Electronic Supplementary Information for:

Ring-opening polymerization of six-membered 1,3-dioxa-2-silacycloalkanes by an organobase catalyst: precision polymerization and monomer regeneration by polymer degradation

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Experimental Section

Materials. Triethylene glycol (TEG; Nacalai Tesque, >98.0%) was distilled from calcium hydride under reduced pressure. 1,8-Diazabicyclo[5,4,0]undec-7-ene (DBU; TCI, >98.0%) was distilled twice from calcium hydride under reduced pressure. Dimethoxydimethysilane (TCI, >98.0%), 1,3-propanediol (TCI, >98.0%), 1,4-butanediol (TCI, >99.0%), 2-methyl-1,3-propanediol (TCI, >98.0%), In(OTf)$_3$ (Sigma-Aldrich, >99.0%), $Ph_3CB(C_6F_5)_4$ (TCI, >98.0%), $B(C_6F_5)_3$ (TCI, >98.0%), trifluoromethanesulfonic acid (CF_3SO_3H; TCI, >98.0%), bis(trifluoromethanesulfonyl)imide (Tf_2NH; TCI, >99.0%), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD; Sigma-Aldrich, >97.5%), *t*-butylimino-tri(pyrrolidino)phosphorane (BTTP; Sigma-Aldrich, >97.0 %), and ethanol (Wako, super dehydrated grade) were used without further purification. Toluene (Wako, super dehydrated grade) was dried by passage through solvent purification columns (Glass Contour).

Synthesis of 1,3-dioxa-2-silacycloalkanes. 1,3-Dixa-2-silacycloalkanes were synthesized by the condensation reaction of dimethoxydimethylsilane and corresponding diols[S1,S2] using In(OTf)$_3$ as a catalyst at room temperature. After condensation, the reaction mixture was concentrated to remove methanol, which was generated as a byproduct. See our previous study[S3] for the synthesis of 2,2,5,5-tetramethyl-1,3-dioxa-2-silacyclohexane (Si6M), 2,2-dimethyl-1,3-dioxa-2-silacyclohexane (Si6), 2,2,4,4,5,5-hexamethyl-1,3-dioxa-2-silacyclopentane (Si5M), 2,2-dimethyl-1,3-dioxa-2-silacycloheptane (Si7), and 2,2-dimethyl-1,3,6-trioxa-2-silacyclooctane (Si8O).

2,2,5-Trimethyl-1,3-dioxa-2-silacyclohexane (Si6mM). Si6mM was synthesized from dimethoxydimethylsilane and 2-methyl-1,3-propanediol and purified by distillation from calcium hydride under reduced pressure. Colorless liquid. Final yield after distillation: 16%. ^{1}H NMR (CDCl$_3$; 400 MHz): δ 3.98 (m, 2H), 3.66 (m, 2H), 2.14 (m, 1H), 0.80 (d, 3H), 0.19 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (CDCl$_3$; 125 MHz): δ 69.5, 35.0, 12.6, –1.4, –3.0.

Polymerization procedures. The following is a typical polymerization procedure. A glass tube equipped with a three-way stopcock was dried using a heat gun (Ishizaki; PJ206A; blow temperature: approximately 450 ºC) under dry nitrogen. Toluene, TEG solution in dichloromethane, and TBD solution in toluene were sequentially added to the tube using dry syringes. After cooling the solution at –30 ºC for 10 min, the polymerization was started by adding Si6M. After a predetermined time, the reaction was quenched with acetic acid. The quenched mixture was diluted with a mixture of dichloromethane and hexane and then washed with water. The volatiles were removed under reduced pressure. The monomer conversion was determined by gravimetry or ^{1}H NMR analysis of the quenched polymerization solution.

Polymer degradation into a monomer. Poly(Si6M) (5.0 g), In(OTf)$_3$ (0.18 g), and dichloromethane (15 mL) were placed in a pear-shaped flask of distillation apparatus (Figure 3A). The mixture was heated at 80 ºC under reduced pressure (30 kPa). Dichloromethane was first distilled off. Subsequently, after temperature was raised (130 ºC) and pressure was lowered (10 kPa), colorless liquid was distilled (4.0 g). Calcium hydride was placed in a flask for the distillate to prevent unintended polymerization.

