

Electronic Supplementary Information

Molecular and kinetic design for the expanded control of molecular weights in ring-opening metathesis polymerization of norbornene-substituted polyhedral oligomeric silsesquioxanes

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S1. Experimental section

S1.1. Materials

Aminopropyl-heptaisobutyl POSS ($\text{NH}_2\text{C}_3\text{H}_6\text{POSS}$) and aminoethylaminopropylisobutyl-heptaisobutyl POSS ($\text{NH}_2\text{C}_2\text{H}_4\text{NHC}_3\text{H}_6\text{POSS}$) were purchased from Hybrid Plastics. All other chemical compounds were purchased from commercial suppliers and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled over sodium naphthalenide and degassed at 10^{-6} Torr. Hexane was distilled over 1,1-diphenylhexyllithium and degassed at 10^{-6} Torr. Lithium chloride (LiCl) was dried with stirring at $150\text{ }^\circ\text{C}$ for 24 h at 10^{-6} Torr. A 1.4 M *sec*-butyllithium (*s*-BuLi) solution in cyclohexane was degassed, appropriately diluted in hexane, divided into clean glass ampules equipped with break-seals at 10^{-6} Torr, and stored at $-30\text{ }^\circ\text{C}$. 1,1-Diphenylethylene (DPE) and benzyl methacrylate (BzMA) were distilled over calcium hydride (CaH_2) at reduced pressure and then redistilled over CaH_2 at 10^{-6} Torr. DPE, LiCl, and BzMA were appropriately diluted in THF, divided into clean glass ampules equipped with break-seals at 10^{-6} Torr, and stored at $-30\text{ }^\circ\text{C}$. 5-Norbornene-*exo*-2,3-dicarboxylic anhydride (*exo*-NBAnh), 12-(5-norbornene-*exo*-2,3-dicarboximido)dodecanoic acid (*exo*-NBC₁₁H₂₂COOH) and $\text{RuCl}_2(\text{pyridine})_2(\text{H}_2\text{IMes})(\text{CHPh})$ (**Ru**) were prepared in our previous work.^{S1}

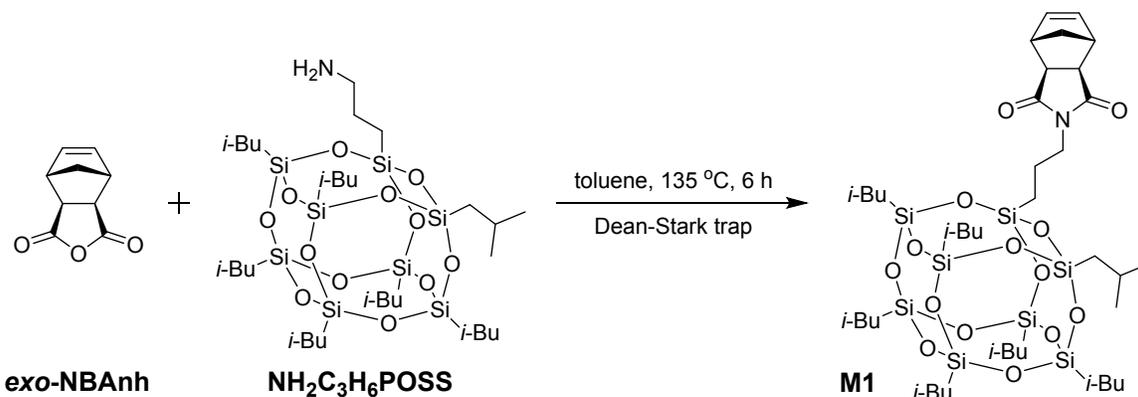
S1.2. Instruments and analyses

A glove box (Seed Tac Korea Co.) retained a nitrogen atmosphere with 0.1–0.3 ppm of H_2O and 1.0–1.5 ppm of O_2 to carry out the ring-opening metathesis polymerization (ROMP). Proton and carbon-13 nuclear magnetic resonance (^1H and ^{13}C NMR) spectra of synthesized compounds were recorded using a JNM-ECX 400 NMR spectrometer (JEOL, 400 MHz) in chloroform-*d*

(CDCl₃, 99.8% atom D, contains 0.03 vol% tetramethylsilane) at 25 °C. Fourier-transform infrared (FT-IR) spectroscopy for potassium bromide (KBr) pellets containing monomers was conducted using a Nicolet iS10 (Thermo Scientific). Elemental analysis (EA) for monomers was conducted using US/Vario Max CN (Elementar; combustion temperature: 1800 °C) and Flash 2000 (Thermo Scientific; combustion temperature: 1000 °C). Conversion (conv), number-average molecular weight (M_n), weight-average molecular weight (M_w), dispersity ($D = M_w/M_n$), and z-average radius of gyration ($R_{g,z}$) of synthesized polymers were determined using a size exclusion chromatography-multiangle laser light scattering (SEC-MALLS) instrument equipped with a 515 HPLC pump (Waters), a set of four Styragel columns connected in series (HR 0.5, HR 1, HR 3, and HR 4 with pore sizes of 50, 100, 500, and 1000 Å, respectively, Waters), a miniDAWN TREOS light scattering detector (Wyatt Technology), and an Optilab T-rEX refractive index detector (Wyatt Technology). The SEC-MALLS instrument was operated in THF/triethylamine (98/2 v/v) with an elution rate of 1.0 mL/min at 40 °C. Refractive index increment (dn/dc) values of polymers were calculated assuming 100% mass recovery of the injected polymer samples. Thermogravimetric analysis (TGA) measurement was performed on a TGA Q50 (TA Instruments) at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurement was performed on a DSC Q20 (TA Instruments) at cooling and heating rates of 2 °C/min under a nitrogen atmosphere. Wide-angle X-ray scattering (WAXS) profiles were recorded using a Rigaku D/max-2500 diffractometer with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$) at 40 kV and 100 mA. Transmission electron microscopy (TEM) measurement was performed on a Tecnai G2 S-Twin (FEI) at an accelerating voltage of 300 kV. Processing of numerical data was performed on an OriginPro 2017 (OriginLab).

S1.3. Synthesis procedures for POSS-substituted monomers

S1.3.1. 3-(5-Norbornene-*exo*-2,3-dicarboximido)propyl-heptaisobutyl POSS (M1)

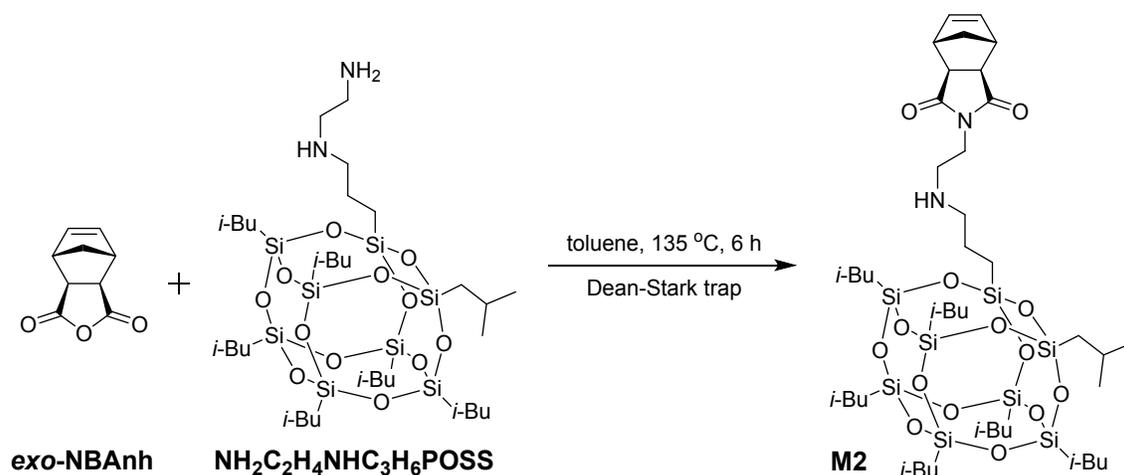


A two-neck 100 mL flask equipped with a Dean-Stark trap was charged with nitrogen for 30 min. To the flask were added toluene (25 mL), *exo*-NBAnh (0.939 g, 5.72 mmol) and $\text{NH}_2\text{C}_3\text{H}_6\text{POSS}$ (5.00 g, 5.72 mmol). The reaction mixture was stirred at 135 °C for 16 h. After the reaction was complete, the solution was cooled and concentrated at reduced pressure. The residual mixture was dissolved in DCM (25 mL) and then washed with 0.1 N HCl (10 mL) and brine (10 mL) in sequence. The organic layer was dried over Na_2SO_4 , filtered, and concentrated at reduced pressure. The recovered solid was precipitated in cool methanol, filtered, and dried under vacuum to afford **M1** as a white powder (5.55 g, 95%).

M1: ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 6.28 (s, 2H), 3.44 (t, 2H, $J = 7.6$ Hz), 3.26 (s, 2H), 2.66 (s, 2H), 1.83 (m, 7H), 1.63 (m, 2H), 1.50 (d, 1H, $J = 8.0$ Hz), 1.22 (d, 1H, $J = 9.6$ Hz), 0.94 (dd, 42H, $J = 6.4, 1.6$ Hz), 0.59 (dd, 16H, $J = 6.8, 2.0$ Hz). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 177.94, 137.89, 47.85, 45.25, 42.76, 41.24, 25.72, 23.92, 22.53, 21.47, 9.86.

