Organocatalytic Controlled/Living Ring-Opening Polymerization of Cyclotrisiloxanes Initiated by Water with Strong Organic Base Catalysts

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Electronic Supplementary Information (ESI)

Contents:

Experimental Section

Materials.

Hexamethylcyclotrisiloxane (D**Error!**, Kanto, 95%) was purified by sublimation by heating under an nitrogen atmosphere prior to use. Octamethylcyclotetrasiloxane (D**Error!**, TCI, >98%), 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane (D**Error!**, Gelest, >95%, mixture of *cis* and *trans* isomers, *cis*/*trans* = 23/77), 1,3,5-trimethyl-1,3,5-tris(3,3,3-trifluoropropyl)cyclotrisiloxane (D**Error!**, TCI, >98.0%, mixture of *cis* and *trans* isomers, *cis*/*trans* = 20/80), *N*,*N*-diisopropylethylamine (DIPEA, TCI, >99.0%), and pyridine (Kanto, >99.0%) were dried over CaH_2 and distilled under reduced pressure prior to use. Decamethylcyclopentasiloxane (D**Error!**, TCI, >99%), hexaphenylcyclotrisiloxane (D**Error!**, TCI, >96.0%), 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane (D**Error!**, Shin-Etsu, mixture of isomers), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, TCI, >98.0%), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, Kanto, >97.0%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene

(TBD, Aldrich, 98%), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, TCI, >95.0%), 1,1,3,3-tetramethylguanidine (TMGa, TCI, >99.0%), 2-*tert*-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diaza- phosphorine (BEMP, Aldrich, >98.0%), *tert*-butylimino-tri(pyrrolidino)phosphorane (*t*Bu-P_1(pyrr), Aldrich, ≥97.0%), 1-ethyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene) (Et-P_2, Aldrich, ≥98.0%), 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (TiBP, Aldrich, 97%), chlorotrimethylsilane (Me_3SiCl, TCI, >98.0%), chlorotriethylsilane (Et_3SiCl, TCI, >97.0%), chlorodimethyl(phenyl)silane ($Me_2PhSiCl$, Gelest, >95%), chlorodimethylsilane (Me_2HSiCl, TCI, >95.0%), chloro(dimethyl)vinylsilane ($Me_2ViSiCl$, TCI, >97.0%), allyl(chloro)dimethylsilane ($AllylMe_2SiCl$, TCI, >96.0%), chloro(chloromethyl)dimethylsilane ($(ClCH_2)Me_2SiCl$, TCI, >98.0%), (bromomethyl)chlorodimethylsilane ($(BrCH_2)Me_2SiCl$, Aldrich, 97%), chlorodimethyl(2,3,4,5,6-pentafluorophenyl)silane ($Me_2(C_6F_5)SiCl$, Wako, >95.0%), chlorotriethoxysilane ($(EtO)_3SiCl$, Aldrich, 98%), dichloro(methyl)phenylsilane (Gelest, 95–100%), dimethylamine (ca. 2.0 mol L^{-1} in ethanol, TCI), propylamine (TCI, >98.0%), isopropylamine (Wako, 99.0%), iodomethane (Wako, 99.5%), benzoic acid (Kanto, >99.5%), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Aldrich, ≥98%), perfluorobenzoic acid (PFBA, TCI, >98.0%), sodium trifluoroacetate (TFANa, Wako, >97.0%), silver trifluoroacetate (TFAAg, Wako, >97.0%), sodium sulfate (Na_2SO_4, Wako, >99.0%), tetrahydrofuran (THF, stabilizer free, Wako, >99.5%), dichloromethane (CH_2Cl_2, stabilized with 2-methylbut-2-ene, Wako, >99.5%), dimethylsulfoxide (DMSO, Wako, Super Dehydrated, >99.0%), diethyl ether (Et_2O, Wako, Super Dehydrated, >99.5%), and acetonitrile (MeCN, Wako, >99.5%) were used as received. 'Dry' CH_2Cl_2 (Wako, super dehydrated, water content < 0.001%) and 'dry' THF (Kanto, dehydrated –Super Plus–, water content < 0.001%) were purified with Glass Contour Solvent Dispensing System and used for most of the polymerizations to exclude experimental errors originated from a variation of water content in a not dehydrated solvent among lots. Amberlyst® A26 (OH^- form, Aldrich) was washed with THF (stabilizer free) several times prior to use.

1,5-Dihydroxy-1,1,3,3,5,5-hexamethyltrisiloxane (D**Error!**-$(OH)_2$),[1] 1,4,6-triazabicyclo[3.3.0]oct-4-ene (TBO),[2] propylenethiourea,[3] *N*,*N'*,*S*-trimethylisothiourea hydroiodide,[4] 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide,[5] and 1,5,7-triazabicyclo[4.3.0]non-6-ene (TBN)[6] were synthesized as previously reported.

Measurements.

NMR

^{1}H (600 MHz), ^{13}C{^{1}H} (150 MHz), ^{29}Si{^{1}H} (119 MHz), and ^{19}F (564 MHz) NMR spectra were recorded on a BRUKER Biospin AVANCE III HD 600 NMR spectrometer with a CryoProbe. Chemical shifts were reported in δ (ppm) and were referenced to tetramethylsilane (0.00 ppm) for ^{1}H, ^{13}C, and ^{29}Si and to (trifluoromethyl)benzene (−63.72 ppm) for ^{19}F.

Size-Exclusion Chromatography (SEC)

Size-exclusion chromatography (SEC) was performed at 45 °C using a Waters ACQUITY Advanced Polymer Chromatography (APC) System consisting of p-Isocratic Solvent Manager (Model AIS), Sample Manager pFTN (Model ASM), Column Manager-S (Model AZC), PDA TS Detector (Model ADT), Refractive Index (RI) Detector (Model URI) equipped with a Waters APC™ XT45 column (linear, 4.6 mm × 150 mm; pore size, 4.5 nm; bead size, 1.7 µm; exclusion limit, 5000), a Waters APC™ 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 APC™ XT450 column (linear, 4.6 mm × 150 mm; pore size, 45.0 nm; bead size, 2.5 µm; exclusion limit, 400 000) in THF at the flow rate of 0.70 mL min^{-1}. The polydispersity ($Đ$) was determined based on a calibration curve prepared by polystyrene (PS) of TSKgel® standard polystyrene oligomer kit (Tosoh) with the weight-average molecular weights (M_w) and ($Đ$)s of 9.64×10^4 g mol^{-1} (1.01) and 5.9×10^2 g mol^{-1} (1.19) and PS of ReadyCal PS Kit for APC (Waters) with M_w ($Đ$)s of 6.25×10^4 g mol^{-1} (1.05), 4.23×10^4 g mol^{-1} (1.02), 3.40×10^4 g mol^{-1} (1.04), 2.75×10^4 g mol^{-1} (1.03), 2.12×10^4 g mol^{-1} (1.02), 1.55×10^4 g mol^{-1} (1.05), 8.90×10^3 g mol^{-1} (1.03), 4.71×10^3 g mol^{-1} (1.08), 3.46×10^3 g mol^{-1} (1.06), 2.25×10^3 g mol^{-1} (1.05), 1.25×10^3 g mol^{-1} (1.12).

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 or reflector mode by accumulating 200 to 2000 laser shots at a 19 kV acceleration voltage and externally calibrated with Tosoh TSKgel® standard Polystyrene TS-502 (M_w = 2.63 kg mol^{-1}, $Đ$ = 1.05) and TS-521 (M_w = 5.06 kg mol^{-1}, $Đ$ = 1.02). In a typical measurement, a solution of 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), a matrix (DCTB, 50 mg mL^{-1}, 20 μL), and a cationization agent (TFAAg, 2.2 mg mL^{-1}, 45 μL). Solution of samples were prepared by mixing polysiloxane (30 mg mL^{-1} in THF, 10 μL), a matrix (DCTB for poly(dimethylsiloxane) (PDMS), poly[methyl(vinyl)siloxane] (PMVS), and poly(methylphenylsiloxane) (PMPS); PFBA for poly[methyl(3,3,3-trifluoropropyl)siloxane] (PMTFPS), 50 mg mL^{-1}, 20 μL), and a cationization agent (TFAAg or TFANa, 2.2 mg mL^{-1}, 45 μL). Approximately 10 μL of the obtained mixture were spotted on a ground steel target plate and dried prior to measurements.

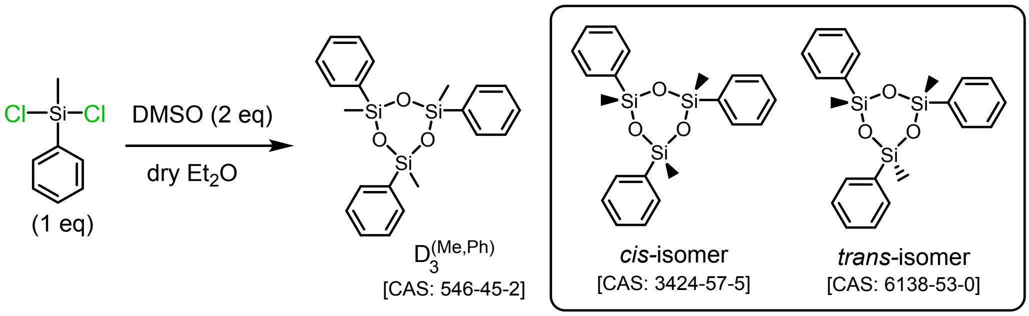
High Resolution Mass Spectrometry (HR-MS)

The high-resolution atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) mass spectra were obtained on a Bruker micrOTOF II.

Differential Scanning Calorimetry (DSC)

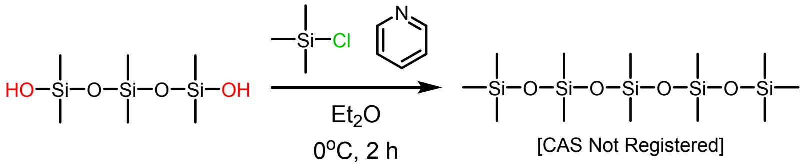
Melting points (m.p.) of the compounds newly synthesized in this study were measured by differential scanning calorimetry (DSC) on a Seiko Instruments DSC 7020. Approximately 3 mg of samples were used for each measurement. The samples were heated from 25 °C to 140 °C at the heating rate of 2 °C min^{-1} under nitrogen atmosphere. The m.p. was determined from the extrapolated onset temperature and the peak temperature of an endothermic peak in the first scan.

Synthesis of 1,3,5-Trimethyl-1,3,5-triphenylcyclotrisioxane (DError!)



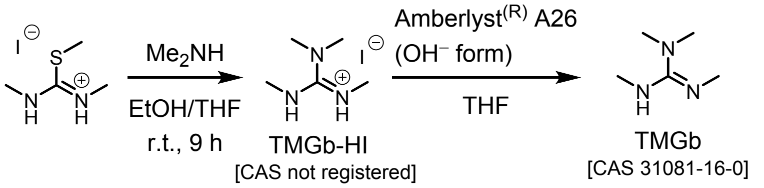
The synthesis of D**Error!** was carried out by modifying previously reported procedures for the synthesis of other cyclotrisiloxanes from dichlorosilanes and DMSO.[7, 8] Dry DMSO (6.88 g, 88.1 mmol) was added dropwise to a solution of dichloro(methyl)phenylsilane (8.42 g, 44.1 mmol) in dry Et_2O (63 mL) at ambient temperature under a nitrogen atmosphere. After 48 min, the reaction mixture was diluted with Et_2O and washed with water several times until acidic by-products were removed. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give a viscous colorless liquid containing isomers of D**Error!** and 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane. The crude product was distilled under reduced pressure to obtain a mixture of *cis*- D**Error!** and *trans*- D**Error!** (*cis*/*trans* = 24/76) as a white solid (1.80 g, 30% yield). B.p. 110–118 °C / 0.06 mmHg (as a mixture of *cis*- D**Error!** and *trans*- D**Error!**). (Lit. 171 °C / 1.5 mmHg).[9] ^{1}H NMR (600 MHz, $CDCl_3$): *cis*-isomer δ 7.49-7.46 (m, 6H, Ar-*H* in *m*-position), 7.36-7.32 (m, 3H, Ar-*H* in *p*-position), 7.26-7.22 (m, 6H, Ar-*H* in *o*-position), 0.55 (s, 9H, Si*Me*); *trans*-isomer 7.73-7.70 (m, 2H, Ar-*H* in *m*-position), 7.60-7.56 (m, 4H, Ar-*H* in *m*-position), 7.46-7.41 (m, 1H, Ar-*H* in *p*-position), 7.45-7.42 (m, 2H, Ar-*H* in *o*-position), 7.42-7.37 (m, 2H, Ar-*H* in *p*-position), 7.35-7.30 (m, 4H, Ar-*H* in *o*-position), 0.47 (s, 6H, Si*Me*), 0.41 (s, 3H, Si*Me*). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): *cis*-isomer δ 135.85 (aromatic, *ipso*-position), 133.33 (aromatic, *o*-position), 130.03 (aromatic, *p*-position), 127.68 (aromatic, *m*-position), −0.06 (Si*Me*); *trans*-isomer δ 136.61 (1C, aromatic, *ipso*-position), 136.20 (2C, aromatic, *ipso*-position), 133.27 (2C, aromatic, *o*-position), 133.20 (1C, aromatic, *o*-position), 130.22 (1C, aromatic, *p*-position), 130.12 (2C, aromatic, *p*-position), 127.96 (1C, aromatic, *m*-position), 127.80 (2C, aromatic, *m*-position), −0.26 (2C, Si*Me*), −0.42 (1C, Si*Me*). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): *cis*-isomer δ −21.02 (*Si*Me); *trans*-isomer δ −21.02 (2Si, *Si*Me), −21.06 (1Si, *Si*Me). HRMS (ESI) calcd for $[C_{21}H_{25}O_3Si_3]^+$ $[M+H]^+$ 409.1111, found 409.1109.