Characterization. The molecular weight distribution of the polymers was measured by gel permeation chromatography (GPC) in toluene at 40 ºC with polystyrene gel columns [TSKgel GMH$_{\mathrm{HR}}$-M × 2 (exclusion limit molecular weight = 4×10^6; bead size = 5 µm; column size = 7.8 mm id × 300 mm); flow rate 1.0 mL/min] connected to a JASCO PU-4580 pump, Tosoh CO-8020 column oven, a Tosoh UV-8020 ultraviolet detector, and a LAB-SYSTEM RI-2000A refractive-index detector. The number-average molecular weight (M_{n}) and the polydispersity ratio [weight-average molecular weight /number-average molecular weight ($M_{\mathrm{w}}/M_{\mathrm{n}}$)] were calculated from the chromatograms with respect to 16 polystyrene standards (Tosoh; molecular weight = 5.0×10^2 to 1.09×10^6, $M_{\mathrm{w}}/M_{\mathrm{n}} < 1.2$). NMR spectra were recorded with JEOL JNM-ECA 500 spectrometer (500.16 MHz for ^{1}H), JEOL JNM-ECZN 500 spectrometer (500.16 MHz for ^{1}H and 125.77 MHz for ^{13}C), or JEOL JNM ECS400 spectrometer (395.88 MHz for ^{1}H) in chloroform-*d* at 30 ºC. Electrospray ionization mass spectrometry (ESI-MS) data were recorded on a Q Exactive Orbitrap (Thermo Scientific) spectrometer. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) data were recorded on a Shimadzu/Kratos Axima-Performance spectrometer using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyliden]malononitrile and sodium trifluoroacetate as matrix and cationizing agent, respectively. Differential scanning calorimetry (DSC) analysis of the polymers was conducted using a Shimadzu DSC-60 Plus differential scanning calorimeter. Thermogravimetric analysis (TGA) was conducted with a NEXTA STA (Hitachi High Tech) under flowing nitrogen at a heating rate of 10 ºC min^{-1}.

Table S1. Polymerization of Si6M using acids or cationizing agents [a]

Entry	$[\mathrm{Si6M}]_0$ (M)	Acids or cationizing agent	Solvent	Temp. (ºC)	Conv. (%)	$M_n \times 10^{-3}$
1	1.2	$B(C_6F_5)_3$	CH_2Cl_2	−30	18	0.2
2[b]	2.4	$B(C_6F_5)_3$	CH_2Cl_2	−78	8	3.3
3	1.2	$Ph_3CB(C_6F_5)_4$	toluene	0	43	0.2
4	1.2		toluene	−30	26	0.2
5	2.4		toluene	−30	78	0.3
6	1.2		toluene	−30	79	0.3
7	1.2	CF_3SO_3H	toluene	−30	62	0.2
8	1.2	Tf_2NH	toluene	−30	62	0.3

[a] [Acid or cationizing agent]$_0$ = 5.0 mM, for 24 h (except for entry 2) or 22.5 h (entry 2). [b] Reference S3.