S1.3.2. 3-(2-(5-Norbornene-*exo*-2,3-dicarboximido)ethylamino)propyl-heptaisobutyl POSS

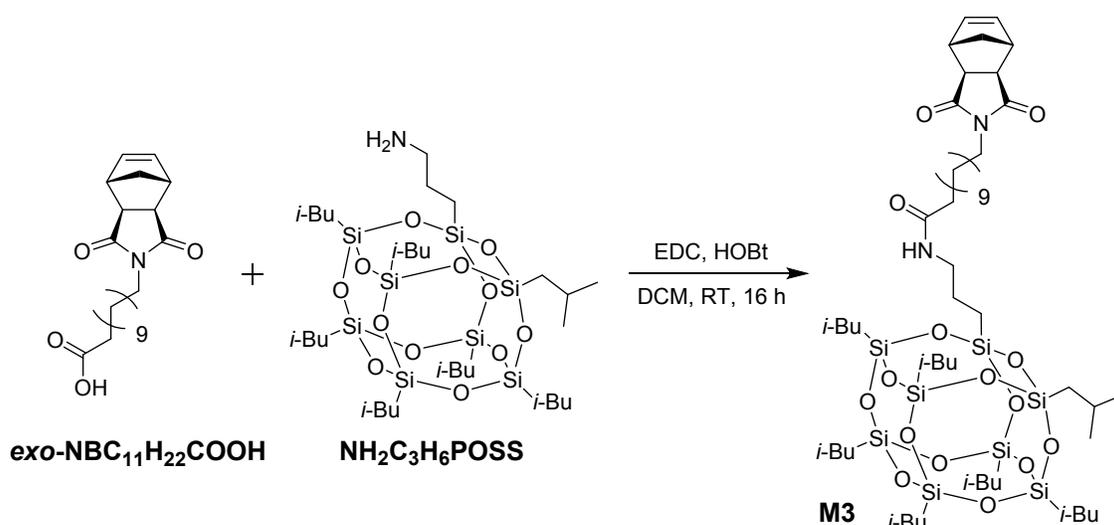
(M2)



A two-neck 100 mL flask equipped with a Dean-Stark trap was charged with nitrogen for 30 min. To the flask were added toluene (25 mL), *exo*-NBAnh (0.895 g, 5.45 mmol) and NH₂C₂H₄NHC₃H₆POSS (5.00 g, 5.45 mmol). The reaction mixture was stirred at 135 °C for 6 h. After the reaction was complete, the solution was cooled and concentrated at reduced pressure. The crude product was purified by silica gel column chromatography in hexane/ethyl acetate (initially 8/2 v/v and subsequently 6/4 v/v). The recovered solid was precipitated in cool methanol, filtered, and dried under vacuum to afford **M2** as a white powder (3.16 g, 54%).

M2: ¹H NMR (CDCl₃ with 0.03% v/v TMS, 400 MHz): δ 6.27 (s, 2H), 3.58 (t, 2H, *J* = 6.2 Hz), 3.25 (s, 2H), 2.78 (t, 2H, *J* = 6.4 Hz), 2.66 (s, 2H), 2.55 (t, 2H, *J* = 7.2 Hz), 1.83 (m, 7H), 1.48 (quint, 2H, *J* = 8 Hz), 1.46 (s, 2H), 0.94 (dd, 42H, *J* = 6.8, 1.2 Hz), 0.58 (d, 16H, *J* = 6.8 Hz). ¹³C NMR (CDCl₃ with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.28, 137.92, 52.02, 47.91, 46.84, 45.36, 42.85, 38.54, 25.75, 23.93, 22.58, 9.63.

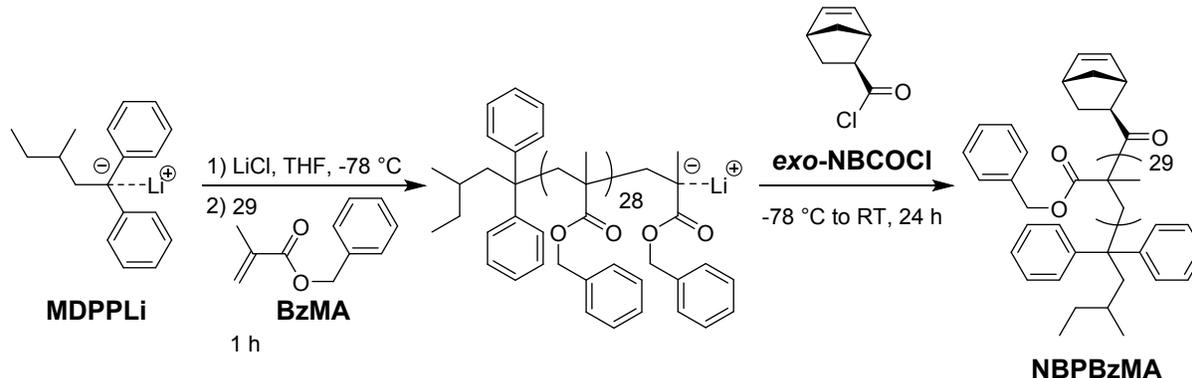
S1.3.3. 3-(12-(5-Norbornene-*exo*-2,3-dicarboximido)dodecanoylamino)propyl-heptaisobutyl POSS (M3)



The synthesis procedure for **M3** is described in our previous report.^{S1}

M3: ¹H NMR (CDCl₃ with 0.03% v/v TMS, 400 MHz): δ (ppm) 6.28 (s, 2H), 5.42 (s, 1H), 3.44 (t, 2H, *J* = 7.6 Hz), 3.26 (s, 2H), 3.29–3.17 (m, 4H), 2.66 (s, 2H), 2.13 (t, 2H, *J* = 7.6 Hz), 1.84 (m, 7H), 1.66–1.44 (m, 8H), 1.24 (m, 14H), 0.95 (d, 42H, *J* = 6.4 Hz), 0.59 (dd, 16H, *J* = 6.8, 1.2 Hz). ¹³C NMR (CDCl₃ with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.08, 172.95, 137.88, 47.86, 45.22, 42.76, 41.73, 38.79, 36.99, 29.65–29.25, 29.14, 27.80, 26.98, 25.89, 25.73, 23.91, 23.14, 22.55, 9.53. Typical NMR spectra of **M3** are offered in our previous report.^{S1}

S1.3.4. *exo*-5-Norbornene-2-carbonyl-end poly(benzyl methacrylate) (NBPBzMA)



The synthesis procedure for **NBPBzMA** is described in our previous report.^{S1}

NBPBzMA: $M_n = 5.44$ kDa ($M_{n,theo} = 4.95$ kDa at $[BzMA]_0/[s-BuLi]_0 = 26.0$). $D = 1.02$. 1H NMR ($CDCl_3$ with 0.03% v/v TMS, 400 MHz): δ (ppm) 7.41–7.01 (br), 6.09–5.66 (br), 5.17–4.50 (br), 2.10–0.40 (br). ^{13}C NMR ($CDCl_3$ with 0.03% v/v TMS, 100 MHz): δ (ppm) 177.14, 135.24, 128.62, 66.86, 54.25, 44.87, 18.57. Typical NMR spectra of **NBPBzMA** are offered in our previous report.^{S1}

S1.4. Polymerization procedures

S1.4.1. Homopolymerization of M1–3 via ROMP

All ROMP experiments were carried out in a glove box charged with nitrogen. The volumes of THF for monomer and initiator were set according to $[M]_0 = 0.1$ or 0.4 M. One of the monomers (**M1–3**) (100 mg) was dissolved in THF in a 10 mL vial, and then the solution was stirred. A 0.01 M solution of **Ru** in THF was rapidly added via syringe to allow polymerization. The volume of added **Ru** was set according to $[M]_0/[I]_0$. At regular time intervals, aliquots (50 μ L) were extracted and transferred into solutions of ethyl vinyl ether (3 droplets) in THF (1 mL) to terminate the reaction. The aliquots were used for SEC analysis to characterize the conversion,

M_n , M_w , and D depending on the reaction time. After final conversion, the resulting polymer was isolated by precipitation in acetonitrile, filtration, and drying under vacuum.

P1: $dn/dc = 0.0658$ mL/g. ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 5.87–5.24 (br), 3.76–2.46 (br), 1.84 (m), 1.62 (s), 1.50 (s), 0.94 (d, $J = 6.4$ Hz), 0.59 (d, $J = 6.8$ Hz). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.07, 131.89, 41.45, 25.76, 23.91, 22.54, 21.41, 9.72.

P2: $dn/dc = 0.0760$ mL/g. ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 5.86–5.30 (br), 3.76–2.44 (br), 1.84 (m), 1.58 (s), 1.51 (s), 0.94 (d, $J = 6.4$ Hz), 0.58 (d, $J = 7.2$ Hz). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.37, 132.31, 52.24, 46.89, 38.69, 25.75, 23.91, 23.24, 22.61, 9.72.

P3: $dn/dc = 0.0670$ mL/g. ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 5.89–5.23 (br), 3.80–2.50 (br), 2.13 (t, $J = 7.4$ Hz), 1.84 (m), 1.68–1.44 (br), 1.25 (s), 0.95 (d, $J = 6.4$ Hz), 0.59 (d, $J = 6.8$ Hz). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 178.32, 173.00, 131.96, 41.78, 38.73, 37.01, 29.86–29.14, 27.82, 27.08, 25.96, 25.75, 23.93, 23.15, 22.56, 9.56. Typical NMR spectra of **P3** are offered in our previous report.¹

S1.4.2. Block copolymerization of M3 and NBPBzMA via sequential ROMP

Three different amounts of **M3** (200 mg/150 mg/100 mg, corresponding to 0.164 mmol/0.120 mmol/0.0821 mmol) were dissolved in THF (0.21 mL/0.16 mL/0.10 mL) in 10 mL vials, and then the solutions were stirred. Three volumes of 0.01 M **Ru** in THF (0.330 μmol /0.250 μmol /0.160 μmol of **Ru**) were rapidly added via syringe to the three monomer solutions in sequence to allow homopolymerization. After the complete conversion of **M3**, three volumes of 0.1 M **NBPBzMA** in THF (100 mg/150 mg/200 mg, corresponding to 0.0184 mmol/0.0276

mmol/0.0368 mmol of **NBPBzMA**) were subsequently added via syringe to the three reaction mixtures in sequence to allow block copolymerization. When precipitation occurred, THF was added to the reaction mixtures to re-dissolve the precipitates. After stirring for 24 h, the polymerization was quenched by adding 2 droplets of ethyl vinyl ether. The resulting polymers were isolated by precipitation in methanol, filtration, and drying under vacuum. A small amount of residual **NBPBzMA** macromonomers in BCP with $f_{\text{wt,P3}}$ of 34% (entry 33 in Table 3) was eliminated by fractional precipitation in acetonitrile/methanol (1/1 v/v).

