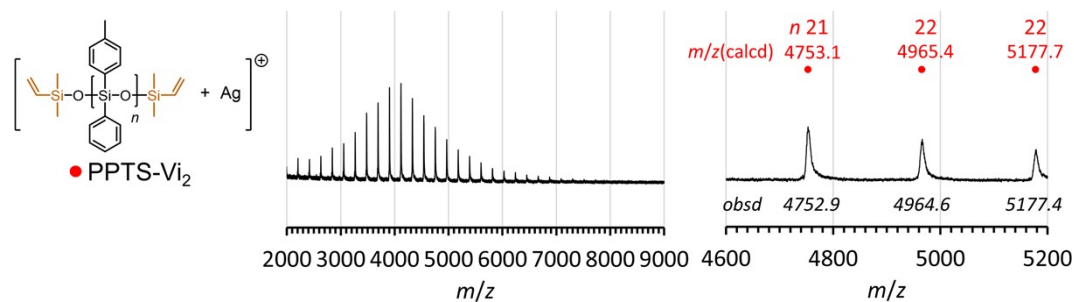
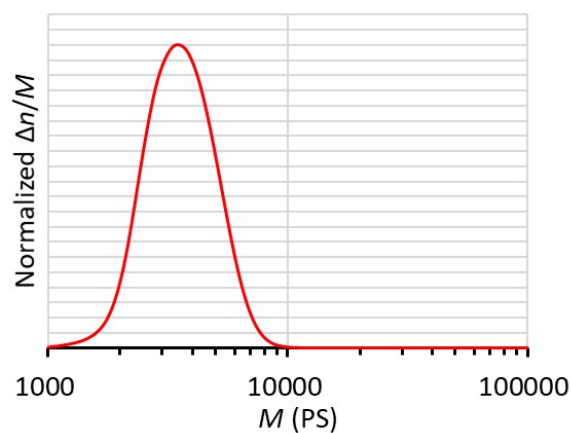
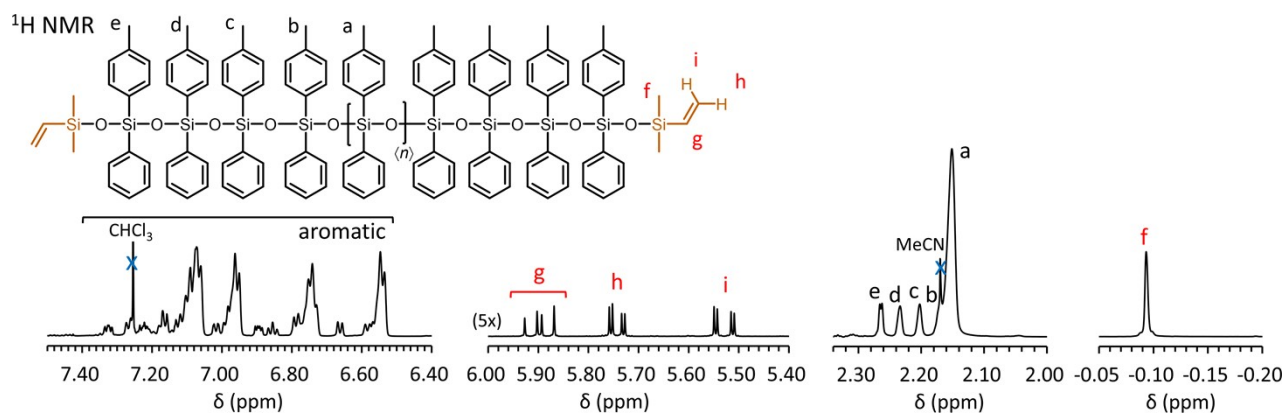


Fig. S3. ^1H NMR spectrum (600 MHz, in CDCl_3), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α,ω -bis[dimethyl(vinyl)silyl]-terminated PPTS (PPTS-Vi_2), $M_{n,\text{NMR}} = 6.58 \text{ kg mol}^{-1}$, $\langle X_{n,\text{PT}} \rangle = 30.1$, $D_M = 1.11_2$. (Integral values, $I_f = 12.0$, $I_{a-c} = 90.3846$)

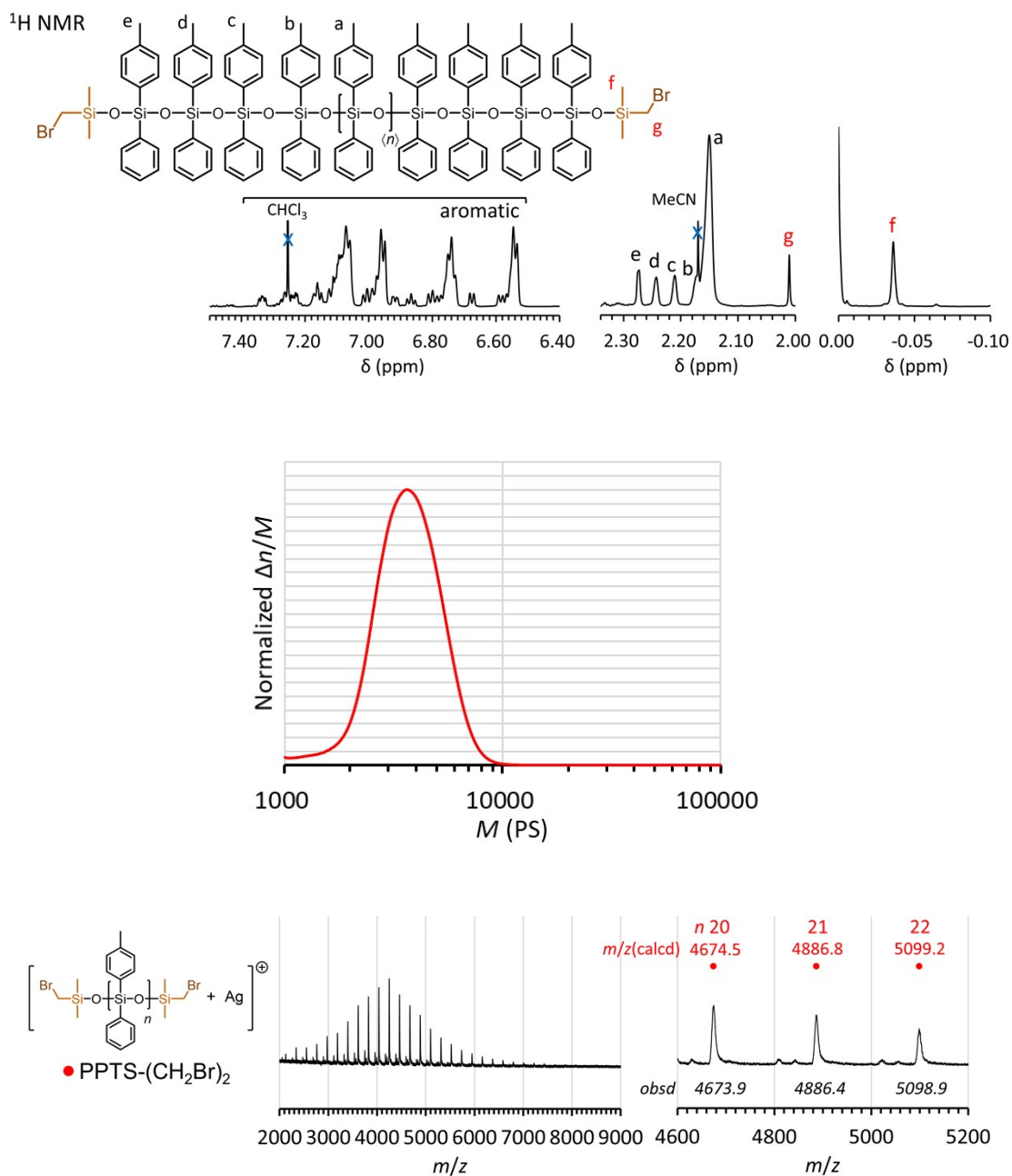


Fig. S4. ¹H NMR spectrum (600 MHz, in CDCl₃), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α,ω -bis[(bromomethyl)dimethylsilyl]-terminated PPTS (PPTS-(CH₂Br)₂, $M_{n,NMR} = 7.04 \text{ kg mol}^{-1}$, $\langle X_{n,PT} \rangle = 32.3$, $D_M = 1.114$). (Integral values, $I_f = 12.0$, $I_{a-e} = 96.9333$)