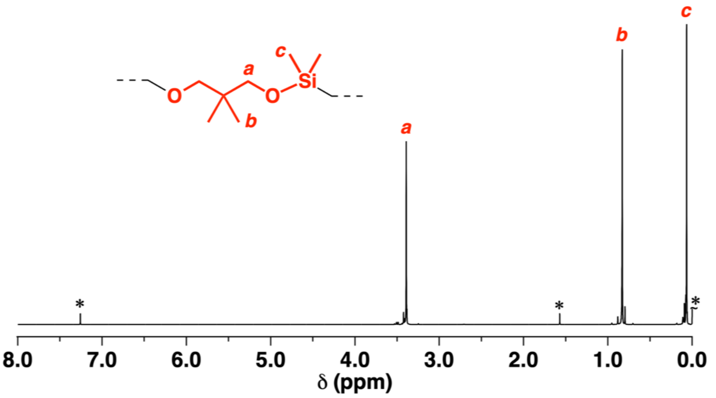
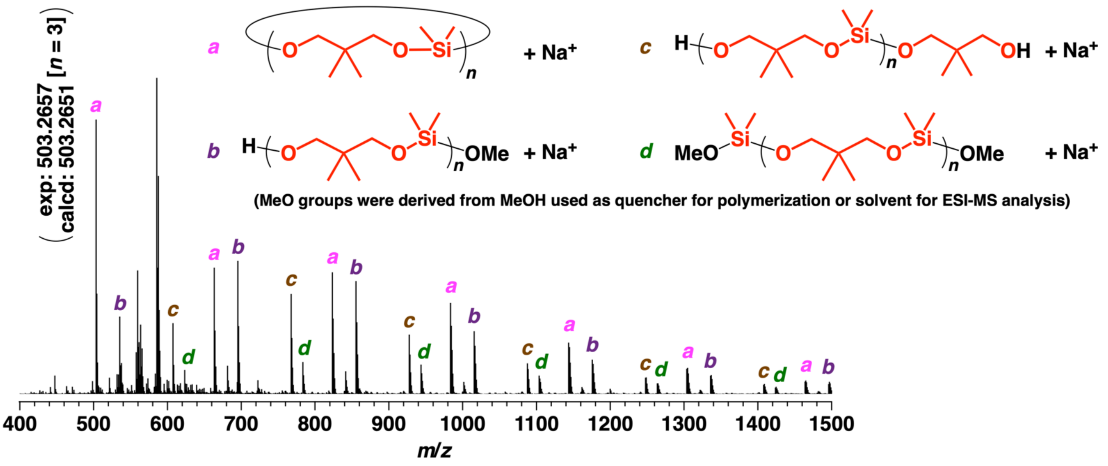


Figure S1. ^{1}H NMR spectrum of the product obtained by the polymerization of Si6M using $Ph_3CB(C_6F_5)_4$ (entry 5 in Table S1; in $CDCl_3$ at 30 ºC; * water, Me_4Si, or $CHCl_3$).



(MeO groups were derived from MeOH used as quencher for polymerization or solvent for ESI-MS analysis)

Figure S2. ESI-MS spectrum of the product obtained by the polymerization of Si6M using $Ph_3CB(C_6F_5)_4$ (entry 5 in Table S1).

Table S2. Polymerization of Si6M using DBU, TBD, or BTTP

Entry	Catalyst	Time (h)	Conv. (%)	$M_n \times 10^{-3}$	M_w/M_n
1	TBD	24	53	22.7	1.19
2	DBU	24	3	0.2	–
3	BTTP	73	7	–	–

^{a} [Si6M]$_0$ = 2.4 M, [alcohol]$_0$ = 5.0 mM (EtOH for entries 1 and 2, TEG for entry 3), [catalyst]$_0$ = 5.0 mM, in toluene at 25 (entries 1 and 2) or –30 (entry 3) ºC.

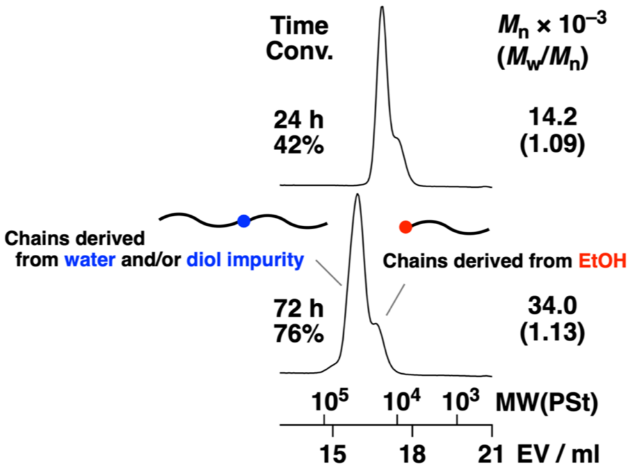


Figure S3. MWD curves of poly(Si6M)s obtained by the polymerization with EtOH as an initiator ([Si6M]$_0$ = 2.4 M, [EtOH]$_0$ = 5.0 mM, [TBD]$_0$ = 5.0 mM, in toluene at –30 ºC). The data correspond to those shown in Figure 2D.