P3-*b*-P(NB-*g*-BzMA): $dn/dc = 0.0847$ mL/g for $f_A = 67$ wt% (entry 31 in Table 3), 0.105 mL/g for $f_A = 50$ wt% (entry 32 in Table 3) and 0.124 mL/g for $f_A = 34$ wt% (entry 33 in Table 3). ^1H NMR (CDCl_3 with 0.03% v/v TMS, 400 MHz): δ (ppm) 7.37–7.00 (br), 5.87–5.36 (br), 3.78–2.50 (br), 2.13 (t, $J = 7.4$ Hz), 1.84 (m), 2.00–0.40 (br). ^{13}C NMR (CDCl_3 with 0.03% v/v TMS, 100 MHz): δ (ppm) 177.16, 173.06, 135.34, 131.89, 128.47, 66.87, 54.21 45.01, 41.80, 37.05, 29.61, 27.88, 27.07, 26.01, 25.80, 23.97, 23.17, 22.56, 18.52, 16.59, 9.57. Typical NMR spectra of **P3-*b*-P(NB-*g*-BzMA)**s with $f_A = 67$, 50 and 34 wt% are offered in our previous report.¹

S1.5. Preparation of self-assembled **P3-*b*-P(NB-*g*-BzMA)** thin films for TEM analysis

P3-*b*-P(NB-*g*-BzMA) solutions in THF (2.5 mg/mL for $f_A = 67$ and 50 wt%; 5.0 mg/mL for $f_A = 34$ wt%) were drop-cast on carbon-coated copper grids, and the samples were placed in a closed chamber containing THF (10 mL) for solvent-vapor annealing at 25 °C. The annealing times were 24 h for $f_A = 67$ wt%, 12 h for $f_A = 50$ wt% and 1 h for $f_A = 34$ wt%. The self-assembled **P3-*b*-P(NB-*g*-BzMA)** thin films were dried at room temperature for 24 h, then directly used for TEM analysis without staining.

S2. Characterization of synthetic compounds

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

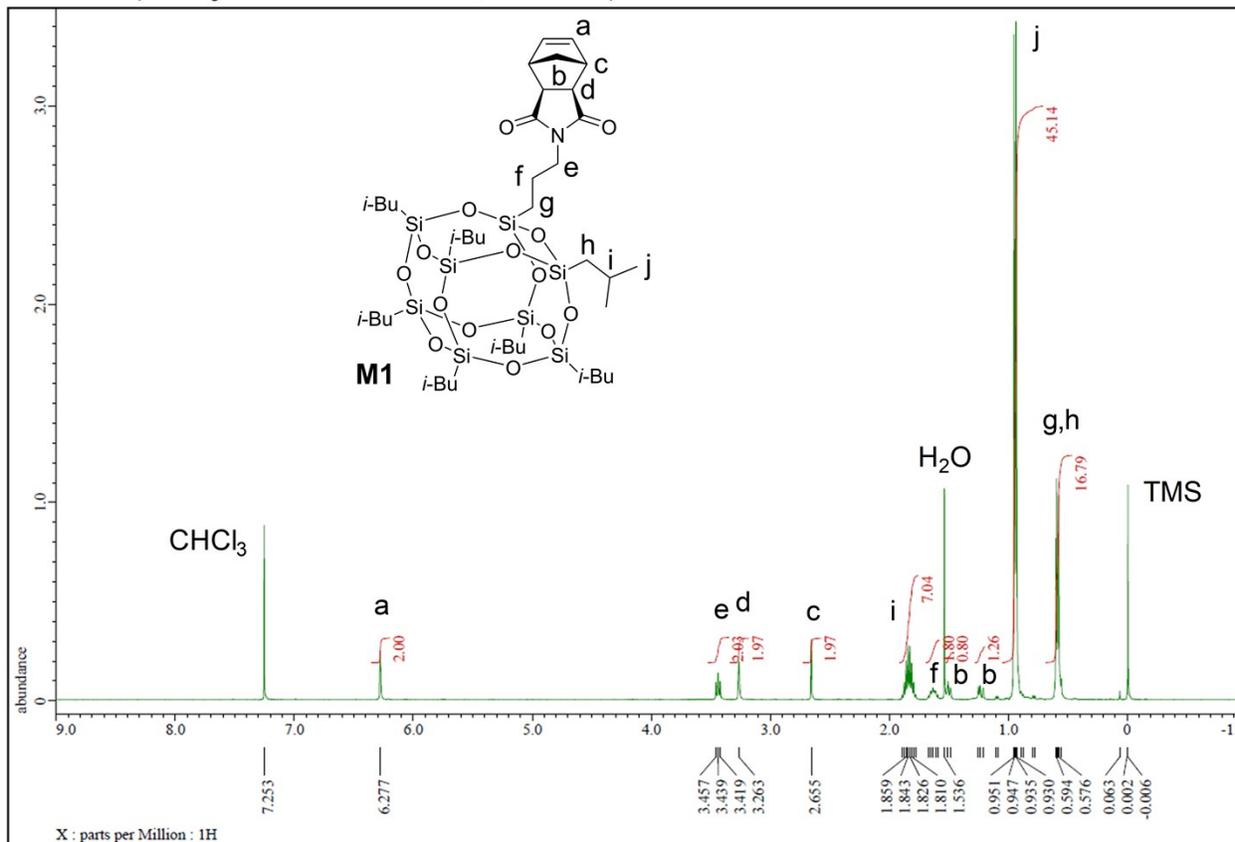


Fig. S1 ^1H NMR spectrum of **M1** in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

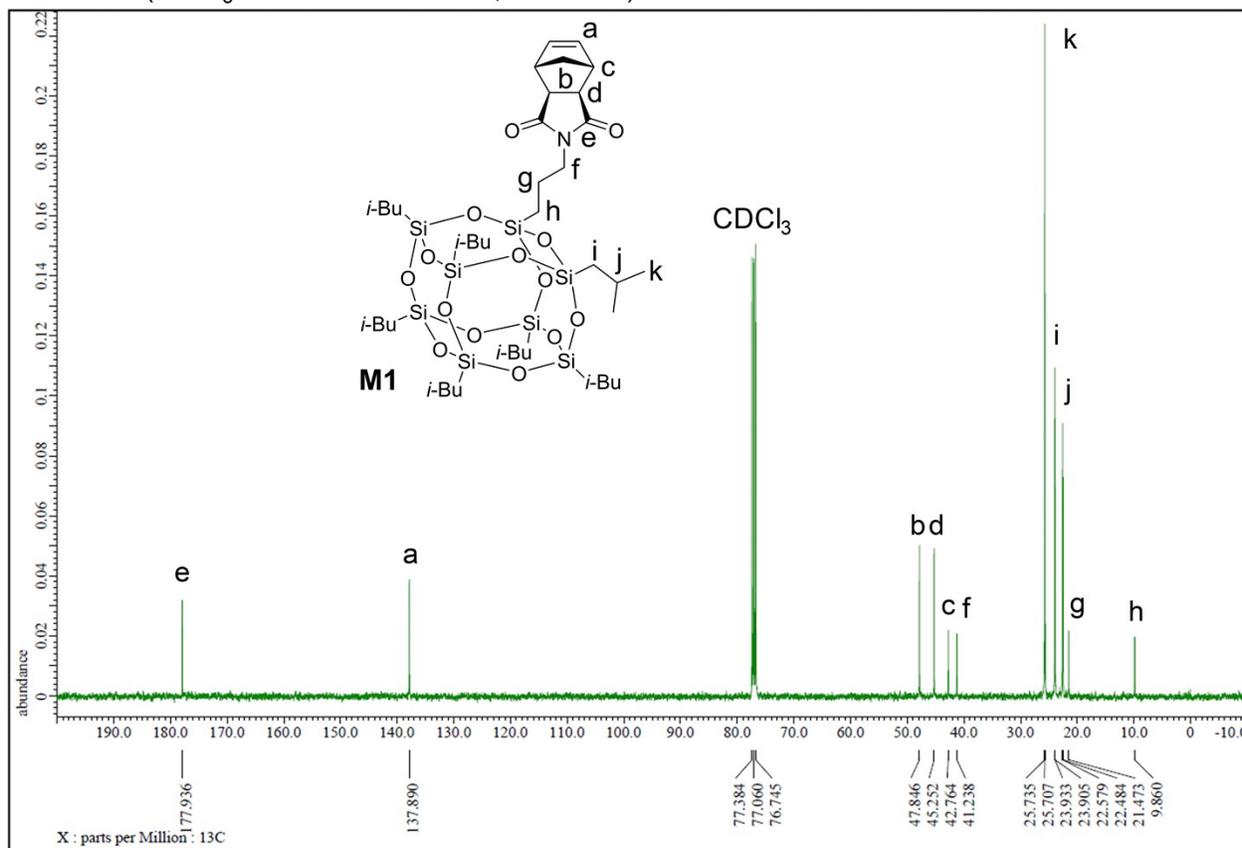


Fig. S2 ^{13}C NMR spectrum of **M1** in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

