Electronic Supplementary Material (ESI) for Polymer Chemistry.
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Supporting information for

Supramolecular organogel formation behaviors of beads-on-string shaped polyazomethines dependent on POSS structures in the main chain

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Synthesis of polymers.

Synthesis of T_8-poly(azomethine)s (**3**)

A typical polymerization is as follows. A mixture of *para*-bis(3-aminopropyl) hexaisobutyl-substituted T_8 cage (**1**) (0.150 g, 0.171 mmol) and terephthalaldehyde (**2a**) (0.0230 g, 0.171 mmol) in *p*-xylene (2.0 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to obtain **3a**. FT-IR (ATR): ν = 737, 834, 1021, 1092, 1227, 1332, 1365, 1401, 1465, 1607, 1644, 1705, 2869, 2952 cm^{-1}.

3b. A mixture of **1** (0.150 g, 0.171 mmol) and isophthalaldehyde (**2b**) (0.0233 g, 0.174 mmol) in *p*-xylene (2.0 mL) was to obtain **3b**. FT-IR (ATR): ν = 738, 835, 1020, 1092, 1227, 1332, 1401, 1465, 1606, 1648, 2869, 2952 cm^{-1}.

3c. A mixture of **1** (0.150 g, 0.172 mmol) and 4,4'-oxydibenzaldehyde (**2c**) (0.0389 g, 0.172 mmol) in *p*-xylene (2.0 mL) was used to obtain **3c**. FT-IR (ATR): ν = 738, 833, 876, 1022, 1092, 1229, 1332, 1365, 1465, 1498, 1592, 1646, 1701, 2869, 2952 cm^{-1}.

Synthesis of DDSQ-poly(azomethine)s (**5**)

A mixture of **4** (0.200 g, 0.150 mmol) and **2a** (0.0201 g, 0.150 mmol) in chloroform (2.0 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to obtain **5a**. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.38-8.33 (m, 2H), 8.09-6.52 (m, 52H), 0.56-0.48 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 191.8, 159.8, 159.2, 153.3, 141.2, 138.7, 138.1, 135.0, 134.7, 134.6, 134.3, 134.3, 134.2, 134.1, 134.1, 134.0, 131.9, 131.8, 130.9, 130.7, 130.5, 130.4, 130.3, 130.3, 130.1, 129.3, 129.2, 128.9, 127.9, 127.8, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 120.4, 114.4, 77.2, 21.0, -0.3, -0.4 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ = -30.5, -78.3, -78.5, -79.4, -79.5 ppm.

5b. A mixture of **4** (0.200 g, 0.150 mmol) and **2b** (0.0200 g, 0.149 mmol) in THF (1.3 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to obtain **5b**. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.41-8.34 (m, 2H), 8.18-6.50 (m, 52H), 0.56-0.48 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 191.7, 159.9, 159.0, 153.3, 137.2, 137.0, 136.9,

135.0, 134.7, 134.6, 134.3, 134.2, 134.1, 134.0, 131.8, 131.4, 131.1, 131.0, 130.9, 130.7, 130.5, 130.4, 130.4, 130.3, 130.3, 129.6, 129.3, 127.9, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 120.4, 120.3, 114.4, 77.2, 30.4, -0.3, -0.4 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ = -29.9, -30.5, -30.6, -78.2, -78.3, -78.5, -79.3, -79.5, -79.5 ppm.

5c. A mixture of **4** (0.201 g, 0.150 mmol) and **2c** (0.0340 g, 0.150 mmol) in chloroform (2.0 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to obtain **5c**. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.30-8.26 (m, 2H), 7.95-6.52 (m, 56H), 0.56-0.48 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 190.7, 190.6, 162.2, 159.5, 159.3, 159.3, 158.2, 153.6, 148.1, 135.0, 134.6, 134.3, 134.2, 134.2, 134.1, 134.0, 132.1, 132.1, 132.0, 131.9, 131.9, 131.1, 130.9, 130.8, 130.8, 130.4, 130.4, 130.3, 130.3, 130.3, 130.1, 127.8, 127.8, 127.8, 127.7, 127.7, 127.6, 127.6, 127.5, 127.5, 127.4, 120.3, 120.1, 119.4, 119.3, 118.5, 114.4, 77.2, -0.3, -0.4 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ = -29.9, -30.5, -30.6, -78.3, -78.5, -79.3, -79.5 ppm.

Synthesis of DDSQ-poly(azomethine)s (**7**)

A mixture of **6** (0.201 g, 0.158 mmol) and **2a** (0.0212 g, 0.158 mmol) in THF (1.2 mL) was stirred at room temperature for 2 h. The solvent was removed under reduced pressure to obtain **7a**. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.07-7.99 (m, 2H), 7.55-7.10 (m, 44H), 3.57-3.47 (m, 4H), 1.89-1.78 (m, 4H), 0.80-0.76 (m, 4H), 0.35-0.28 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 191.9, 160.4, 159.7, 141.6, 138.0, 137.4, 134.1, 134.1, 133.9, 132.0, 131.0, 130.4, 129.8, 128.5, 128.1, 127.8, 127.7, 77.2, 64.2, 30.4, 24.2, 14.4, -0.8 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ = -17.4, -78.6, -79.5, -79.5 ppm. FT-IR (ATR): ν = 572, 694, 726, 801, 1072, 1261, 1298, 1430, 1594, 1641, 1702, 2832, 2925, 3010, 3050, 3072 cm^{-1}.

7b. A mixture of **6** (0.200 g, 0.158 mmol) and **2b** (0.0211 g, 0.157 mmol) in THF (1.2 mL) was used to obtain **7b**. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.07-7.99 (m, 2H), 7.79-7.08 (m, 44H), 3.55-3.48 (m, 4H), 1.86-1.78 (m, 4H), 0.82-0.75 (m, 4H), 0.35-0.27 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 191.9, 160.3, 159.4, 136.6, 134.0, 133.9, 132.0, 132.0, 131.1, 131.0,

130.4, 129.5, 129.2, 128.7, 128.3, 128.2, 127.8, 127.7, 77.2, 64.1, 63.9, 24.4, 24.2, 14.5, 14.4, 14.3, -0.7, -0.8 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ = -17.4, -17.5, -78.6, -79.5, -79.5 ppm. FT-IR (ATR): ν = 571, 694, 726, 798, 997, 1027, 1071, 1261, 1430, 1594, 1645, 2830, 2925, 3008, 3049, 3072 cm^{-1}.