Synthesis of Dodecamethylpentasiloxane



Chlorotrimethylsilane (481 µL, 3.79 mmol) was added dropwise to a solution of D**Error!**-$(OH)_2$ (0.38 g, 1.6 mmol) and dry pyridine (509 µL, 6.32 mmol) in dry CH_2Cl_2 (878 µL) at 0 °C. The reaction was continued for 2 h at 0 °C. The reaction mixture was diluted with CH_2Cl_2 (10 mL) and washed with water (5 mL × 3). The organic phase was separated, dried over Na_2SO_4, and filtered. The solvent was removed from the filtrate with an evaporator. The residue was purified by distillation at reduced pressure to obtain the targeted compound as a colorless liquid (0.27 g, 44% yield). B.p. 72–75 °C / 4 mmHg. (Lit. 110–113°C / 21 mmHg).[10] ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.09 (s, 18H, Si*Me*$_3$), 0.07 (s, 6H, Me_3Si-O-$SiMe_2$-O-Si*Me*$_2$-), 0.05 (s, 12H, Me_3Si-O-Si*Me*$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 1.80 (Si*Me*$_3$), 1.16 (Me_3Si-O-Si*Me*$_2$), 1.07 (Me_3Si-O-$SiMe_2$-O-Si*Me*$_2$-). ^{29}Si{^{1}H} NMR (119 MHz, $CDCl_3$): δ 7.28 (*Si*Me_3), −21.38 (Me_3Si-O-*Si*Me_2), −22.15 (Me_3Si-O-$SiMe_2$-O-*Si*Me_2-). HRMS (APCI) calcd for $[C_{12}H_{37}O_4Si_5]^+$ $[M+H]^+$ 385.1538, found 385.1538.

Synthesis of 1,1,2,3-Tetramethylguanidine (TMGb)

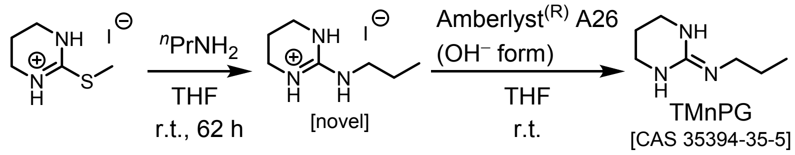


Dimethylamine in ethanol (2.0 mol L^{-1}, 42.3 mL, 85 mmol) was added to *N,N′,S*-trimethylisothiourea hydroiodide (10.41 g, 42.30 mmol) under a nitrogen atmosphere at ambient temperature, and the mixture was stirred for 9 h at the same temperature. After ceasing the evolution of methanethiol, the reaction mixture was concentrated *in vacuo* to obtain crude 1,1,2,3-tetramethylguanidine hydroiodide (TMGb-HI) as a yellow solid. One third of the crude product (3.43 g, 14.1 mmol) was suspended in THF (40 mL, stabilizer-free) and neutralized with Amberlyst® A26 (OH^- form, 0.8 mequiv mL^{-1}, 24.0 mL-wet volume, 19.2 mmol). The resultant solution was filtered, concentrated, and distilled under reduced pressure in the presence of CaH_2 (0.40 g) to give TMGb (0.63 g, *y*. 38%) as a colorless crystalline solid.

TMGb-HI: m.p. 104–113°C (Lit. 120–120.5°C).[11] ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.41 (br s, 2H, N*H*), 2.90 (br s, 6H, -N*Me*$_2$), 2.82 (br s, 3H, -NH*Me*), 2.81 (br s, 3H, -NH*Me*). ^{13}C{^{1}H} NMR (151 MHz, DMSO-d_6): δ 160.41 (quaternary), 39.50 (-N*Me*$_2$), 30.92 (-NH*Me*). HRMS (APCI) calcd for $[C_5H_{14}N_3]^+$ $[M-I]^+$ 116.1187, found 116.1186; calcd for $[C_5H_{14}N_3I_2]^-$ $[M+I]^-$ 369.9283, found 369.9281.

TMGb: m.p. 43–47 °C, b.p. 68–71 °C / 8.3 mmHg. *Hygroscopic*. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.82 (s, 6H, -NH*Me* and -N=*Me*), 2.68 (s, 6H, -N*Me*$_2$). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 160.57 (quaternary), 39.63 (-N*Me*$_2$), 32.83 (-NH*Me* and -C=N*Me*). HRMS (APCI) calcd for $[C_5H_{14}N_3]^+$ $[M+H]^+$ 116.1187, found 116.1185.

Synthesis of 1,3-Trimethylene-2-propylguanidine (TMnPG)



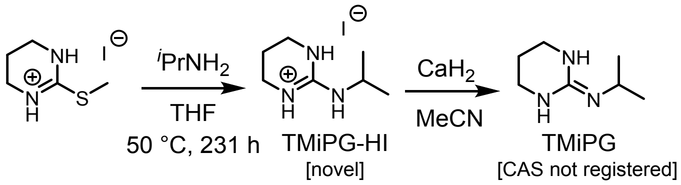
1,2-Trimethylene-3-propylguanidine hydroiodide (TMnPG-HI) was synthesized by modifying a typical procedure to synthesize guanidine.[12] Propylamine (6.10 mL, 74.2 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (9.15 g, 35.4 mmol) in THF (50 mL, with stabilizer) at ambient temperature under a nitrogen atmosphere. The reaction mixture was stirred for 62 h at ambient temperature and then concentrated, washed with *n*-hexane, and dried *in vacuo* to give crude TMnPG-HI as a white solid. The crude product was again dissolved in THF (100 mL, with stabilizer) and stirred with Amberlyst® A26 (OH^- form, 0.8 mequiv mL^{-1}, 50 mL-wet volume, 40 mmol) for 4 h at ambient temperature. The solution was filtered and the filtrate was concentrated *in vacuo*. The residue was distilled under reduced pressure in the presence of CaH_2 to obtain 1,2-trimethylene-3-propylguanidine (TMnPG) (3.54 g, 71% yield) as a yellowish solid.

TMnPG-HI: m.p. 53–56 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 7.59 (br s, 2H, N*H*$(CH_2)_3$N*H*), 7.18 (br s, 1H, N*H*^{n}Pr), 3.24 (t, J = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.01 (dt, J = 5.0 Hz and 7.0 Hz, 3H, C*H*$_2$CH$_2$CH$_3$), 1.81 (quintet, J = 5.8 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.47 (sextet, J = 7.3 Hz, 2H, C*H*$_2$CH$_3$), 0.87 (t, J = 7.4 Hz, 3H, C*H*$_3$).

^{13}C{^{1}H} NMR (151 MHz, DMSO-*d*$_6$): *δ* 152.99 (*C*N^{n}Pr), 42.41 (N*C*H$_2$CH$_2$CH$_3$), 38.54 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 22.33 (*C*H$_2$CH$_3$), 20.17 (NHCH$_2$*C*H$_2$CH$_2$NH), 11.53 (*C*H$_3$). HRMS (APCI) calcd for $[\mathrm{C_7H_{16}N_3}]^+$ $[\mathrm{M{-}I}]^+$ 142.1344, found 142.1346; calcd for $[\mathrm{I}]^-$ $[\mathrm{M{-}TMnPG{-}H}]^-$ 126.9050, found 126.9053.

TMnPG: m.p. 94–99 °C (Lit. ~50 °C).[13] B.p. 118–121°C / 1.1 mmHg (Lit. 138°C / 0.5 mmHg).[13] *Hygroscopic*. ^{1}H NMR (600 MHz, CDCl$_3$): *δ* 3.36 (t, *J* = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 3.27 (t, *J* = 6.9 Hz, 3H, C*H*$_2$CH$_2$CH$_3$), 1.91 (quintet, *J* = 5.8 Hz Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.62 (sextet, *J* = 7.2 Hz, 2H, C*H*$_2$CH$_3$), 0.99 (t, *J* = 7.4 Hz, 3H, C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, CDCl$_3$): *δ* 153.22 (*C*N^{n}Pr), 43.06 (N*C*H$_2$CH$_2$CH$_3$), 38.28 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 22.26 (*C*H$_2$CH$_3$), 20.13 (NHCH$_2$*C*H$_2$CH$_2$NH), 11.30 (*C*H$_3$). HRMS (APCI) calcd for $[\mathrm{C_7H_{16}N_3}]^+$ $[\mathrm{M{+}H}]^+$ 142.1344, found 142.1341.

Synthesis of 1,3-Trimethylene-2-isopropylguanidine (TMiPG)



Isopropylamine (2.07 g, 35.0 mmol) was added to a suspension of 2-methylthio-1,4,5,6-tetrahydropyrimidine hydroiodide (4.52 g, 17.5 mmol) in dry THF (26 mL) at ambient temperature under a nitrogen atmosphere. The reaction mixture was stirred for 231 h at 50 °C, and then concentrated *in vacuo*. The residue was washed with *n*-hexane and dried *in vacuo* to give 1,2-trimethylene-3-isopropylguanidine hydroiodide (TMiPG-HI) as a light brown solid (4.17 g, 88% yield). The crude product was dissolved in MeCN (6 mL) and stirred with CaH$_2$ (0.84 g) at 60 °C for 3.5 h. The solution was concentrated *in vacuo*. The residue was distilled by heating at 190 °C and 0.75 mmHg to obtain 1,3-trimethylene-2-isopropylguanidine (TMiPG, 0.38 g, 7.6% yield) as a white solid.

TMiPG-HI: m.p. 67–76°C. ^{1}H NMR (600 MHz, DMSO-*d*$_6$): *δ* 7.50 (br s, 2H, N*H*(CH$_2$)$_3$N*H*), 7.10 (br d, *J* = 7.9 Hz, 1H, N*H*^{i}Pr), 3.63 (septet, *J* = 6.9 Hz, 1H, NC*H*), 3.26 (t, *J* = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 1.82 (quintet, *J* = 5.8 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N), 1.12 (d, *J* = 6.3 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, DMSO-*d*$_6$): *δ* 152.14 (*C*N^{i}Pr), 42.86 (N*C*H), 38.56 (NH*C*H$_2$CH$_2$*C*H$_2$NH), 22.91 (*C*H$_3$), 20.16 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (APCI) calcd for $[\mathrm{C_7H_{16}N_3}]^+$ $[\mathrm{M{-}I}]^+$ 142.1344, found 142.1343; calcd for $[\mathrm{I}]^-$ $[\mathrm{M{-}TMiPG{-}H}]^-$ 126.9050, found 126.9052.

TMiPG: m.p. 125–127 °C. *Hygroscopic*. ^{1}H NMR (600 MHz, DMSO-*d*$_6$): *δ* 3.62 (septet, *J* = 6.4 Hz, 1H, NC*H*), 3.10 (t, *J* = 5.8 Hz, 4H, NC*H*$_2$CH$_2$C*H*$_2$N), 1.57 (quintet, *J* = 5.7 Hz, 2H, NCH$_2$C*H*$_2$CH$_2$N), 0.99 (d, *J* = 6.4 Hz, 6H, C*H*$_3$). ^{13}C{^{1}H} NMR (151 MHz, DMSO-*d*$_6$): *δ* 153.36 (*C*N^{i}Pr), 41.41 (N*C*H), 41.00 (N*C*H$_2$CH$_2$*C*H$_2$N), 23.65 (*C*H$_3$), 21.78 (NHCH$_2$*C*H$_2$CH$_2$NH). HRMS (APCI) calcd for $[\mathrm{C_7H_{16}N_3}]^+$ $[\mathrm{M{+}H}]^+$ 142.1344, found 142.1342.

Homopolymerization of DError! (Tables 1 and 2)

A typical polymerization was carried out as follows. D**Error!** (221 mg, 991 μmol), dry THF (358 μL) and a THF solution of H$_2$O (1/99 (v/v), 179 μL, 99.1 μmol) was added to a flask equipped with a needle-bulb under a N$_2$ atmosphere. A THF solution of TMnPG (100 mg mL^{-1}, 14.0 μL, 9.91 μmol) was added to initiate the polymerization at 30 °C. After stirring for 90 min, pyridine (63.9 μL, 756 μmol, 8 equiv) as a scavenger of hydrochloric acid and Me$_2$PhSiCl (83.2 μL, 496 μmol, 5 equiv) as an end-capping agent were added to the reaction mixture to end-cap the propagating polymers. The end-capping reaction was continued for 15 min at 30 °C. The mixture was concentrated, washed with MeOH (5 mL) four times, and the supernatant was carefully removed with a Pasteur pipette. The remaining product was concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated PDMS (PDMS-($OSiMe_2Ph)_2$) (189 mg, 75.9% yield, $M_{\mathrm{n,NMR}}$ = 2.60 kg mol^{-1}, *Đ*= 1.12) as a colorless liquid. ^{1}H and ^{29}Si{^{1}H} NMR spectra of the product are shown in Figure 3.

For the synthesis of α,ω-dihydroxy-terminated PDMS (PDMS-$(OH)_2$), benzoic acid (12.1 mg, 10 equiv, 99.12 μmol) was added to the reaction mixture instead of pyridine and $Me_2PhSiCl$. The reaction mixture was stirred for 5 min to neutralize the catalyst. The mixture was concentrated, washed with MeCN (3 mL) three times since addition of MeOH causes partial condensation of PDMS-$(OH)_2$. The upper MeCN layer was carefully removed with a Pasteur pipette. The product was concentrated *in vacuo* to obtain PDMS-$(OH)_2$ (135 mg, 60.7% yield, $M_{\mathrm{n,NMR}}$ = 2.68 kg mol^{-1}, *Đ*= 1.09) as a colorless liquid. ^{1}H and ^{29}Si{^{1}H} NMR spectra of the product are shown in Figure 3.

The model polymerization of D**Error!** in the presence of dodecamethylpentasiloxane (38.2 mg, 44.8 μL, 99.1 μmol) were carried out in the same manner using D**Error!** (221 mg, 991 μmol), a THF solution of H_2O (1/99 (v/v), 179 μL, 99.1 μmol), dry THF (313 μL), a THF solution of TMnPG (100 mg mL^{-1}, 14.0 μL, 9.91 μmol), pyridine (63.9 μL, 756 μmol), and $Me_2PhSiCl$ (83.2 μL, 496 μmol). The product was PDMS-($OSiMe_2Ph)_2$) (173 mg, 69.5% yield, $M_{\mathrm{n,NMR}}$ = 2.90 kg mol^{-1}, *Đ*= 1.13).

The polymerizations of D**Error!** under different conditions were similarly carried out as described in the typical procedure using THF solutions of the strong organic bases under the conditions listed in Tables 1 and 2.

The low-molecular-weight part of the products are also removed with the purification procedures when M_n of the product is low as shown in Figure S1.

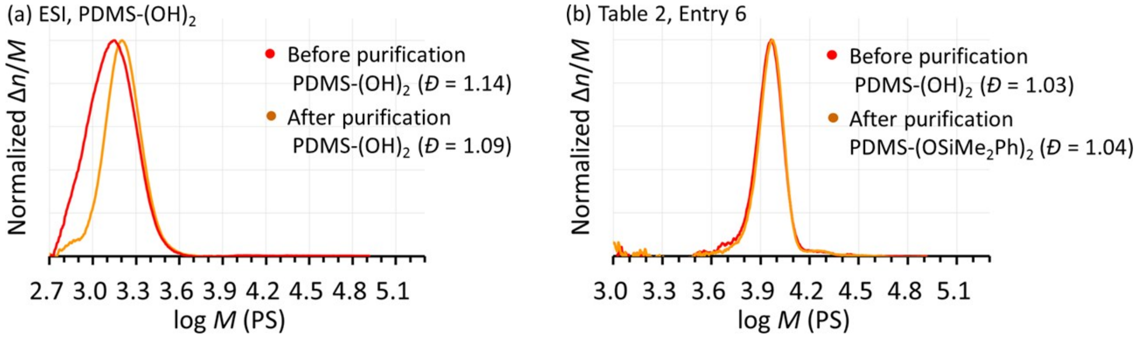


Figure S1. The change in the molecular weight distribution of (a) PDMS-$(OH)_2$ obtained in the polymerization described in the section of 'Homopolymerization of D**Error!**' and (b) PDMS-$(OSiMe_2Ph)_2$ obtained in the polymerization shown in entry 6 of Table 2 before and after the purification.