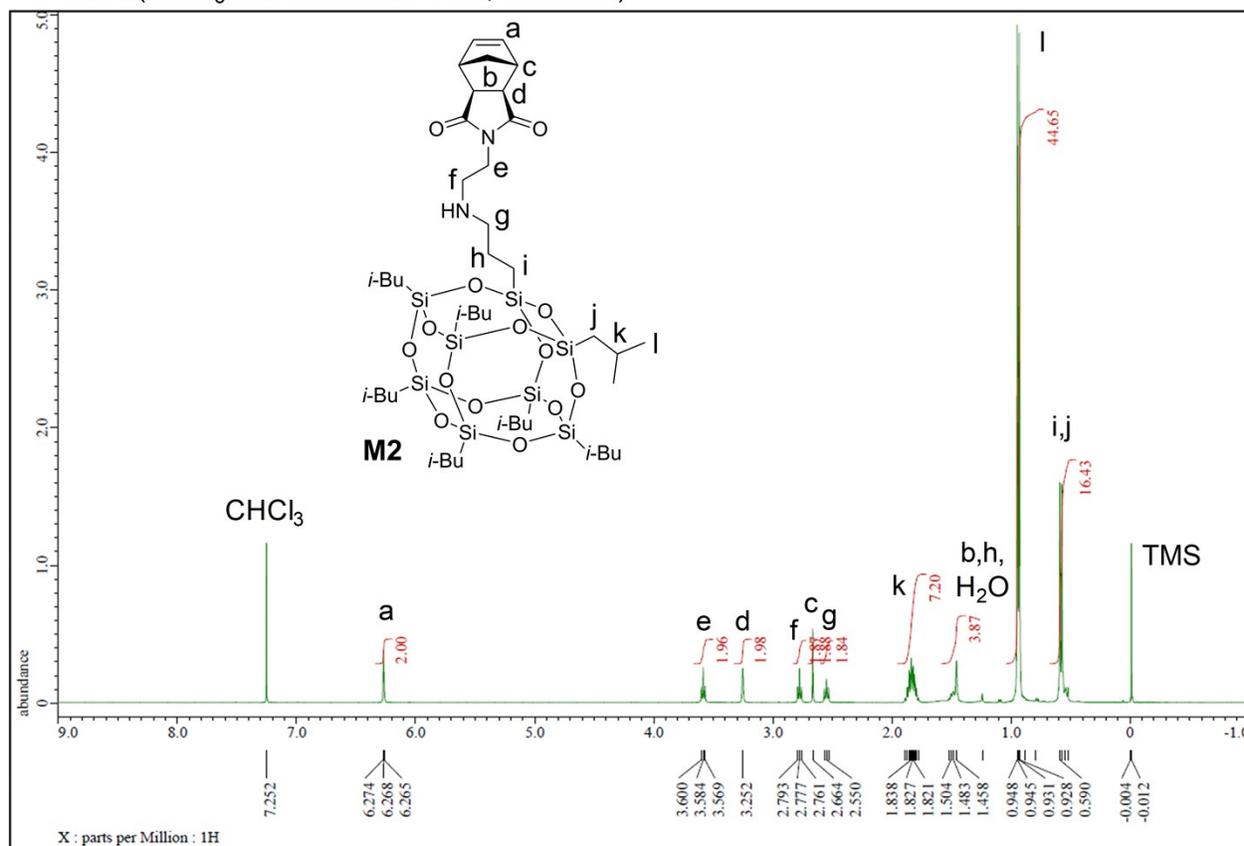


Fig. S3 ^1H NMR spectrum of **M2** in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

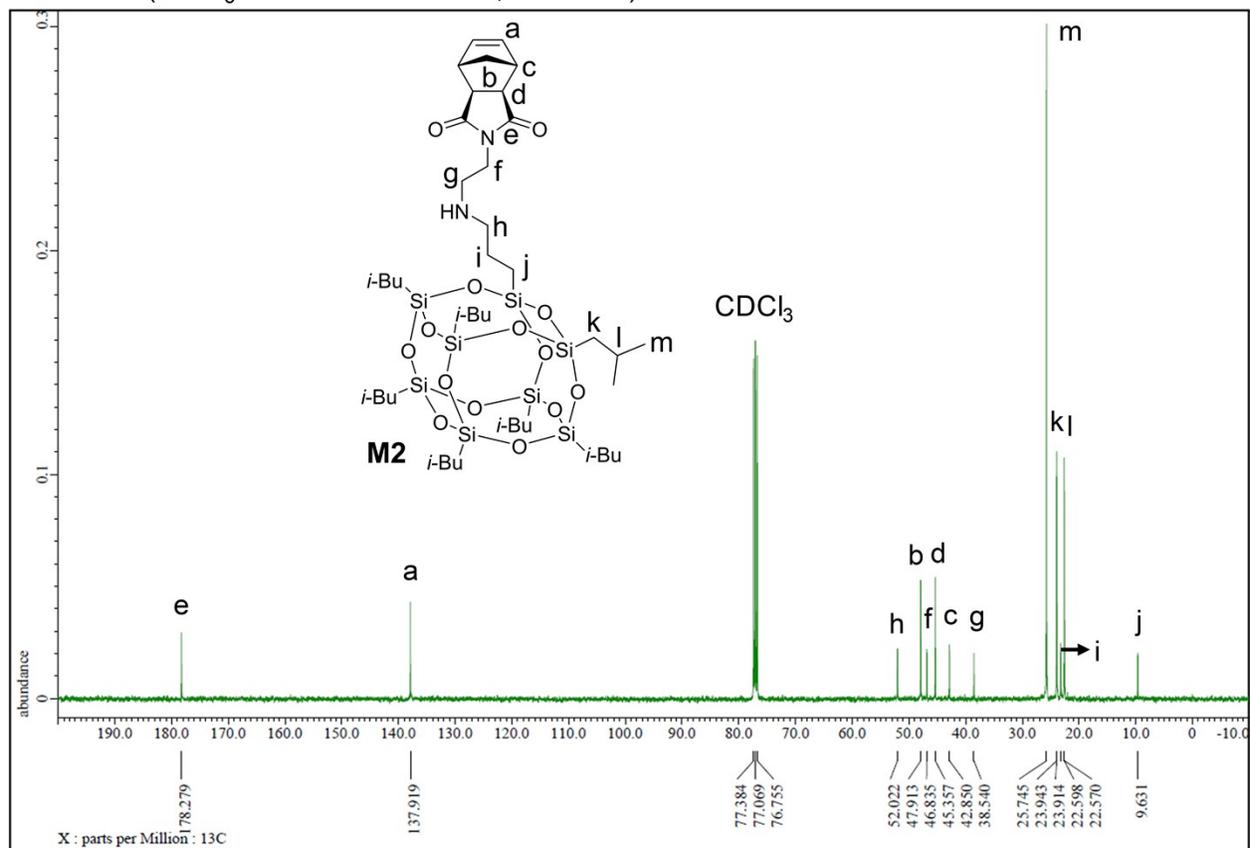


Fig. S4 ^{13}C NMR spectrum of **M2** in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

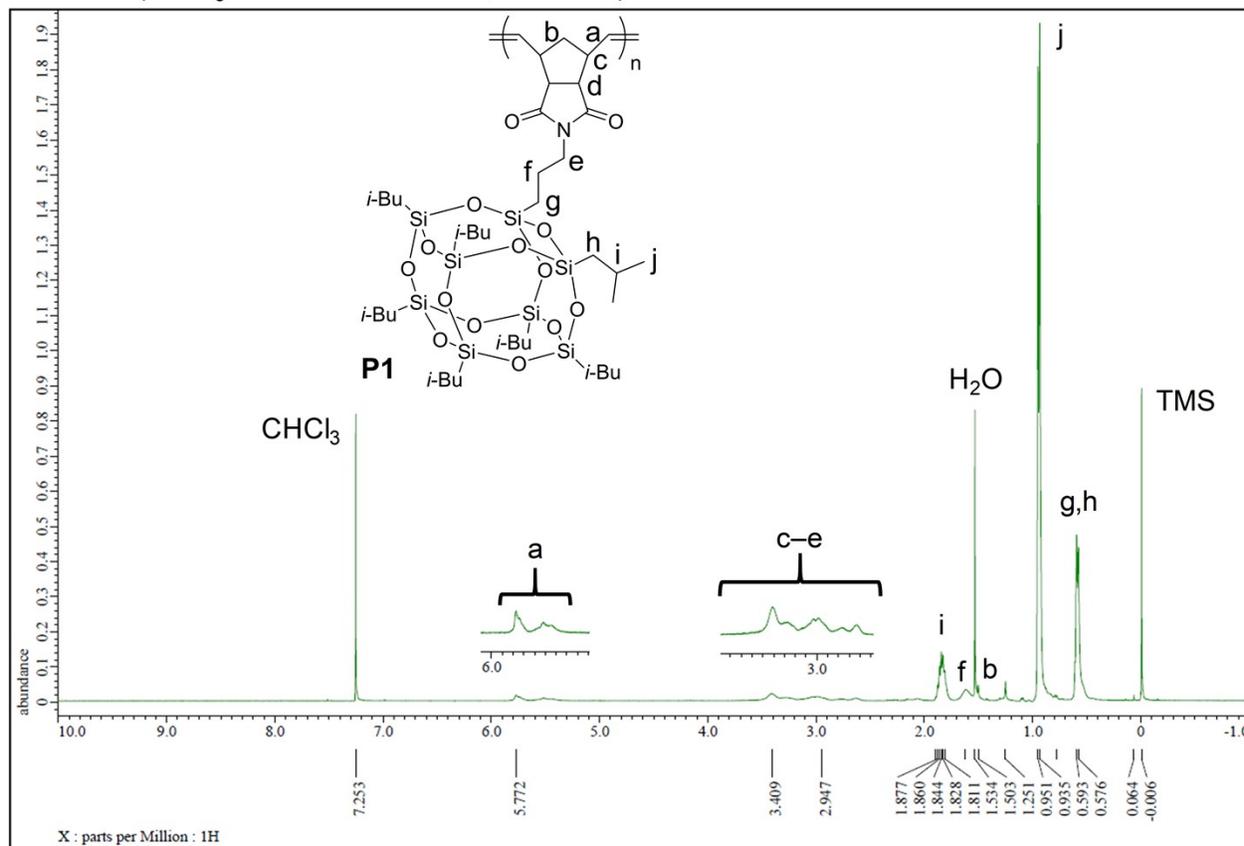


Fig. S5 ^1H NMR spectrum of **P1** in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