7c. A mixture of **6** (0.200 g, 0.158 mmol) and **2c** (0.0357 g, 0.158 mmol) in THF (1.2 mL) was used to obtain **7c**. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.00-7.97 (m, 2H), 7.61-6.90 (m, 48H), 3.51-3.48 (m, 4H), 1.87-1.77 (m, 4H), 0.79-0.75 (m, 4H), 0.35-0.29 (m, 6H) ppm; ^{13}C-NMR ($CDCl_3$, 100 MHz): δ = 159.8, 159.6, 158.6, 134.2, 134.2, 134.1, 134.1, 134.0, 134.0, 133.7, 132.0, 132.0, 131.1, 131.1, 130.4, 130.3, 130.1, 129.9, 129.7, 129.4, 128.0, 127.9, 127.8, 127.7, 127.7, 127.6, 127.5, 120.1, 119.7, 119.1, 118.9, 118.8, 118.8, 118.7, 118.1, 77.2, 68.0, 64.0, 63.9, 25.6, 24.3, 14.3, -0.7, -0.8 ppm; ^{29}Si-NMR ($CDCl_3$, 80 MHz): δ = -17.3, -78.6, -79.5, -79.5, -79.6 ppm. FT-IR (ATR): ν = 572, 694, 726, 997, 1027, 1072, 1238, 1300, 1374, 1430, 1498, 1594, 1645, 1739, 2829, 2925, 3008, 3027, 3049, 3072 cm^{-1}.

X-ray crystallographic data for single crystalline products

The single crystal was mounted on a glass fiber. Intensity data were collected at room temperature on a Rigaku XtaLAB mini with graphite monochromated Mo Kα radiation. Readout was performed in the 0.073 mm pixel mode. The data were collected to a maximum 2θ value of 55.0°. Data were processed using the Crystal Clear program[27] and CrysAlisPro.[28] An empirical absorption correction[29] was applied. The data were corrected for Lorentz and polarization effects. The structure was solved by Direct Methods[30] and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on $F2$ was based on observed reflections and variable parameters. All calculations were performed using the CrystalStructure[30] crystallographic software package except for refinement, which was performed using SHELXL2013[31] The disordered structures were refined with SHELXL2016[32] by using $Olex_2$[33] as the graphical interface.

(27) CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998–β014). Tokyo 196-8666, Japan.

(28) CrysAlisPro: Data Collection and Processing Software, Rigaku Oxford Diffraction, 2020, Tokyo 196-8666, Japan.

(29) SIR2011: M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2012**, *45*, 357.

(30) CrystalStructure 4.1: Crystal Structure Analysis Package, Rigaku Corporation (β000–β014). Tokyo 196-8666, Japan.

(31) SHELXL2013: G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 11β.

(32) SHELXL2016: G. M. Sheldrick, *Acta Cryst.* **2015**, *C27*, 3.

(33) Olex2: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339.

Crystallographic data

Table S1. Crystallographic data of bis(3-aminopropyl)-DDSQ (**6**) measured at -180 °C.

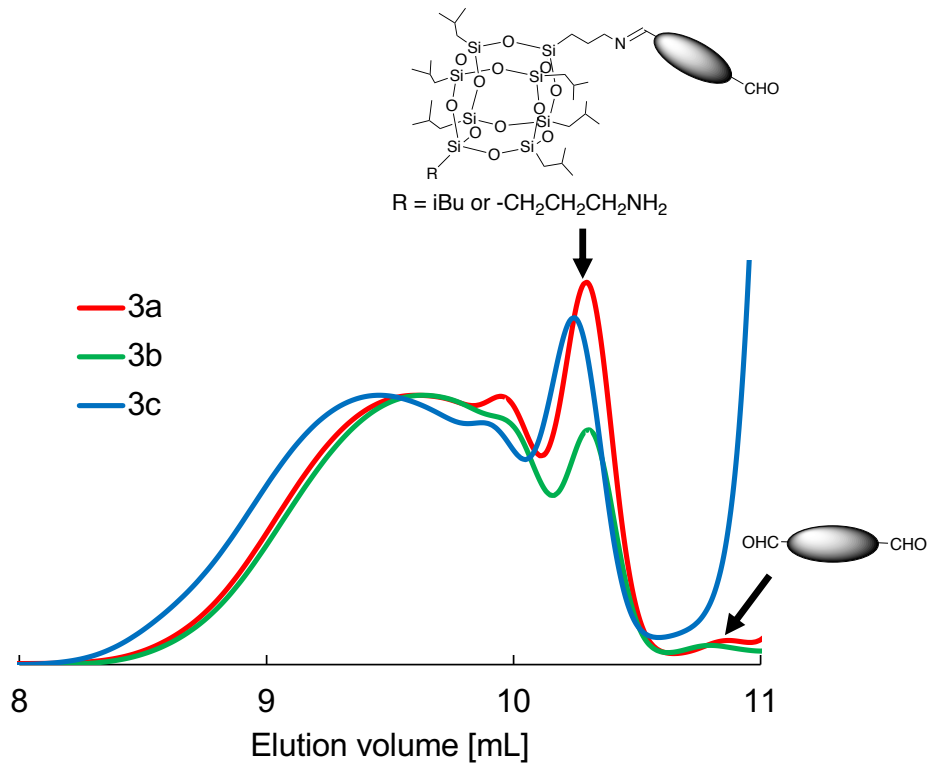
Crystal data	Bis(3-aminopropyl)DDSQ (**6**)
Empirical formula	$C_{56}H_{62}N_2O_{14}Si_{10}$
Formula weight	1267.97
Crystal Dimension, mm^3	0.17 × 0.24 × 0.34
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	10.0808(7)
b, Å	24.2770(15)
c, Å	25.8121(19)
α, deg	90
β, deg	90
γ, deg	90
Volume, $Å^3$	6317.0(7)
D_{calcd}, g cm^{-3}	1.333
Z	4
F(000)	2656.00
Data collection	
Temperature, °C	-180.0
$2\theta_{max}$, deg	52.742
T_{min}/T_{max}	0.917/0.991
Refinement	
No. of observed data	12910
No. of parameters	827
R1[a], wR2 [b]	0.0671, 0.1875
Goodness of fit indicator	1.013

[a] $R1 = \Sigma \mid |Fo| - |Fc| \mid / \Sigma|Fo|$, [b] $wR2 = [\Sigma w ((Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$, $w = [\delta^2(Fo^2)]^{-1}$

Table S2. Selected distances, and angles of bis(3-aminopropyl)-DDSQ (**6**) measured at -180 °C.