Synthesis of Telechelic PDMSs (Table 2)

The synthesis of telechelic PDMSs was carried out in the same manner as written in the section of 'Homopolymerization of D**Error!**'. Non-dehydrated CH_2Cl_2 (358 μL, stabilized with stabilized with 2-methylbut-2-ene) was used instead of dry THF. The polymerizations were carried out with D**Error!** (221 mg, 991 μmol) in a vial with a screw cap under air.

PDMS-$(OSiMe_2H)_2$ (Table 2, entry 10): PDMS-$(OSiMe_2H)_2$ (157 mg, 67.1 % yield, $M_{\mathrm{n,NMR}}$ = 2.95 kg mol^{-1}, *Đ*= 1.15) was obtained as a colorless liquid by end-capping with Me_2HSiCl (55.0 μL, 496 μmol). MeCN instead of MeOH was used for the purification. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S9.

PDMS-(OSiMe$_2$Vi)$_2$ (Table 2, entry 11): PDMS-(OSiMe$_2$Vi)$_2$ (165 mg, 69.0% yield, $M_{n,NMR}$ = 3.00 kg mol^{-1}, $Đ$ = 1.14) was obtained as a colorless liquid by end-capping with Me$_2$ViSiCl (66.9 μL, 496 μmol). ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S10.

PDMS-(OSiAllylMe$_2$)$_2$ (Table 2, entry 12): PDMS-(OSiAllylMe$_2$)$_2$ (162 mg, 66.8% yield, $M_{n,NMR}$ = 2.77 kg mol^{-1}, $Đ$ = 1.13) was obtained as a colorless liquid by end-capping with AllylMe$_2$SiCl (74.5 μL, 496 μmol). ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S11.

PDMS-[OSi(CH$_2$Cl)Me$_2$]$_2$ (Table 2, entry 13): PDMS-[OSi(CH$_2$Cl)Me$_2$]$_2$ (192 mg, 78.8% yield, $M_{n,NMR}$ = 3.14 kg mol^{-1}, $Đ$ = 1.10) was obtained as a colorless liquid using (ClCH$_2$)Me$_2$SiCl (65.2 μL, 496 μmol) as an end-capping agent and DIPEA (129 μL, 756 μmol) as a scavenger of hydrochloric acid. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S12.

PDMS-[OSi(CH$_2$Br)Me]$_2$ (Table 2, entry 14): PDMS-[OSi(CH$_2$Br)Me$_2$]$_2$ (172 mg, 68.0% yield, $M_{n,NMR}$ = 3.08 kg mol^{-1}, $Đ$ = 1.13) was obtained as a colorless liquid by end-capping with Me$_2$(BrCH$_2$)SiCl (74.5 μL, 496 μmol). ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S13.

PDMS-(OSiMe$_2$C$_6$F$_5$)$_2$ (Table 2, entry 15): PDMS-(OSiMe$_2$C$_6$F$_5$)$_2$ (194 mg, 72.8% yield, $M_{n,NMR}$ = 3.38 kg mol^{-1}, $Đ$ = 1.13) was obtained as a colorless liquid using Me$_2$(C$_6$F$_5$)SiCl (91.7 μL, 496 μmol) as an end-capping agent and DIPEA (129 μL, 756 μmol) as a scavenger of hydrochloric acid. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S14.

PDMS-[Si(OEt)$_3$]$_2$ (Table 2, entry 16): PDMS-[Si(OEt)$_3$]$_2$ (115 mg, 45.1% yield, $M_{n,NMR}$ = 3.25 kg mol^{-1}, $Đ$ = 1.11) was obtained as a colorless liquid by end-capping with (EtO)$_3$SiCl (97.3 μL, 496 μmol) as an end-capping agent. MeCN instead of MeOH was used for the purification. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S15.

Homopolymerization of DError! (Table 3, entry 1)

DError! (145 mg, 354 μmol), dry CH$_2$Cl$_2$ (164 μL) and a THF solution of H$_2$O (1/99 (v/v), 64 μL, 99 μmol) was added to a flask equipped with a needle-bulb under a N$_2$ atmosphere. A THF solution of TMnPG (2.5 mg mL^{-1}, 20.0 μL, 0.35 μmol) was added to initiate the polymerization at 30 °C. After stirring for 219 min, pyridine (22.8 μL, 283 μmol, 8 equiv) as a scavenger of hydrochloric acid and Et$_3$SiCl (29.7 μL, 177 μmol, 5 equiv) as an end-capping agent were added to the reaction mixture. The end-capping reaction was continued for 150 min at 30 °C. The mixture was concentrated, washed with MeOH (5 mL) four times, and the supernatant was carefully removed with a Pasteur pipette. The remaining product was concentrated *in vacuo* to obtain α,ω-bis(triethylsilyl)-terminated PMPS (PMPS-(OSiEt$_3$)$_2$) (107 mg, 69.8% yield, $M_{n,NMR}$ = 5.60 kg mol^{-1}, $Đ$ = 1.16) as a colorless liquid. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S16. The formation of 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane (D**Error!**) in the polymerization was observed in the ^{1}H NMR spectrum of the crude product as shown in Figure S2.

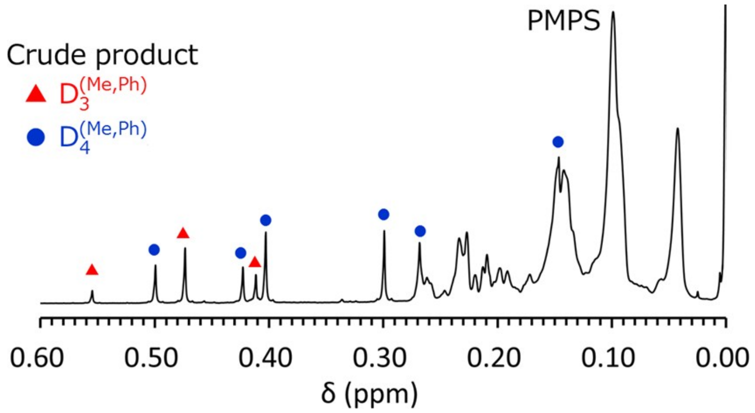


Figure S2. ^{1}H NMR spectrum of the crude product in the polymerization of D**Error!** taken just before the addition of the end-capping reaction observed in $CDCl_3$.

Homopolymerization of D**Error!** (Table 3, entry 3)

D**Error!** (253 µL, 229 mg, 885 µmol), dry CH_2Cl_2 (282 µL) and a THF solution of H_2O (1/99 (v/v), 160 µL, 88.5 µmol) was added to a flask equipped with a needle-bulb under a N_2 atmosphere. A THF solution of TMnPG (2.5 mg mL^{-1}, 50.0 µL, 0.885 µmol) was added to initiate the polymerization at 30 °C. After stirring for 72 min, pyridine (57.0 µL, 708 µmol, 8 equiv) as a scavenger of hydrochloric acid and $Me_2PhSiCl$ (74.3 µL, 443 µmol, 5 equiv) as an end-capping agent were added to the reaction mixture. The end-capping reaction was continued for 120 min at 30 °C. The mixture was concentrated, washed with MeOH (5 mL) four times, and the supernatant was carefully removed with a Pasteur pipette. The remaining product was concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated PMVS (PMVS-$(OSiMe_2Ph)_2$) (116 mg, 45.6% yield, $M_{n,NMR}$ = 3.64 kg mol^{-1}, $Đ$ = 1.11) as a colorless liquid. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S17. The formation of D**Error!** in the polymerization was observed in the ^{1}H NMR spectrum of the crude product as shown in Figure S3.

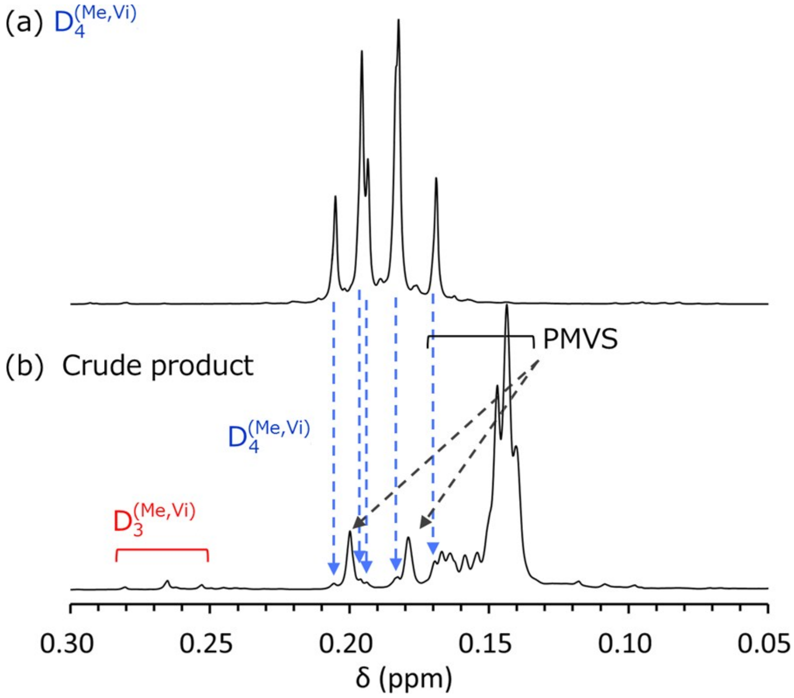


Figure S3. ^{1}H NMR spectrum of (a) D**Error!** and (b) the crude product in the polymerization of D**Error!** taken just before the addition of the end-capping agent observed in $CDCl_3$.

Homopolymerization of DError! (Table 3, entry 5)

D**Error!** (415 mg, 885 μmol), dry CH_2Cl_2 (411 μL) and a THF solution of H_2O (1/99 (v/v), 159 μL, 88.5 μmol) was added to a flask equipped with a needle-bulb under a N_2 atmosphere. A THF solution of TMnPG (2.5 mg mL^{-1}, 20.0 μL, 0.354 μmol) was added to initiate the polymerization at 30 °C. After stirring for 40 min, pyridine (57.0 μL, 708 μmol, 8 equiv) as a scavenger of hydrochloric acid and $Me_2PhSiCl$ (74.3 μL, 443 μmol, 5 equiv) as an end-capping agent were added to the reaction mixture. The end-capping reaction was continued for 120 min at 30 °C. The mixture was concentrated, washed with MeOH (5 mL) four times, and the supernatant was carefully removed with a Pasteur pipette. The remaining product was concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated PMTFPS (PMTFPS-$(OSiMe_2Ph)_2$) (222 mg, 50.4% yield, $M_{n,NMR}$ = 6.00 kg mol^{-1}, $Đ$ = 1.12) as a colorless liquid. ^{1}H NMR, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S18.

Attempts of Homopolymerization of DError!, DError!, and DError! (Table 3, entry 7–9)

D**Error!** (197 mg, 664 μmol), dry CH_2Cl_2 (320 μL), and a THF solution of H_2O (1/99 (v/v), 160 μL, 88.5 μmol) were added to a flask equipped with a needle-bulb under a N_2 atmosphere. A THF solution of TMnPG (100 mg mL^{-1}, 12.5 μL, 8.85 μmol) was added to initiate the polymerization at 30 °C. After stirring for 1500 min (25 h), a small aliquot (~50 μL) was taken and mixed with an excess amount of benzoic acid and $CDCl_3$ (~0.60 mL) prior to ^{1}H NMR measurements to determine the conversion of D**Error!**.

The reactions of D**Error!** and D**Error!** were carried out in the same manner. For the reaction of D**Error!**, D**Error!** (229 mg, 664 μmol), dry CH_2Cl_2 (282 μL), and a THF solution of H_2O (1/99 (v/v), 160 μL, 88.5 μmol) were used. For the reaction of D**Error!**, D**Error!** (197 mg, 531 μmol), dry CH_2Cl_2 (320 μL), a THF solution of H_2O (1/99 (v/v), 160 μL, 88.5 μmol) were used.

Statistical Copolymerization of DError! and DError! (Table 3, entry 10)

By the semi-batch method

D**Error!** (208 mg, 935 μmol), dry CH_2Cl_2 (347 μL) and a THF solution of H_2O (1/99 (v/v), 67.4 μL 37.4 μmol) was added to a flask equipped with a needle-bulb under a N_2 atmosphere. A THF solution of TMnPG (2.50 mg mL^{-1}, 106 μL, 1.87 μmol) was added to initiate the polymerization at 30 °C. D**Error!** (10.0 μL, 37.4 μmol) was added to the reaction mixture eight times at 28, 60, 95, 135, 182, 238, 308, and 401 min after the initiation. After 540 min of stirring, pyridine (24.1 μL, 299 μmol) and $Me_2PhSiCl$ (31.4 μL, 187 μmol) were added to the reaction mixture. The end-capping reaction was continued for 14 h with stirring at 30 °C. The mixture was concentrated and washed with MeOH (5 mL) four times. The residue was concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] (163 mg, 55.0% yield, $M_{n,NMR}$ = 6.34 kg mol^{-1}, $Đ$ = 1.13) as a colorless liquid. ^1H and $^{29}Si\{^1H\}$ NMR spectra of the product are shown in Figures S19 and S20.

By the premix method

D**Error!** (197 mg, 885 μmol), D**Error!** (237 μL, 885 μmol), dry CH_2Cl_2 (328 μL) and a THF solution of H_2O (1/99 (v/v), 63.8 μL, 35.4 μmol) was added to a flask equipped with a needle-bulb under a N_2 atmosphere. A THF solution of TMnPG (2.50 mg mL^{-1}, 100 μL, 1.77 μmol) was added to initiate the polymerization at 30 °C. After 25 h of stirring, pyridine (22.8 μL, 283 μmol) and $Me_2PhSiCl$ (29.7 μL, 177 μmol) were added to the reaction mixture. The end-capping reaction was continued for 1 h with stirring at 30 °C. The mixture was concentrated and washed with MeOH (5 mL) four times. The residue was concentrated *in vacuo* to obtain α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] (316 mg, 72.6% yield, $M_{n,NMR}$ = 12.9 kg mol^{-1}, $Đ$ = 1.37) as a colorless liquid. ^1H and $^{29}Si\{^1H\}$ NMR spectra of the product are shown in Figures S19 and S20. Small amounts of aliquots were taken during the polymerization to measure the conversion of D**Error!** and D**Error!** and the molecular weight distributions of the crude products. Figure S4 shows the first-order kinetic plot of the polymerization. It is obvious that D**Error!** polymerized almost selectively and quantitatively in the first 75 min of the polymerization. The observed SEC traces indicated The occurrence of the backbiting and the condensation after the quantitative consumption of D**Error!** as shown in Figure S5.