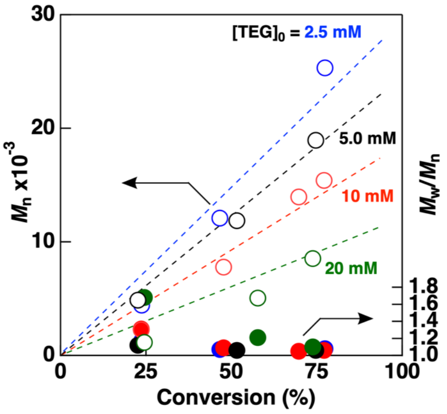


Figure S4. Polymerization of Si6M at different concentrations of TEG ([Si6M]$_0$ = 2.4 M, [TEG]$_0$ = 2.5 (blue), 5.0 (black), 10 (red), or 20 (green) mM, [TBD]$_0$ = 5.0 mM, in toluene at –30 ºC). The data obtained at [TEG]$_0$ of 5.0 mM are the same as those shown in Figure 2A, 2B, and 2C.

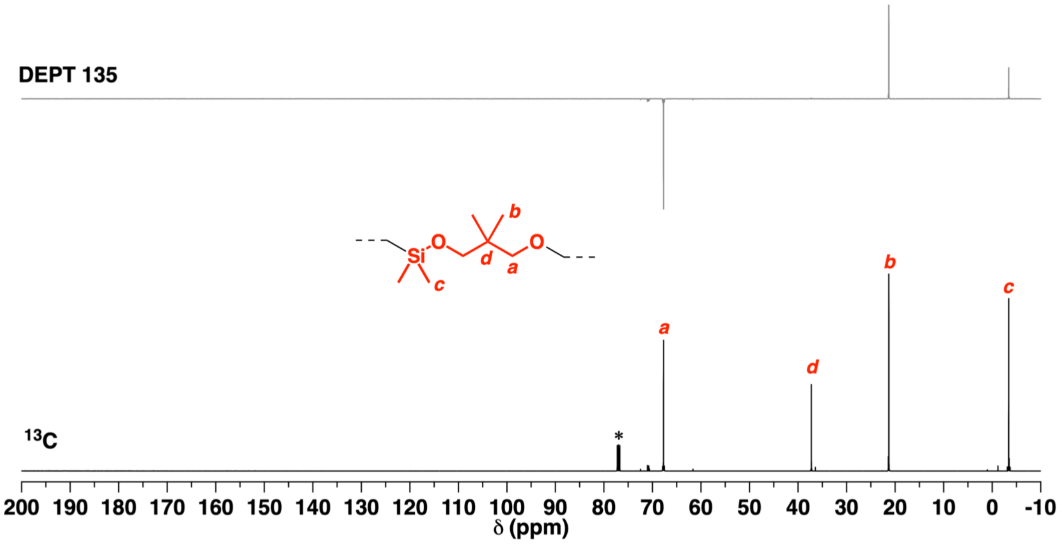


Figure S5. ^{13}C and DEPT 135 NMR spectra of poly(Si6M) (the sample shown in Figure 1A and 1B; monomer conversion = 20%, M_n(GPC) = 7.4 × 10^3; the same sample as that shown in Figure 1C).