	distances (Å)		angles (°)
Si-O	1.621(5)	O-Si-O	109.5(3)
	1.611(5)		110.3(3)
	1.614(5)		108.6(3)
	1.616(5)		111.6(3)
	1.618(5)		110.4(3)
	1.617(5)		110.0(3)
	1.597(5)		108.5(3)
	1.618(5)		109.5(3)
	1.602(6)		108.6(3)
	1.597(6)		108.2(3)
	1.578(6)		109.2(3)
Si-O	1.598(6)	O-Si-O	108.3(3)
	1.611(6)		109.4(3)
	1.611(6)		109.1(3)
	1.600(5)		108.8(3)
	1.611(5)		110.3(3)
	1.610(5)		109.1(3)
	1.619(5)		108.8(3)
	1.606(6)		110.2(3)
	1.595(6)		109.1(3)
	1.602(6)		109.2(3)
	1.595(5)		111.1(3)
	1.611(6)		108.9(3)
	1.599(6)		108.8(3)
	1.614(6)		110.3(3)
	1.617(6)		111.5(4)
	1.604(5)		
	1.595(5)		
N-C	1.45(7)		
	1.56(5)		

(a)



(b)

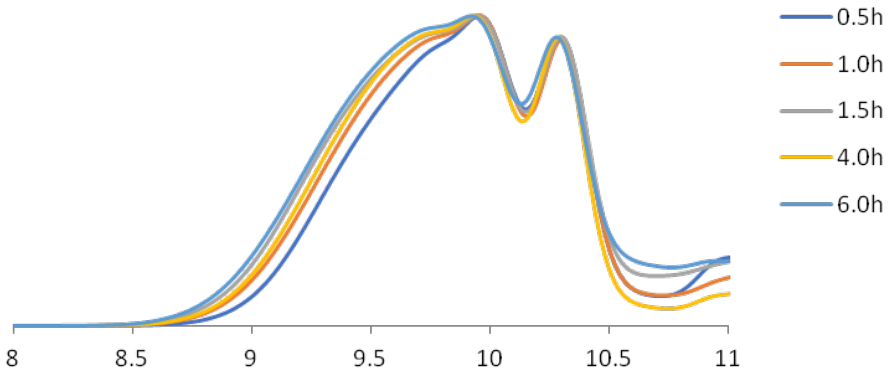


Figure S1 (a) SEC traces of the polymerization solutions of **3** at the feed ratio of 1.0 in p-xylene for 2 h at room temperature, measured by Shodex KF-805 column using THF as an eluent with UV detection at 254 nm. Beside the main polymeric fraction, oligomeric fractions appeared at 10.4 mL, corresponding to 1:1 adducts of the dialdehyde with **1** or 3-aminopropyl-heptaisobutyl-substituted T_8 cage. Small fractions at 11.0 mL corresponds to the dialdehydes (**2**). (b) SEC traces of the polymerization solutions of 1 and 3a at the feed ratio of 1.0 in toluene for various polymerization times at room temperature.

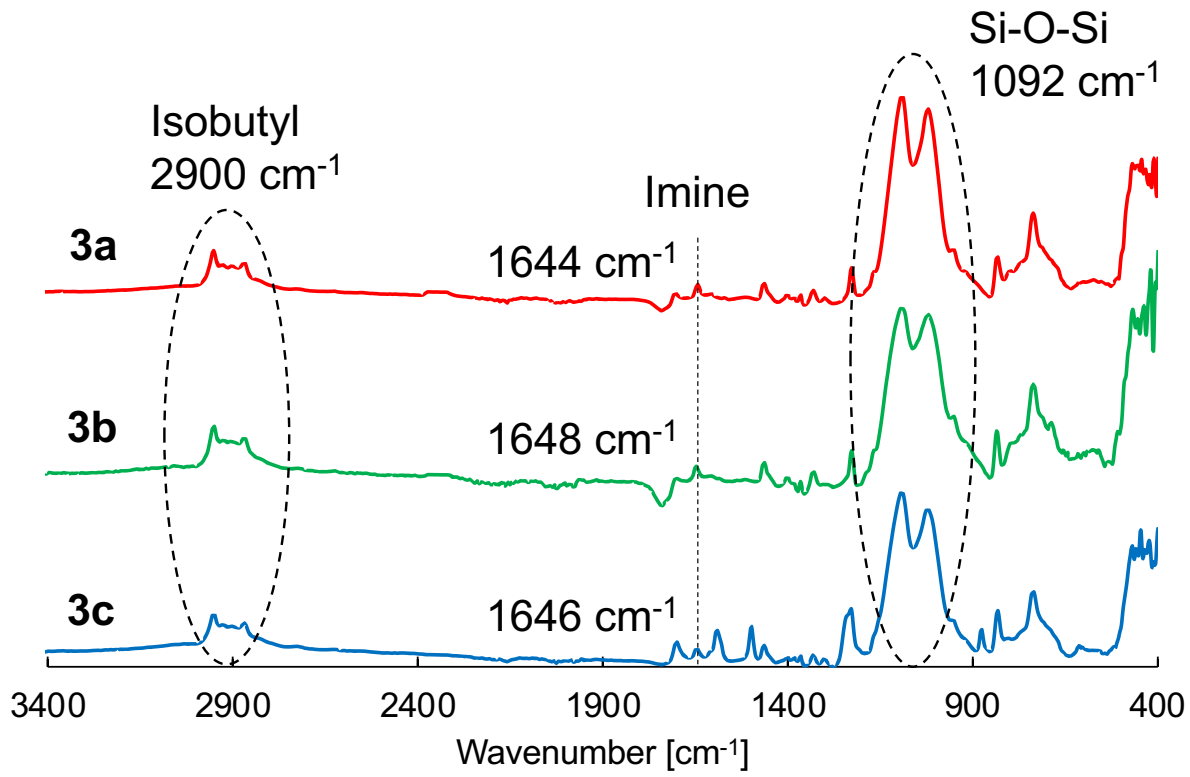
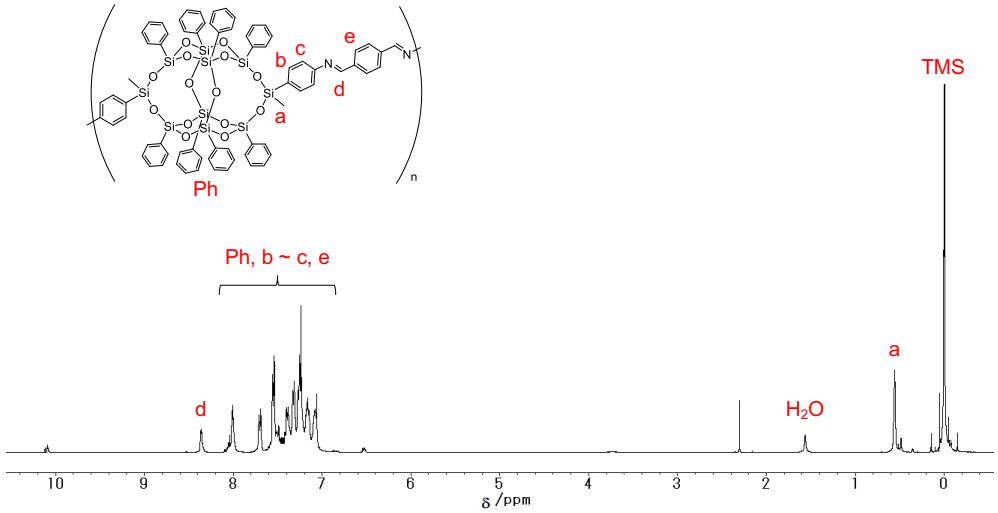
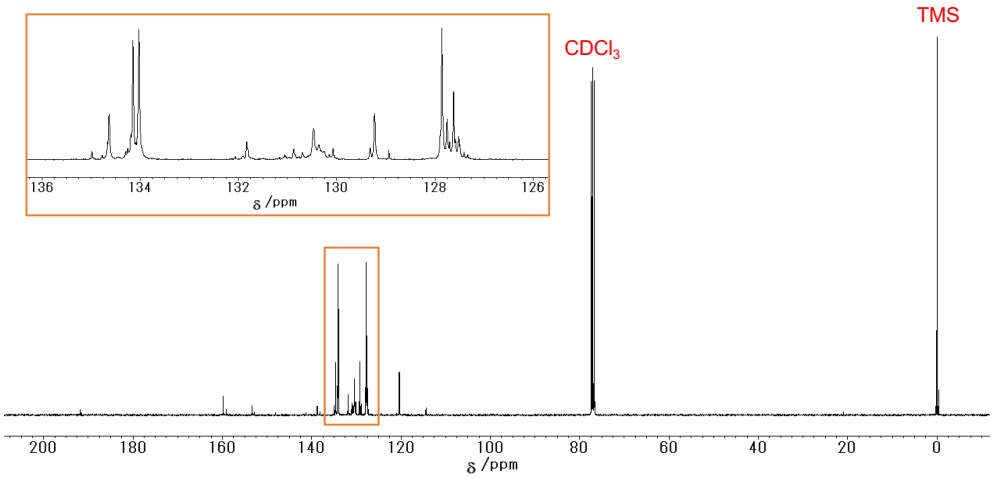