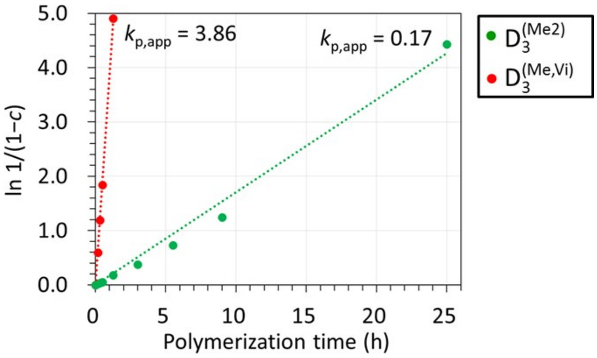


Figure S4. (a) First-order kinetic plot for the copolymerization of D**Error!** and D**Error!** catalyzed by TMnPG in CH_2Cl_2/THF (67/33 (v/v)) at 30 °C under the conditions of [D**Error!**]$_0$ = [D**Error!**]$_0$ = 1.80 mol L^{-1} and [D**Error!**]$_0$/[D**Error!**]$_0$/[H_2O]$_0$/[TMnPG]$_0$ = 25/25/1/0.05.

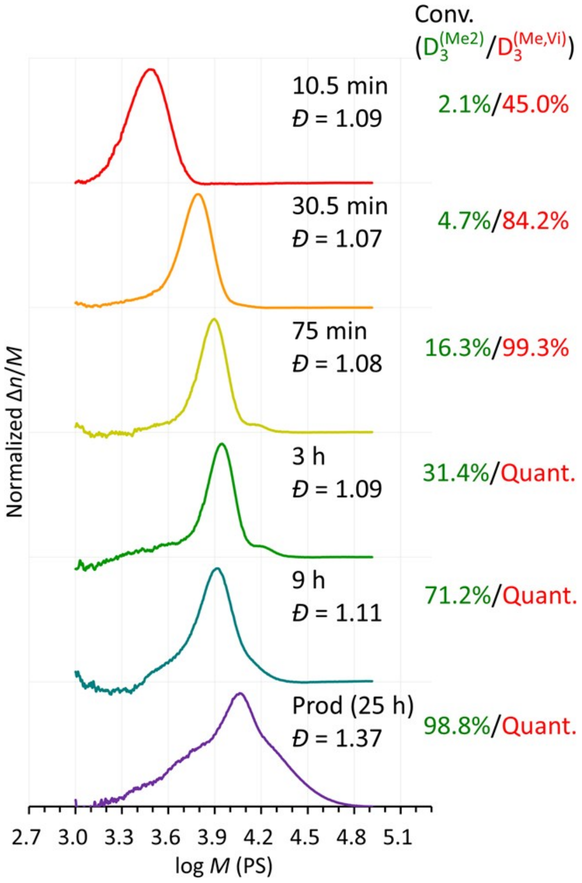


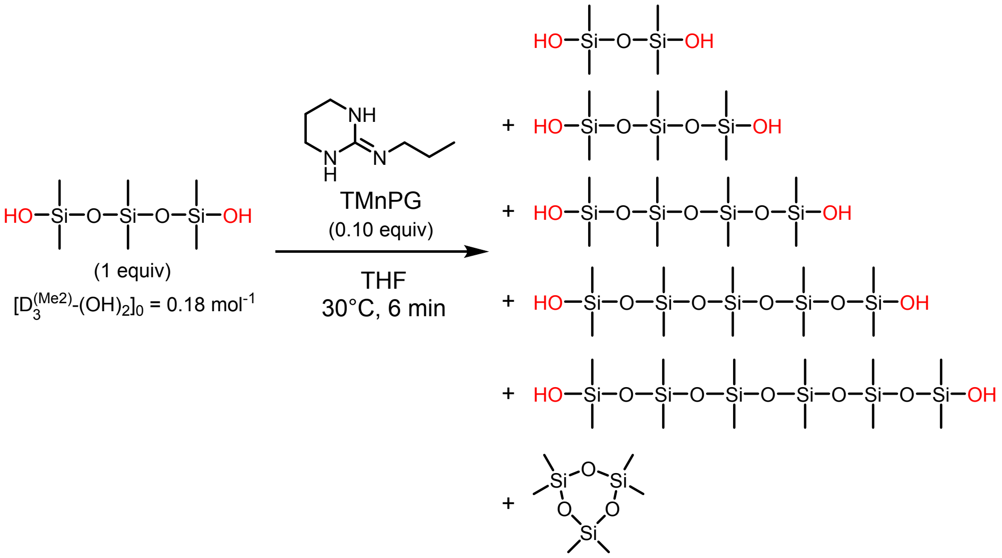
Figure S5. SEC chromatograms of the products obtained in the copolymerization of D**Error!** and D**Error!** based on the premixed method ([D**Error!**]$_0$/[D**Error!**]$_0$/[H_2O]$_0$/[TMnPG]$_0$ = 25/25/1/0.05 in CH_2Cl_2/THF = 67/33 (v/v) at 30 °C).

Block Copolymerization of D**Error!** and Other D_3 Monomers (Table 3, entries 11 and 12).

D**Error!** (221 mg, 991 μmol), dry CH_2Cl_2 (465 μL) and a THF solution of H_2O (1/99 (v/v), 71.4 μL 39.7 μmol) was added to a flask equipped with a needle-bulb under a N_2 atmosphere. A THF solution of TMnPG (100 mg mL^{-1}, 14.0 μL, 9.91 μmol) was added to initiate the polymerization at 30 °C. After 75 min of stirring, D**Error!** (177 mg, 270 μmol) was directly added to the reaction mixture and the mixture was stirred for 44 min. Pyridine (24.6 μL, 317 μmol) and Et_3SiCl (33.2 μL, 198 μmol) were added to the reaction mixture. The end-capping reaction was continued for 24 h with stirring at 30 °C. The mixture was concentrated, washed with MeOH (5 mL) five times. The residue was concentrated *in vacuo* to obtain α,ω-bis(triethylsilyl)-terminated PDPS-*b*-PDMS-*b*-PDPS (321 mg, 78.7% yield, $M_{\mathrm{n,NMR}}$ = 10.8 kg mol^{-1}, $Đ$ = 1.06) as a white solid. ^{1}H and ^{29}Si{^{1}H} NMR spectra of the product are shown in Figure S22.

α,ω-Bis[dimethyl(phenyl)silyl]-terminated PMVS-*b*-PDMS-*b*-PMVS (260 mg, 56.8% yield, $M_{\mathrm{n,NMR}}$ = 11.2 kg mol^{-1}, $Đ$ = 1.07) was synthesized in the same manner using D**Error!** (217 mg, 974 μmol), a THF solution of H_2O (1/99 (v/v), 70.2 μL, 38.9 μmol), CH_2Cl_2 (367 μL), a THF solution of TMnPG (2.5 mg mL^{-1}, 110 μL, 1.95 μmol), D**Error!** (260 μL, 974 μmol), pyridine (24.2 μL, 312 μmol), and $Me_2PhSiCl$ (32.7 μL, 195 μmol) under the conditions shown in Table 3, entry 11. ^{1}H and ^{29}Si{^{1}H} NMR spectra of the product are shown in Figures S19 and S20.

Model Reaction for the Intermolecular Transfer of a Terminal Dimethylsiloxy Unit of α,ω-Dihydroxy-Terminated PDMS



A THF solution of TMnPG (100 mg mL^{-1}, 14.3 μL, 10.1 μmol) was added to a solution of D**Error!**-(OH)$_2$ (24.3 mg, 101 μmol) in dry THF (547 μL) under a N_2 atmosphere at 30 °C. Small aliquots (~120 μL) were taken at 2 min, 4 min and 6 min from the initiation and mixed with an excess amount of benzoic acid and $CDCl_3$ (~0.48 mL) prior to ^{1}H NMR measurements. 1,3-Dihydroxy-1,1,3,3-tetramethyldisiloxane, 1,7-dihydroxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxane, 1,9-dihydroxy-1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane, 1,11-dihydroxy-1,1,3,3,5,5,7,7,9,9,11,11-dodecamethylhexasiloxane were gradually generated as the reaction was continued as observed in the ^{1}H NMR spectra shown in Figure S6.

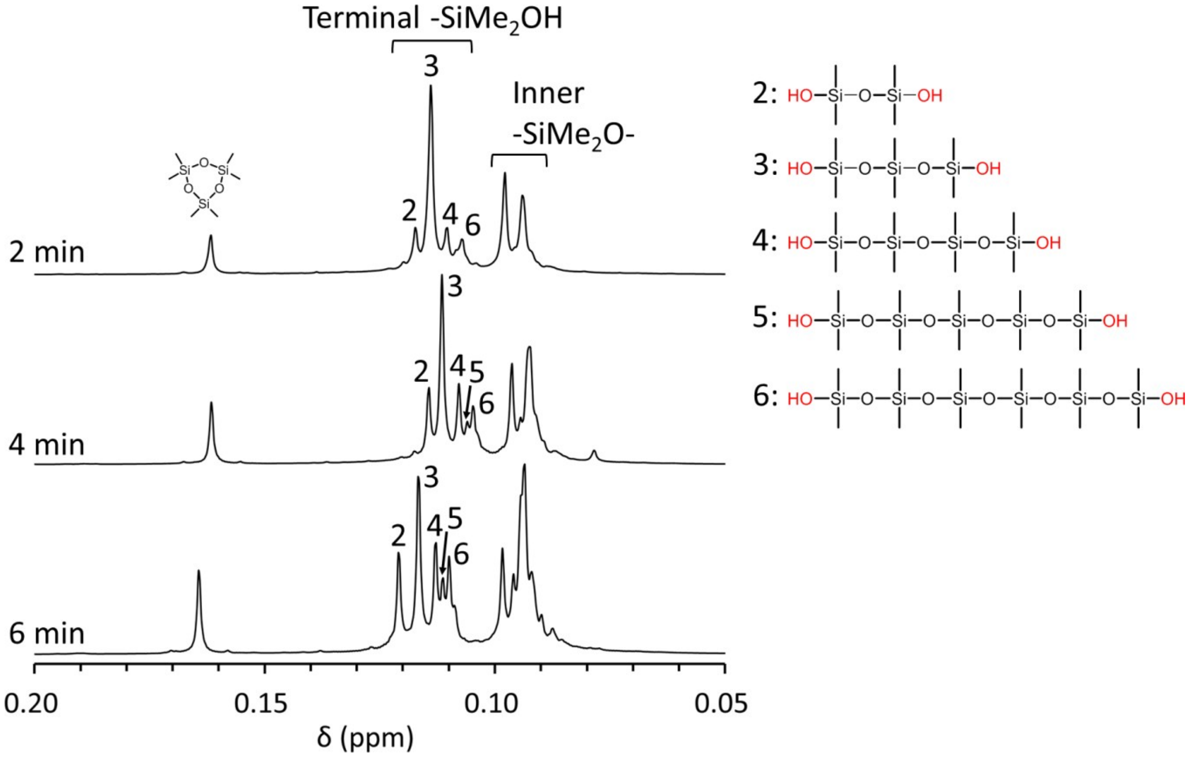
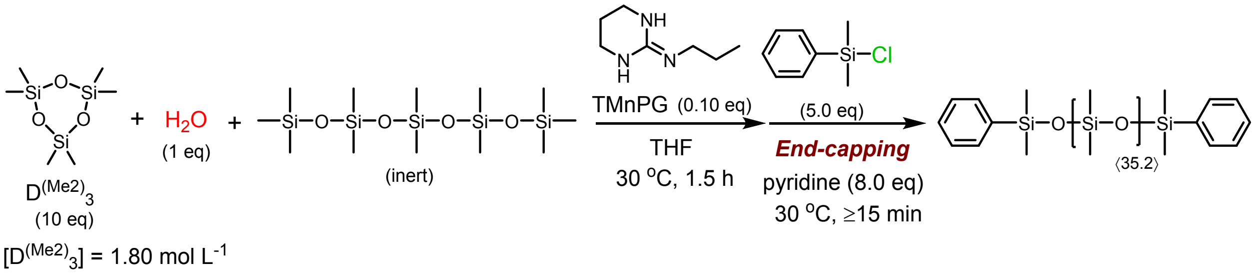


Figure S6. ^{1}H NMR spectra of the reaction mixtures obtained in the model reaction for the intermolecular transfer of terminal dimethylsiloxy units using D**Error!**-(OH)$_2$ and TMnPG in THF at 30 °C observed in $CDCl_3$/THF ~ 4/1.

Model Reaction for the Intermolecular Chain-Transfer in the Polymerization of DError!



In order to confirm whether the intermolecular chain-transfer (Scheme 2f) occur, a model polymerization of D**Error!** (221 mg, 991 µmol) in the presence of dodecamethylpentasiloxane (38.2 mg, 99.1 µmol) was carried out under the same conditions as the one described in the section '**Homopolymerization of DError!**'. The product was α,ω-bisdimethyl(phenyl)silyl-terminated PDMS (173 mg, 69.5% yield, $M_{\mathrm{n,NMR}}$ = 2.90 kg mol^{-1}, Đ = 1.13) .and did not contain trimethylsilyl-terminated PDMS as shown in Figure S7. α,ω-Bistrimethylsilyl-terminated PDMS (131 mg, 55.2% yield, $M_{\mathrm{n,NMR}}$ = 2.64 kg mol^{-1}, Đ = 1.14) as a reference material was synthesized using chlorotrimethylsilane in the same manner as the polymerization described in the section '**Synthesis of Telechelic PDMSs**'. ^{1}H, ^{29}Si{^{1}H} NMR, and MALDI-TOF MS spectra of the product are shown in Figure S8.