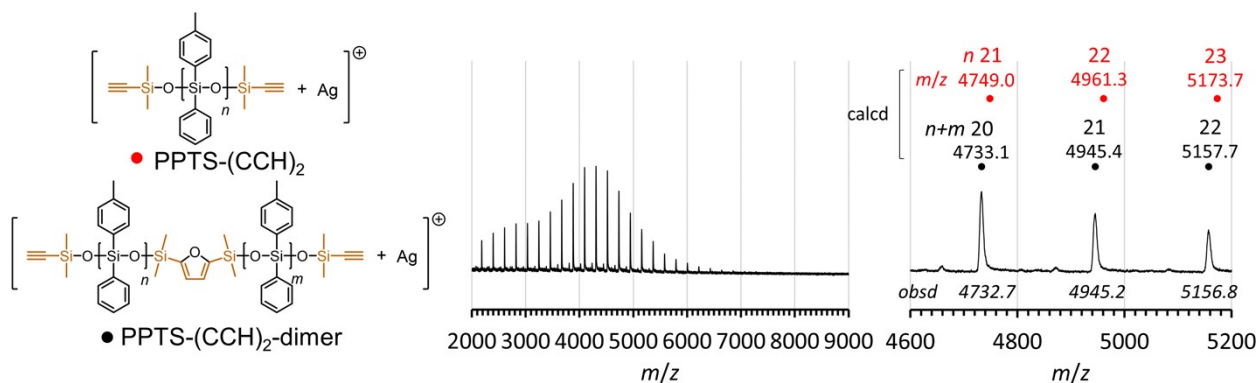
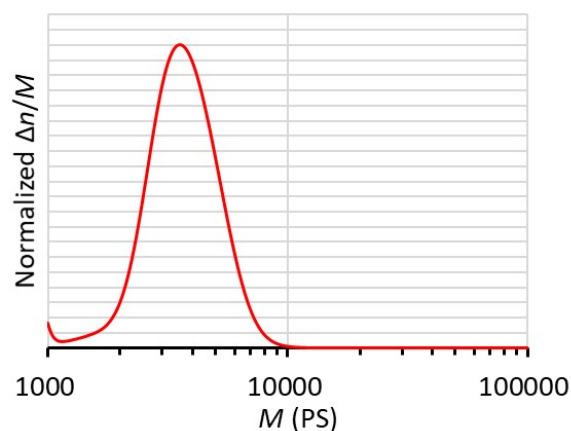
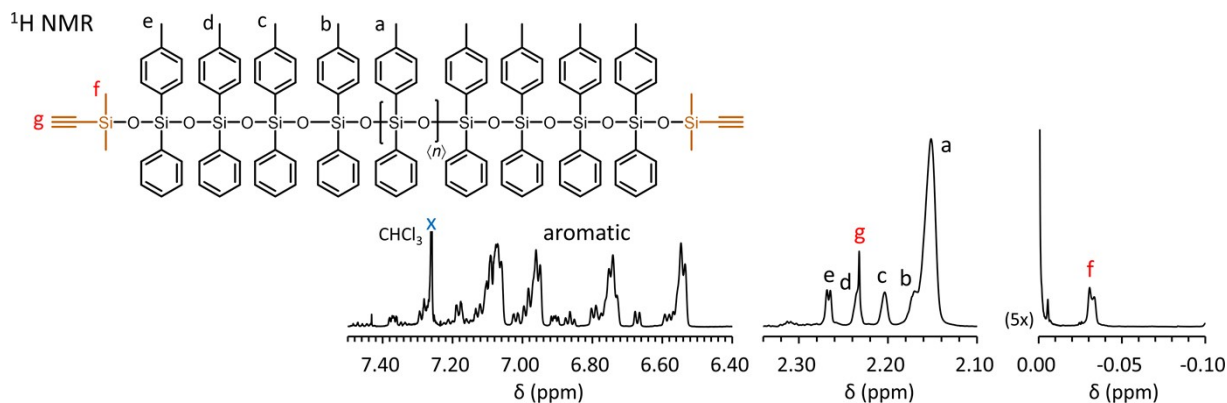


Fig. S5. ^1H NMR spectrum (600 MHz, in CDCl_3), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α,ω -bis[ethynyldimethylsilyl]-terminated PPTS ($\text{PPTS}-(\text{CCH})_2$, $M_{n,\text{NMR}} = 6.22 \text{ kg mol}^{-1}$, $\langle X_{n,\text{PT}} \rangle = 28.4$, $D_M = 1.11_3$). (Integral values, $I_f = 12.0$, $I_{a-e} = 85.2487$)

In the MALDI-TOF MS spectrum, $\text{PPTS}-(\text{CCH})_2$ was detected as a dimer with one additional oxygen atom. The original $\text{PPTS}-(\text{CCH})_2$ possibly dimerized and connected with an oxygen atom to form a furan ring on the ionization.

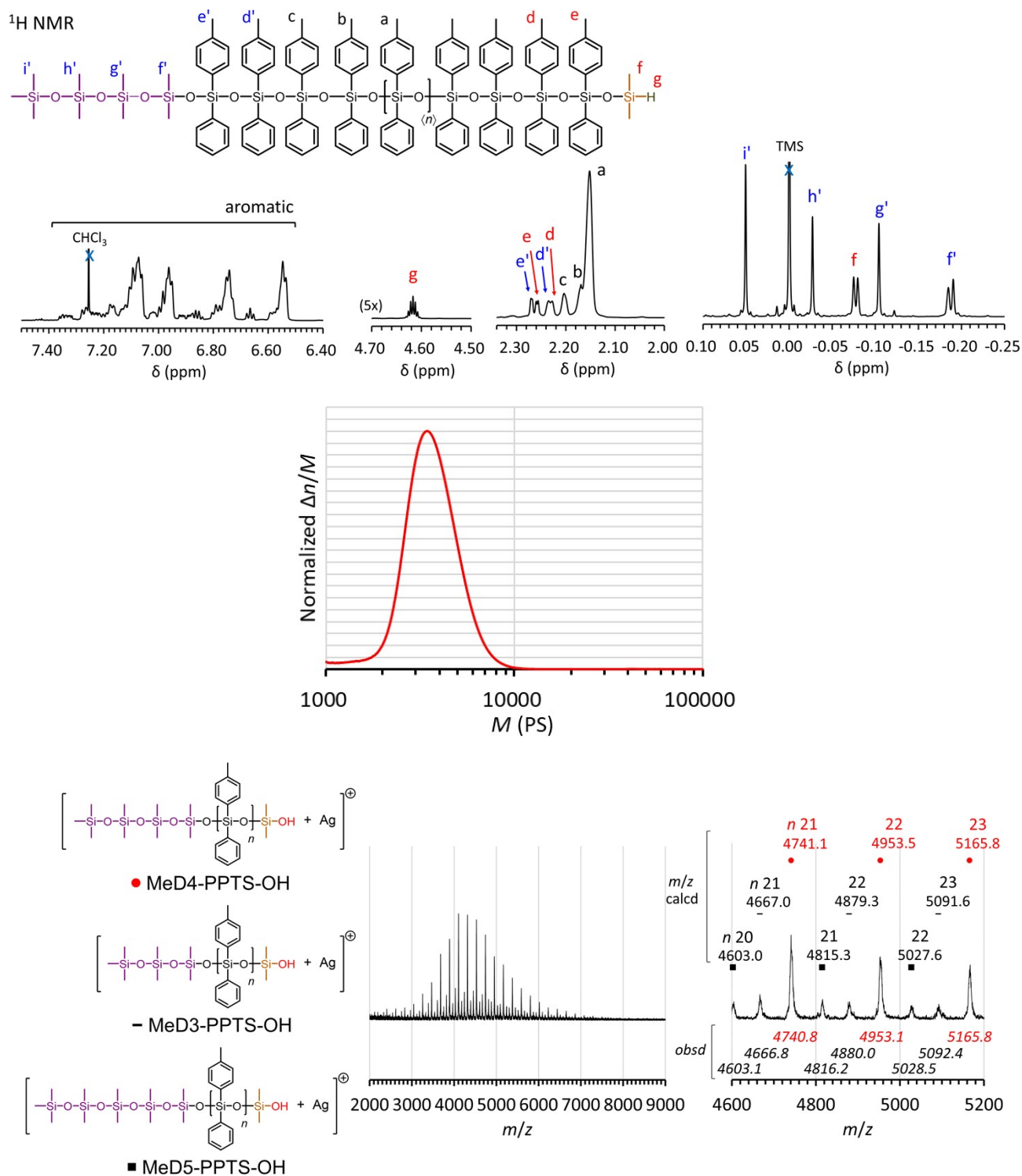


Fig. S6. ¹H NMR spectrum (600 MHz, in CDCl₃), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α -(1,1,3,3,5,5,7,7-nonamethyltetrasiloxyl)- ω -hydrodimethylsilyl-terminated PPTS ($M_{n,NMR} = 6.32 \text{ kg mol}^{-1}$, $\langle X_{n,PT} \rangle = 28.0$, $D_M = 1.11_0$). (Integral values, $I_f = 6.2747$, $I_{f'} = 6.0559$, $I_{g'} = 5.5905$, $I_{h'} = 5.6981$, $I_{i'} = 8.3352$)

In the MALDI-TOF MS measurement, the terminal Si-H bonds were converted to Si-OH bonds on the ionization. The spectrum revealed that the product contains PPTS with one more and one less dimethylsilyloxy unit (MeD5-PPTS-OH and MeD3-PPTS-OH, respectively), which indicated that the intermolecular transfer of a terminal hydroxysilyl group (Scheme S1c) occurred between MeD4OH in the initial stages of the polymerization.