Figure S2 FT-IR spectra of **3**.

(a)



(b)



(c)

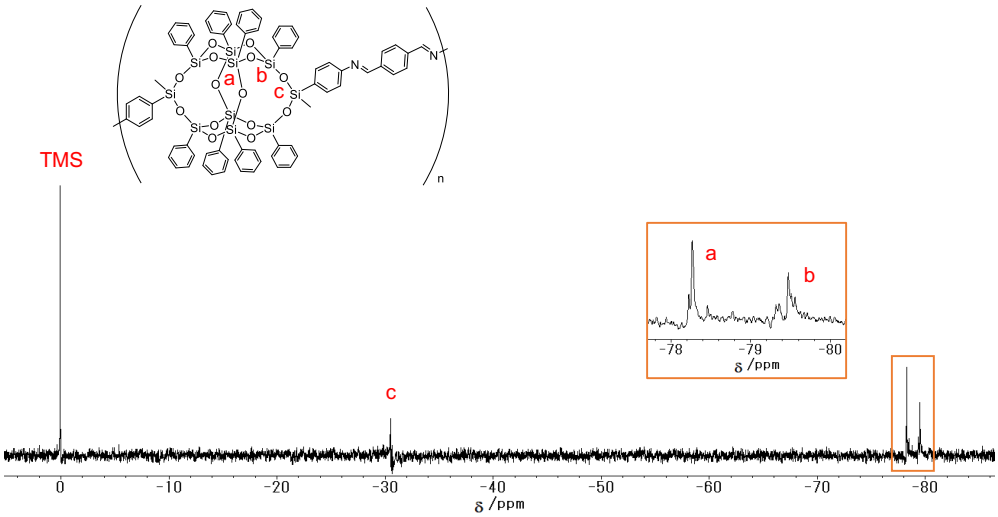
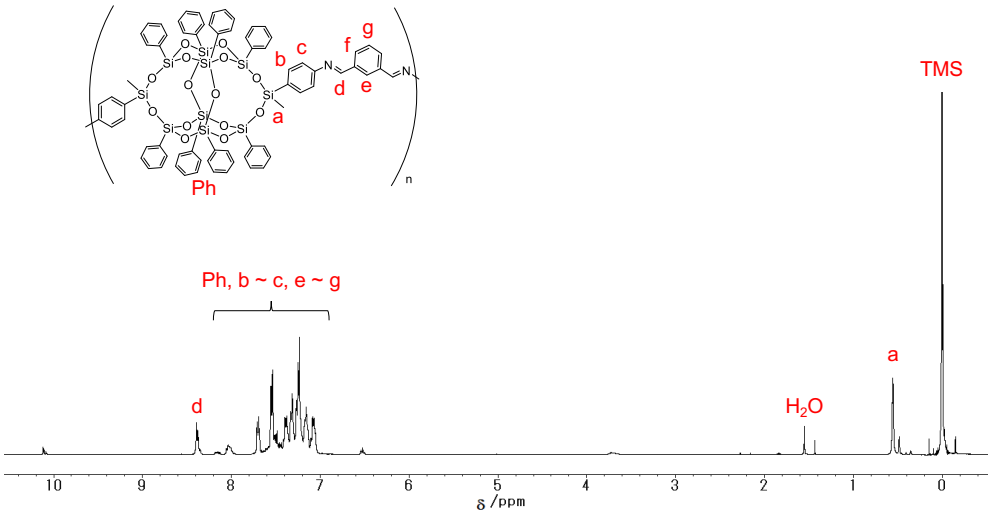
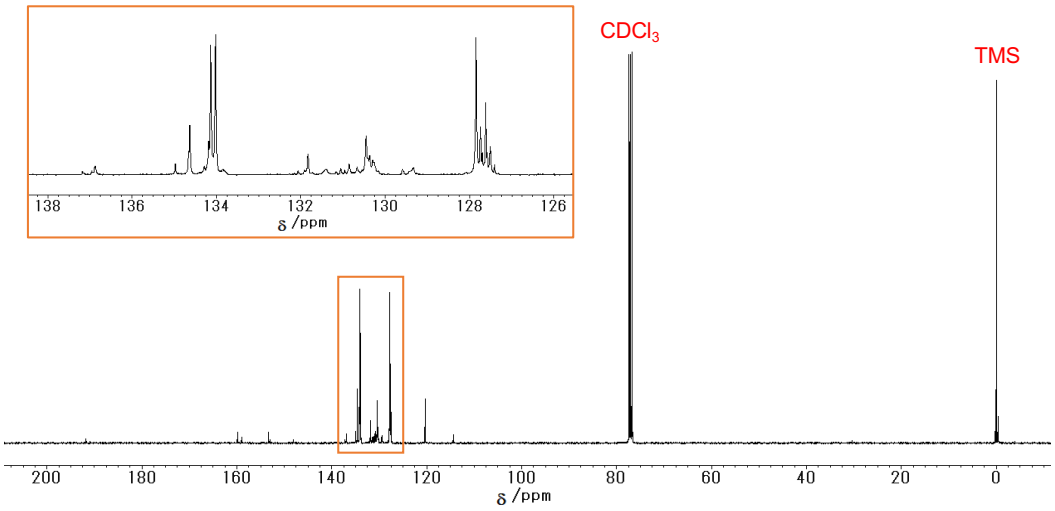