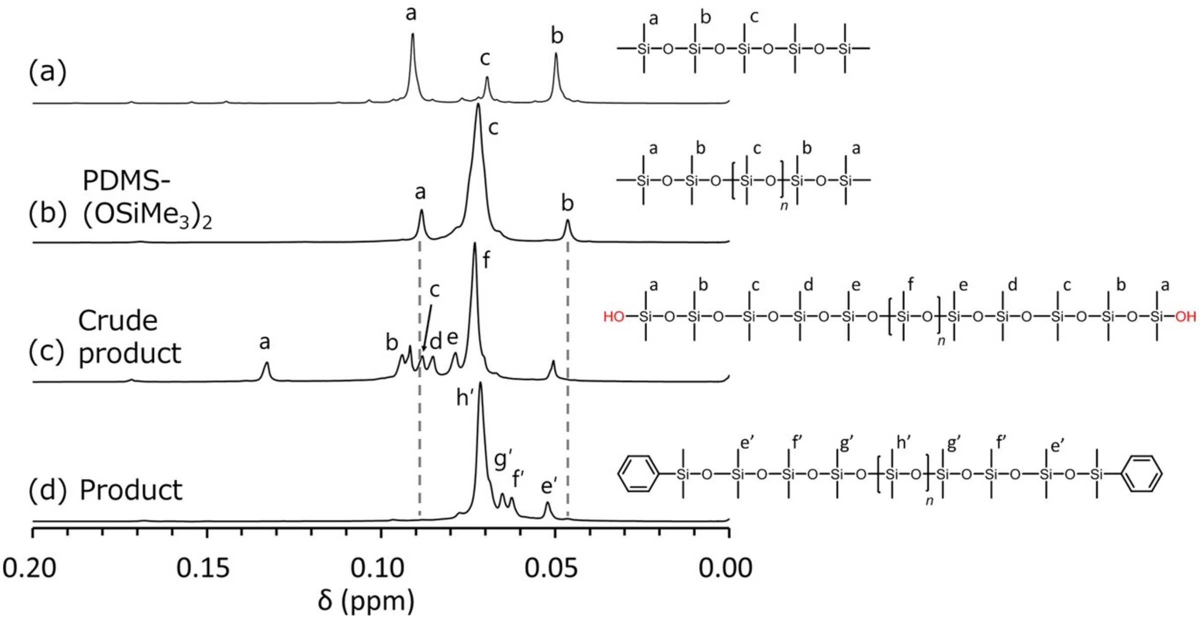


Figure S7. ^{1}H NMR spectra of (a) dodecamethylpentasiloxane, (b) α,ω-bis trimethylsilyl-terminated PDMS, (c) the reaction mixture taken just before the addition of the end-capping agent, and (d) the product obtained in the model reaction for the intermolecular chain-transfer reaction observed in $CDCl_3$.

Determination of $M_{n,NMR}$ by ^{1}H NMR Measurements.

The M_n ($M_{n,NMR}$) of the synthesized polysiloxanes were determined by ^{1}H NMR analysis.

For PDMS-$(OH)_2$, the integral values of the peak a (I_a) and peaks b–f ($I_{b–f}$) in Figure 3a were compared. $M_{n,NMR}$ = 74.13[2(I_a + $I_{b–f}$) / I_a] + 18.016

For PDMS-$(OSiMe_2Ph)_2$, the integral values of the peak d′ ($I_{d'}$) and peaks e′–h′ ($I_{e'–h'}$) in Figure 3b were compared. $M_{n,NMR}$ = 74.13(2$I_{e'–h'}$ / $I_{d'}$) + 286.52

For PDMS-$(OSiMe_2H)_2$, the integral values of the peak b (I_b) and peaks c and d (I_{c+d}) in Figure S9 were compared. $M_{n,NMR}$ = 74.13(2I_{c+d} / I_b) + 134.33

For PDMS-$(OSiMe_2Vi)_2$, the integral values of the peak d (I_d) and peaks e and f (I_{e+f}) in Figure S10 were compared. $M_{n,NMR}$ = 74.13(2I_{e+f} / I_d)] + 186.40

For PDMS-$(OSiMe_2Allyl)_2$, the integral values of the peak d (I_d) and peaks e and f (I_{e+f}) in Figure S11 were compared. $M_{n,NMR}$ = 74.13(2I_{e+f} / I_d) + 214.46

For PDMS-$[OSi(CH_2Cl)Me_2]_2$, the integral values of the peak b (I_b) and peaks c and d (I_{c+d}) in Figure S12 were compared. $M_{n,NMR}$ = 74.13(2I_{e+f} / I_d) + 231.26

For PDMS-$[OSi(CH_2Br)Me_2]_2$, the integral values of the peak b (I_b) and peaks c–e ($I_{c–e}$) in Figure S13 were compared. $M_{n,NMR}$ = 74.13(2$I_{c–e}$ / I_d) + 320.17

For PDMS-$(OSiMe_2C_6F_5)_2$, the integral values of the peak a (I_a) and peaks b–f ($I_{b–f}$) in Figure S14 were compared. $M_{n,NMR}$ = 74.13(2$I_{b–f}$ / I_a) + 466.43

For PDMS-[Si(OEt)$_3$]$_2$, the integral values of the peak c (I_c) and peaks d–f ($I_\mathrm{d–f}$) in Figure S15 were compared. $M_\mathrm{n,NMR} = 74.13[2(I_\mathrm{d–f} + I_\mathrm{c})/ I_\mathrm{c}] + 342.54$

For PMPS-(OSiEt$_3$)$_2$, the integral values of the peak a (I_a) and peaks c and d ($I_\mathrm{c+d}$) in Figure S16 were compared. $M_\mathrm{n,NMR} = 136.23(6I_\mathrm{c+d} / I_\mathrm{a}) + 246.54$

For PMVS-(OSiMe$_2$Ph)$_2$, the integral values of the peak b (I_c) and peaks e and f ($I_\mathrm{e+f}$) in Figure S17 were compared. $M_\mathrm{n,NMR} = 86.17(4I_\mathrm{e+f} / I_\mathrm{c}) + 286.52$

For PMTFPS-(OSiMe$_2$Ph)$_2$, the integral values of the peak d (I_d) and peaks e–i ($I_\mathrm{e–i}$) in Figure S18 were compared. $M_\mathrm{n,NMR} = 156.18(4I_\mathrm{e+f} / I_\mathrm{c}) + 286.52$

For α,ω-bis[dimethyl(phenyl)silyl]-terminated PMVS-*b*-PDMS-*b*-PMVS and α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane], the integral values of the peak a (I_a), peak b (I_b), and peak d (I_d) in Figure S19 were compared. $M_\mathrm{n,NMR} = 74.13(2I_\mathrm{d} / I_\mathrm{a}) + 86.17(4I_\mathrm{b} / I_\mathrm{a}) + 286.52$

For α,ω-bis(triethylsilyl)-terminated PDPS-*b*-PDMS-*b*-PDPS, the integral values of the peak a (I_a), peak c–i (I_b), and peak aromatic (I_aromatic) in Figure S22 were compared. $M_\mathrm{n,NMR} = 74.13(2I_\mathrm{c–i} / I_\mathrm{a}) + 86.17(6I_\mathrm{aromatic} /5\ I_\mathrm{a}) + 594.89$

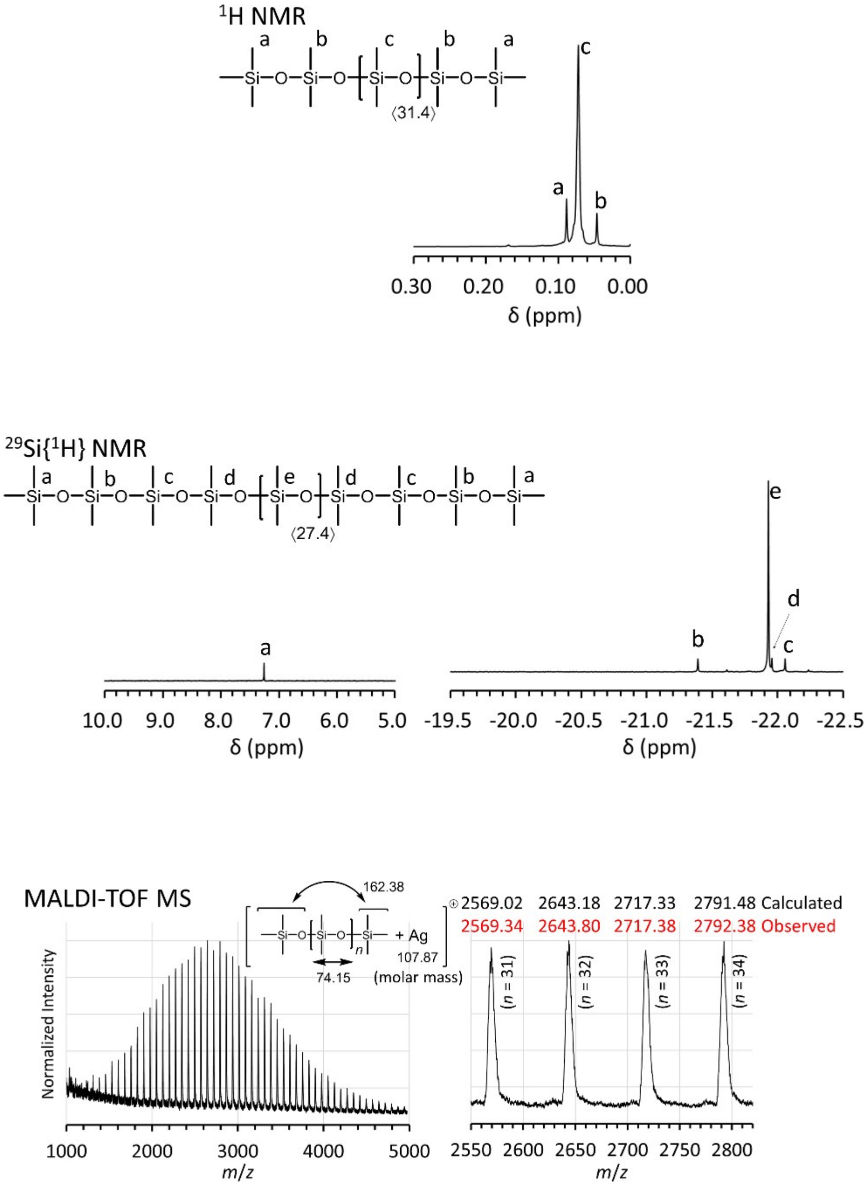


Figure S8. ^{1}H and ^{29}Si{^{1}H} NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PDMS-$(OSiMe_3)_2$ synthesized with Me_3SiCl ($M_{n,NMR}$ = 2.64 kg mol^{-1}, $Đ$ = 1.14).

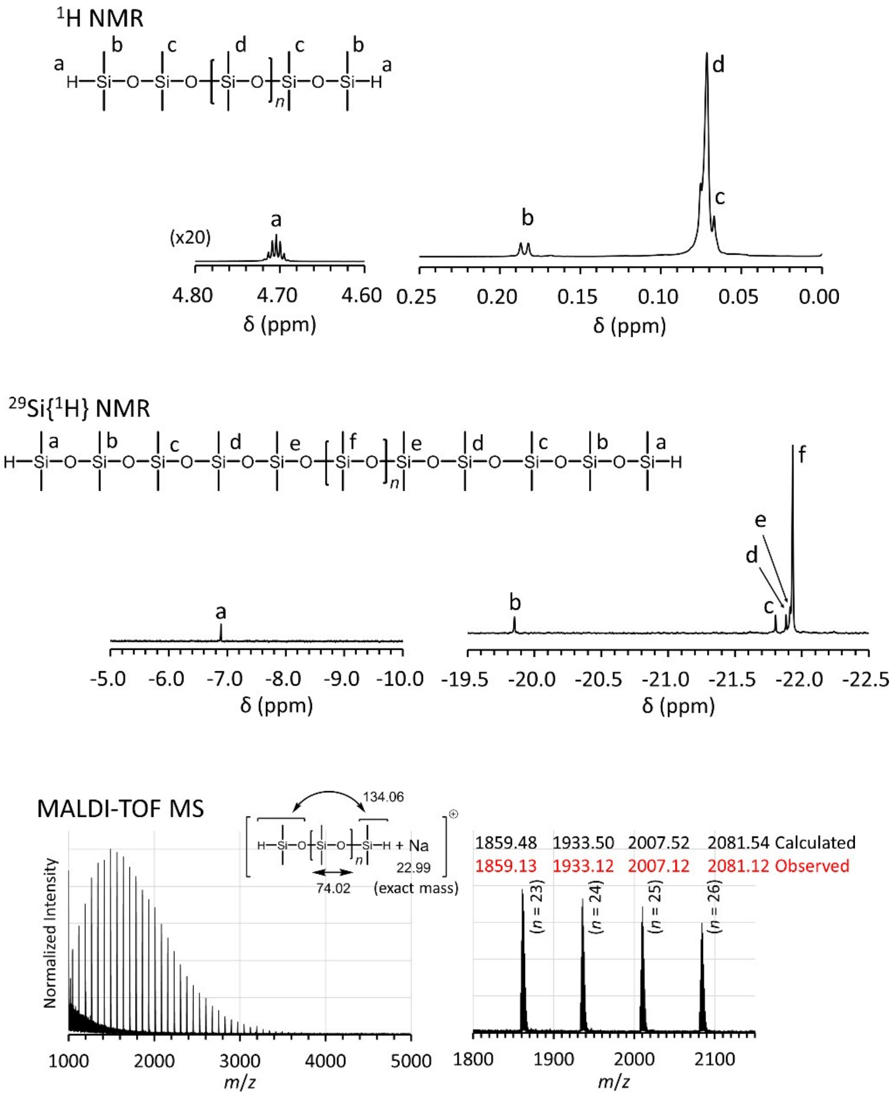


Figure S9. ^{1}H and $^{29}Si\{^{1}H\}$ NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the reflector mode using DCTB as a matrix and TFANa as a cationization agent) spectra of PDMS-$(OSiMe_2H)_2$ (Table 2, entry 10, $M_{n,NMR}$ = 2.95 kg mol^{-1}, $Đ$ = 1.15).

