Electronic Supplementary Information

Metal-Free Synthesis of Alternating Silylether–Carbosilane Copolymers Using Unsaturated Ketones

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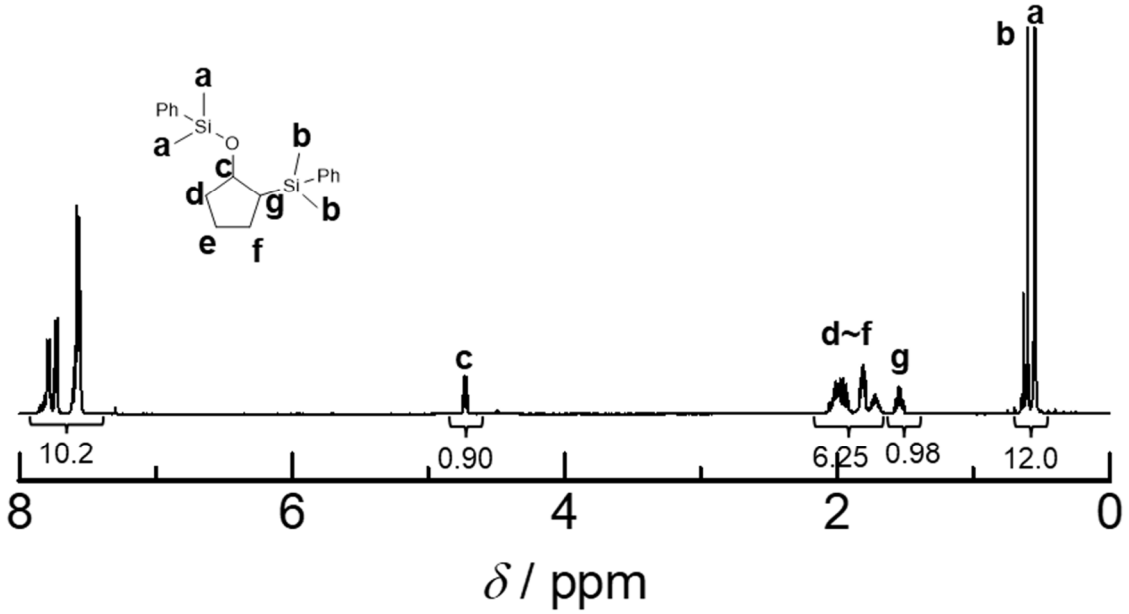


Fig. S1 ^{1}H NMR spectra of the product obtained by model reaction between CP and DMPS.

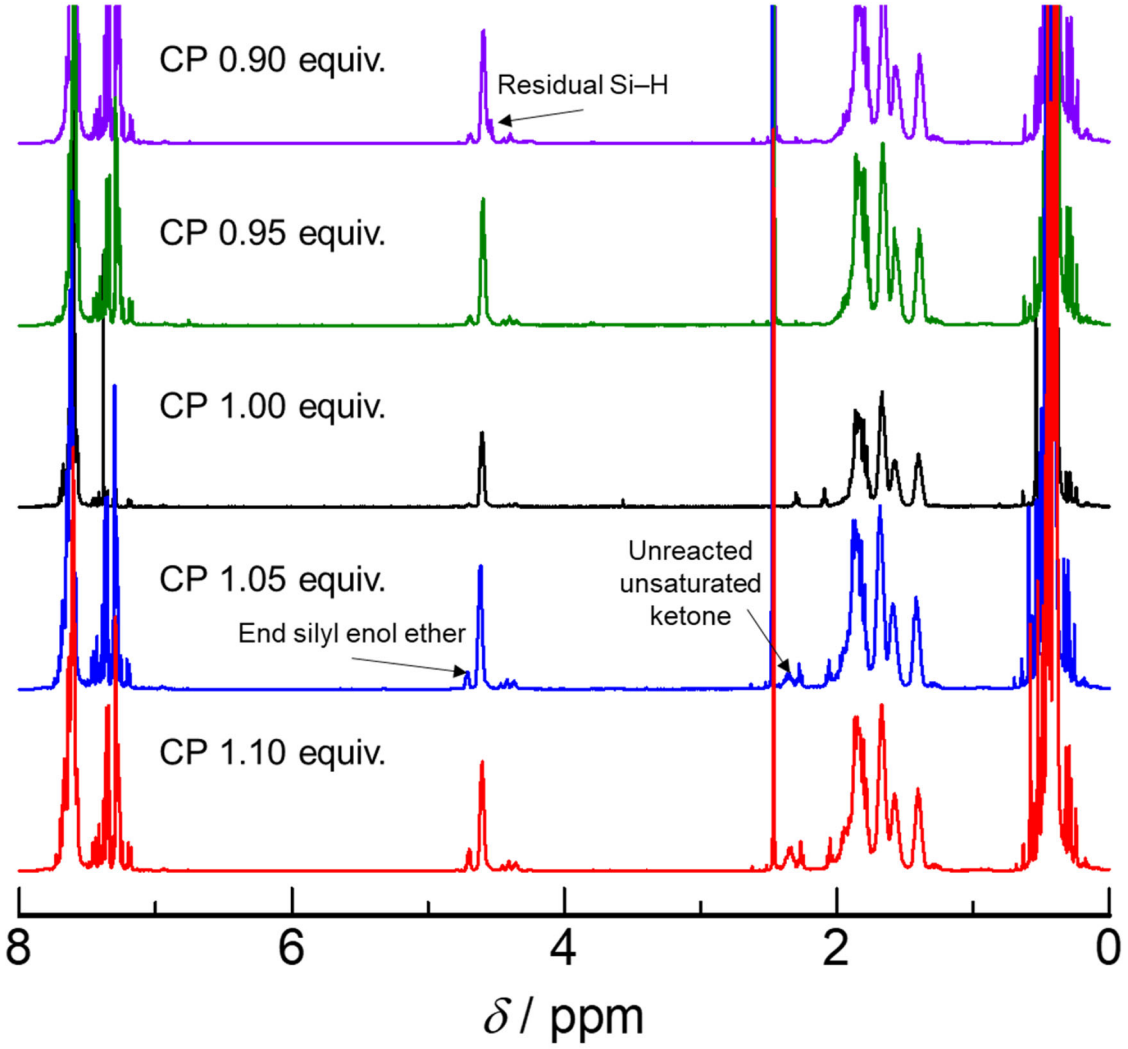
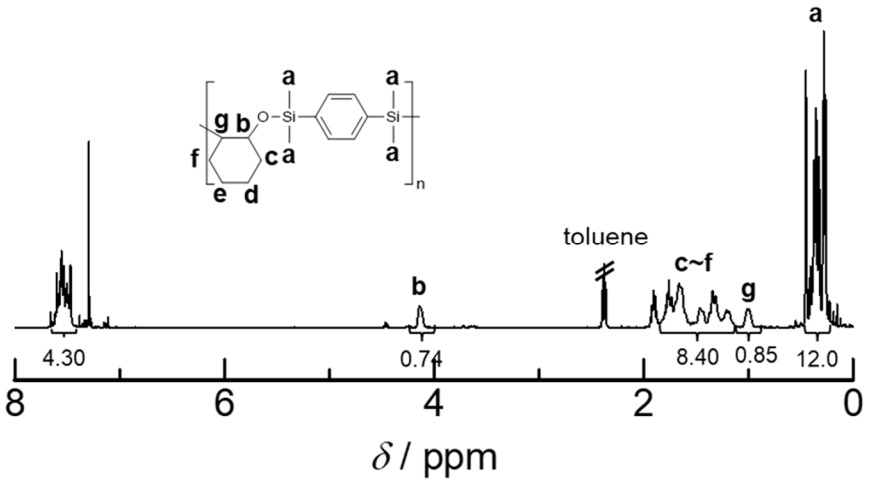
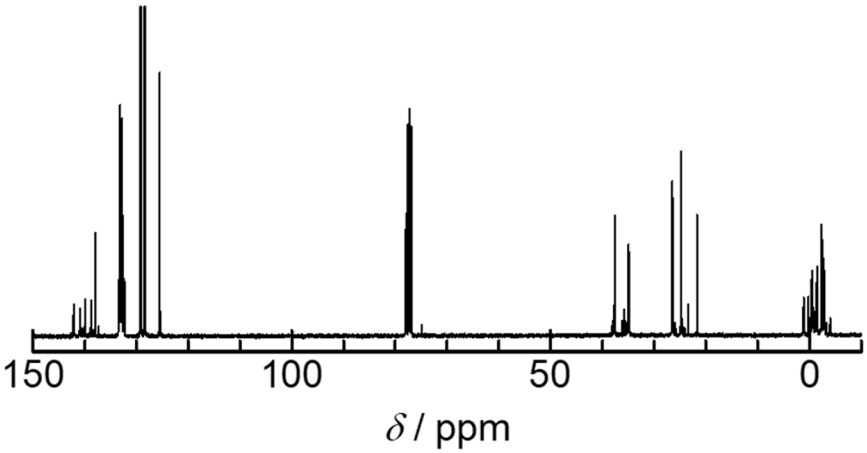


Fig. S2 ^{1}H NMR spectra of CP-DMSB for stoichiometric imbalance tests and their end group analysis (entries 1-5, Table 1).

(a)



(b)



(c)

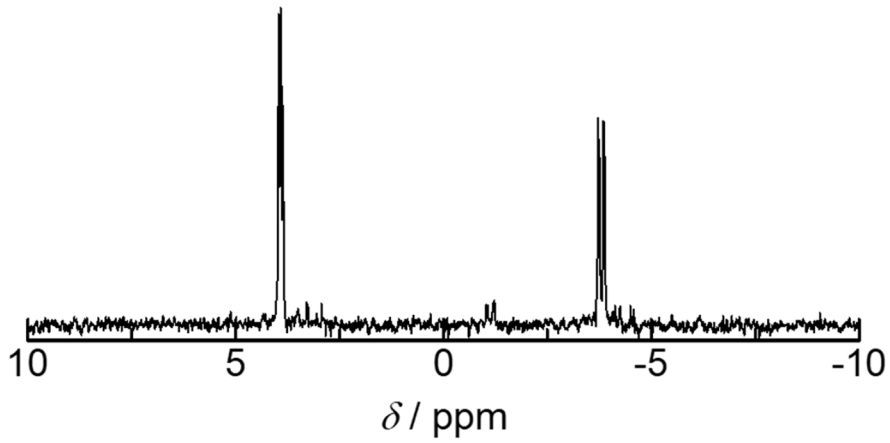


Fig. S3 NMR spectra of CP–DMSB (entry 1, Table 3): (a) ^{1}H, (b) ^{13}C, and (c) ^{29}Si..