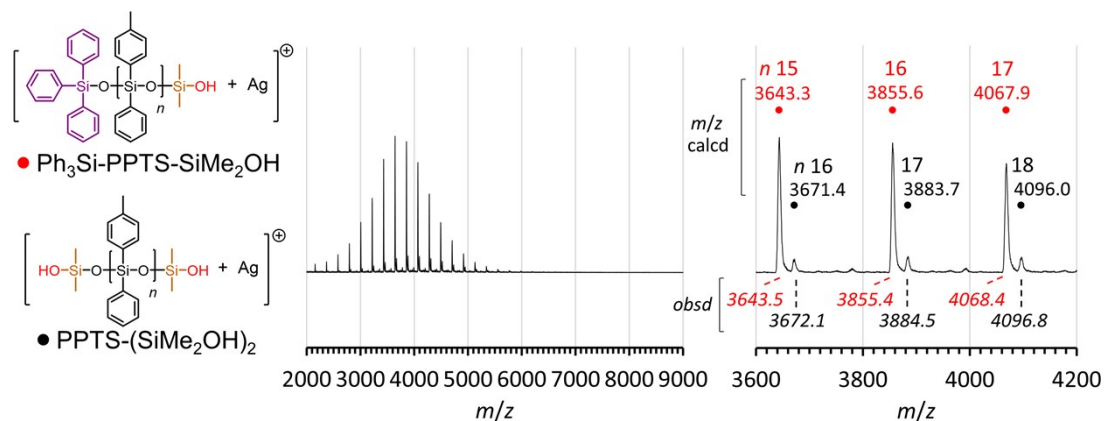
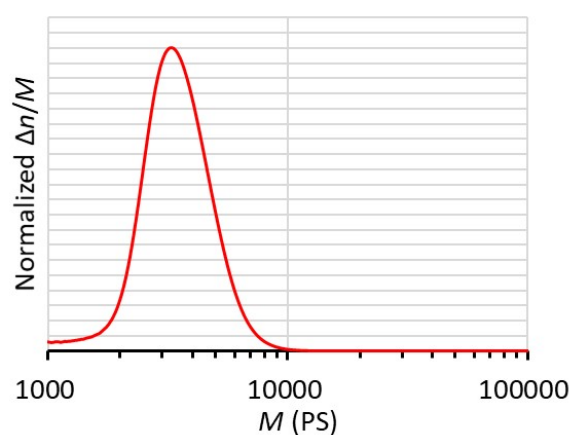
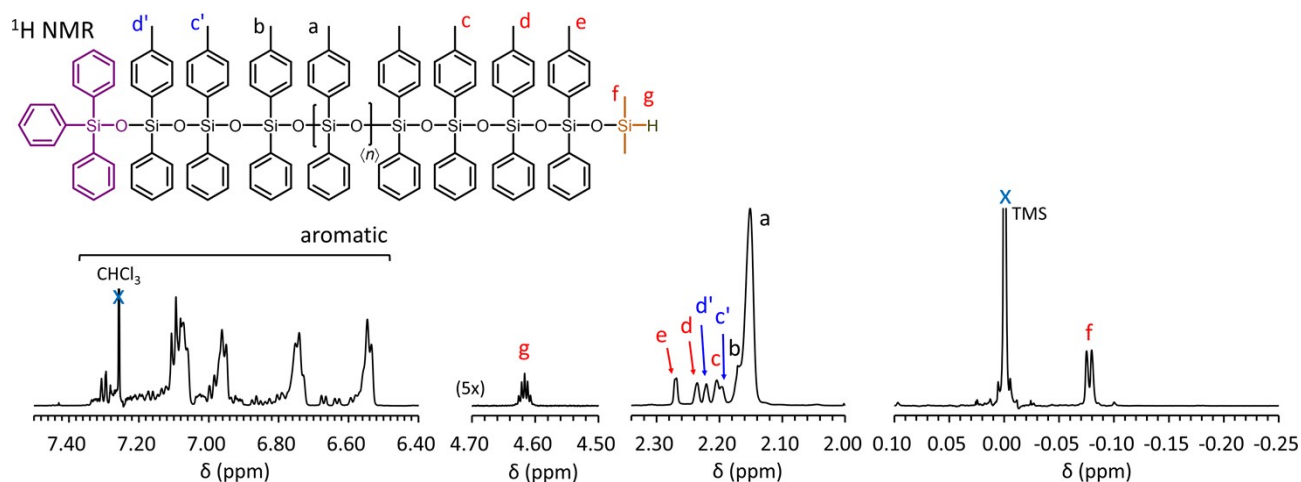


Fig. S7. ¹H NMR spectrum (600 MHz, in CDCl₃), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α-triphenylsilyl-ω-hydrodimethylsilyl-terminated PPTS ($M_{n,\text{NMR}} = 5.326 \text{ kg mol}^{-1}$, $\langle X_{n,\text{PT}} \rangle = 23.2$, $D_M = 1.11_4$). (Integral values, $I_c + I_{c'}$ = 6.1211, $I_d + I_{d'}$ = 6.1244, I_e = 3.7764, I_f = 12.0, I_{a-e} = 70.9080)

In the MALDI-TOF MS measurement, the terminal Si-H bonds were converted to Si-OH bonds on ionization. The spectrum revealed that the product contains a small amount of PPTS with two dimethyl(hydro)siloxy groups, which should be generated by the polymerization initiated by a trace amount of water generated from a condensation of Ph_3SiOH (Scheme S1d).

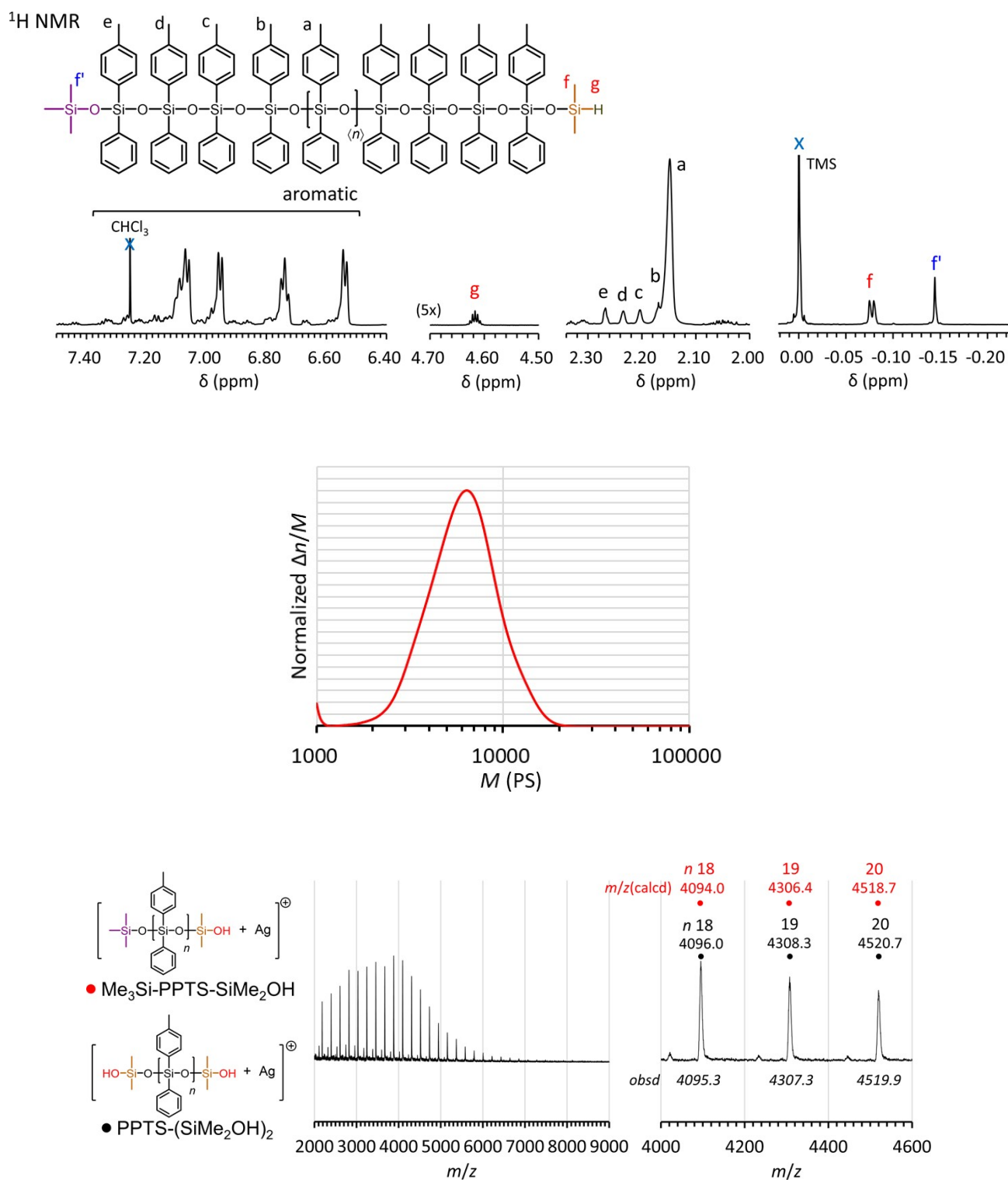


Fig. S8. $^1\text{H NMR}$ spectrum (600 MHz, in CDCl_3), molar-mass distribution, and MALDI-TOF MS spectra (measured in linear mode using DCTB as the matrix and TFAAg as the cationization agent) of α -trimethylsilyl- ω -hydrodimethylsilyl-terminated PPTS ($M_{n,\text{NMR}} = 11.1 \text{ kg mol}^{-1}$, $\langle X_{n,\text{PT}} \rangle = 51.4$, $D_M = 1.18_3$). (Integral values, $I_{a-e} = 154.1866$, $I_f = 8.3019$, $I_g = 6.4654$)