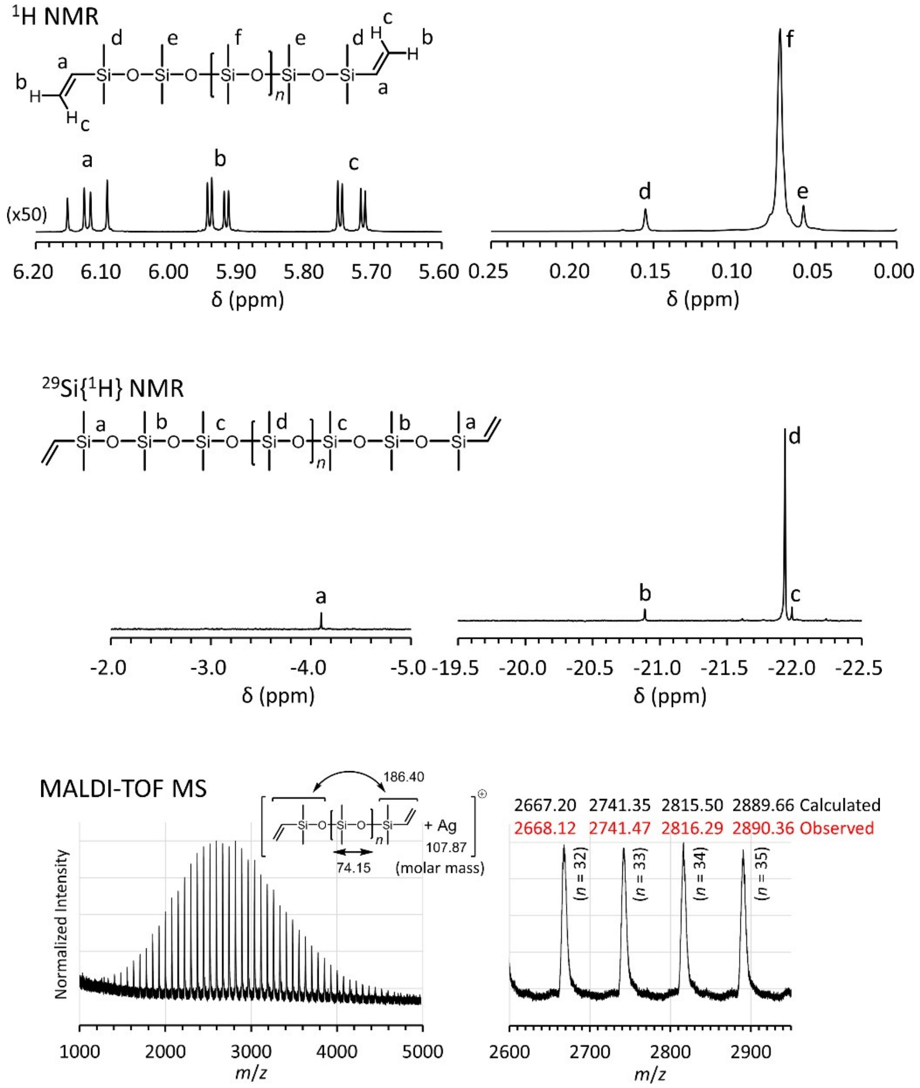


Figure S10. ^{1}H and ^{29}Si{^{1}H} NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PDMS-($OSiMe_2Vi$)$_2$ (Table 2, entry 11, $M_{\mathrm{n,NMR}}$ = 3.00 kg mol^{-1}, $Đ$ = 1.14).

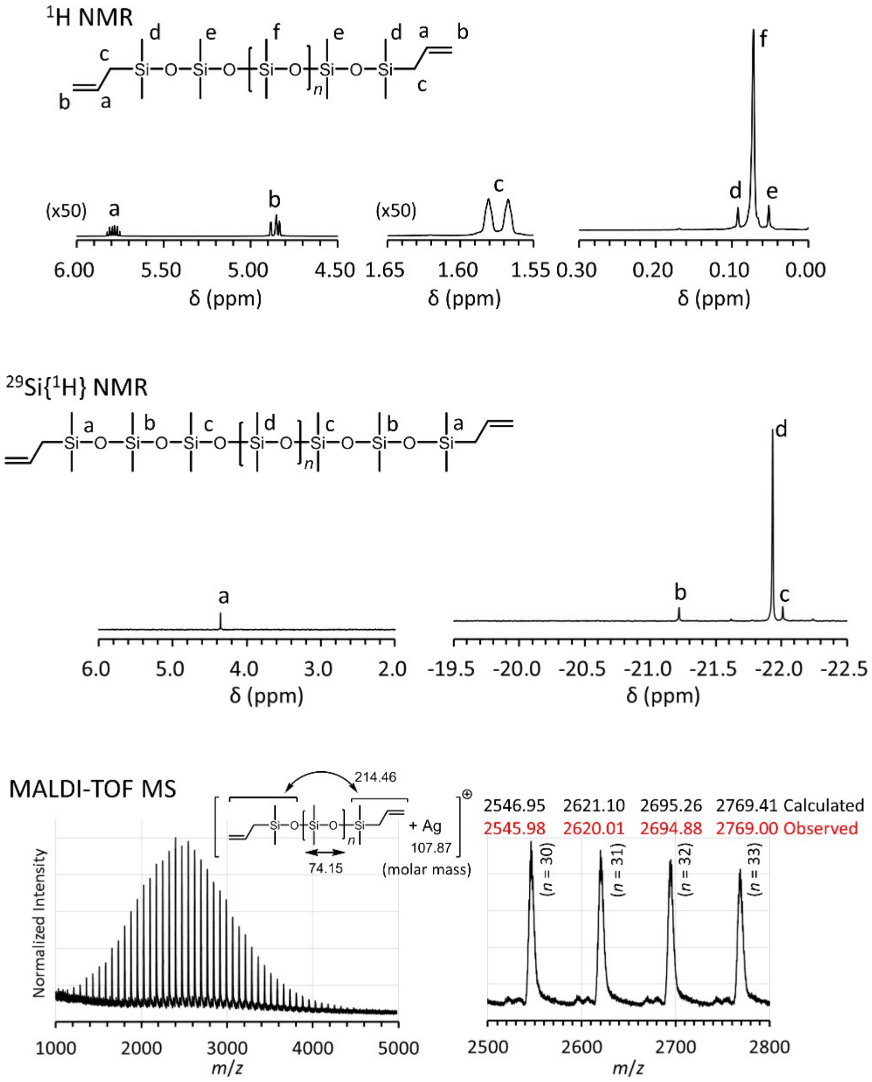


Figure S11. ^{1}H and ^{29}Si{^{1}H} NMR (in CDCl$_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PDMS-(OSiAllylMe$_2$)$_2$ (Table 2, entry 12, $M_{\mathrm{n,NMR}}$ = 2.77 kg mol^{-1}, $Đ$ = 1.13).

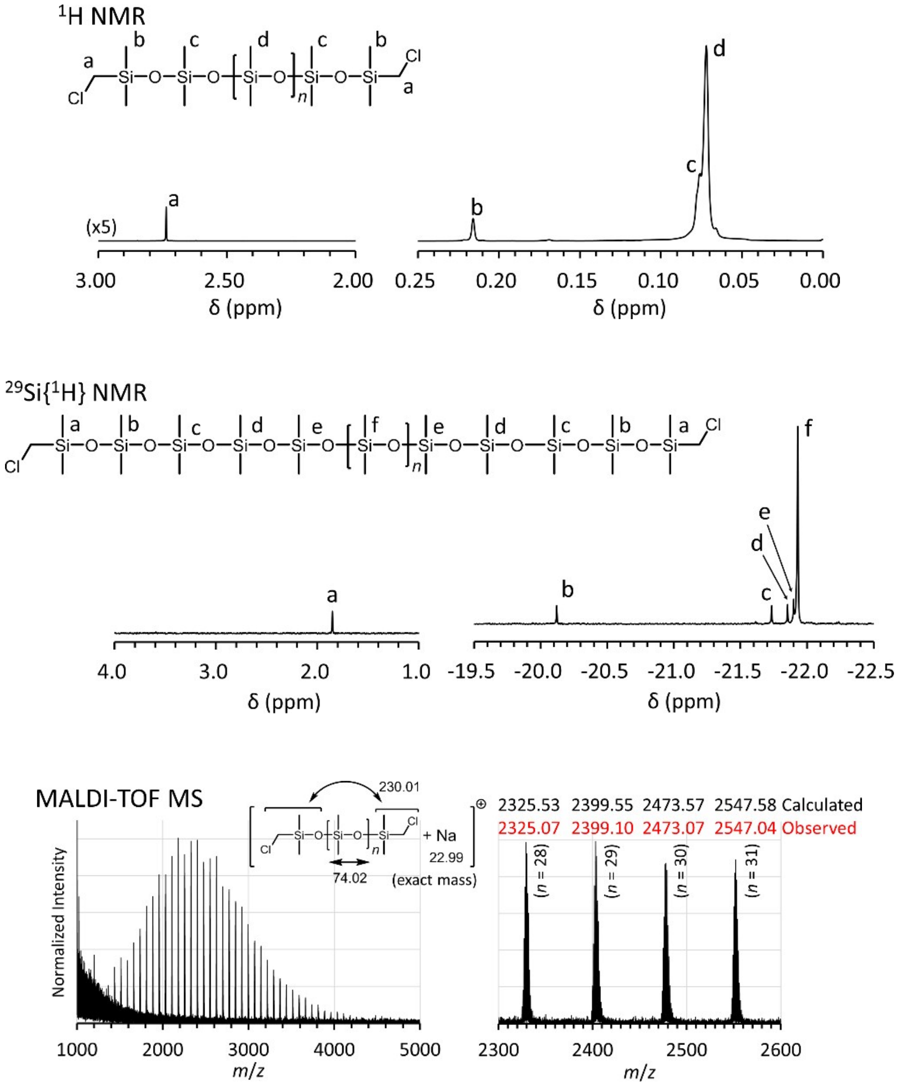


Figure S12. ^{1}H and ^{29}Si{^{1}H} NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the reflector mode using DCTB as a matrix and TFANa as a cationization agent) spectra of PDMS-[OSi(CH_2Cl)Me_2]$_2$ (Table 2, entry 13, $M_{n,NMR}$ = 3.14 kg mol^{-1}, $Đ$ = 1.10).

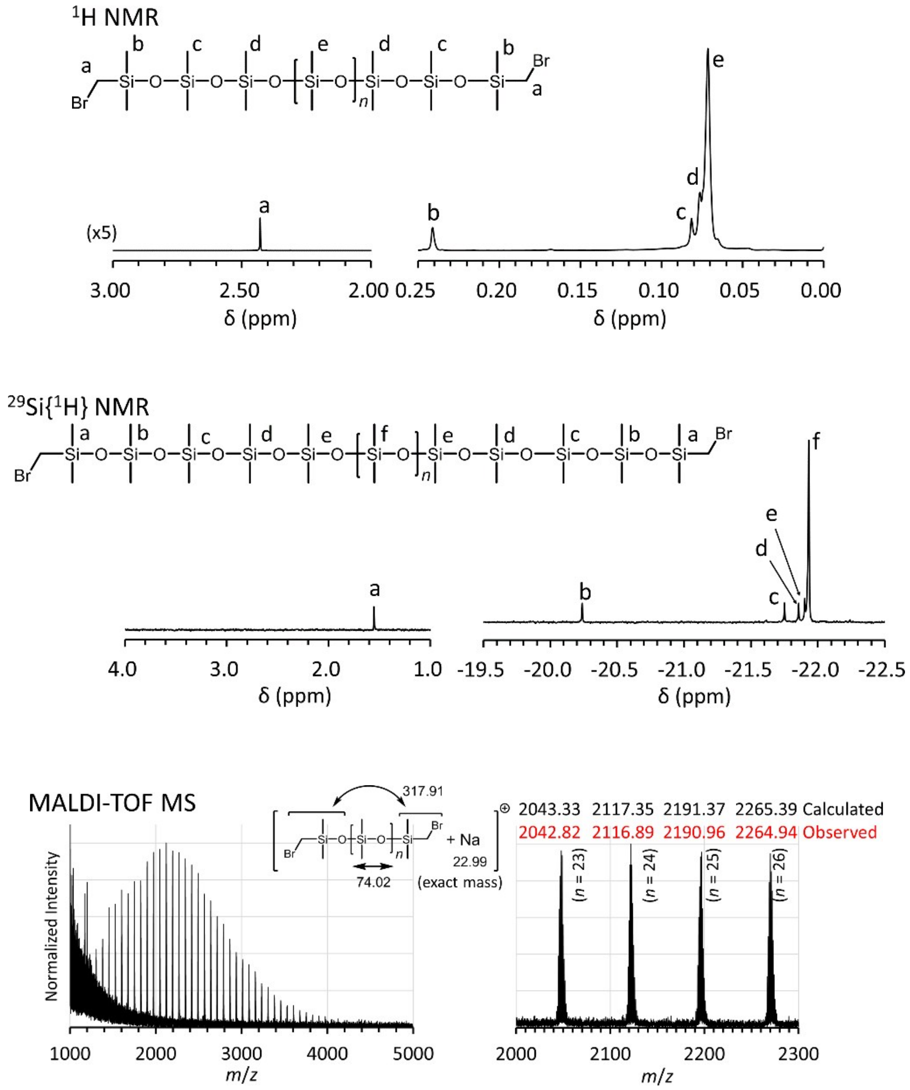


Figure S13. ^{1}H and ^{29}Si{^{1}H} NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the reflector mode using DCTB as a matrix and TFANa as a cationization agent) spectra of PDMS-[OSi(CH_2Br)Me_2]$_2$ (Table 2, entry 14, $M_{n,NMR} = 3.08$ kg mol^{-1}, $Đ = 1.13$).

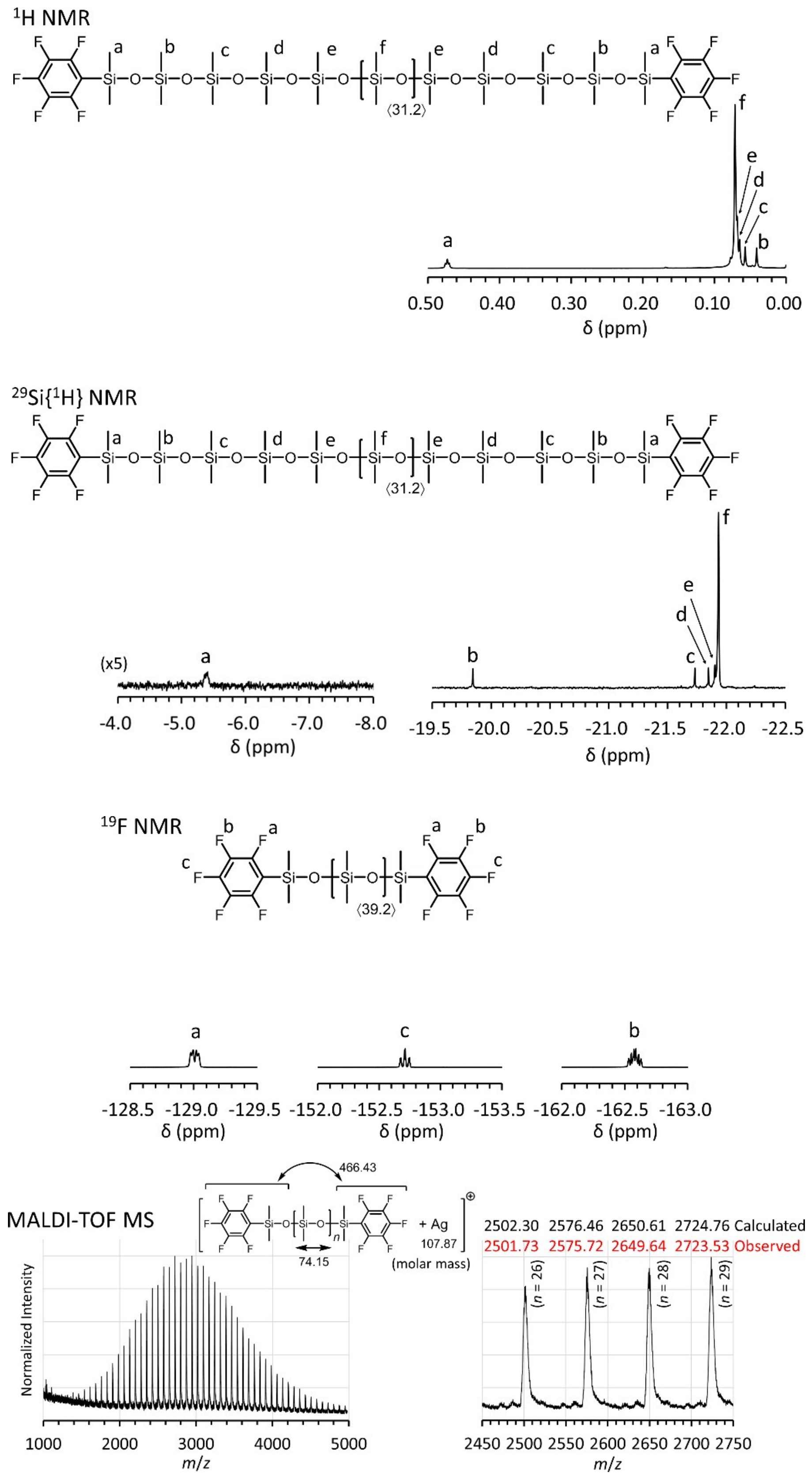


Figure S14. ^{1}H, ^{29}Si{^{1}H}, and ^{19}F NMR (in CDCl$_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PDMS-(OSiMe$_2$C$_6$F$_5$)$_2$ (Table 2, entry 15, $M_{\mathrm{n,NMR}}$ = 3.38 kg mol^{-1}, $Đ$ = 1.13).