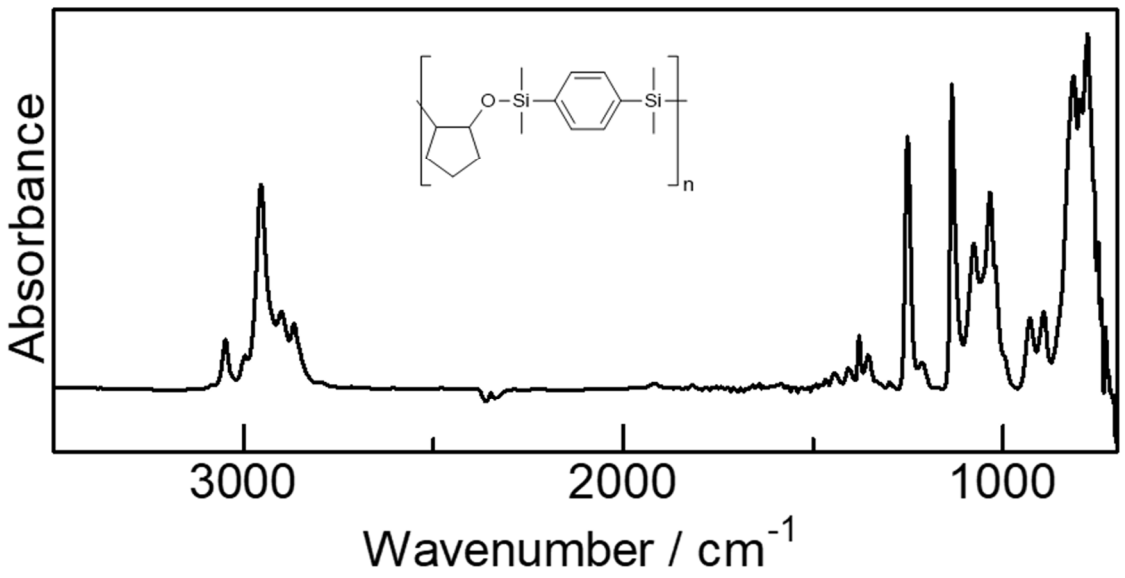
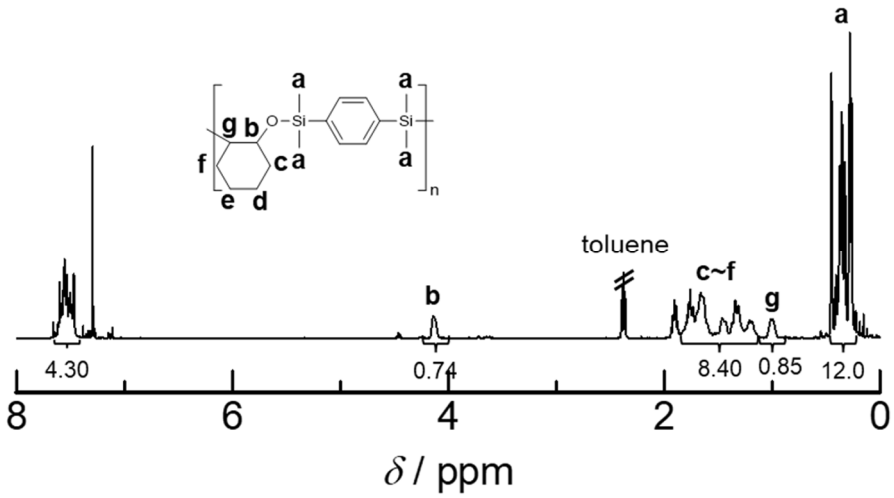


Fig. S4 FT-IR spectra of CP–DMSB (entry 1, Table 3).

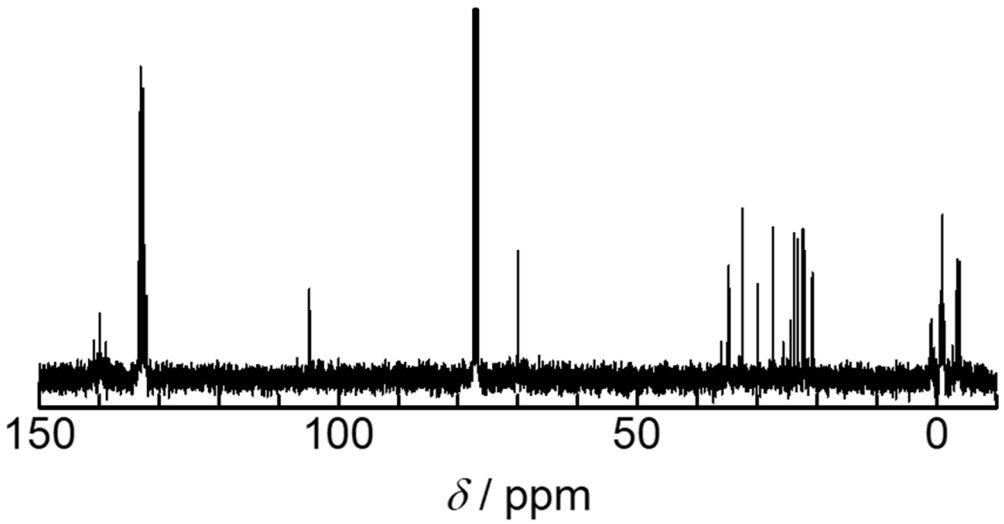
CP–DMSB (**1a**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77–7.68 (m, 4H), 4.70 (d, 1H), 1.97–1.89 (m, 3H), 1.77 (m, 2H), 1.68 (m, 1H), 1.50 (m, 1H), 0.61–0.49 (m, 12H). **^{13}C NMR** (400 MHz, $CDCl_3$): δ 133.19, 132.81, 129.21, 128.41, 77.88, 37.59, 34.91, 26.47, 24.80, -0.58, -1.51, -2.32, -2.80. **^{29}Si NMR** (400 MHz, $CDCl_3$): δ 5.13, -2.60. **FT-IR** ν_{max} (cm^{-1}): 3048, 2954, 2901, 2868, 1379, 1252, 1135, 1077, 1035, 930, 893, 815, 777.

(a)



(b)



(c)

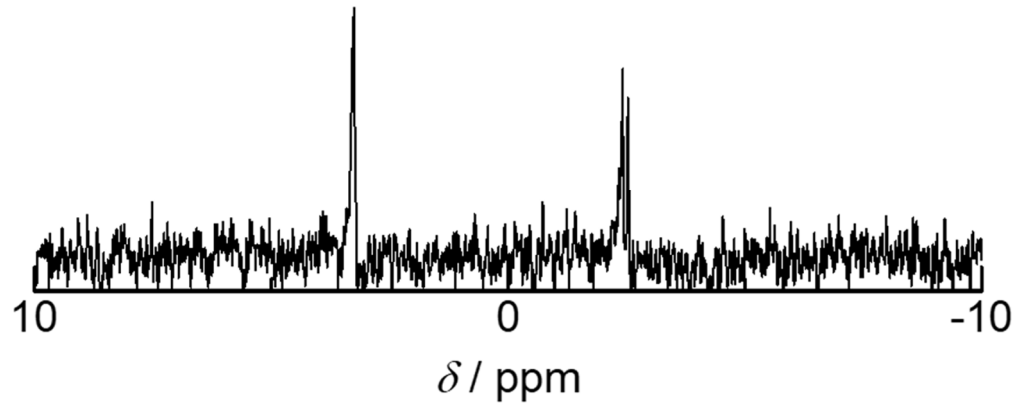


Fig. S5 NMR spectra of CH–DMSB (entry 2, Table 3): (a) ^{1}H, (b) ^{12}C, and (c) ^{29}Si..

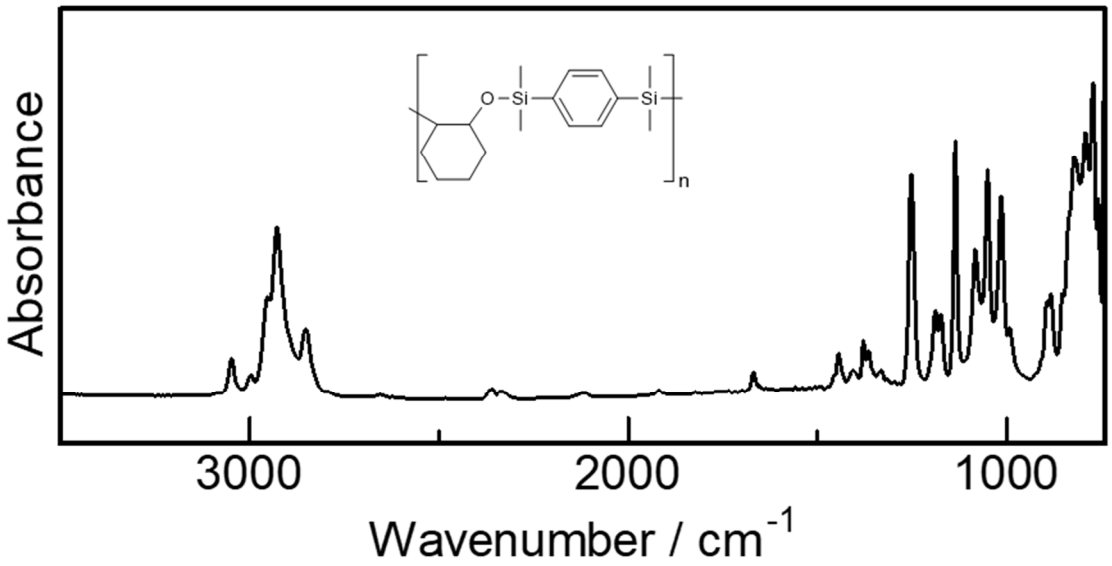
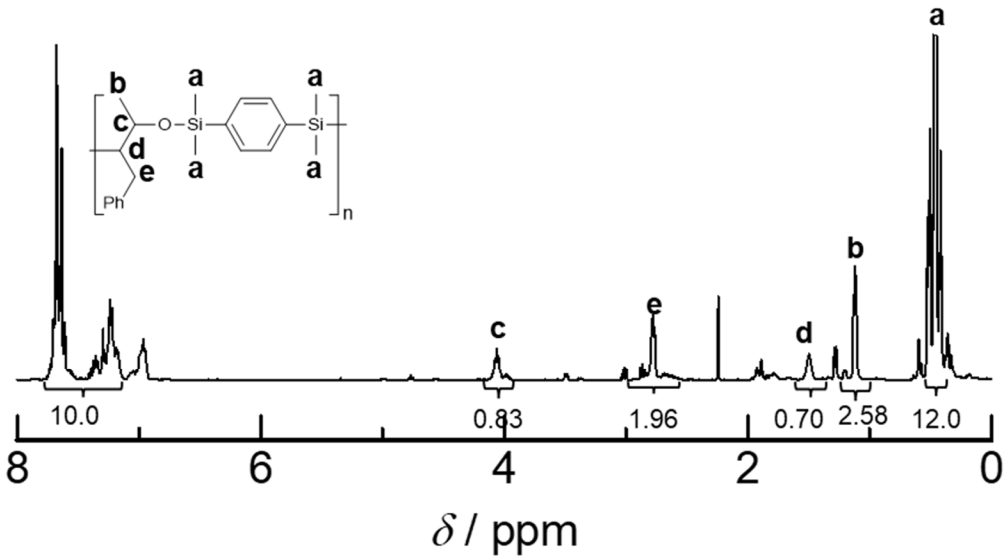