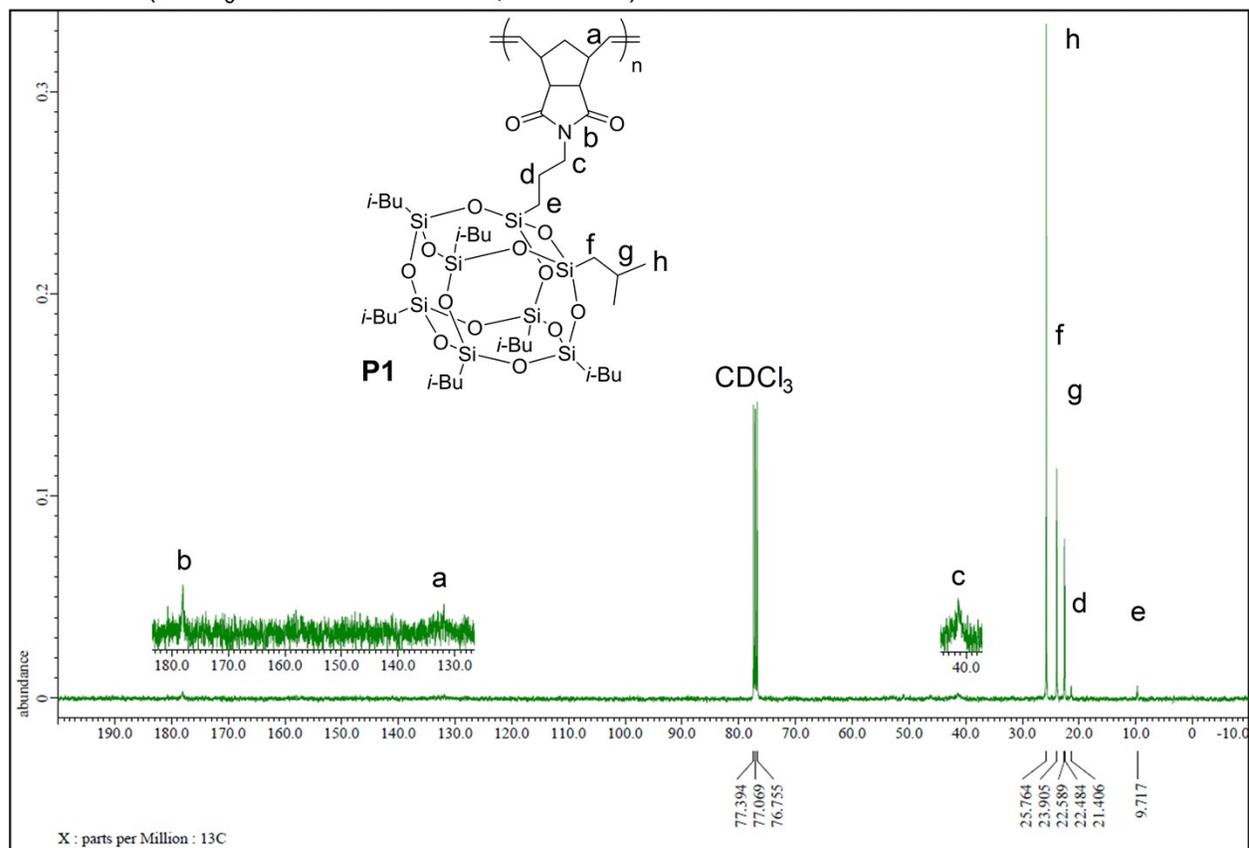


Fig. S6 ^{13}C NMR spectrum of **P1** in CDCl_3 .

^1H NMR (CDCl_3 with 0.03 vol% TMS, 400 MHz)

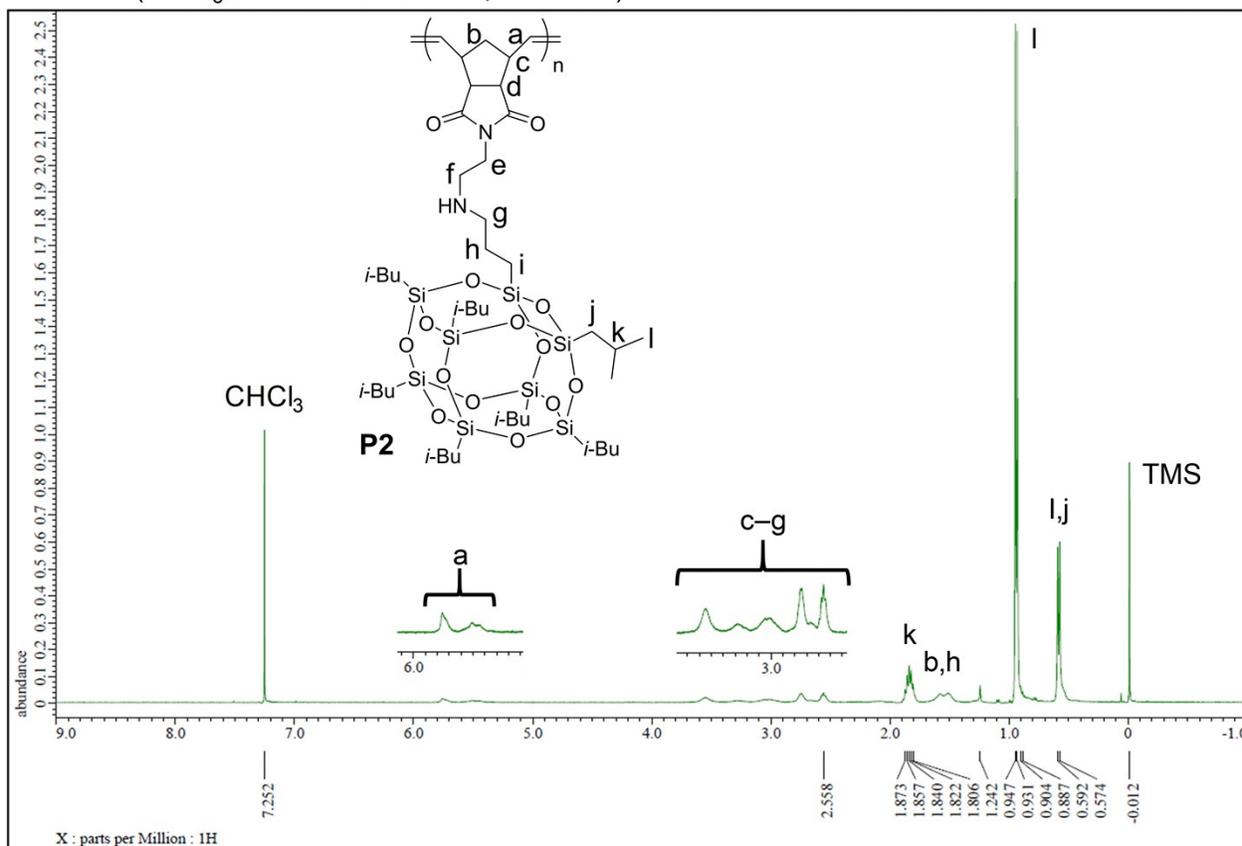


Fig. S7 ^1H NMR spectrum of **P2** in CDCl_3 .

^{13}C NMR (CDCl_3 with 0.03 vol% TMS, 100 MHz)

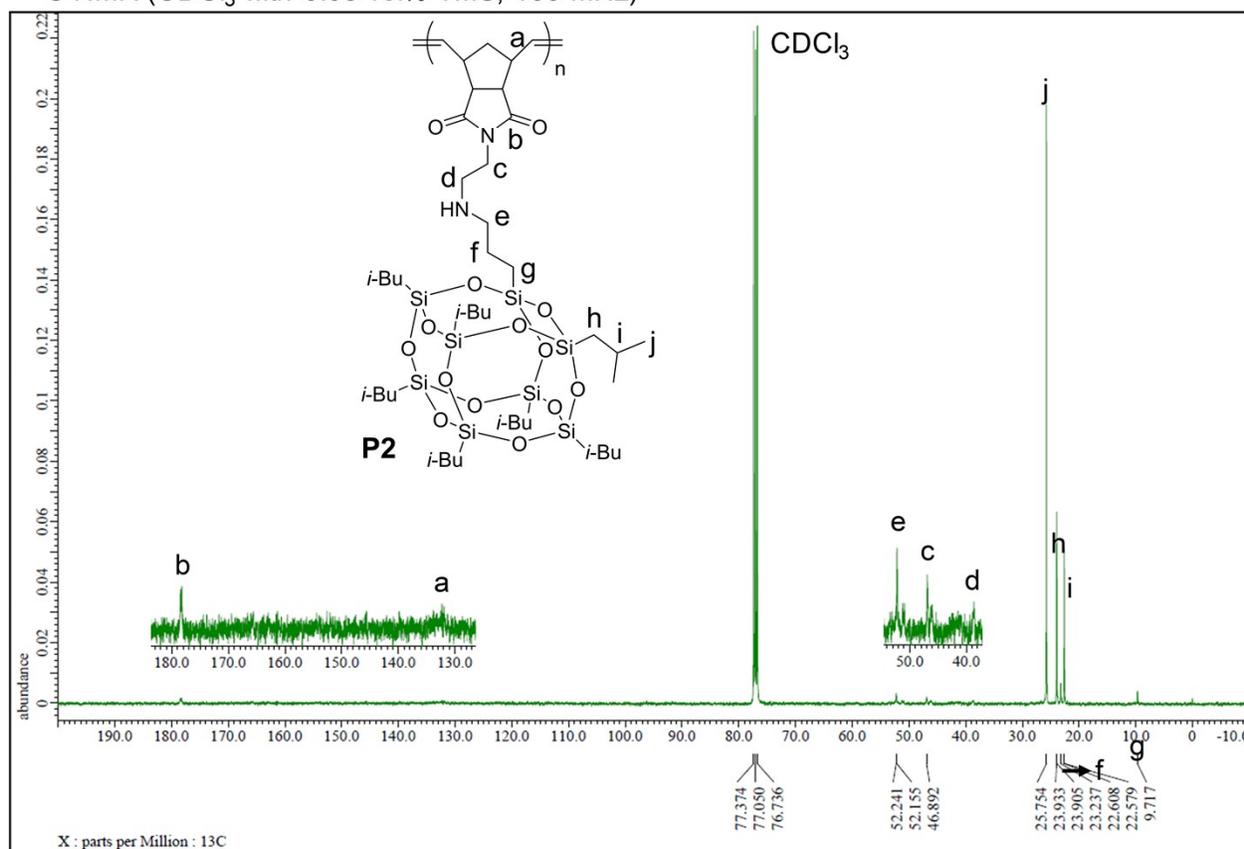


Fig. S8 ^{13}C NMR spectrum of **P2** in CDCl_3 .