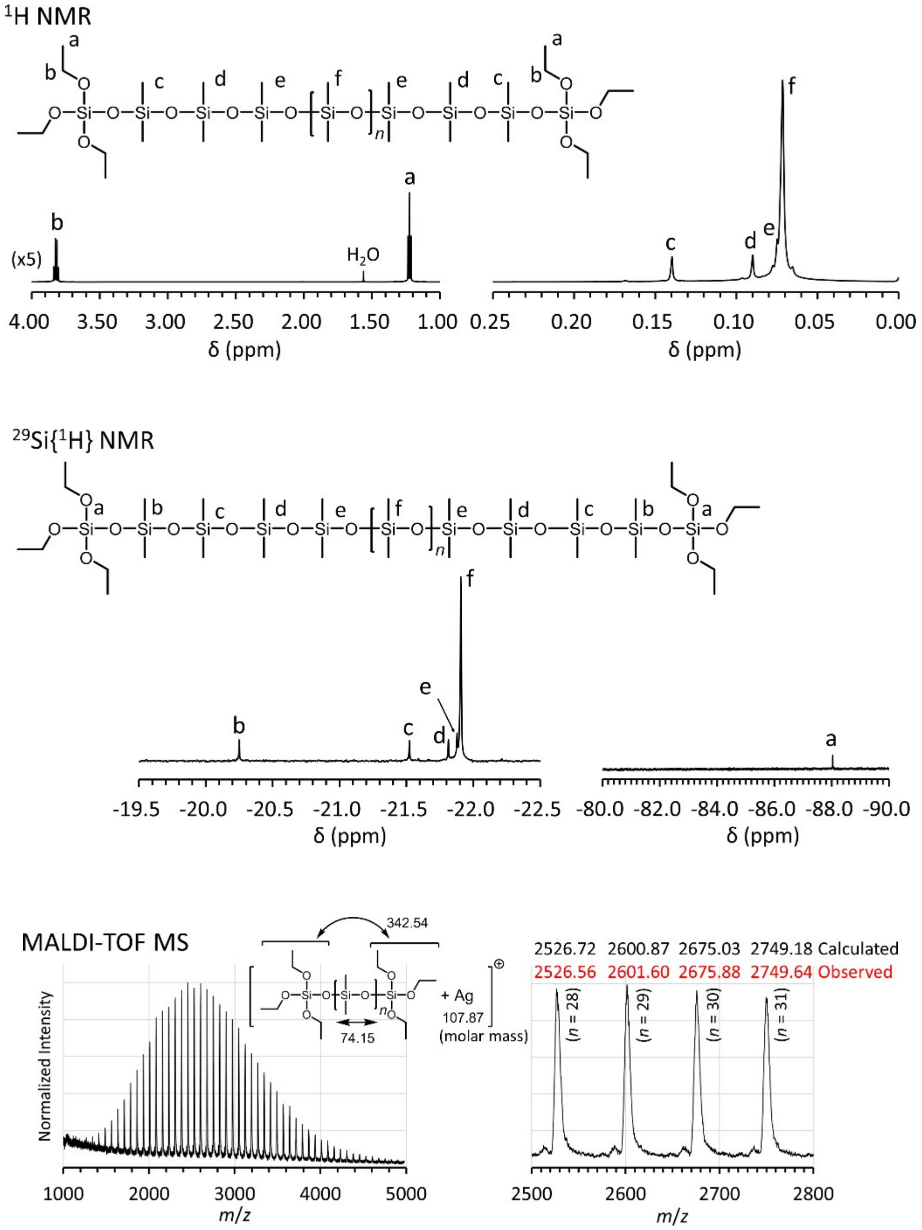


Figure S15. ^{1}H and ^{29}Si{^{1}H} NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) of PDMS-$[Si(OEt)_3]_2$ (Table 2, entry 16, $M_{n,NMR}$ = 3.25 kg mol^{-1}, $Đ$ = 1.11).

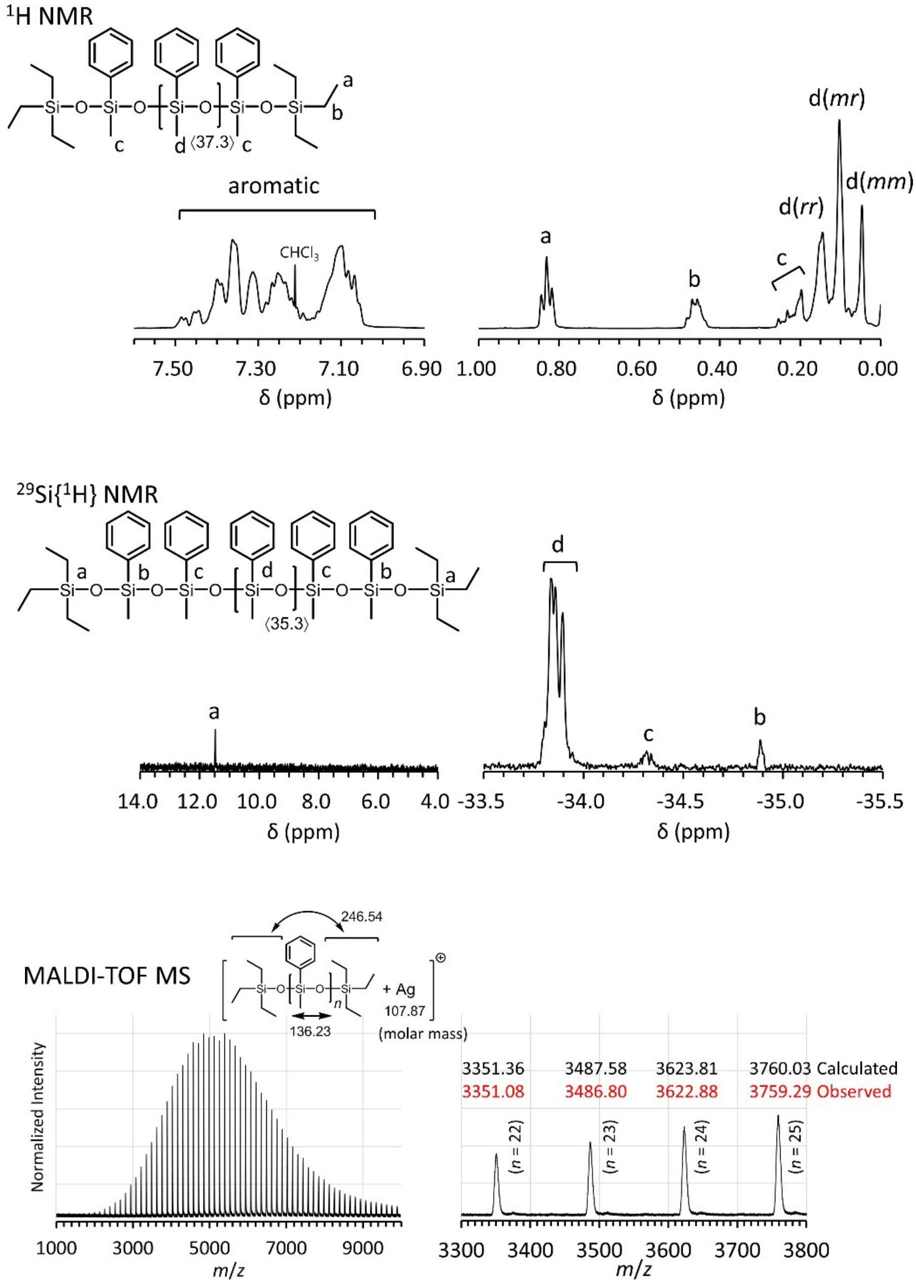


Figure S16. ¹H and ²⁹Si{¹H} NMR (in $CDCl_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PMPS-$(OSiEt_3)_2$ (Table 3, entry 1, $M_{n,NMR}$ = 5.60 kg mol^{-1}, $Đ$ = 1.16).

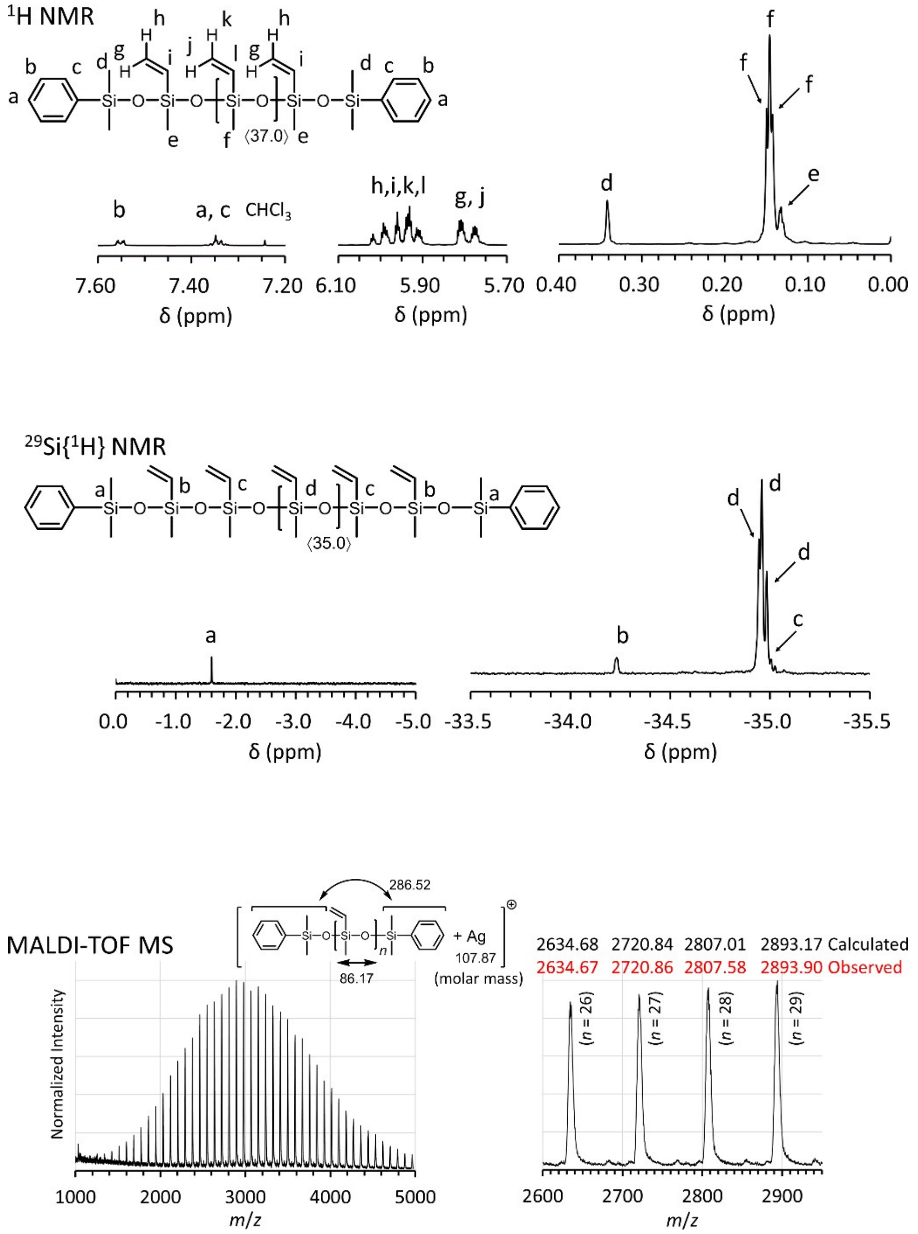


Figure S17. ^{1}H and ^{29}Si{^{1}H} NMR (in CDCl$_3$), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PMVS-(OSiMe$_2$Ph)$_2$ (Table 3, entry 3, $M_{\mathrm{n,NMR}}$ = 3.64 kg mol^{-1}, $Đ$ = 1.11).