Fig. S6 FT-IR spectra of CH–DMSB (entry 2, Table 3).

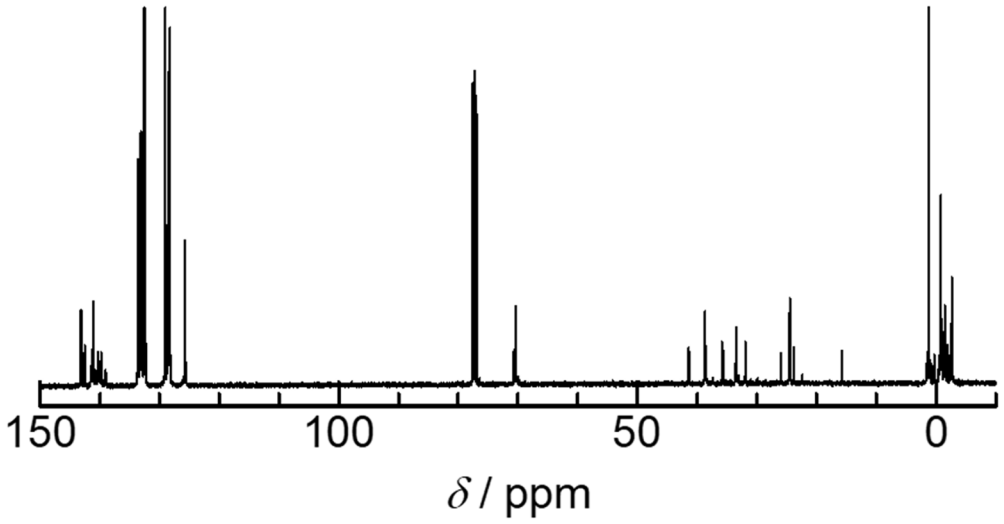
CH–DMSB (**1b**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.47 (m, 4H), 4.70 (s, 1H), 1.79–1.18 (m, 8H), 1.00 (m, 1H), 0.45–0.26 (m, 12H). **^{13}C NMR** (400 MHz, $CDCl_3$): δ 133.19, 133.12, 132.68, 132.64, 69.96, 34.99, 32.45, 27.30, 22.09, 20.74, 0.88, -0.98, -3.49, -3.83. **^{29}Si NMR** (400 MHz, $CDCl_3$): δ 3.26, -2.42. **FT-IR** ν_{max} (cm^{-1}): 3048, 2953, 2928, 2852, 1444, 1379, 1253, 1189, 1174, 1136, 1083, 1050, 1014, 883, 822, 792, 771.

(a)



(b)



(c)

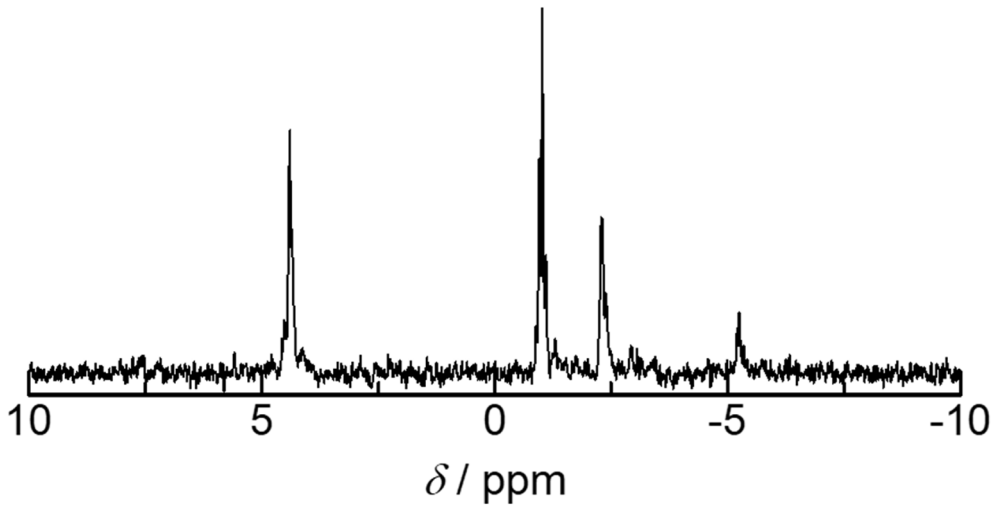


Fig. S7 NMR spectra of TBA–DMSB (entry 6, Table 3): (a) ^{1}H, (b) ^{13}C, and (c) ^{29}Si.

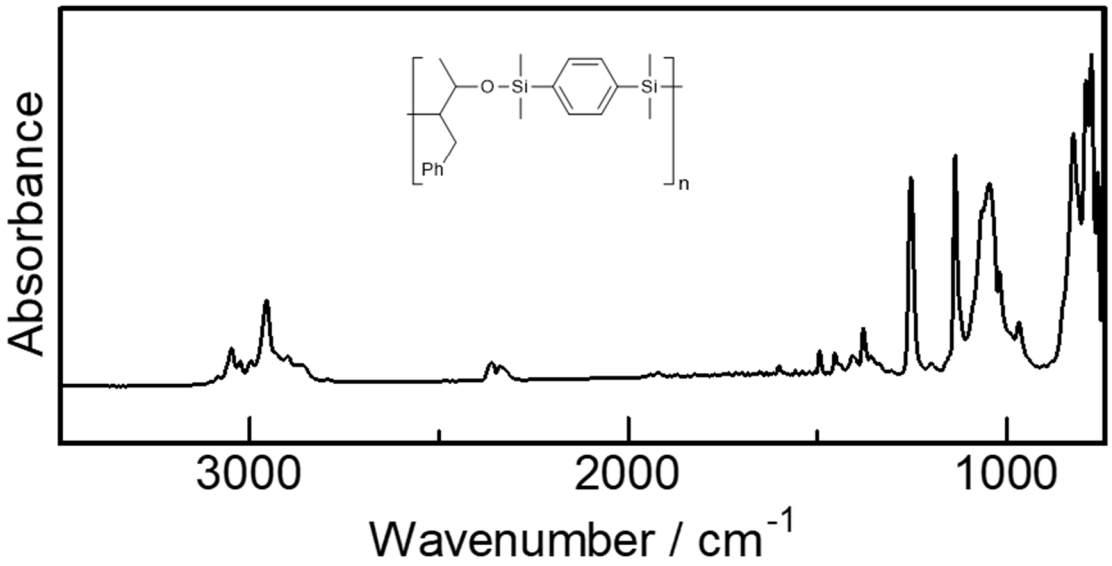
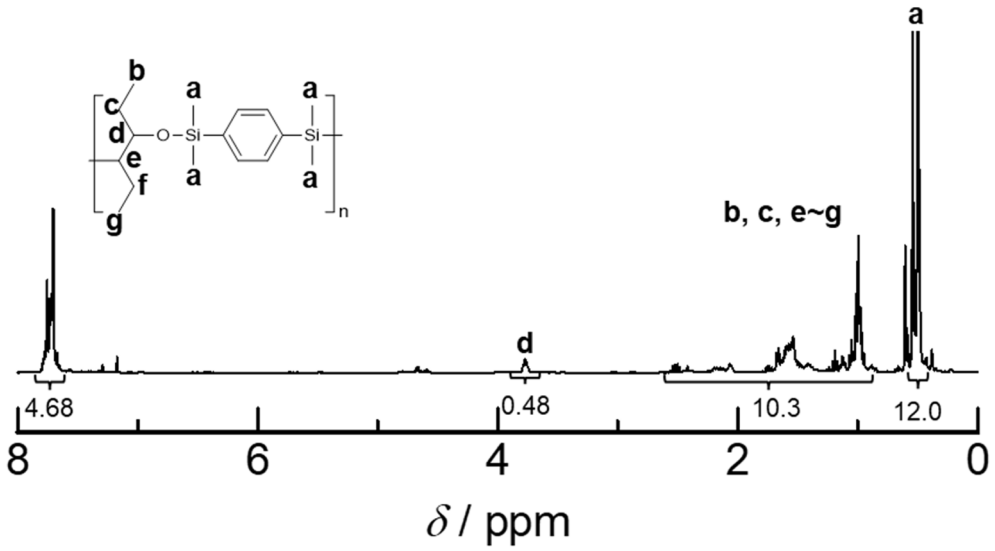


Fig. S8 FT-IR spectra of TBA–DMSB (entry 6, Table 3).