Figure S3 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **5a** in $CDCl_3$.

(a)



(b)



(c)

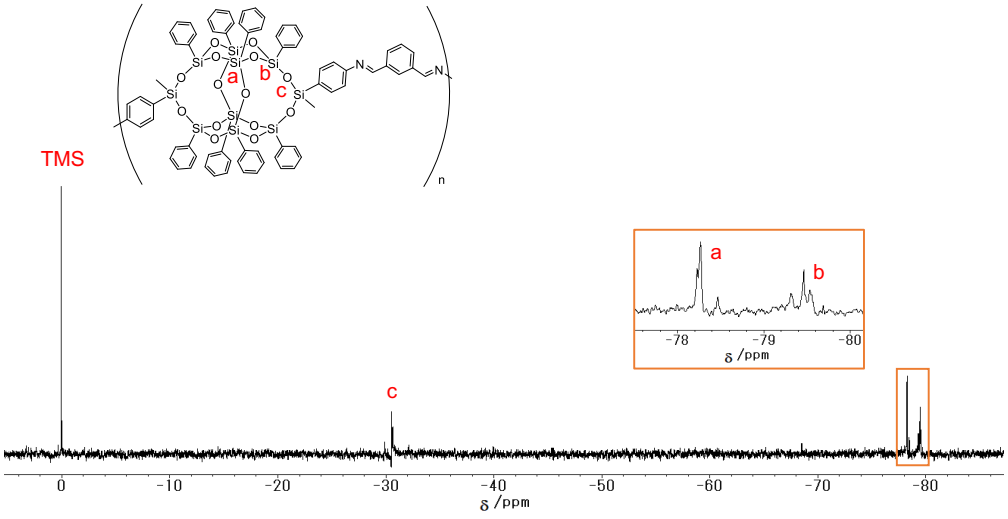
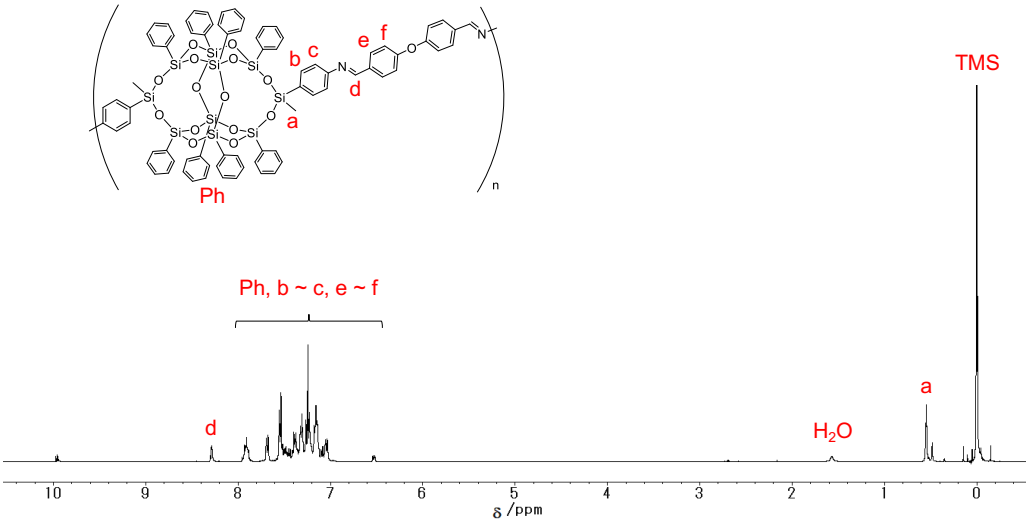
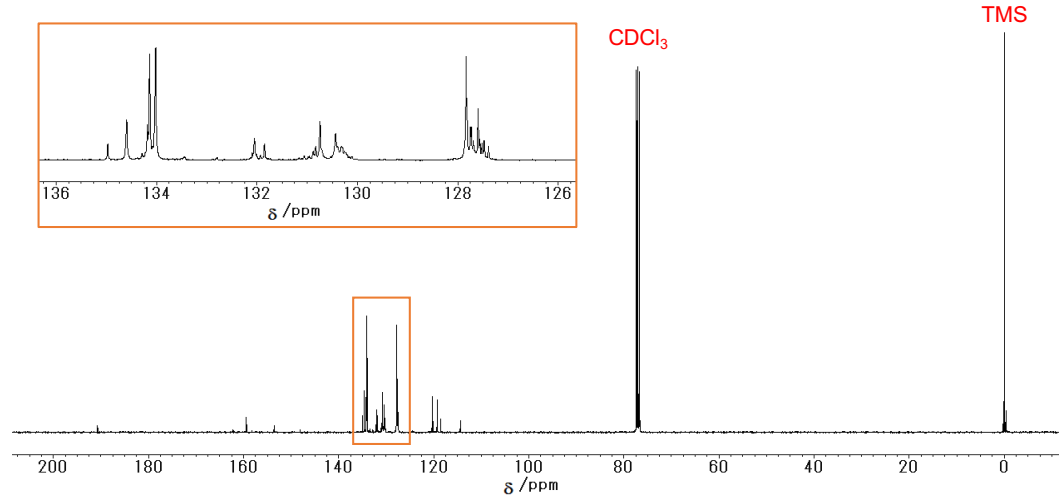


Figure S4 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **5b** in $CDCl_3$.