In the MALDI-TOF MS measurement, the terminal Si-H bonds were converted to Si-OH bonds. The ratio of the desired PPTS ($\text{Me}_3\text{Si-PPTS-SiMe}_2\text{H}$) and the undesired PPTS ($\text{PPTS-(SiMe}_2\text{H)}_2$) could not be determined from the observed spectrum, because the peaks due to the two polymers were overlapping.

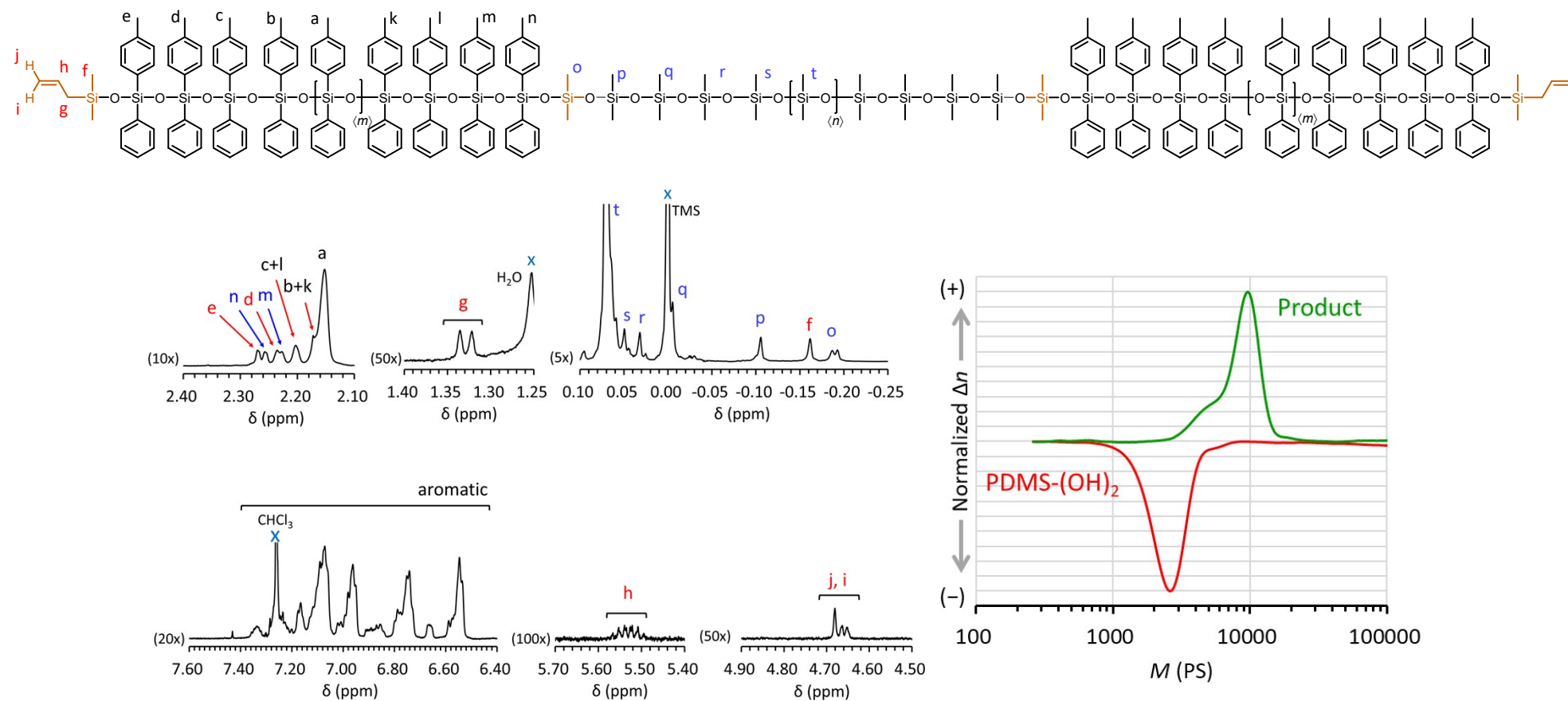


Fig. S9. ^1H NMR spectrum (600 MHz in CDCl_3) and molar-mass distribution of the product of the polymerization of PT3 using $\text{PDMS}-(\text{OH})_2$ ($\langle X_{n,D} \rangle = 77.9$, $D_M = 1.13_4$) as a macroinitiator (Table 3, entry 1, $M_{n,\text{NMR}} = 16.9 \text{ kg mol}^{-1}$, $\langle X_{n,D}/X_{n,\text{PT}} \rangle = 77.9/51.2$, $D_M = 1.15_4$). (Integral values, $I_f = 12.0$, $I_{a-e} + I_{k-n} = 135.9821$, $I_{o+t} = 446.8303$)

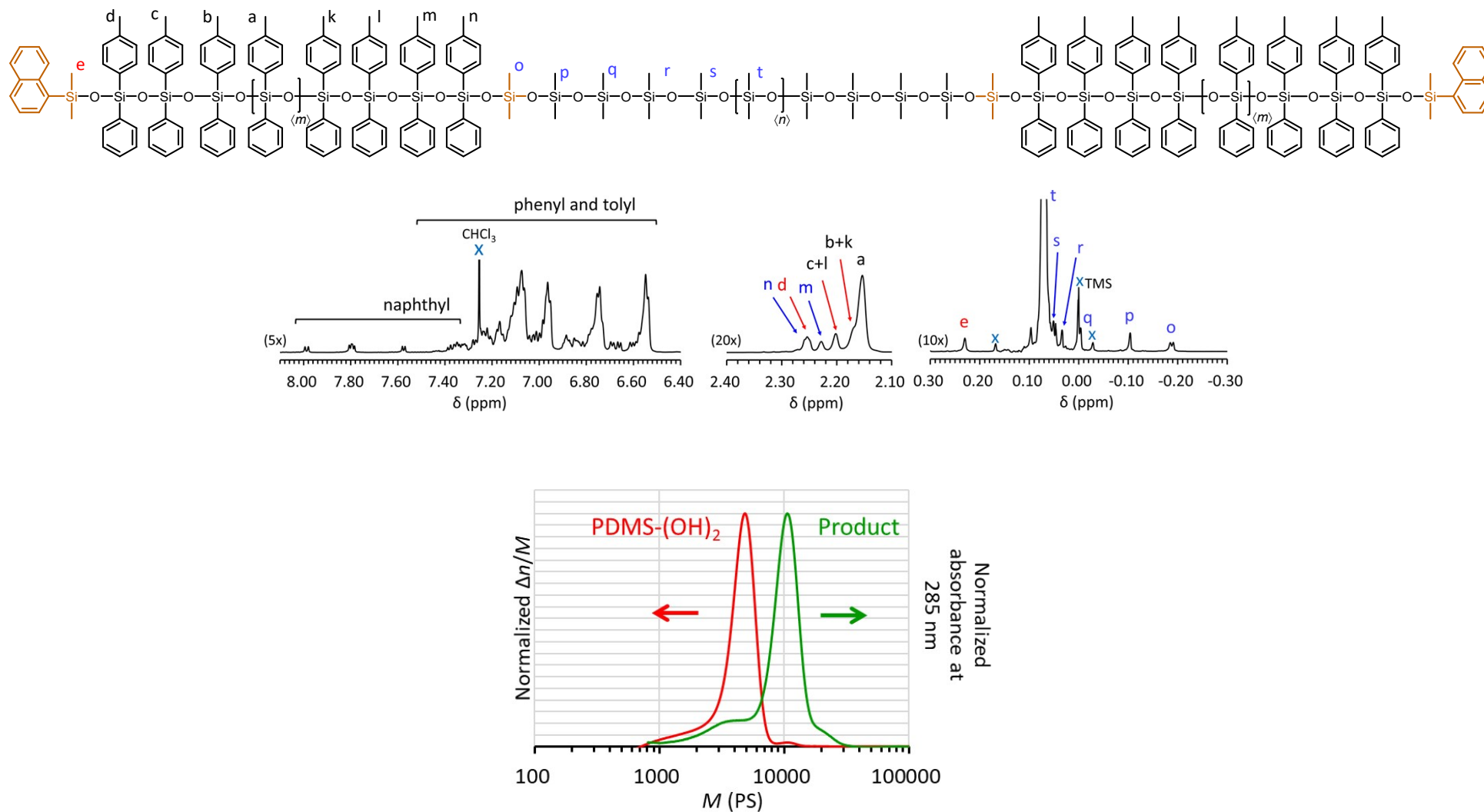


Fig. S10. ^1H NMR spectrum (600 MHz in CDCl_3) and molar-mass distribution of the product of the polymerization of PT3 using PDMS-(OH)₂ ($\langle X_{n,D} \rangle = 142.9$, $D_M = 1.16_2$) as a macroinitiator (Table 3, entry 2, $M_{n,\text{NMR}} = 18.9 \text{ kg mol}^{-1}$, $\langle X_{n,D}/X_{n,PT} \rangle = 143/37.4$, $D_M = 1.17_8$). (Integral values, $I_f = 12.0$, $I_{a-e} + I_{k-n} = 160.9674$, $I_{o+t} = 405.0483$)