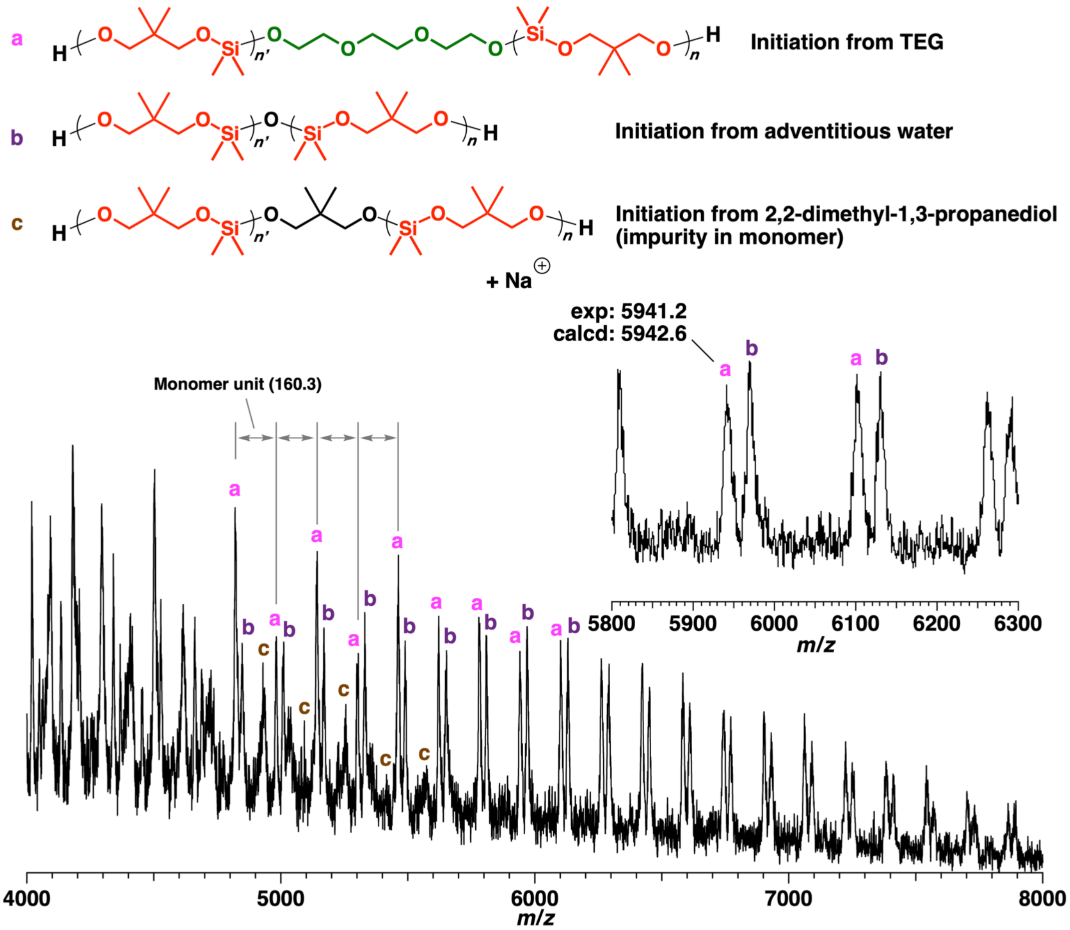


Figure S6. MALDI-TOF-MS analysis of the poly(Si6M) obtained with TEG as an initiator (the sample shown in Figure 1A and 1B; monomer conversion = 20%, M_n(GPC) = 7.4 × 10^3).

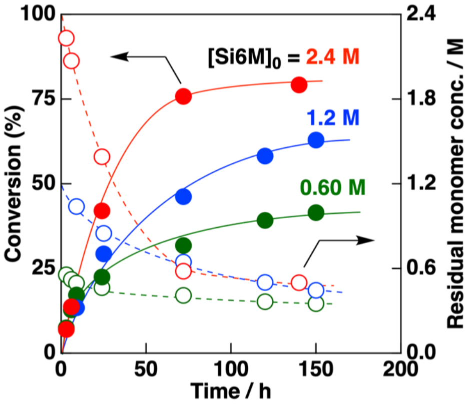


Figure S7. Polymerization of Si6M at different monomer concentrations (filled: monomer conversion, open: residual monomer concentrations; $[\mathrm{Si6M}]_0$ = 0.60 (green), 1.2 (blue), or 2.4 (red) M, $[\mathrm{EtOH}]_0$ = 5.0 mM, $[\mathrm{TBD}]_0$ = 5.0 mM, in toluene at –30 °C).