(a)



(b)



(c)

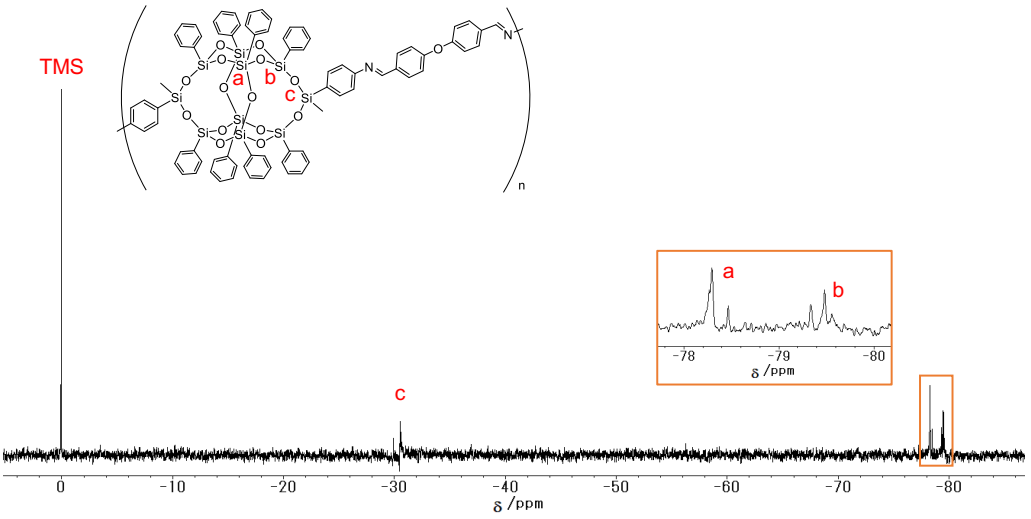


Figure S5 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **5c** in $CDCl_3$.

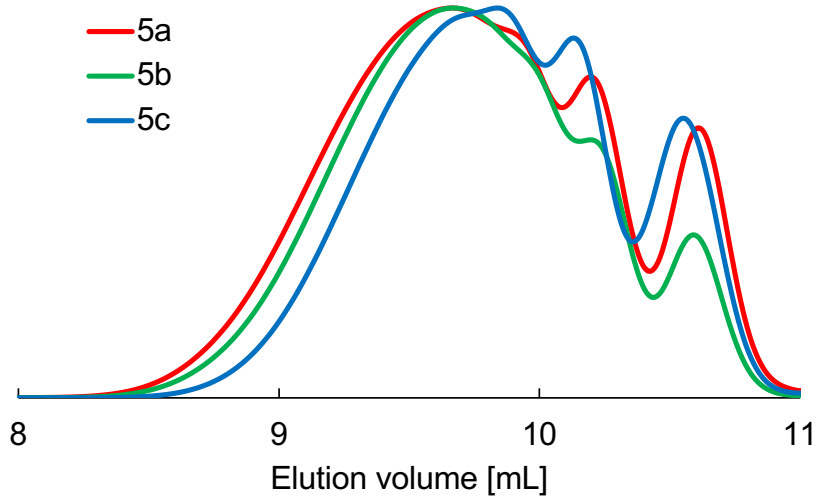


Figure S6 SEC traces of the polymerization solutions of **5** using THF as an eluent with UV detection at 254 nm.