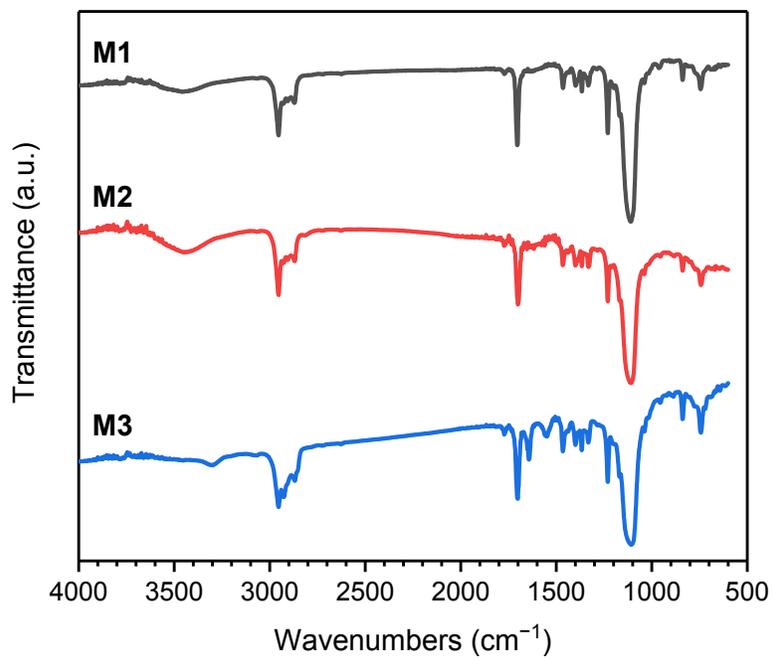


Fig. S9 FT-IR spectra of **M1–3**.

Table S1 Results of EA for **M1–3**

M	Chemical formula	Observed (calculated) proportion of element except for Si ₈ O ₁₂ (wt%)			
		C	H	N	O
M1	C ₄₀ H ₇₇ NO ₁₄ Si ₈	47.2 (47.1)	7.8 (7.6)	1.5 (1.4)	3.3 (3.1)
M2	C ₄₂ H ₈₂ N ₂ O ₁₄ Si ₈	47.2 (47.4)	7.9 (7.8)	2.6 (2.6)	3.0 (3.0)
M3	C ₅₂ H ₁₀₀ N ₂ O ₁₅ Si ₈	50.9 (51.3)	7.8 (8.3)	2.5 (2.3)	3.8 (3.9)

^aThe elements of Si₈O₁₂ nanocage were not detected in EA due to its conversion to silica at combustion temperatures.

S3. Details of kinetic analysis for ROMP of M1–3 ($[M]_0 = 0.1$ M)

Table S2 ROMP of M1 initiated by Ru (I) in THF at 25 °C ($[M]_0 = 0.1$ M)

Entry	$[M]_0/[I]_0$	t^a (s)	Conv ^b (%)	$M_{n,theo}^c$ (kDa)	M_n^b (kDa)	\bar{D}^b	$M_{n,theo}/M_n$	$\ln([M]_0/[M]_t)$
S1	50	15	40.0	20	22	1.06	0.909	0.510
S2	50	30	58.9	30	32	1.03	0.938	0.889
S3	50	60	84.1	43	46	1.03	0.929	1.84
S4	50	120	97.8	50	54	1.03	0.922	3.82
S5	50	240	100	51	55	1.02	0.927	–
S6	100	15	32.0	33	38	1.05	0.868	0.386
S7	100	30	50.5	52	57	1.01	0.912	0.703
S8	100	60	76.0	78	86	1.01	0.907	1.43
S9	100	120	92.1	94	108	1.01	0.870	2.67
S10	100	240	99.1	101	115	1.01	0.878	4.71
S11	100	480	100	102	118	1.01	0.864	–
S12	250	15	18.0	46	65	1.01	0.708	0.198
S13	250	30	38.1	97	125	1.01	0.776	0.480
S14	250	60	62.2	159	199	1.01	0.799	0.973
S15	250	120	85.1	217	280	1.01	0.775	1.90
S16	250	240	96.6	247	312	1.01	0.792	3.38
S17	250	480	100	255	324	1.01	0.787	–
S18	500	15	13.8	70	106	1.02	0.660	0.182
S19	500	30	30.3	155	208	1.02	0.745	0.361
S20	500	60	51.6	263	343	1.02	0.767	0.726
S21	500	120	77.6	396	495	1.02	0.800	1.50
S22	500	240	93.7	478	605	1.03	0.790	2.76
S23	500	480	98.8	504	626	1.04	0.805	4.42
S24	500	960	100	510	634	1.04	0.804	–
S25	1000	15	13.6	139	181	1.06	0.768	0.146
S26	1000	30	27.8	284	333	1.02	0.853	0.326
S27	1000	60	49.0	500	543	1.03	0.921	0.673
S28	1000	120	71.8	733	797	1.03	0.920	1.27
S29	1000	240	87.2	890	972	1.04	0.916	2.06
S30	1000	480	96.2	982	1078	1.05	0.913	3.27
S31	1000	960	100	1020	1138	1.06	0.896	–

^at: Polymerization time. ^bDetermined by SEC-MALLS. ^c $M_{n,theo} = [M]_0/[I]_0 \times \text{conv}/100\% \times \text{MW of M1}$.

Table S3 ROMP of **M2** initiated by **Ru** (**I**) in THF at 25 °C ($[\mathbf{M2}]_0 = 0.1 \text{ M}$)

Entry	$[\mathbf{M2}]_0/[\mathbf{I}]_0$	t^a (s)	Conv ^b (%)	$M_{n,theo}^c$ (kDa)	M_n^b (kDa)	D^b	$M_{n,theo}/M_n$	$\ln([\mathbf{M2}]_0/[\mathbf{M2}]_t)$
S32	50	120	23.3	12	16	1.07	0.750	0.265
S33	50	240	38.2	20	26	1.03	0.769	0.481
S34	50	480	59.2	31	40	1.03	0.775	0.896
S35	50	960	82.7	44	56	1.04	0.786	1.75
S36	50	1920	97.1	52	67	1.04	0.776	3.54
S37	50	3840	100	53	71	1.04	0.746	–
S38	100	240	23.7	25	30	1.03	0.833	0.271
S39	100	480	39.4	42	49	1.02	0.857	0.501
S40	100	960	62.2	66	80	1.02	0.825	0.973
S41	100	1920	86.3	92	112	1.04	0.821	1.99
S42	100	3840	98.1	104	126	1.05	0.825	3.96
S43	100	7680	100	106	132	1.06	0.803	–
S44	250	480	18.9	50	55	1.03	0.909	0.207
S45	250	960	32.5	85	96	1.02	0.885	0.387
S46	250	1920	54.5	143	166	1.03	0.861	0.772
S47	250	3840	84.1	221	262	1.05	0.844	1.78
S48	250	7680	96.9	258	312	1.10	0.827	3.47
S49	500	960	24.7	131	130	1.04	1.01	0.284
S50	500	1920	42.8	228	218	1.06	1.04	0.559
S51	500	3840	68.7	365	345	1.11	1.06	1.16
S52	500	7680	86.0	457	502	1.14	0.910	1.97
S53	1000	1920	24.9	265	270	1.04	0.981	0.286
S54	1000	3840	38.6	410	436	1.05	0.940	0.488
S55	1000	7680	62.6	666	736	1.13	0.904	0.984

^at: Polymerization time. ^bDetermined by SEC-MALLS. ^c $M_{n,theo} = [\mathbf{M2}]_0/[\mathbf{I}]_0 \times \text{conv}/100\% \times \text{MW of } \mathbf{M2}$.

Table S4 ROMP of **M3** initiated by **Ru** (I) in THF at 25 °C ($[\mathbf{M3}]_0 = 0.1$ M)

Entry	$[\mathbf{M3}]_0/[\mathbf{I}]_0$	t^a (s)	conv ^b (%)	$M_{n,theo}^c$ (kDa)	M_n^b (kDa)	\bar{D}^b	$M_{n,theo}/M_n$	$\ln([\mathbf{M3}]_0/[\mathbf{M3}]_t)$
S56	50	15	45.5	28	30	1.04	0.933	0.607
S57	50	30	70.4	43	47	1.04	0.915	1.22
S58	50	60	91.4	56	62	1.02	0.903	2.45
S59	50	120	99.3	60	68	1.02	0.882	4.96
S60	50	240	100	61	69	1.01	0.844	–
S61	100	15	42.6	52	58	1.02	0.897	0.555
S62	100	30	68.4	83	90	1.01	0.922	1.15
S63	100	60	89.3	109	115	1.01	0.948	2.23
S64	100	120	98.8	120	127	1.01	0.945	4.42
S65	100	240	100	122	125	1.01	0.976	–
S66	250	15	34.9	106	118	1.03	0.898	0.429
S67	250	30	60.5	184	192	1.02	0.958	0.929
S68	250	60	86.2	262	259	1.02	1.01	1.98
S69	250	120	97.9	298	295	1.04	1.01	3.77
S70	250	240	100	305	302	1.05	1.01	–
S71	500	15	29.5	180	202	1.01	0.892	0.349
S72	500	30	54.1	329	337	1.03	0.876	0.779
S73	500	60	78.6	479	459	1.04	1.04	1.54
S74	500	120	95.3	580	544	1.06	1.07	3.06
S75	500	240	100	609	570	1.08	1.06	–
S76	1000	15	20.9	255	289	1.03	0.882	0.234
S77	1000	30	41.9	510	517	1.05	0.986	0.543
S78	1000	60	67.9	827	739	1.08	1.25	1.14
S79	1000	120	89.5	1090	854	1.13	1.27	2.41
S80	1000	240	98.9	1205	902	1.14	1.34	4.51
S81	1000	480	100	1218	910	1.15	1.34	–

^a t : Polymerization time. ^b \bar{D} : Determined by SEC-MALLS. ^c $M_{n,theo} = [\mathbf{M3}]_0/[\mathbf{I}]_0 \times \text{conv}/100\% \times \text{MW of } \mathbf{M3}$.