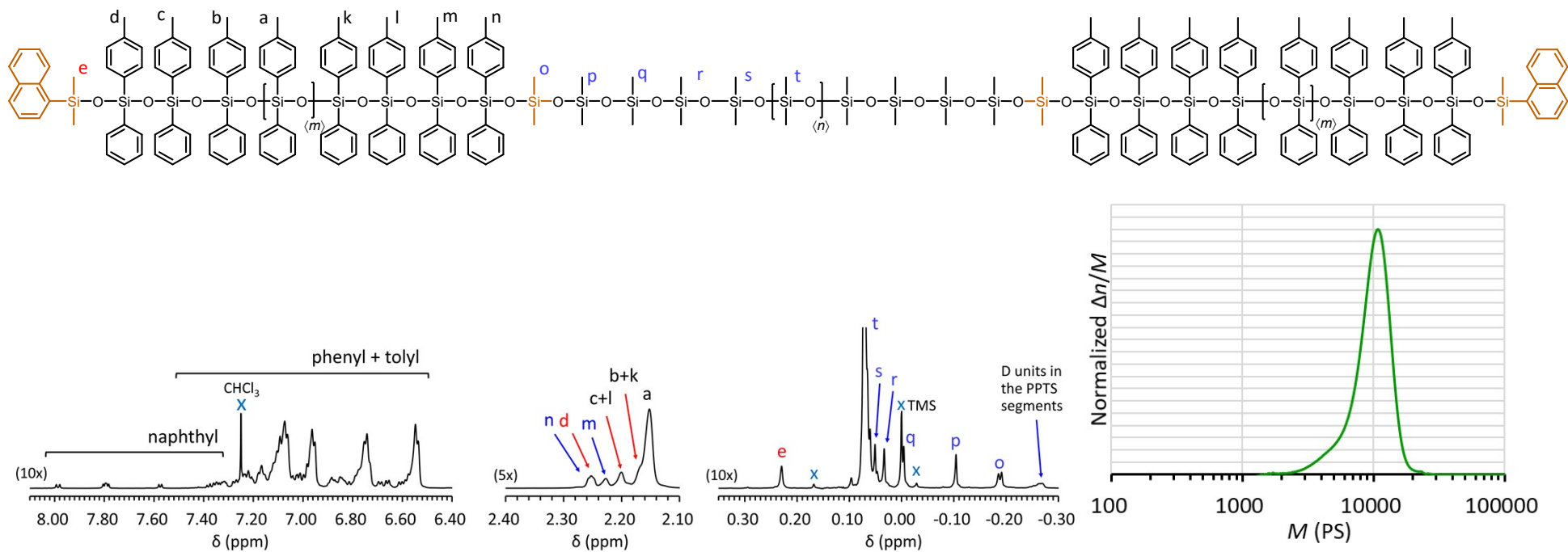


Fig. S11. ¹H NMR spectrum (600 MHz in CDCl₃) and molar-mass distribution of the product of the two-stage copolymerization of D3 and PT3 using water as the initiator and TMnPG as the catalyst (Table 3, entry 3, $M_{n,NMR} = 16.4 \text{ kg mol}^{-1}$, $\langle X_{n,D}/X_{n,PT} \rangle = 67.5/53.7$, $D_M = 1.10_4$). (Integral values, $I_f = 12.0$, $I_{a-e} + I_{k-n} = 111.1666$, $I_{o+t} = 847.4166$)

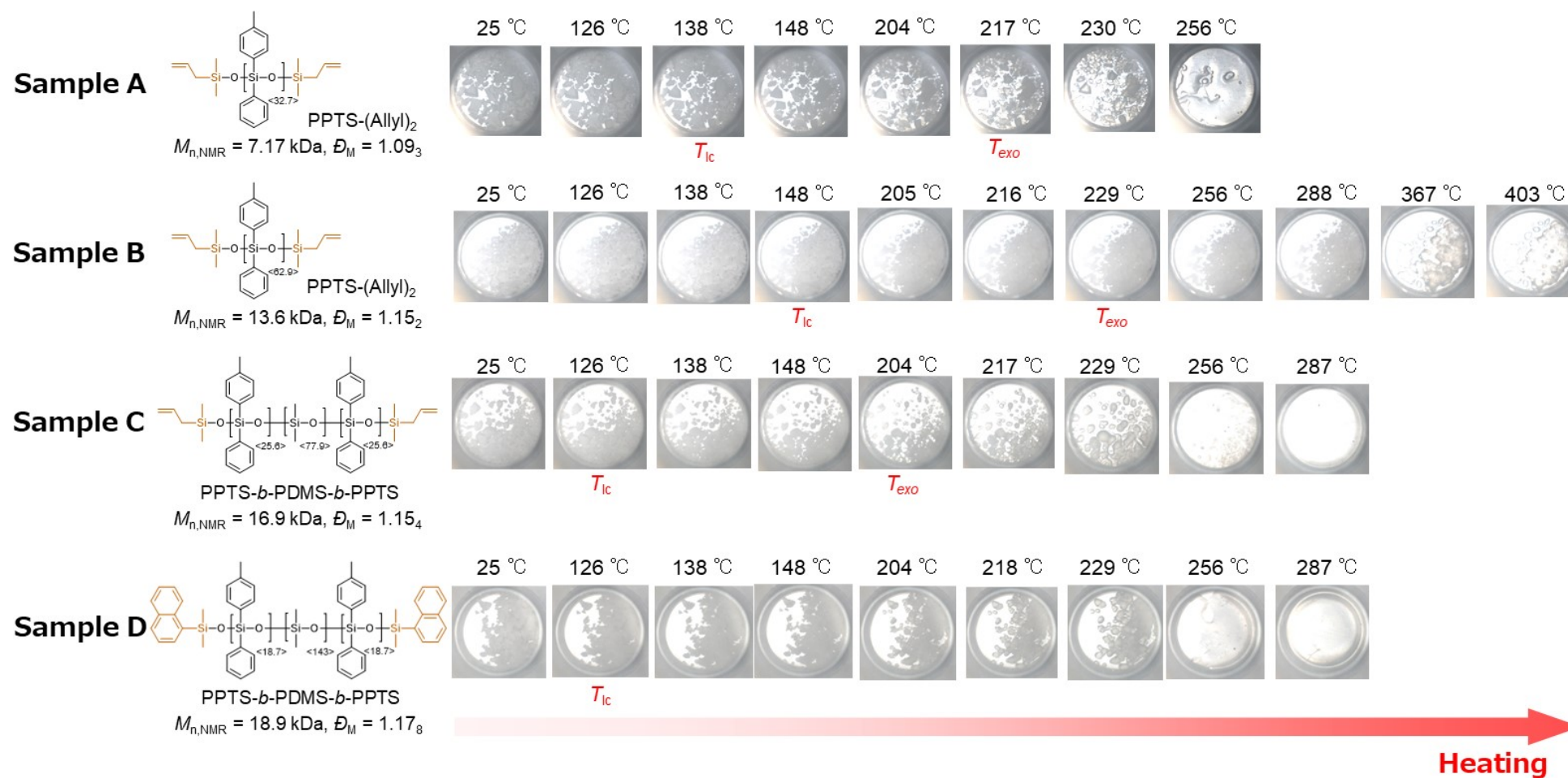
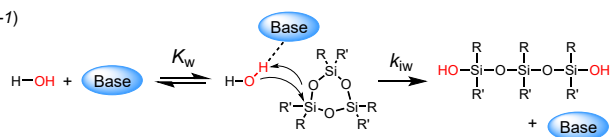