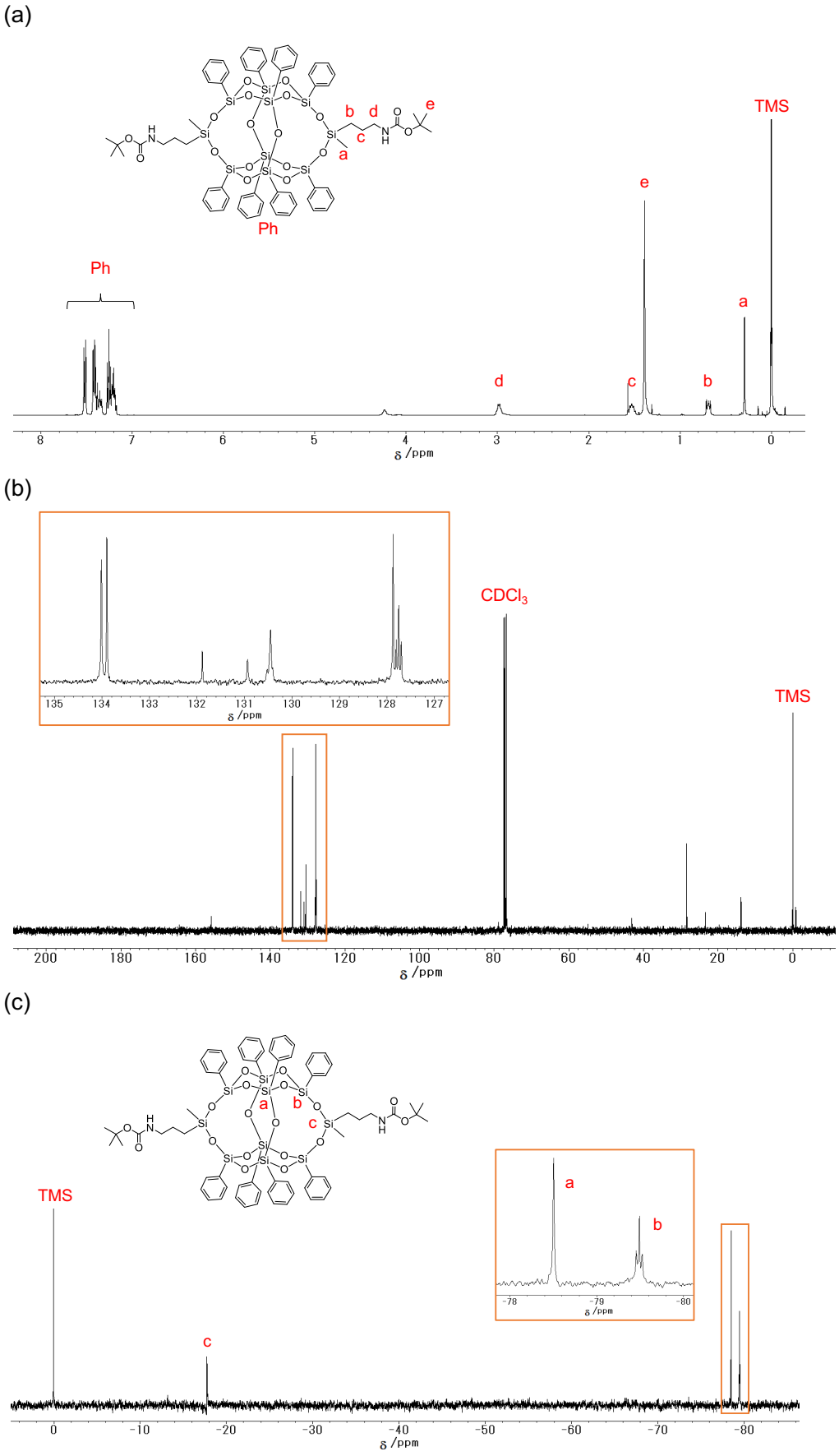
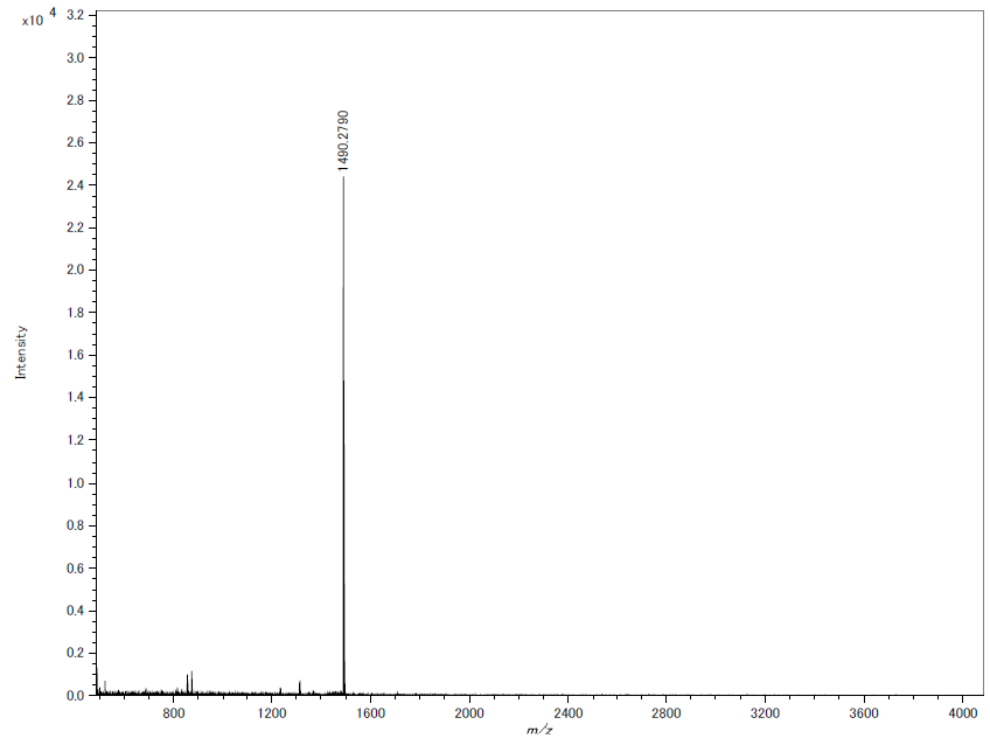


Figure S7 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of the protected bis(3-aminopropyl)-DDSQ in $CDCl_3$.

(a)



(b)

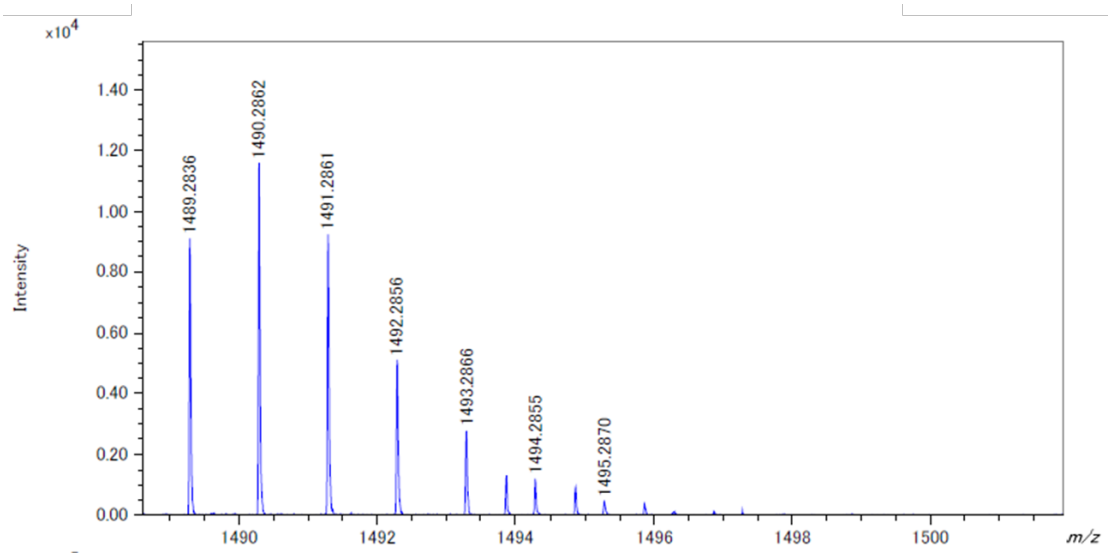
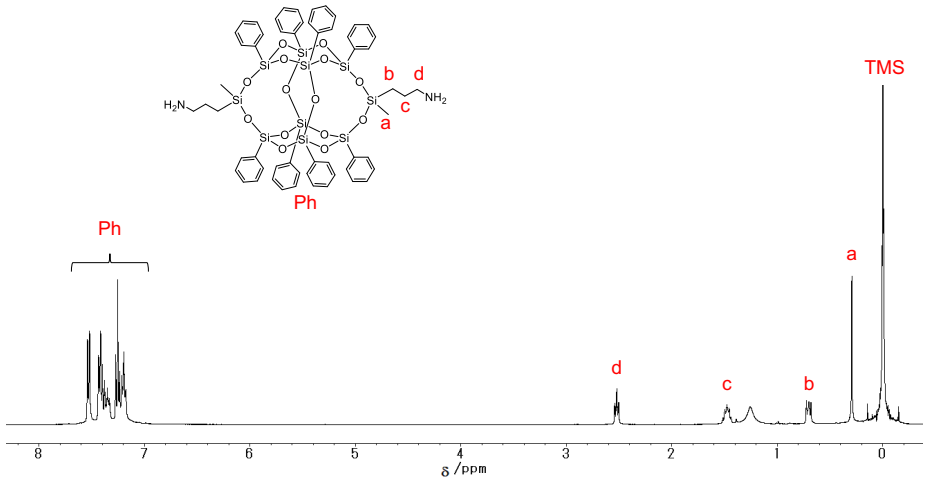
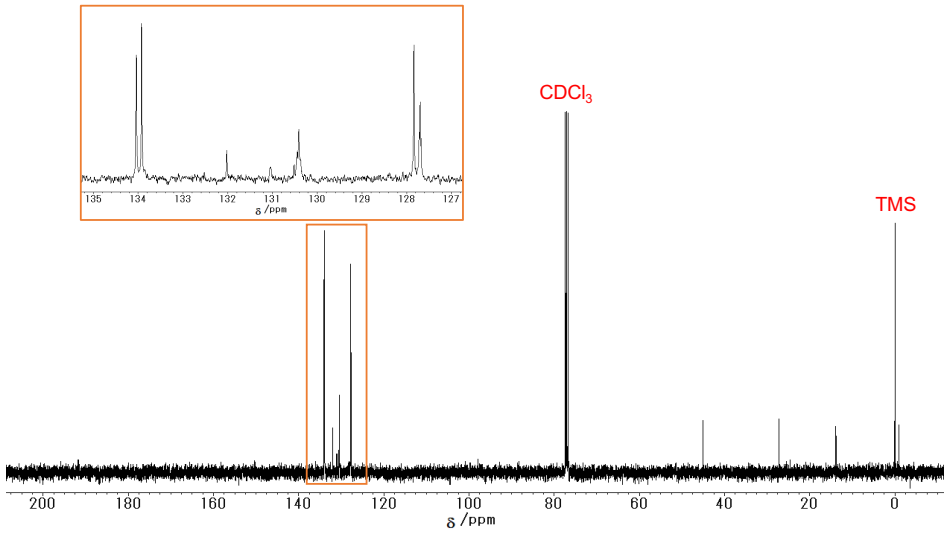