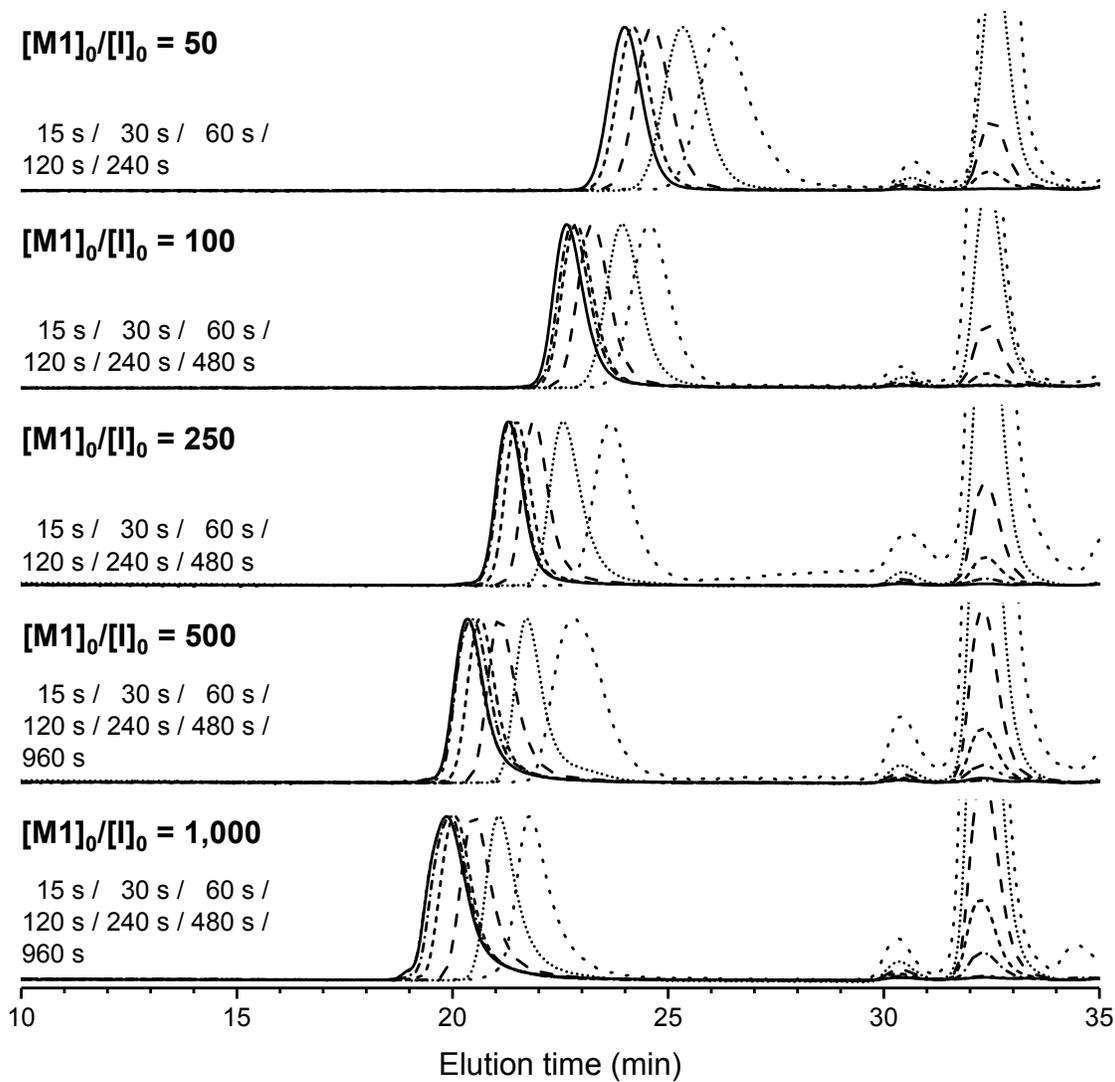


Fig. S10 SEC-dRI traces of **P1** aliquots (entry S11–31) extracted from the homopolymerization mixtures ($[M1]_0 = 0.1$ M) at different time intervals.

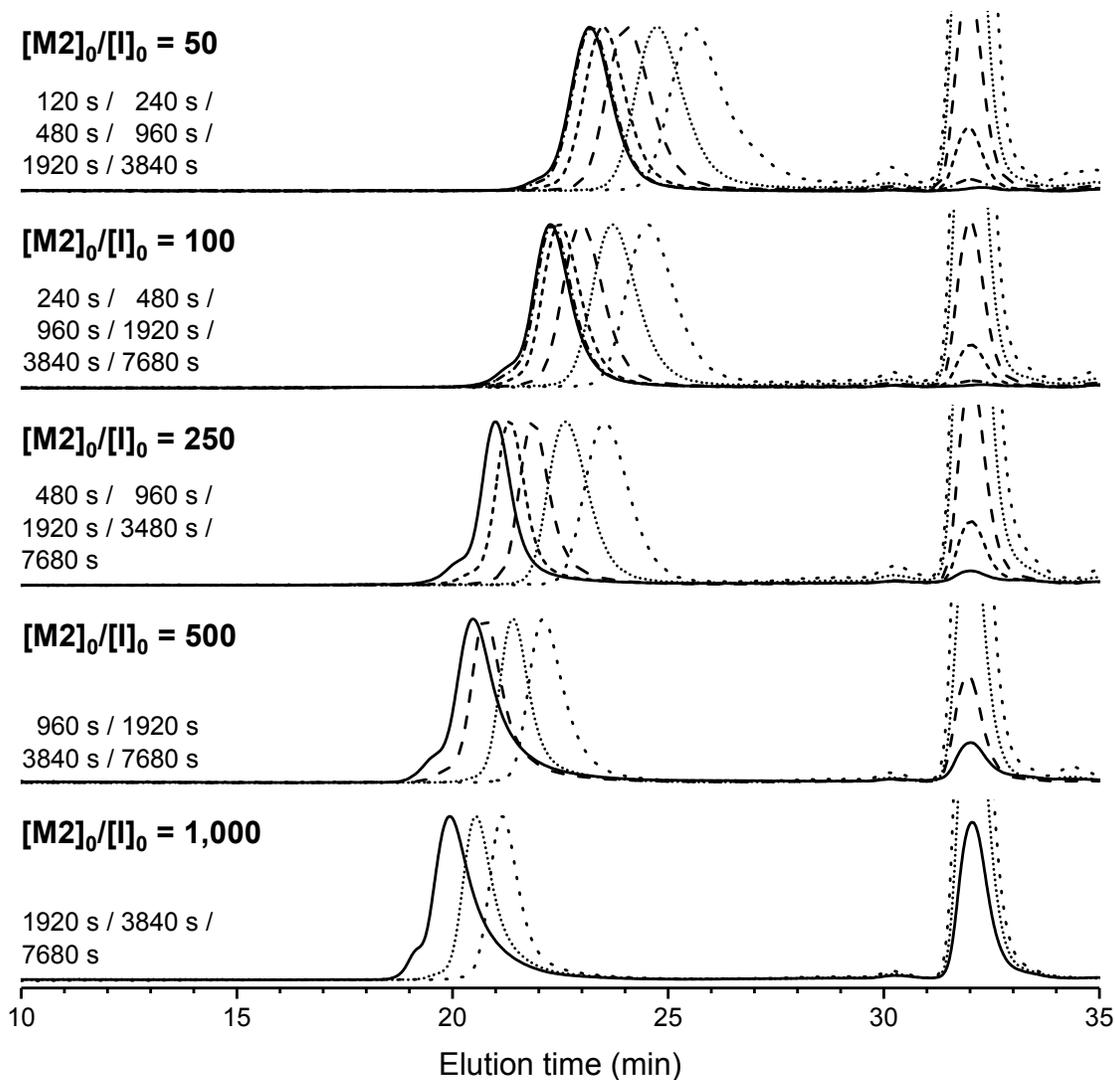


Fig. S11 SEC-dRI traces of **P2** aliquots (entry S32–55) extracted from the homopolymerization mixtures ($[M2]_0 = 0.1$ M) at different time intervals.