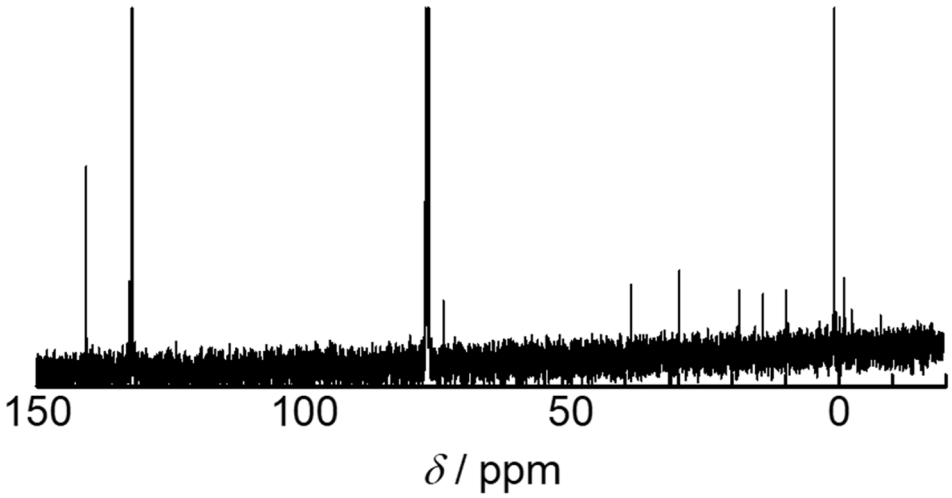
TBA–DMSB (**1f**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.17 (m, 9H), 4.06 (q, 1H), 2.77 (m, 2H), 1.49 (s, 1H), 1.12 (m, 3H), 0.53–0.41 (m, 12H). **^{13}C NMR** (400 MHz, $CDCl_3$): δ 143.16, 142.55, 141.07, 133.60, 133.12, 132.52, 129.02, 128.46, 128.27, 125.79, 77.47, 38.67, 33.41, 24.48, 24.80, -0.80, -1.49, -2.02, -2.65. **^{29}Si NMR** (400 MHz, $CDCl_3$): δ 4.41, -1.01, -2.29, -5.25. **FT-IR** ν_{max} (cm^{-1}): 3048, 2956, 2899, 2869, 1379, 1253, 1136, 1046, 968, 823, 791, 776.

(a)



(b)



(c)

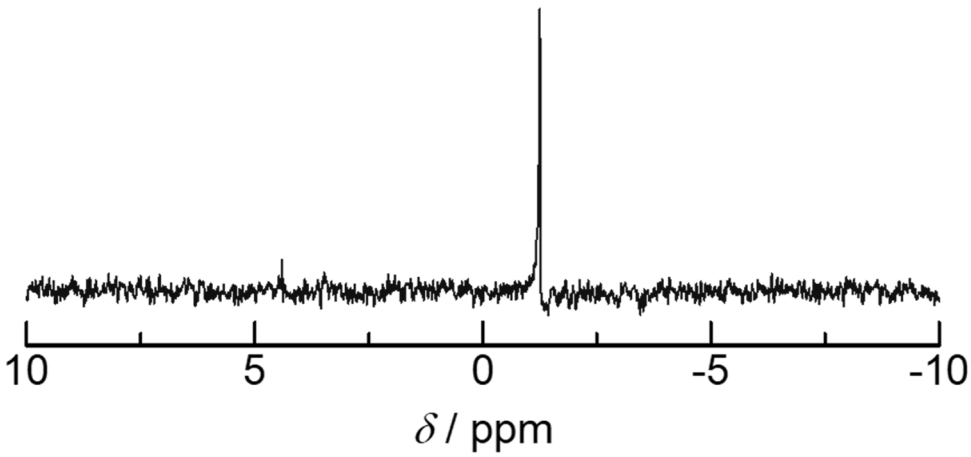


Fig. S9 NMR spectra of 4H3o–DMSB (entry 7, Table 3): (a) ^{1}H, (b) ^{13}C, and (c) ^{29}Si.

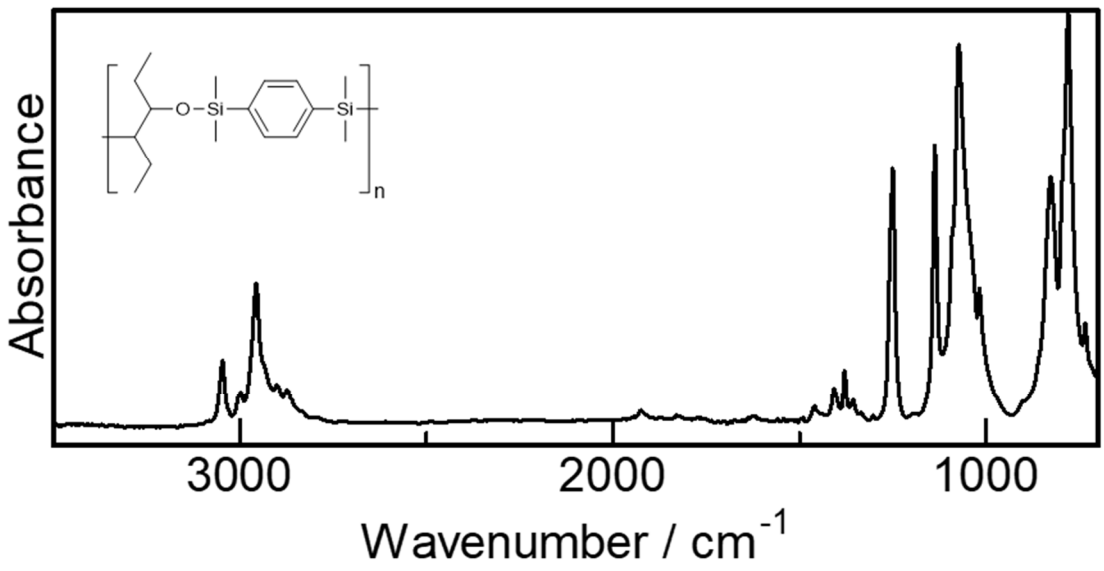


Fig. S10 FT-IR spectra of 4H3o–DMSB (entry 7, Table 3).

4H3o–DMSB (**1g**)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80–7.67 (m, 4H), 3.77 (q, 1H), 2.56–0.85 (m, 11H), 0.54–0.49 (m, 12H). **^{13}C NMR** (400 MHz, $CDCl_3$): δ 140.85, 132.79, 132.46, 132.25, 74.05, 38.93, 29.85, 18.74, 14.23, 9.83, 0.91, 0.62, -0.94, -2.32. **^{29}Si NMR** (400 MHz, $CDCl_3$): δ 4.41, -1.25. **FT-IR** ν_{max} (cm^{-1}): 3046, 2956, 2900, 2873, 1408, 1380, 1251, 1139, 1074, 1019, 827, 782, 736.

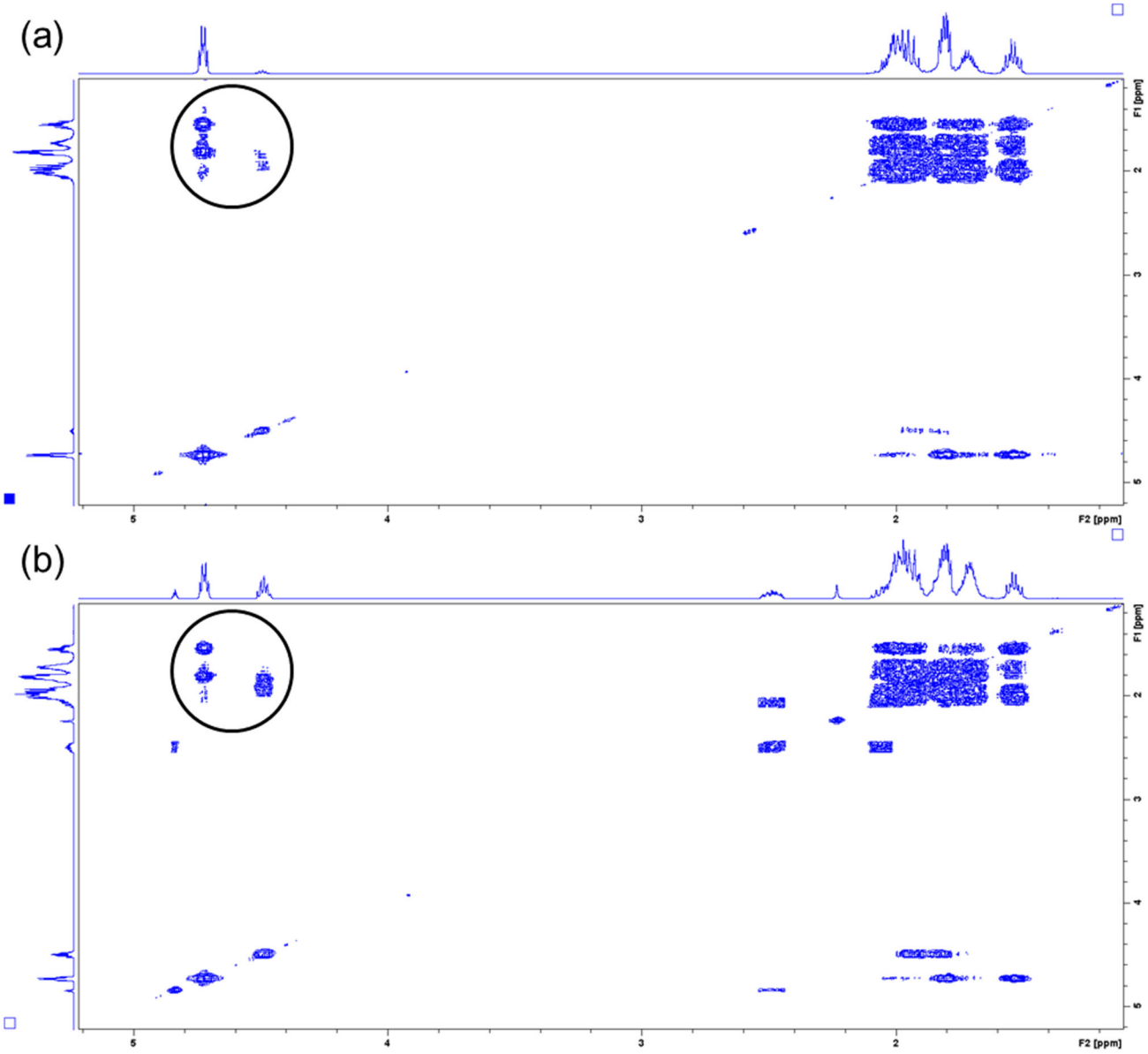


Fig. S11 ^{1}H-COSY NMR spectra of CP–DMSB polymerized in (a) toluene and (b) $CHCl_3$.