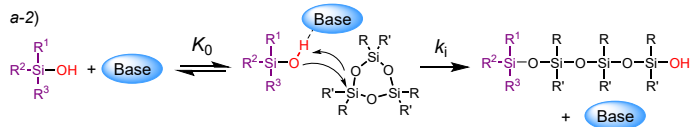
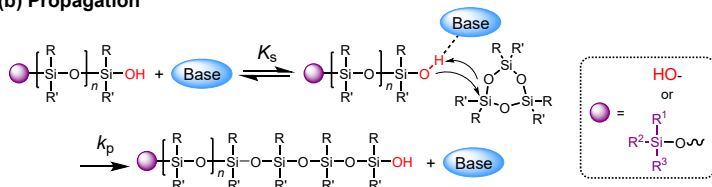
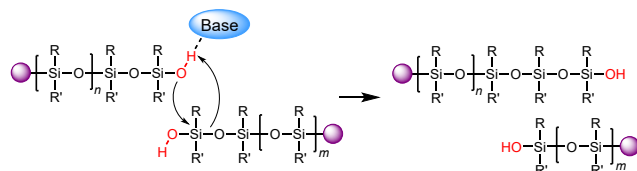
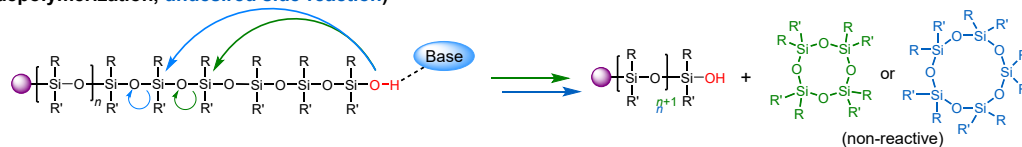
Fig. S12. Photographs of samples A (PPTS-(Allyl)₂), B (PPTS-(Allyl)₂), C (PPTS-*b*-PDMS-*b*-PPTS), and D (PPTS-*b*-PDMS-*b*-PPTS) on aluminium pans during TGA (under a N₂ flow (200 mL min⁻¹), heating rate = 10 °C min⁻¹). The photographs show the correlation between the appearance of the samples and the transitions to a liquid-crystalline state (T_{lc}) and the exothermic transition temperature (T_{exo}) observed in DSC on the first heating.

(a) Initiation

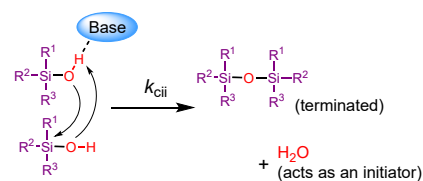
a-1)



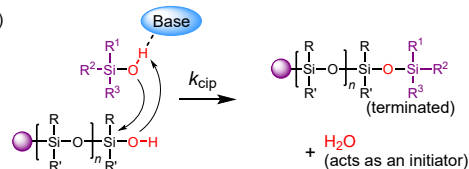
a-2)

**(b) Propagation****(c) Intermolecular transfer of a terminal hydroxysilyl group (disproportionation, allowable side-reaction)****(e) Backbiting (depolymerization, undesired side-reaction)****(d) Condensation (undesired side-reaction)**

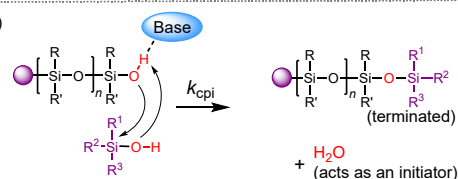
d-1)



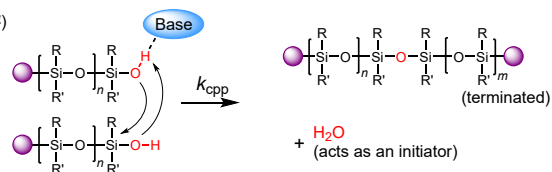
d-2)



d-3)



d-4)



Scheme S1. Possible and plausible elementary reactions in the polymerization of cyclotrisiloxanes using water or a silanol as the initiator and a strong organic base as the catalyst.^{S7}

Determination of the conversion of PT3 to PPTS and PT4 in the polymerizations of PT3.

The conversion of PT3 to PPTS and PT4 was calculated by following equations.

$$\text{Conv(to PPTS)} = I_{\text{PPTS}} / (I_{\text{PT3}} + I_{\text{PT4}} + I_{\text{PPTS}})$$

$$\text{Conv(to PT4)} = I_{\text{PT4}} / (I_{\text{PT3}} + I_{\text{PT4}} + I_{\text{PPTS}})$$

The values of I_{PT3} , I_{PT4} , and I_{PPTS} are the integral values between 2.34₅–2.32₂ ppm, 2.32₂–2.29₆ ppm, and 2.29₆–2.10 ppm, respectively.

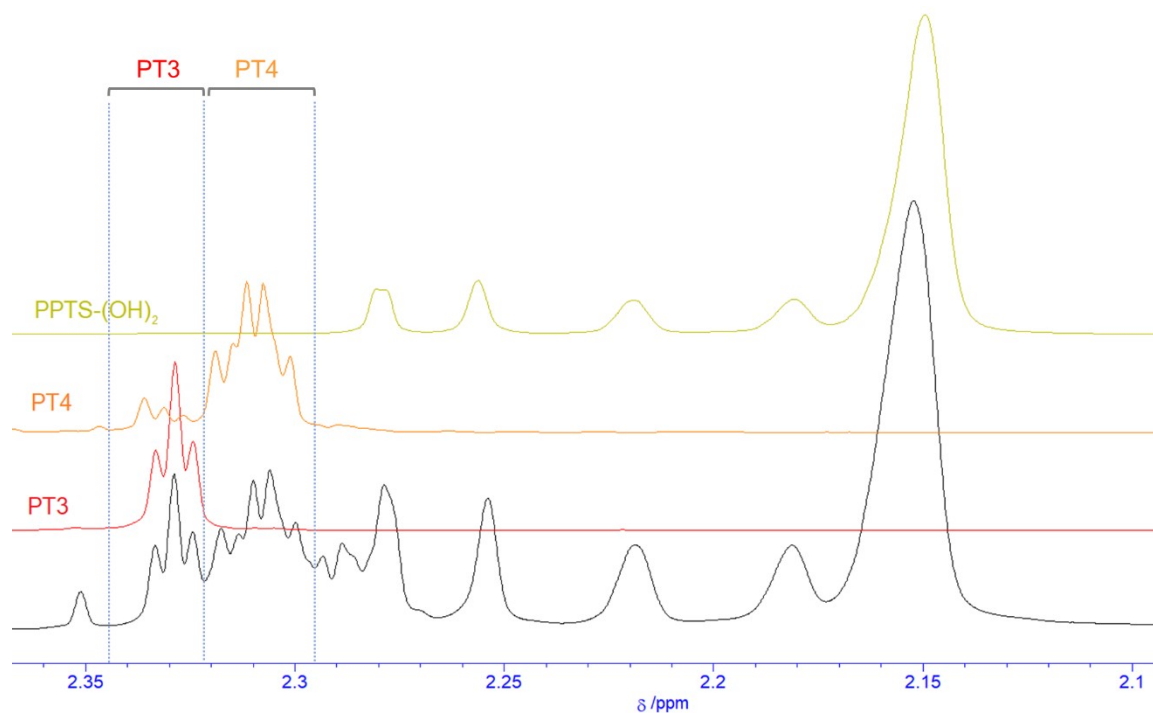


Fig. S13. ¹H NMR spectra (600 MHz, in CDCl₃) of the reaction mixture in the polymerization of PT3 using water as an initiator and TMnPG as a catalyst (black). The spectra of PT3, PT4, and PPTS-(OH)₂ are also shown.

Progress of the polymerization of PT3 at $-20\text{ }^{\circ}\text{C}$ (Table 1, entry 2).

The polymerization almost did not proceed even after 21 h of reaction due to the low solubility of PT3 and the generated oligomers in THF at a low temperature. The samples obtained at 1.5 h and 21 h showed similar ^1H NMR spectra as shown in Fig. S14.

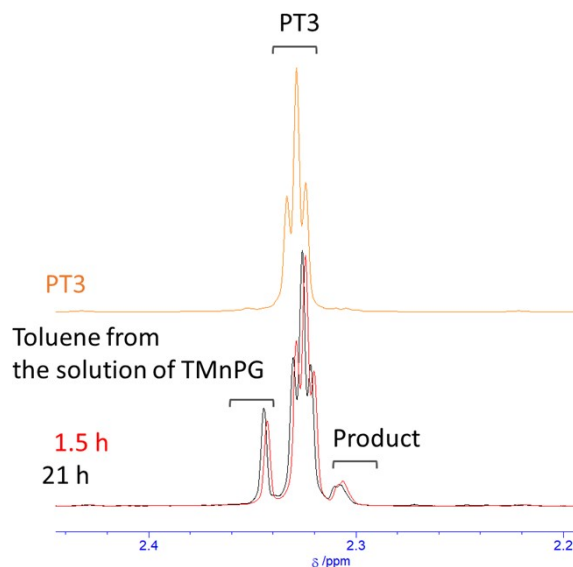


Fig. S14. ^1H NMR spectra (600 MHz, in CDCl_3) of PT3 (orange) and the reaction mixture in the polymerization of PT3 using water as an initiator and TMnPG as a catalyst at $-20\text{ }^{\circ}\text{C}$ (Table 1, entry 2; red (obtained at 1.5 h) and black (obtained at 21 h)).