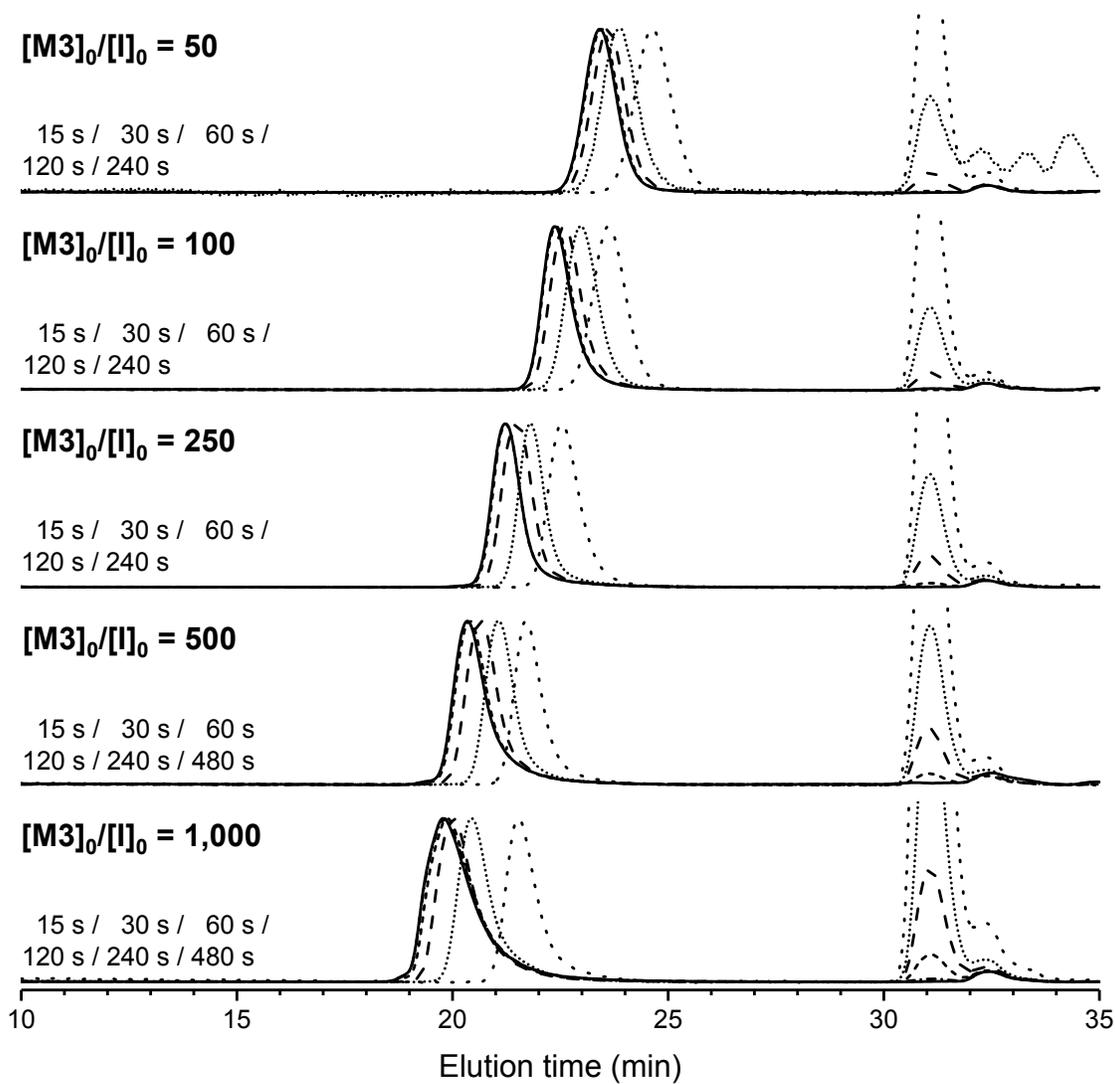


Fig. S12 SEC-dRI traces of **P3** aliquots (entry S56–81) extracted from the homopolymerization mixtures ($[M3]_0 = 0.1$ M) at different time intervals.

S4. Physical properties of P1–3s

Table S5 $R_{g,z}$ values for P1–3s in 3.5 mg/mL THF solutions

Entry	M_w^a		$R_{g,z}^a$		
	(kDa)	DP _w	logDP _w	(nm)	log($R_{g,z}$ /nm)
P1					
17	109	107	2.03	13.2	1.12
18	278	272	2.43	21.7	1.34
19	545	534	2.73	29.4	1.47
20	1145	1122	3.05	38.2	1.58
P2					
7	140	132	2.12	14.1	1.15
8	342	321	2.51	21.9	1.34
9	572	538	2.73	27.6	1.44
10	834	784	2.89	34.2	1.53
P3					
27	126	103	2.01	9.7	0.987
28	335	275	2.44	16.4	1.21
29	701	576	2.76	28.2	1.45
30	1481	1216	3.08	52.7	1.72

^aDetermined from SEC-MALLS.

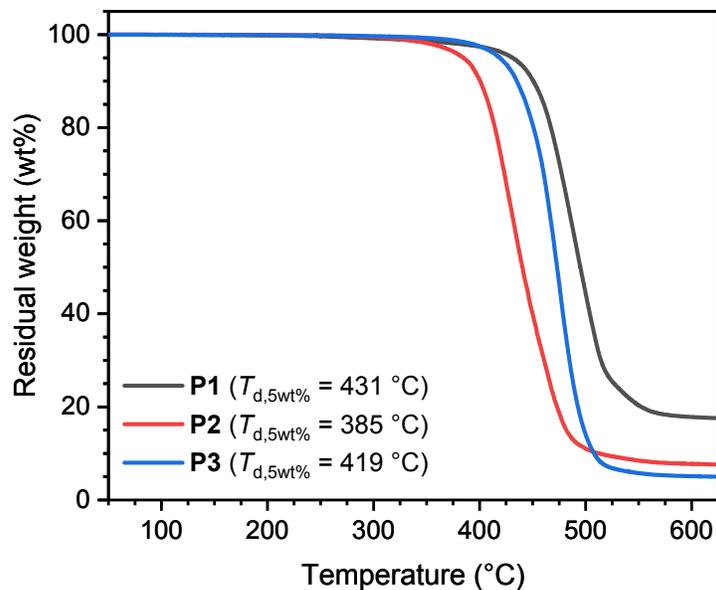


Fig. S13 TGA thermograms of **P1** ($M_n = 1042$ kDa; $D = 1.10$), **P2** ($M_n = 736$ kDa; $D = 1.13$) and **P3** ($M_n = 1236$ kDa; $D = 1.20$) recorded at a heating rate of 10 °C/min under a nitrogen atmosphere. Temperatures for 5 wt% loss were indicated as $T_{d,5wt\%}$.

Results and discussion on TGA analysis.

The thermal degradation behaviors of **P1** ($M_n = 1042$ kDa; $D = 1.10$), **P2** ($M_n = 736$ kDa; $D = 1.13$) and **P3** ($M_n = 1236$ kDa; $D = 1.20$) were examined by TGA at a heating rate of 10 °C/min under a nitrogen atmosphere (Fig. S12). According to a previous study on the thermal degradation of POSS, the weight loss of octaalkyl-substituted POSSs occurs by evaporation at temperatures above their melting points. In particular, the weight loss of octaisobutyl POSS generally begins at approximately 200 °C.^{S2} However, POSS molecules bound to the polymer chain must be evaporated after Si–C bond cleavage. In the TGA thermograms of **P1–3**, the degradation temperatures at the initial 5 wt% loss ($T_{d,5wt\%}$) were observed to be 431 °C for **P1**, 385 °C for **P2**, and 419 °C for **P3**, which correspond the temperatures for Si–C bond cleavage. The lowest thermal stability of **P2** indicated the catalytic effect of the secondary amine on the

Si–C bond cleavage. The thermal stability of **P3**, which has fewer catalytic amide groups, is between the stabilities of **P1** and **P2**. The residual weights (16% for **P1**, 6% for **P2**, and 4% for **P3**) even after heating to 800 °C resulted from the conversion of POSS residues to amorphous silica.^{S2}

S5. Additional TEM micrographs of P3-*b*-P(NB-*g*-BzMA)

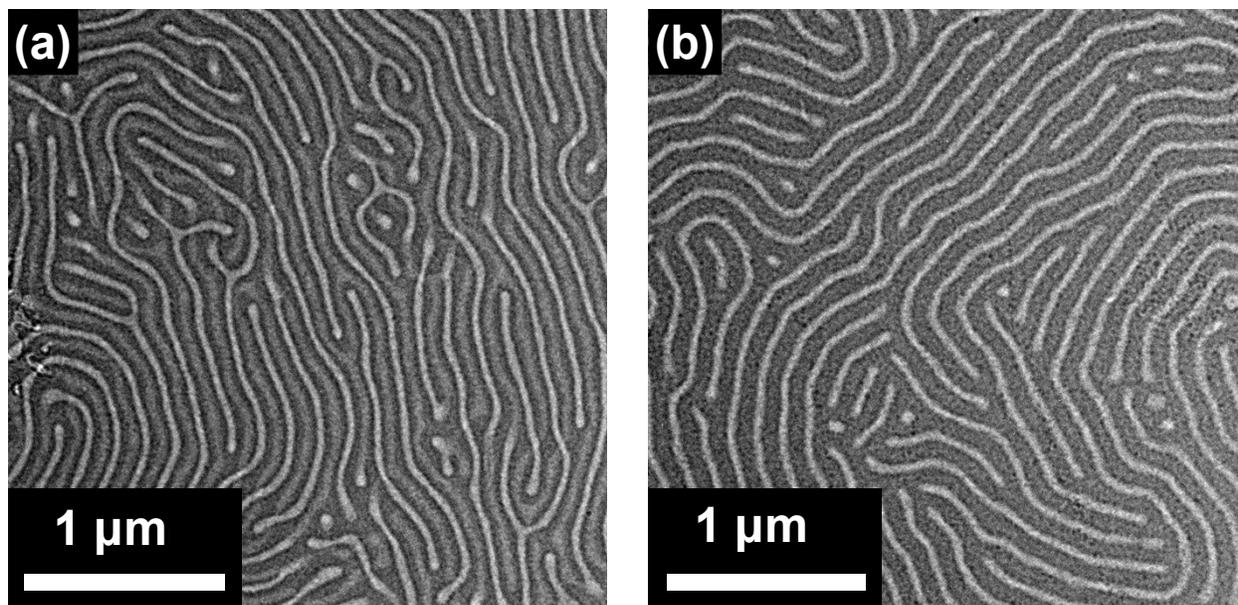


Fig. S14 (a) TEM micrographs of thin films of self-assembled **P3-*b*-P(NB-*g*-BzMA)** with $f_A = 67$ wt% ($M_n = 890$ kDa; $D = 1.07$) displaying (a) a bilayer and (b) a monolayer of **P(NB-*g*-BzMA)** cylinders.

S6. References

- S1 C.-G. Chae, Y.-G. Yu, H.-B. Seo, M.-J. Kim, R. H. Grubbs and J.-S. Lee, *Macromolecules*, 2018, **51**, 3458–3466.
- S2 A. Fina, D. Tabuani, F. Carniato, A. Frache, E. Boccaleri and G. Camino, *Thermochim. Acta*, 2006, **440**, 36–42.