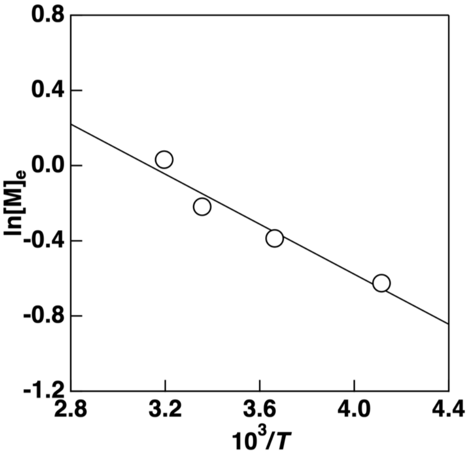


Figure S8. Dependence of the equilibrium concentration on polymerization temperature. $[\mathrm{Si6M}]_0$ = 2.4 M, $[\mathrm{TEG}]_0$ = 5.0 mM, $[\mathrm{TBD}]_0$ = 5.0 mM, in toluene at –30, 0, 25, and 40 ºC. The data correspond to those shown in Figure 2D.

Note for Figure S8: From the relationship of $\ln[\mathrm{M}]_e = \Delta H/RT - \Delta S^o/R$, where $[\mathrm{M}]_e$, ΔH, and ΔS^o are the equilibrium monomer concentration, the heat of polymerization, and the entropy change of polymerization, respectively,[S4] ΔH of –5.5 kJ mol^{-1} and ΔS^o of –17 J mol^{-1} K^{-1} were determined. The ceiling temperature based on $[\mathrm{M}]_e$ of 1.0 M was 46 ºC.

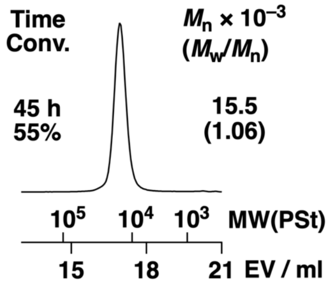


Figure S9. MWD curve of the polymer obtained by the polymerization of the Si6M monomer regenerated by polymer degradation ($[\mathrm{Si6M}]_0$ = 2.4 M, $[\mathrm{TEG}]_0$ = 5.0 mM, $[\mathrm{TBD}]_0$ = 5.0 mM, in toluene at –30 ºC). In the polymer degradation reaction, the regenerated monomer was collected in a flask containing calcium hydride. The monomer was used for repolymerization without any further purification.

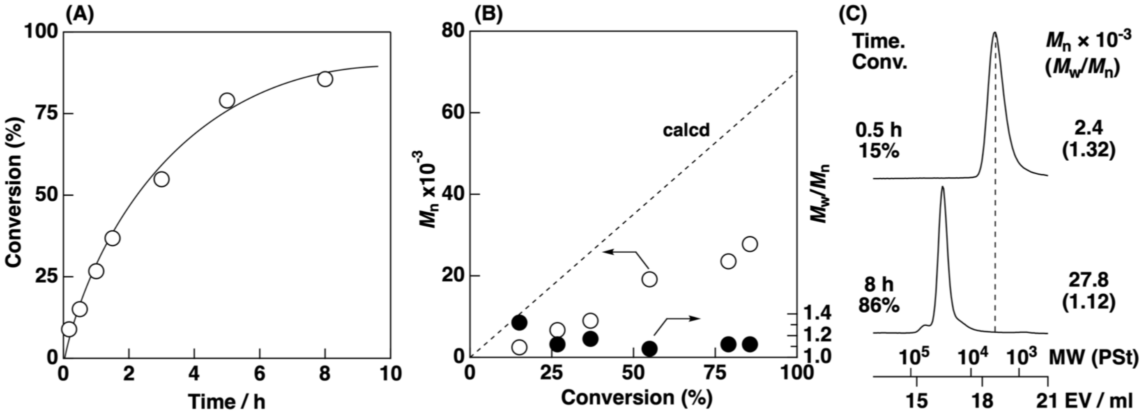


Figure S10. (A) Time–conversion plots for the polymerization of Si6mM, (B) the M_n (open circle) and M_w/M_n (filled circle) values of poly(Si6mM)s, and (C) the MWD curves of poly(Si6mM)s ($[\mathrm{Si6mM}]_0$ = 2.4 M, $[\mathrm{TEG}]_0$ = 5.0 mM, $[\mathrm{TBD}]_0$ = 5.0 mM, in toluene at –30 °C).