Progress of the polymerization of PT3 catalyzed by $t\text{BuP}_1(\text{pyrr})$ (Table 1, entry 7).

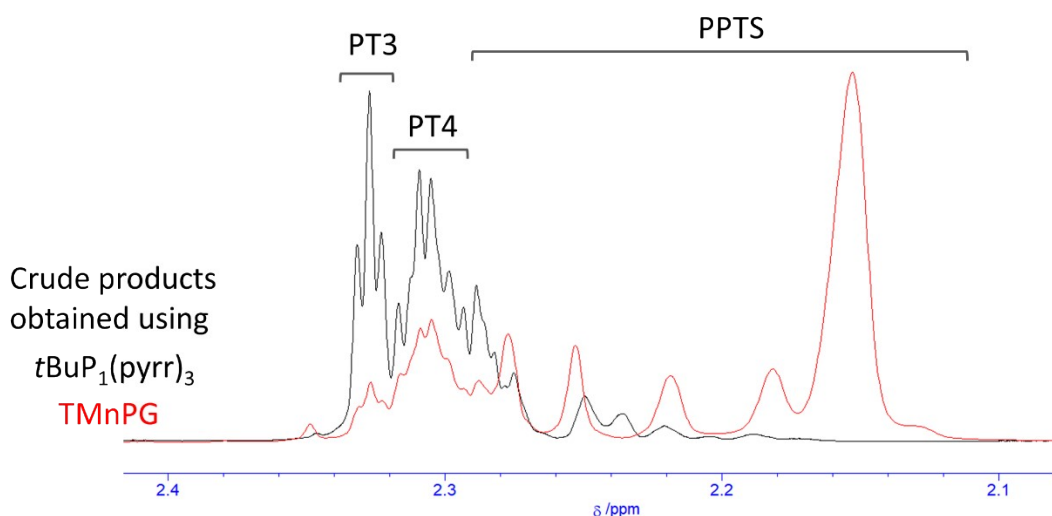


Fig. S15. ^1H NMR spectra (600 MHz, in CDCl_3) of the crude products obtained in the polymerization of PT3 catalyzed by $t\text{BuP}_1(\text{pyrr})$ (black, 5.2 h, conv. to PPTS = 26.2% and PT4 = 45.4%) and TMnPG (red, 24 h, conv. to PPTS = 76.3% and PT4 = 18.1%) with $[\text{PT3}]_0/[\text{H}_2\text{O}]_0/[\text{catalyst}]_0 = 10/1/0.40$ and $[\text{PT3}]_0 = 0.27 \text{ mol}^{-1}$ at room temperature.

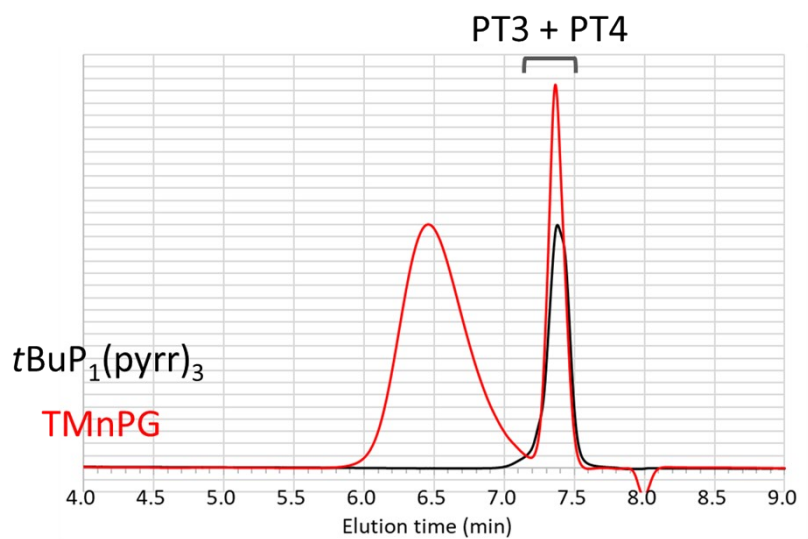


Fig. S16. SEC traces of the crude products obtained in the polymerization of PT3 catalyzed by $t\text{BuP}_1(\text{pyrr})$ (black, 5.2 h, conv. to PPTS = 26.2% and PT4 = 45.4%) and TMnPG (red, 24 h, conv. to PPTS = 76.3% and PT4 = 18.1%) with $[\text{PT3}]_0/[\text{H}_2\text{O}]_0/[\text{catalyst}]_0 = 10/1/0.40$ and $[\text{PT3}]_0 = 0.27 \text{ mol}^{-1}$ at room temperature.

Progress of the polymerization of PT3 initiated by Me₃SiOLi (Table 2, entry 4).

The polymerization was conducted as described in the section of 'Polymerization of PT3 initiated by lithium trimethylsilylanolate (Me₃SiOLi)'. After 21 days (504 h) from the initiation, we observed the ¹H NMR spectrum of the crude product mixed with excess amounts of chlorodimethyl(vinyl)silane and pyridine. The conversion of PT3 to PPTS reached 26.2%, while that to PT4 was 0% as determined from the ¹H NMR spectrum of the crude product shown in the following figure (Fig. S17). The $\langle X_{n,PT} \rangle$ and $M_{n,NMR}$ were determined to be 10.7 and 2.49 kg mol⁻¹. The D_M of the crude product was not calculated, because the SEC trace of the polymeric product was overlapping with the signal due to PT3 (Fig. S18).

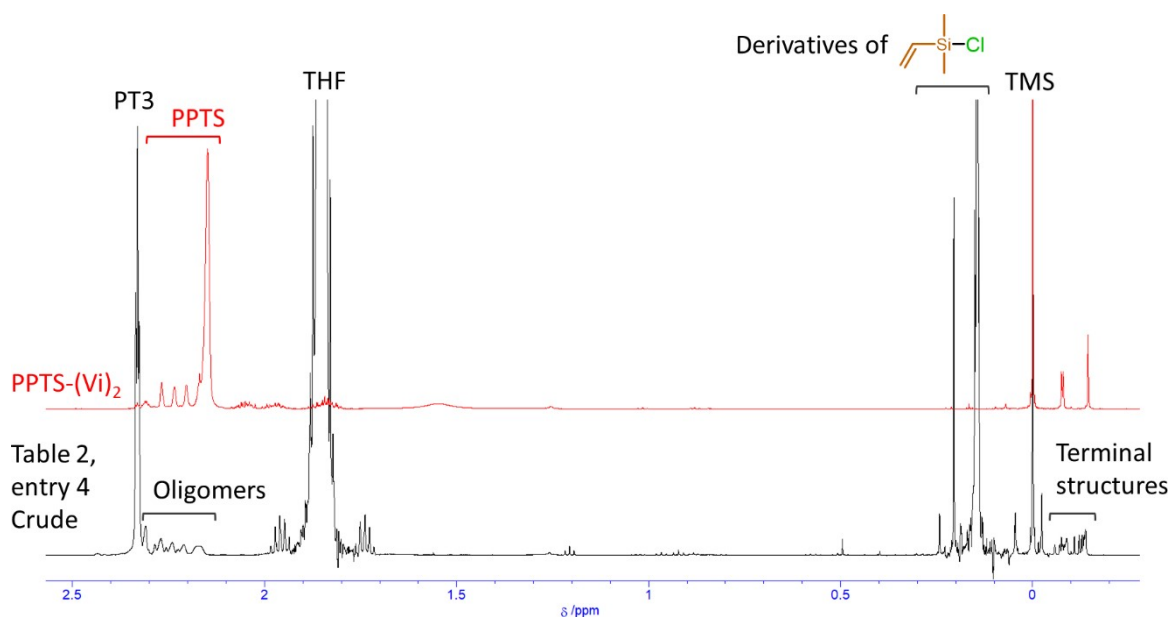


Fig. S17. ¹H NMR spectra (600 MHz, in CDCl₃) of (top) PPTS-(Vi)₂ ($M_{n,NMR} = 6.58$ kg mol⁻¹, $\langle X_{n,PT} \rangle = 30.1$, $D_M = 1.11_2$) and (bottom) the reaction mixture in the polymerization of PT3 using lithium trimethylsilylanolate as an initiator and chlorodimethyl(vinyl)silane as an end-capping agent (Table 2, entry 4). The signal due to PT4 was not observed.