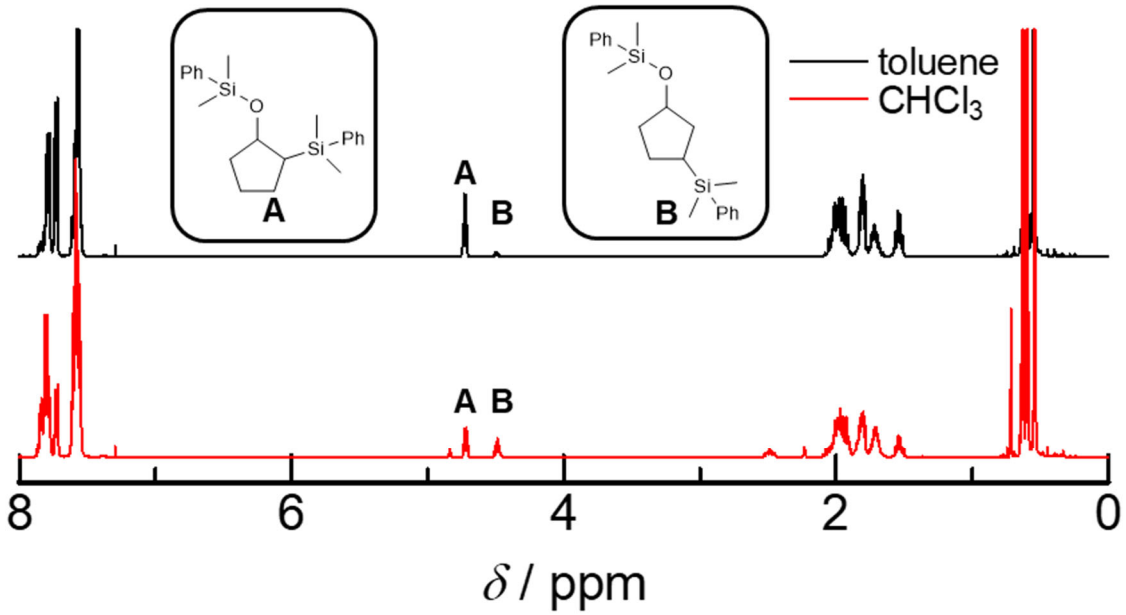
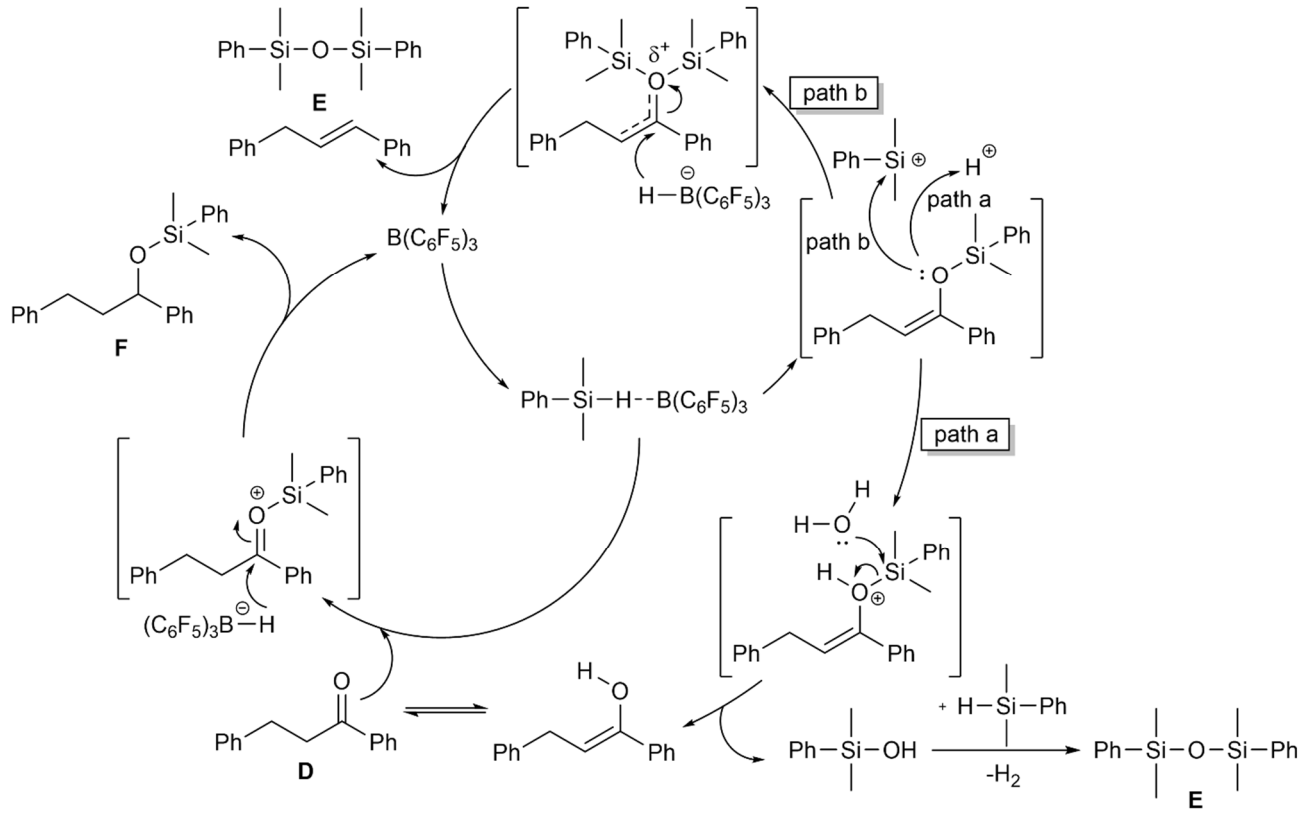
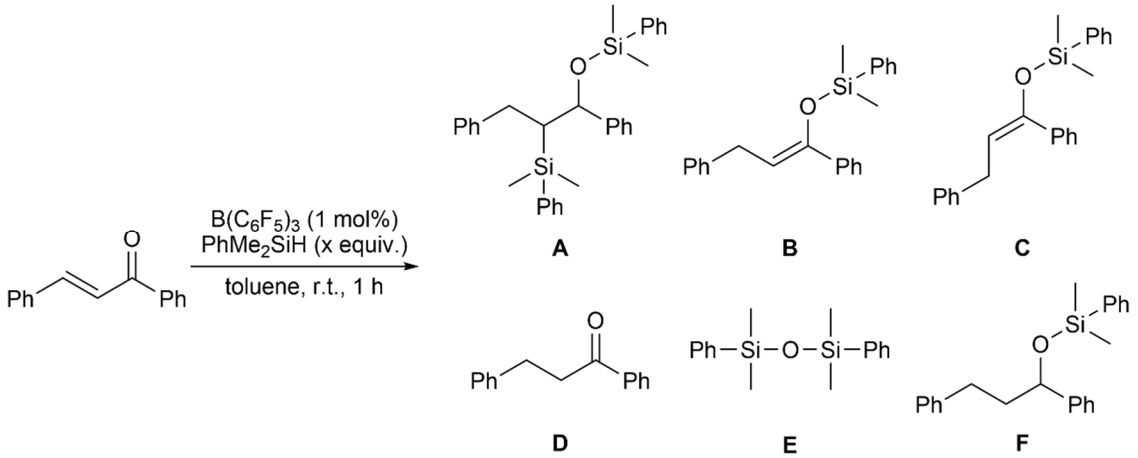


Fig. S12 ^{1}H NMR spectra of CP-DMSB: entries 2 (black) and 4 (red) in Table 2.



Scheme S1. Plausible by-products reaction mechanism for chalcone and DMPS.

Table S1. Hydrosilylation of chalcone with dimethylphenylsilane.[a]



x [equiv.]	**A** [%][b]	**B** [%][b]	**C** [%][b]	**D** [%][b]	**E** [%][b]	**F** [%][b]
1.0	n.d.	75	6	7	5	n.d.
2.0	n.d.	53	2	trace	17	10

[a]Reaction conditions: chalcone (1.0 mmol), dimethylphenylsilane (x mmol), $B(C_6F_5)_3$ (0.01 mmol), toluene (1.0 mL). [b]Determined using ^1H NMR.

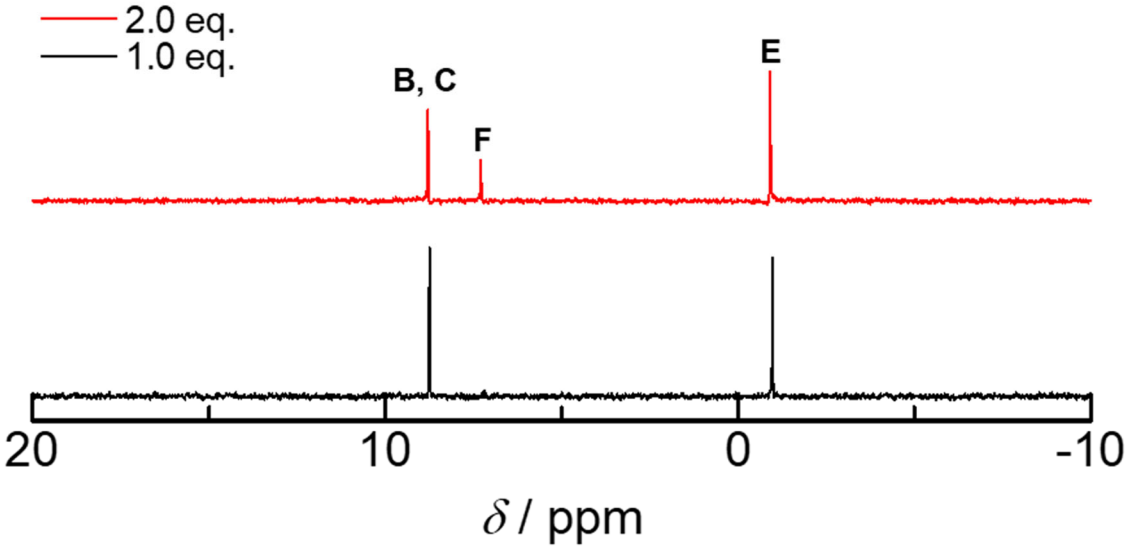


Fig. S13 ^{29}Si NMR spectra of the products in Table S1.