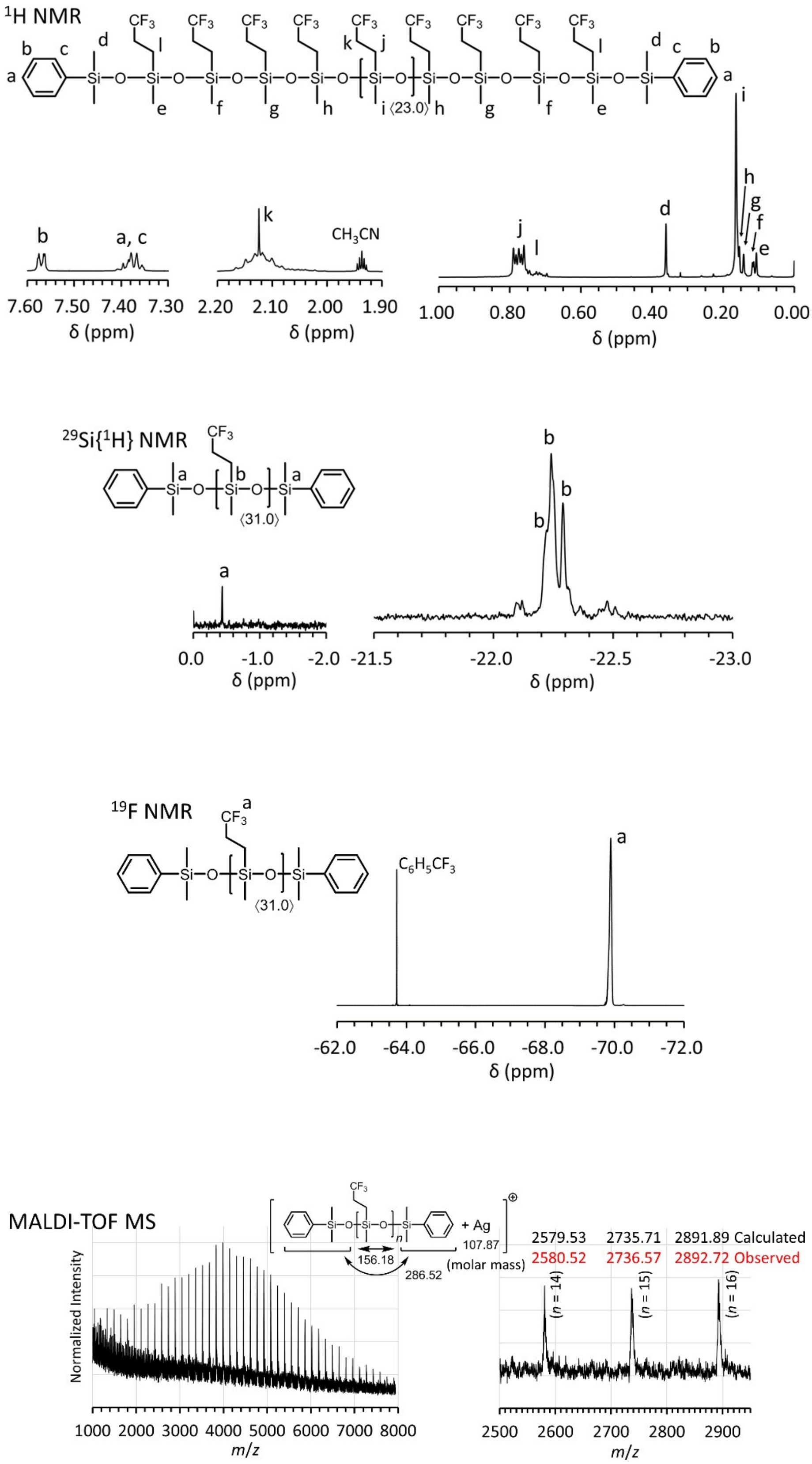


Figure S18. ^{1}H, ^{29}Si{^{1}H}, and ^{19}F NMR (in CD_3CN), and MALDI-TOF MS (measured in the linear mode using DCTB as a matrix and TFAAg as a cationization agent) spectra of PMTFPS-($OSiMe_2Ph$)$_2$. (Table 3, entry 5, $M_{n,NMR}$ = 6.00 kg mol^{-1}, $Đ$ = 1.12).

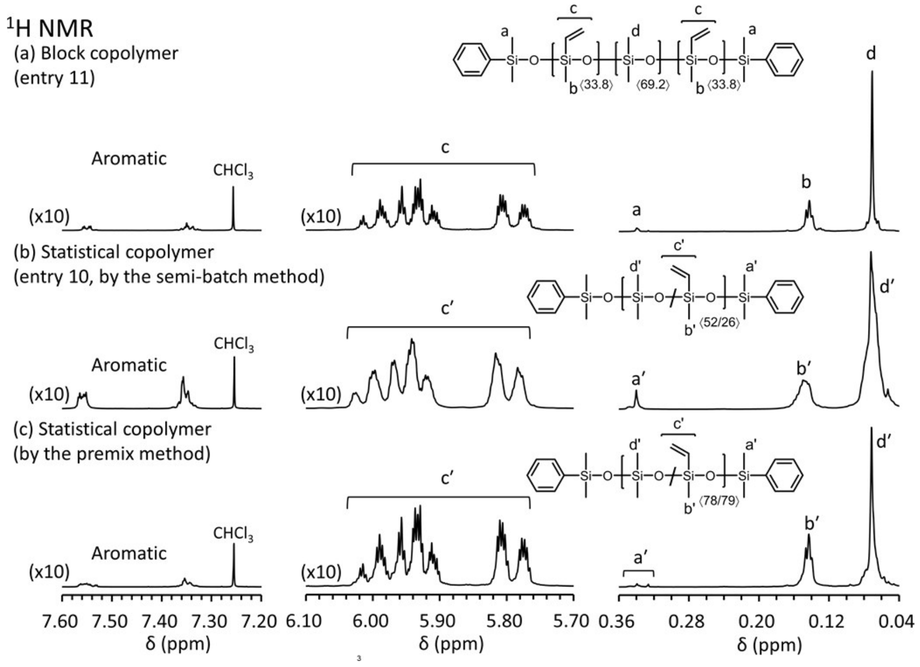


Figure S19. ^{1}H NMR spectra of (a) α,ω-bis[dimethyl(phenyl)silyl]-terminated PMVS-*b*-PDMS-*b*-PMVS (Table 3, entry 11, $M_{\mathrm{n,NMR}}$ = 11.2 kg mol^{-1}, $Đ$ = 1.07), (b) α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] obtained by the semi-batch method (Table 3, entry 10, $M_{\mathrm{n,NMR}}$ = 6.34 kg mol^{-1}, $Đ$ = 1.13), and (c) α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] obtained by the premix method ($M_{\mathrm{n,NMR}}$ = 12.9 kg mol^{-1}, $Đ$ = 1.37) measured in CDCl$_3$.

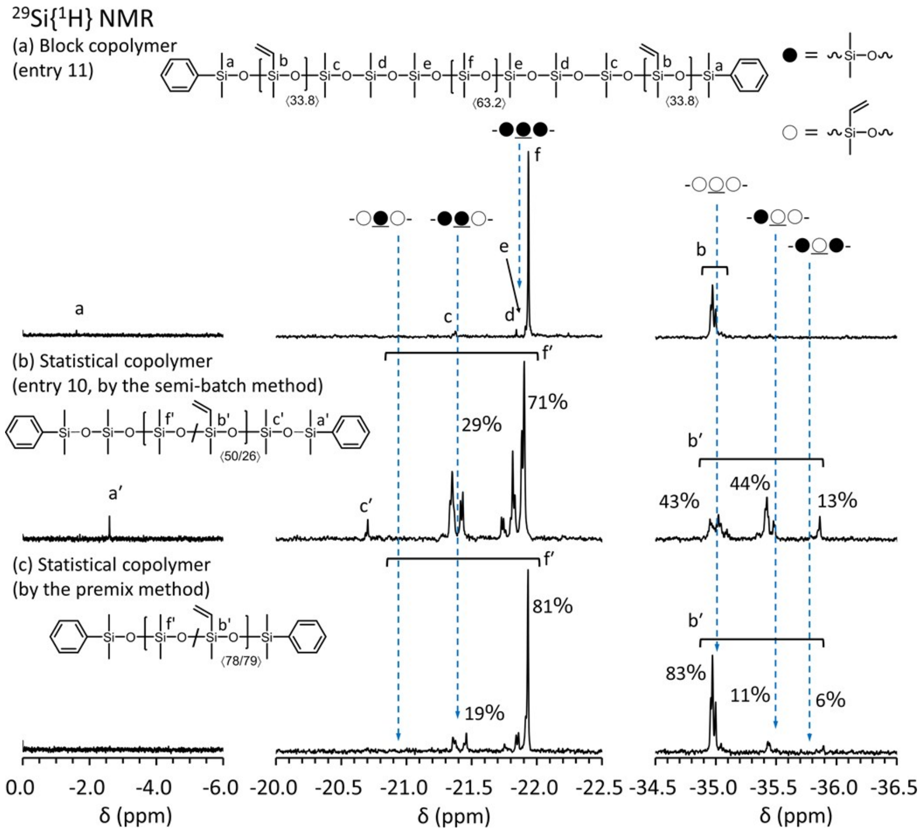


Figure S20. ^{29}Si{^{1}H} NMR spectra of (a) α,ω-bis[dimethyl(phenyl)silyl]-terminated PMVS-*b*-PDMS-*b*-PMVS (Table 3, entry 11, $M_{\mathrm{n,NMR}}$ = 11.2 kg mol^{-1}, $Đ$ = 1.07), (b) α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] obtained by the semi-batch method (Table 3, entry 10, $M_{\mathrm{n,NMR}}$ = 6.34 kg mol^{-1}, $Đ$ = 1.13), and (c) α,ω-bis[dimethyl(phenyl)silyl]-terminated poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] obtained by the premix method ($M_{\mathrm{n,NMR}}$ = 12.9 kg mol^{-1}, $Đ$ = 1.37) measured in CDCl$_3$.

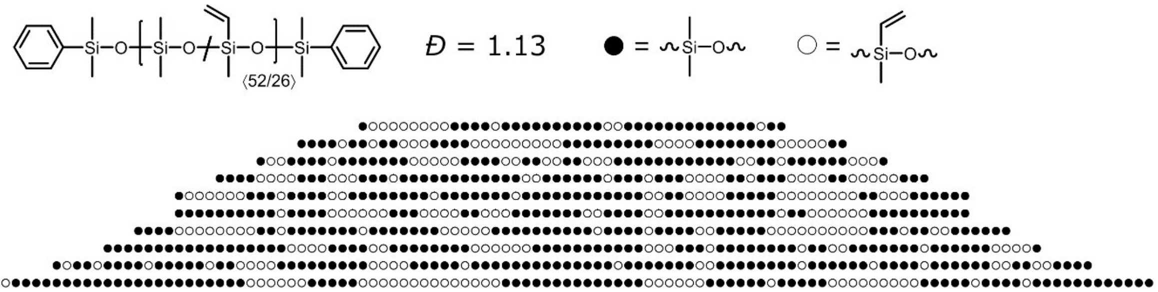


Figure S21. A monomeric sequence of the poly[dimethylsiloxane-*co*-methyl(vinyl)siloxane] (Table 3, entry 10) simulated based on the population of the triad monomeric sequences observed in the ^{29}Si{^{1}H} NMR measurement, $n(\mathrm{D}^{(\mathrm{Me2})})/n(\mathrm{D}^{(\mathrm{Me,Vi})})$, and $Đ$.

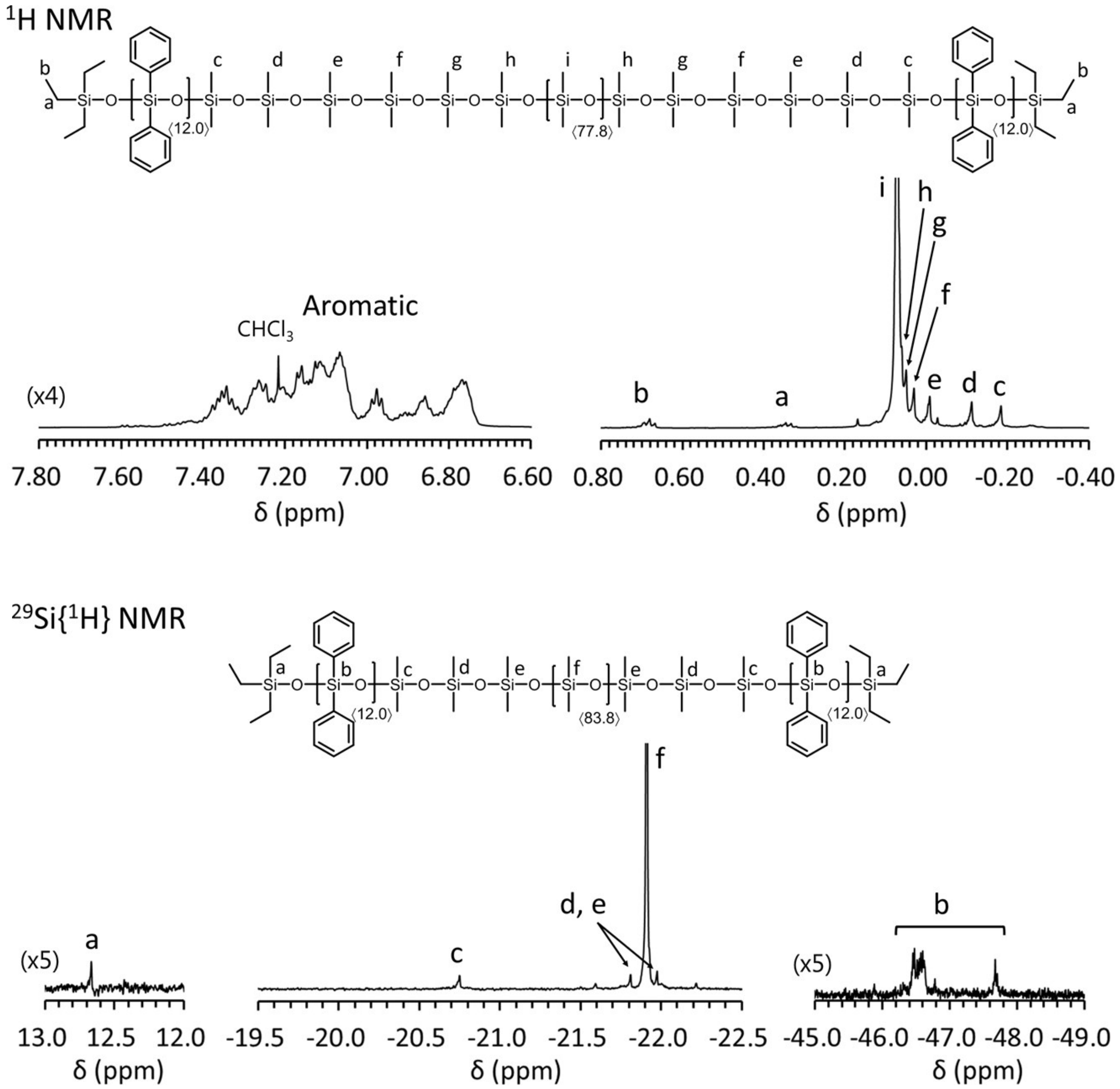


Figure S22. ^{1}H and ^{29}Si{^{1}H} NMR spectra of α,ω-bis(triethylsilyl)-terminated PDPS-*b*-PDMS-*b*-PDPS (Table 3, entry 12, $M_{\mathrm{n,NMR}}$ = 11.7 kg mol^{-1}, $Đ$ = 1.06) measured in CDCl$_3$.

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