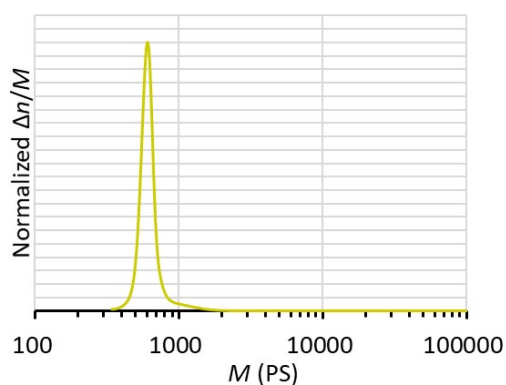


Fig. S18. Molar-mass distribution of the crude product obtained at 21 days (504 h) from the initiation in the ROP of PT3 using lithium trimethylsilylanolate (Me₃SiOLi) as the initiator and a [PT3]₀/[Me₃SiOLi]₀ ratio of 10/1 in THF at room temperature (Table 2, entry 4; $\langle X_{n,PT} \rangle = 10.7$).

Change in molar-mass distributions of PPTS before and after the reprecipitation in MeCN.

These data are measured only for the polymerizations shown in Table 1, entry 5; Table 2 entry 3; and Table 3, entry 3. Unlike the result of the polymerization shown in Table 1, entry 1 and Fig 1, the molar-mass distributions of the three polymers just slightly changed as shown in Fig. S17. The amounts of PPTS with relative molar mass of up to 4000 were reduced by the reprecipitation, while that of PPTS-*b*-PDMS-*b*-PPTS with relative molar mass of up to 6000 was reduced.

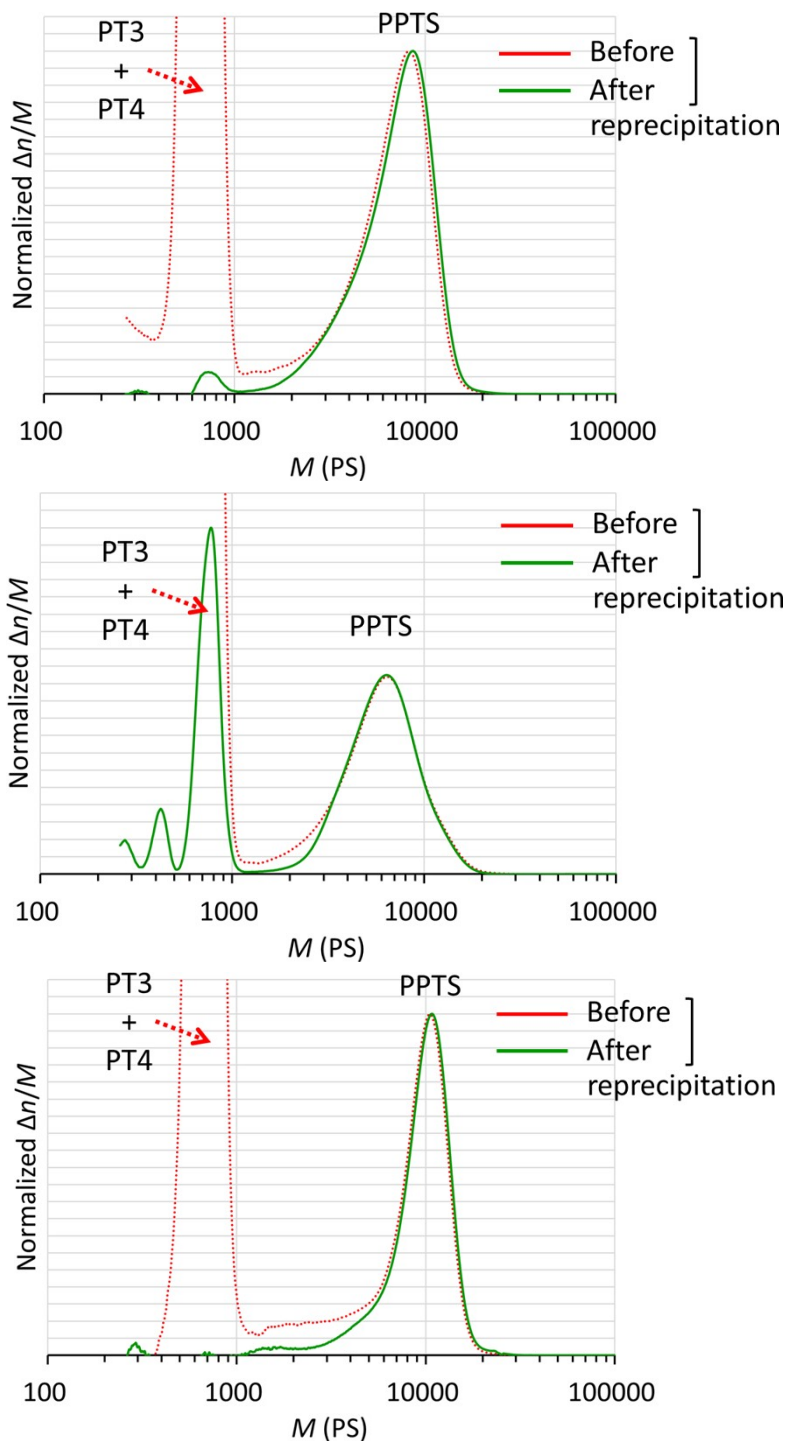


Fig. S19. Change in the molar-mass distributions of the PPTS and PPTS-*b*-PDMS-*b*-PPTS before and after reprecipitation in MeCN. (top) PPTS shown in Table 1, entry 5; (middle) PPTS shown in Table 2, entry 1; and (bottom) PPTS-*b*-PDMS-*b*-PPTS shown in Table 3, entry 2.

Thermogravimetric analysis of PPTS using alumina pans

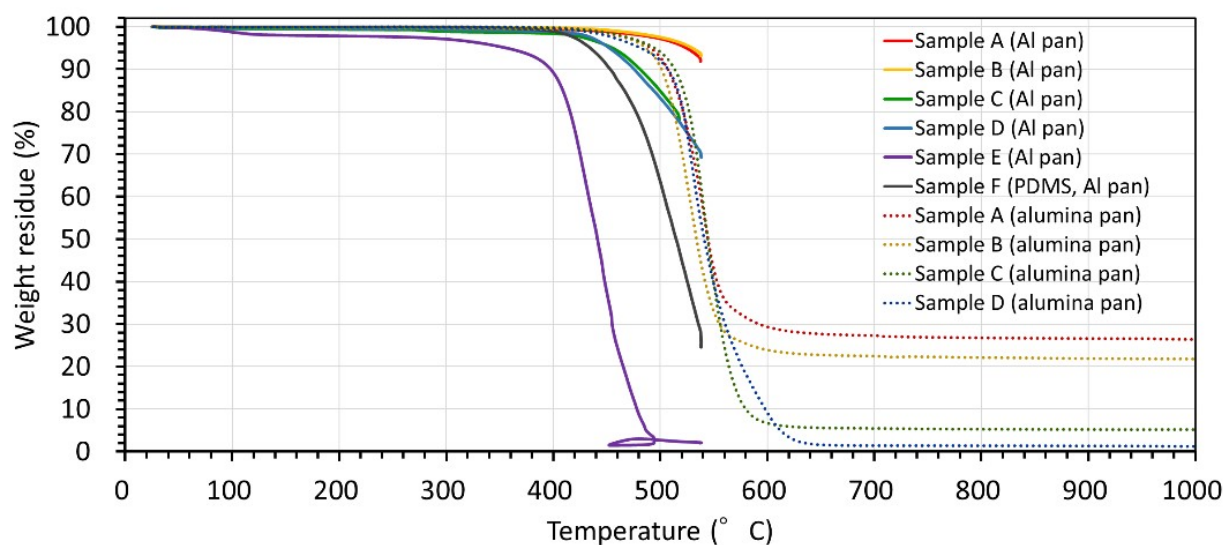


Fig. S20. Thermogravimetric results for PPTS, PPTS-*b*-PDMS-*b*-PPTS, and PDMS in aluminium and alumina pans. Samples A (PPTS-(Allyl)₂, $M_{n,NMR} = 7.17 \text{ kg mol}^{-1}$, $D_M = 1.08_5$), B (PPTS-(Allyl)₂, $M_{n,NMR} = 13.6 \text{ kg mol}^{-1}$, $D_M = 1.15_2$; Table 1, entry 4), C (PPTS-*b*-PDMS-*b*-PPTS, $\langle X_{n,D}/X_{n,PT} \rangle = 77.9/51.2$; Table 3, entry 1), D (PPTS-*b*-PDMS-*b*-PPTS, $\langle X_{n,D}/X_{n,PT} \rangle = 143/37.4$; Table 3, entry 2), E (α,ω -bis(silanol)-terminated PPTS, $M_{n,NMR} = 8.75 \text{ kg mol}^{-1}$, $D_M = 1.12_7$; Fig. S1), and F (α,ω -bis[dimethyl(vinyl)silyl]-terminated PDMS, $M_{n,NMR} = 6.22 \text{ kg mol}^{-1}$, $\langle X_{n,D} \rangle = 81.4$, $D_M = 1.09_4$).

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