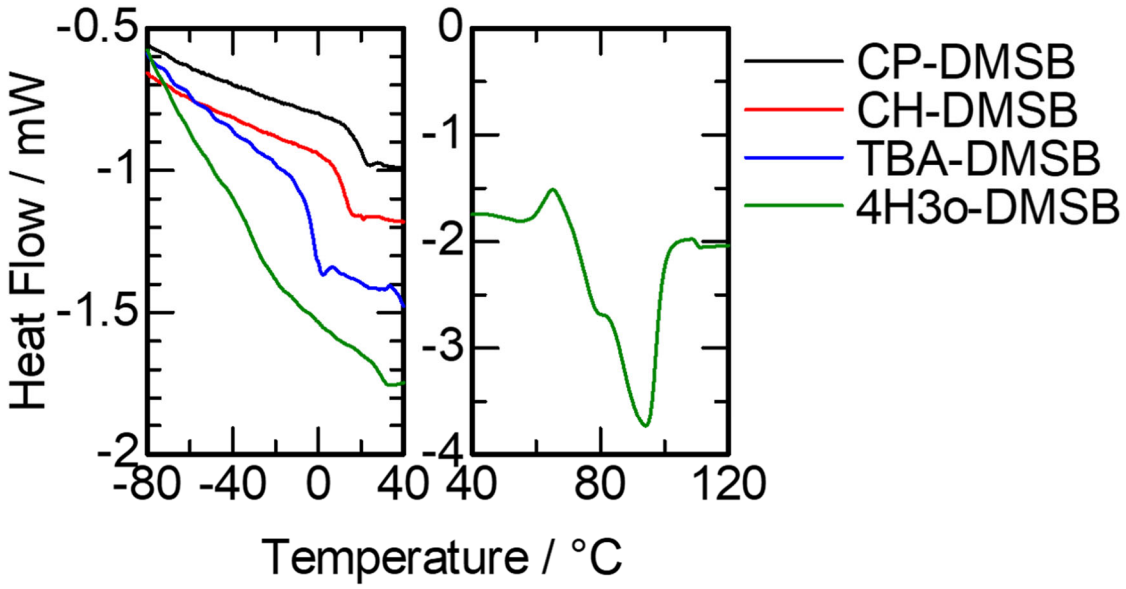


Fig. S14 DSC curves of CP–DMSB (black), CH–DMSB (red), TBA–DMSB (blue), and 4H3o-DMSB (green).

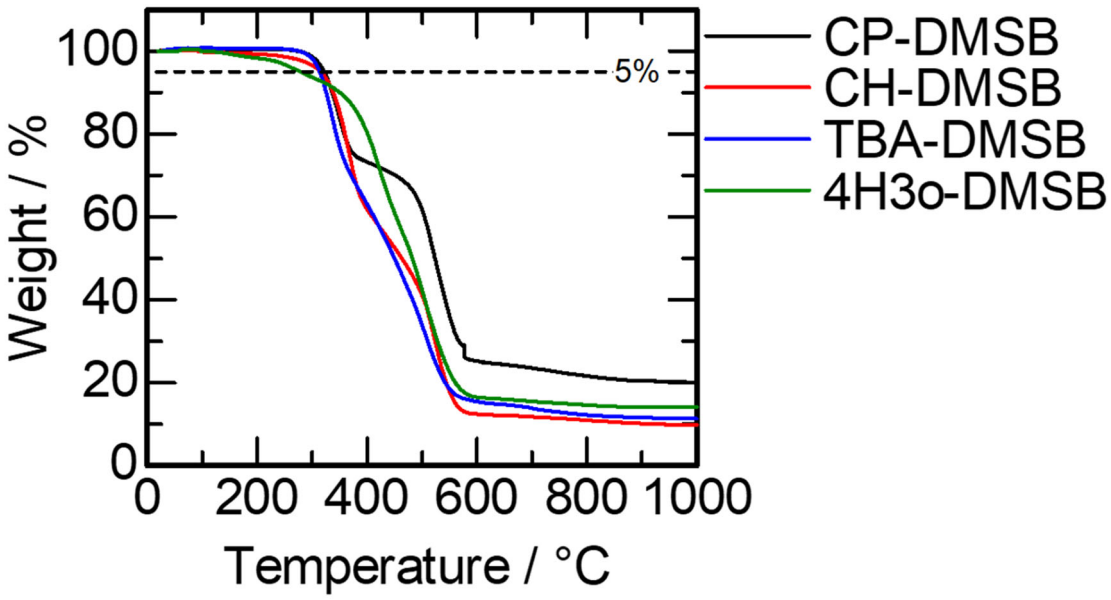


Fig. S15 TGA curves of CP–DMSB (black), CH–DMSB (red), TBA–DMSB (blue), and 4H3o-DMSB (green).

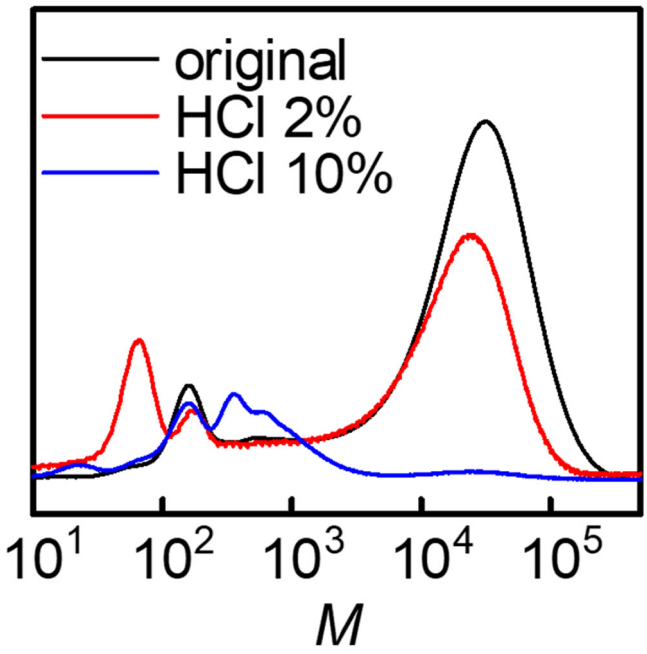


Fig. S16 SEC curves of CP–DMSB (black), acid-catalyzed hydrolysis (2 vol%, HCl aq., pH = 2) (red), and acid-catalyzed hydrolysis (10 vol%, HCl aq., pH = 2) (blue).

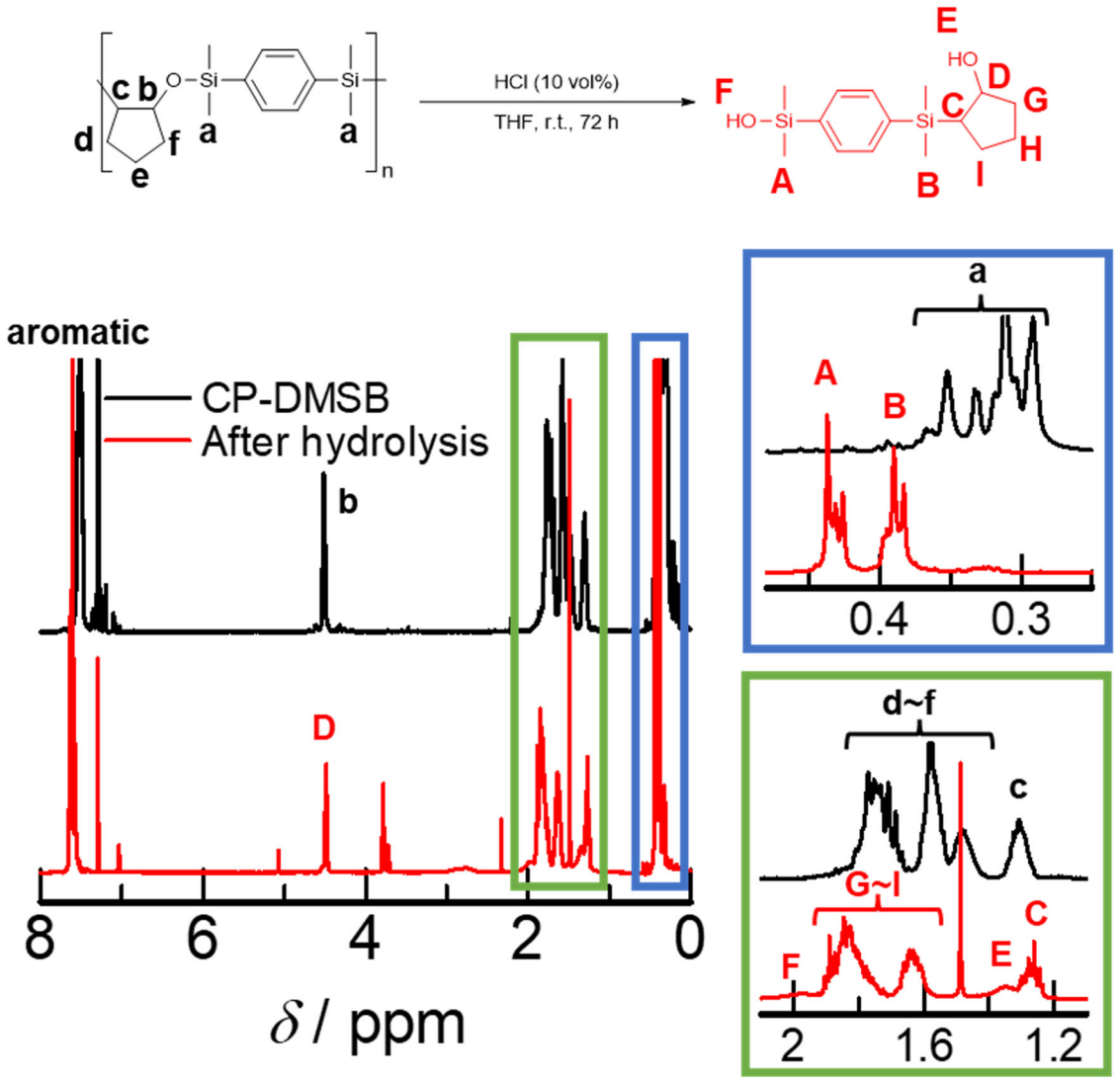
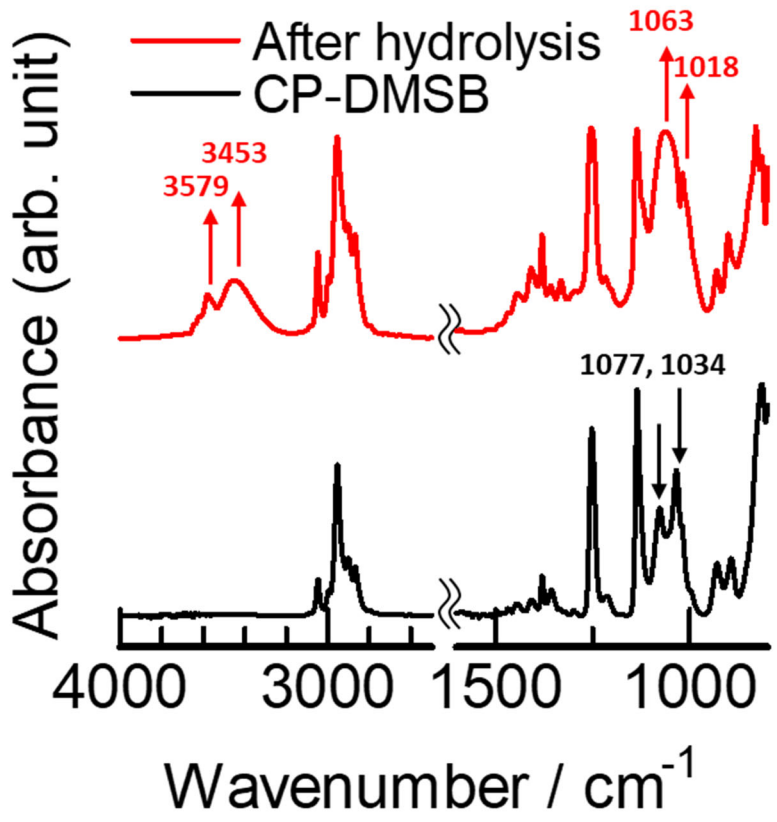