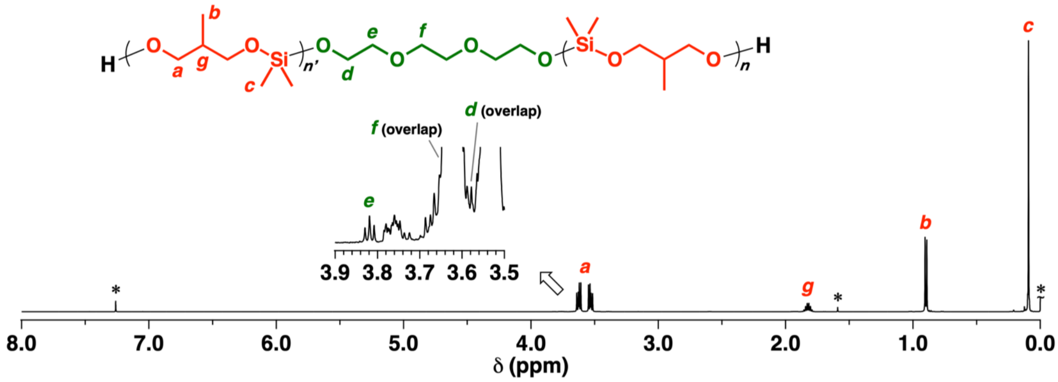


Figure S11. ^{1}H NMR spectrum of poly(Si6mM) (the sample shown in Figure S10C, lower; in $CDCl_3$ at 30 ºC; * water, Me_4Si, or $CHCl_3$).

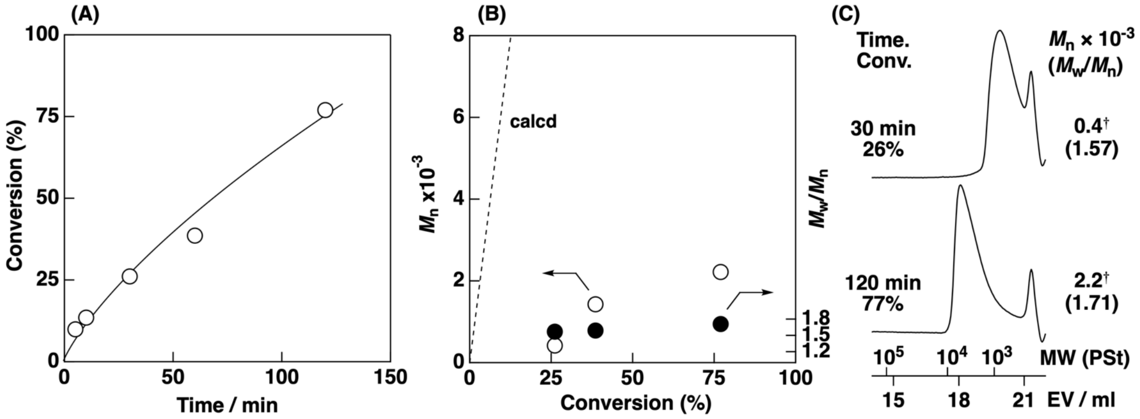


Figure S12. (A) Time–conversion plots for the polymerization of Si6, (B) the M_n (open circle) and M_w/M_n (filled circle) values of poly(Si6)s, and (C) the MWD curves of poly(Si6)s ([Si6]$_0$ = 2.4 M, [TEG]$_0$ = 5.0 mM, [TBD]$_0$ = 5.0 mM, in toluene at –30 °C). † A value for the main peak.