Fig. S17 (top) Chemical structures and (bottom) ^{1}H NMR spectra of the degraded products obtained from hydrolysis.



Wavenumber / cm^{-1}	Assignment
3579	Hydroxyl group (O–H stretching)
3453	Silanol (Si–OH)
1063	Silanol (Si—O bond)
1018	Alcohol (C–O stretching)
1077	Silyl ether (Si–O–C asymmetric stretching)
1034	Silyl ether (Si–O–C symmetric stretching)

Fig. S18 (top) FT-IR spectra and (bottom) peak assignment of the degraded products obtained from hydrolysis.

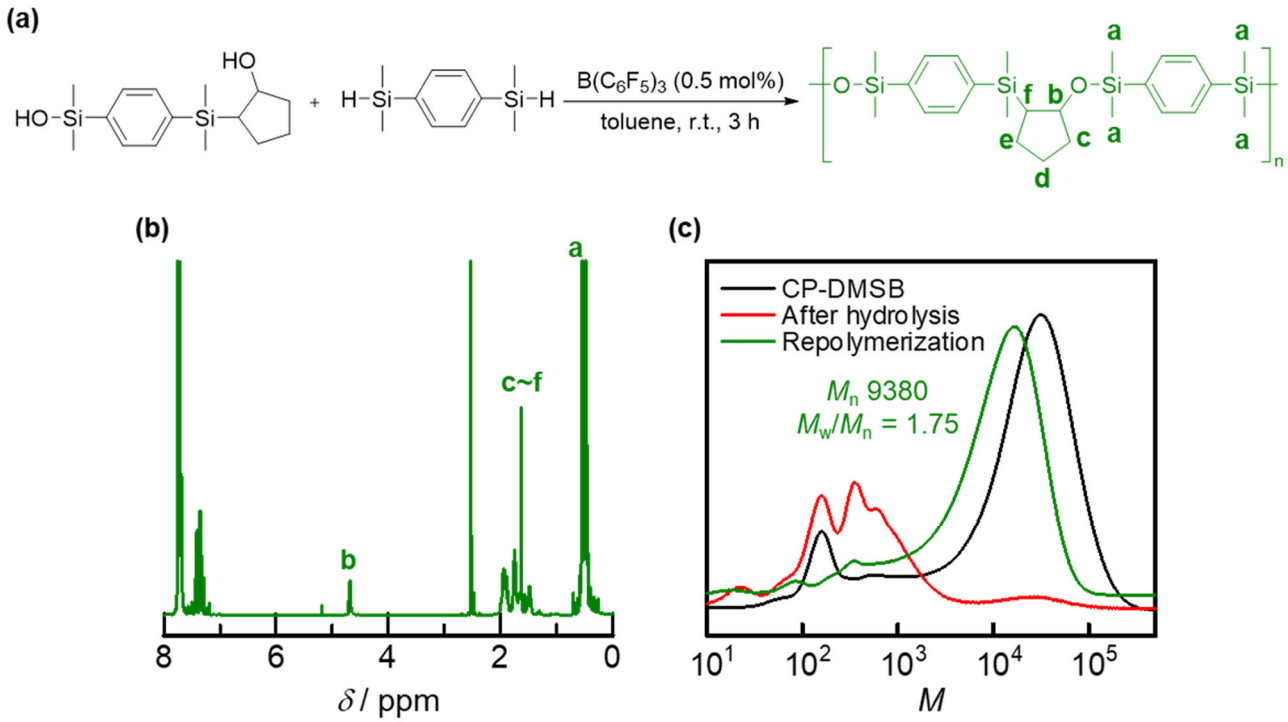


Fig. S19 (a) Polymerization scheme for degraded products, (b) ^{1}H NMR spectra for the polymer obtained from degraded products, and (c) SEC curves for repolymerized products.

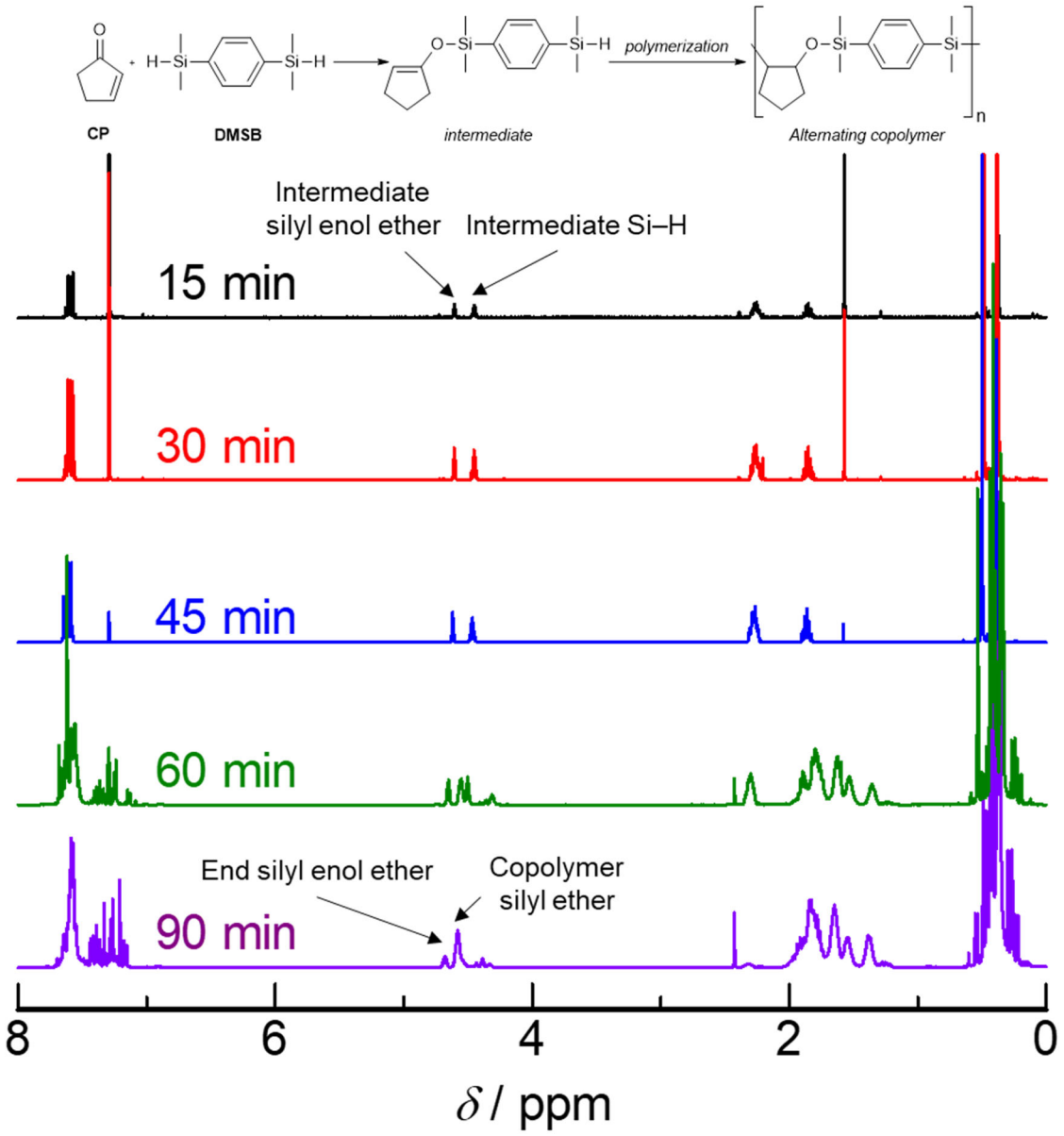


Fig. S20 ^{1}H NMR spectra for the equimolar reaction of CP and DMSB at different reaction time with low total monomer concentration (0.5 M).

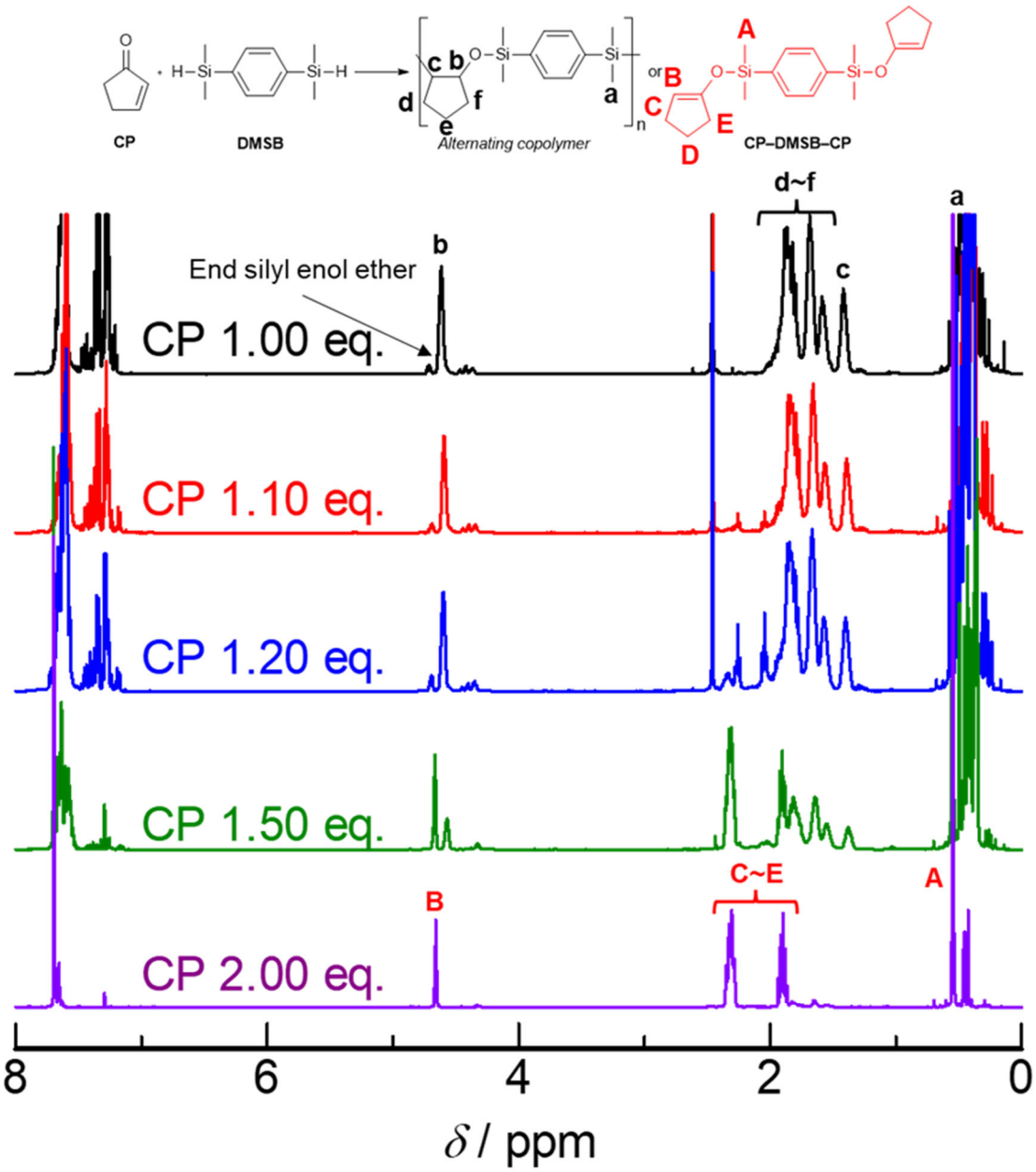
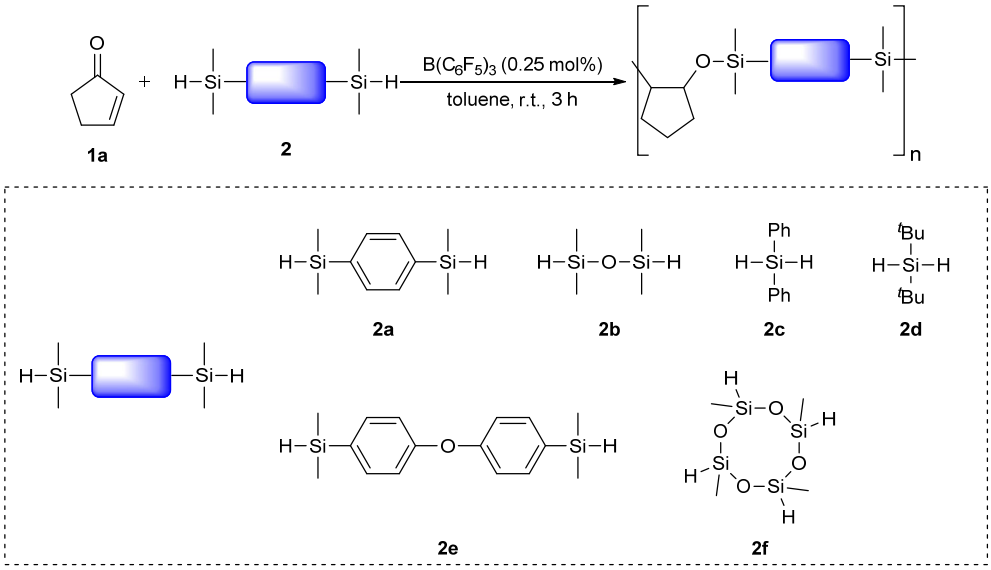


Fig. S21 ^{1}H NMR spectra for the reaction of CP and DMSB at different amounts of CP and their structure analysis.

Table S2. Polymerization of CP with various disilane monomers.



disilane	M_n[b] / 10^3	M_w[b] / 10^3	M_w / M_n[b]	yield [%][c]	T_g [°C][d]	T_{d5} [°C][e]
2a	21.3	42.3	2.0	40	13	322
2b	-	-	-	-	-	-
2c	-	-	-	-	-	-
2d	-	-	-	-	-	-
2e[f]	17.9	32.7	1.8	84	13 (m.p. 48)	315
2f	2.22[g]	-	-	39	-71	199

[a]Polymerization conditions: CP(2.0 mmol), disilane (2.0 mmol) and $B(C_6F_5)_3$ (0.005 mmol) in 2.0 mL of toluene. [b]Determined using SEC calibrated with polystyrene standards in THF at a flow rate of 0.2 mL min^{-1} at 40 °C. [c]Isolated yields. [d]Glass transition temperature (T_g) were measured by differential scanning calorimetry (DSC). [e]Thermal decomposition temperature (T_{d5}) determined using thermogravimetric analysis (TGA). T_{d5} indicates the temperature at a weight loss of 5% of the samples. [f](Oxybis(4,1-phenylene))bis(dimethylsilane) (OPDS). [g]Number-average molecular weight calculated using ^{1}H NMR, considering the terminated silyl enol ether.

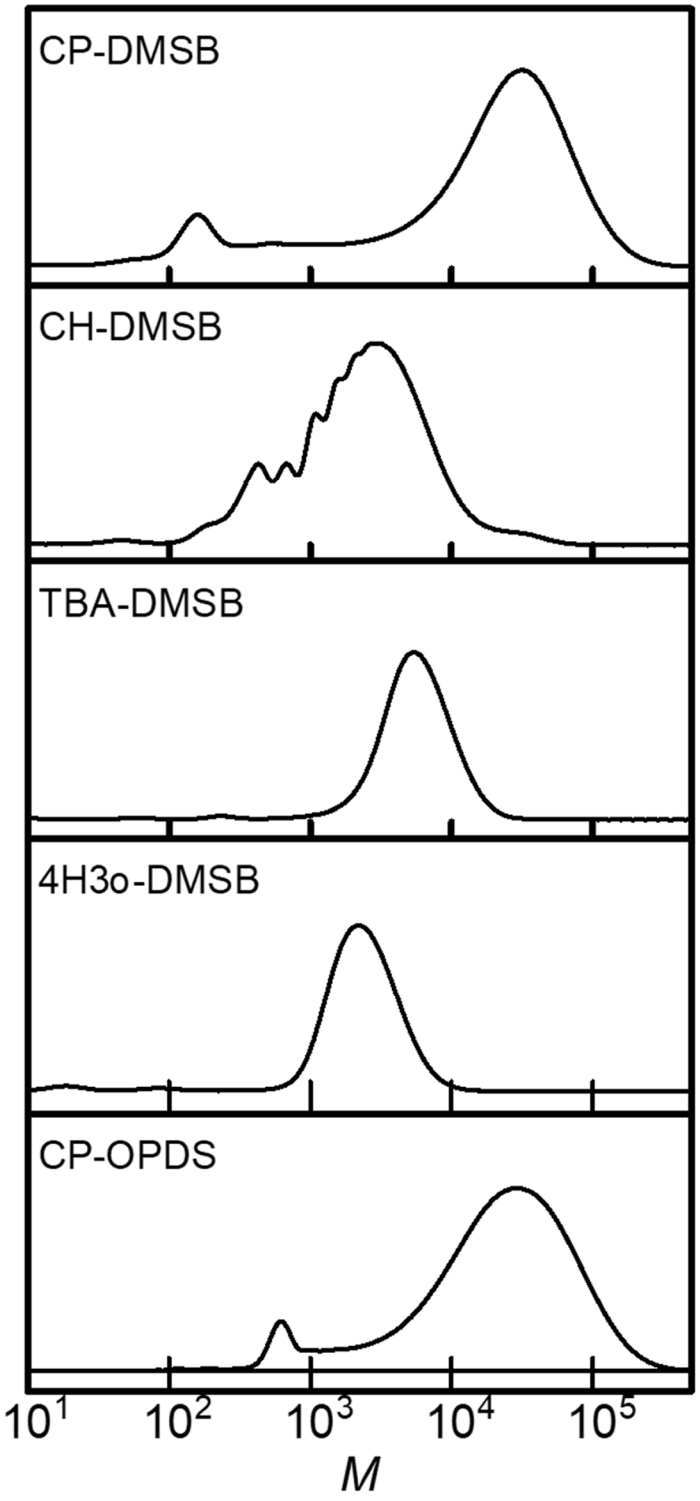


Fig. S22 SEC curves of silylether copolymers.