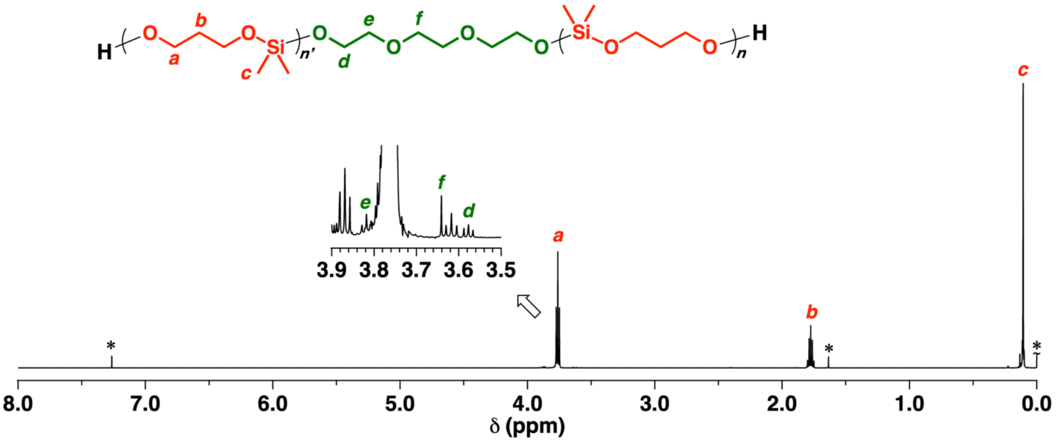


Figure S13. ^{1}H NMR spectrum of poly(Si6) (the sample shown in Figure S12C, lower; in CDCl$_3$ at 30 °C; * water, Me$_4$Si, or CHCl$_3$).

Table S3. Polymerization of Si5M, Si7, or Si8O by BTTP ^{a}

Entry	Monomer	Time (h)	Conv. (%)	$M_n \times 10^{-3}$	M_w/M_n
1	Si5M	73	18	–	–
2	Si7	73	4	–	–
3	Si8O	73	2	–	–

^{a} [Monomer]$_0$ = 2.4 M, [TEG]$_0$ = 5.0 mM, [BTTP]$_0$ = 5.0 mM, in toluene at –30 °C.

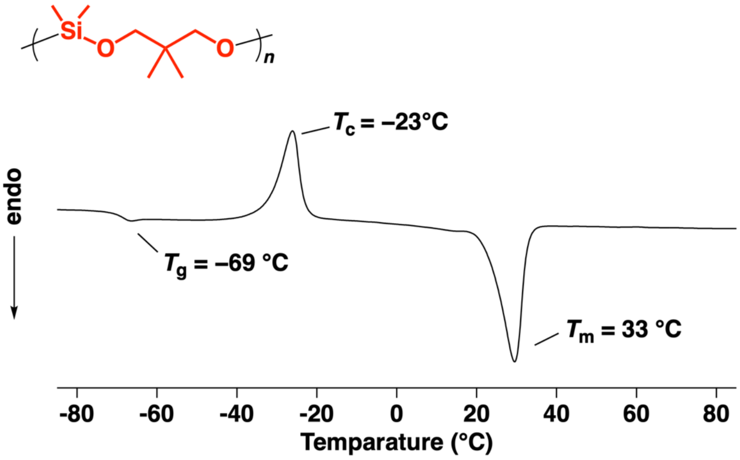


Figure S14. DSC analysis of poly(Si6M) (M_n = 27.1 × 10^3; the second heating scan, 10 ºC min^{-1}).

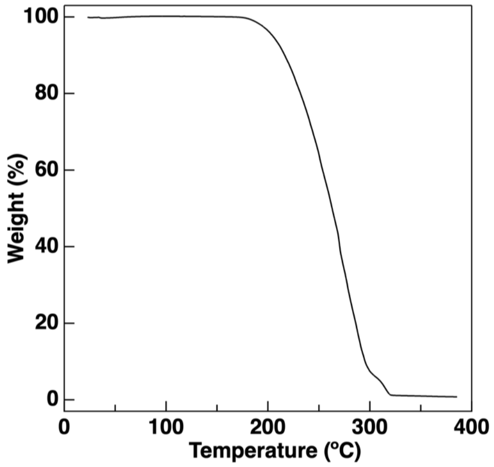


Figure S15. TGA curve of poly(Si6M) (entry 1 in Table 1; heating rate: 10 ºC min^{-1}).

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S3. R. Hada, A. Kanazawa, and S. Aoshima, *Macromolecules*, 2022, **55**, 5474–5484.
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