Figure S8 MALDI-TOF MS spectra of the protected bis(3-aminopropyl)-DDSQ: (a) full spectrum and (b) expand view.

(a)



(b)



(c)

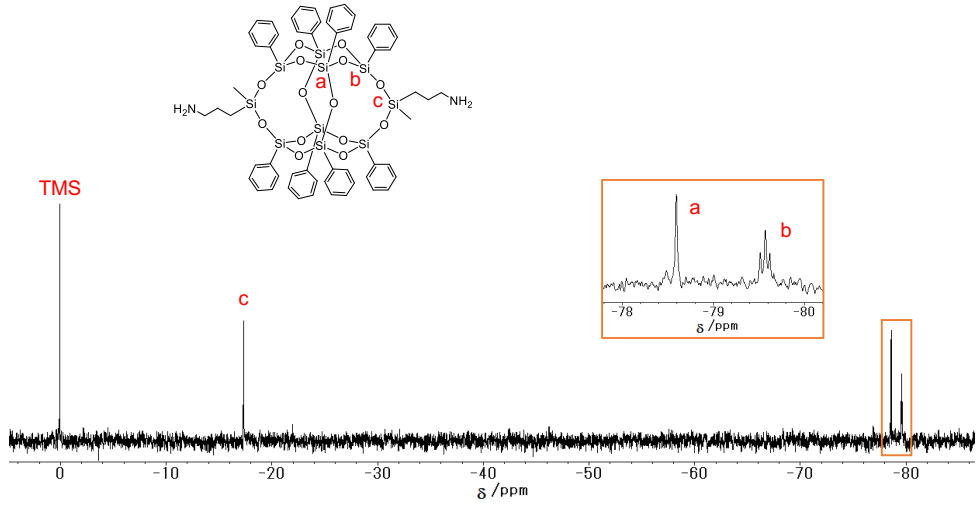


Figure S9 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **6** in $CDCl_3$.

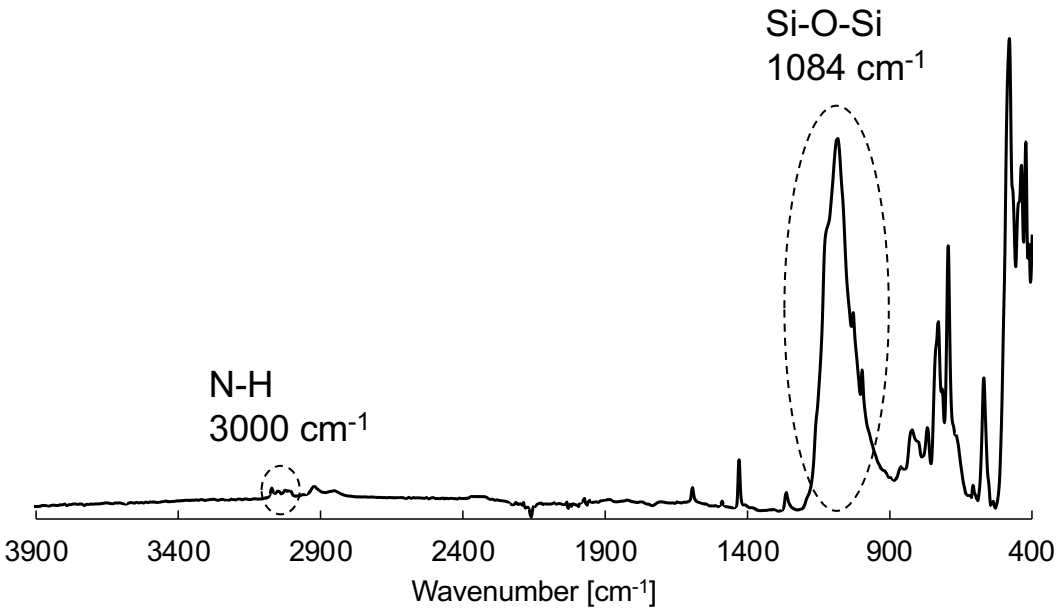


Figure S10 FT-IR spectrum of **6**

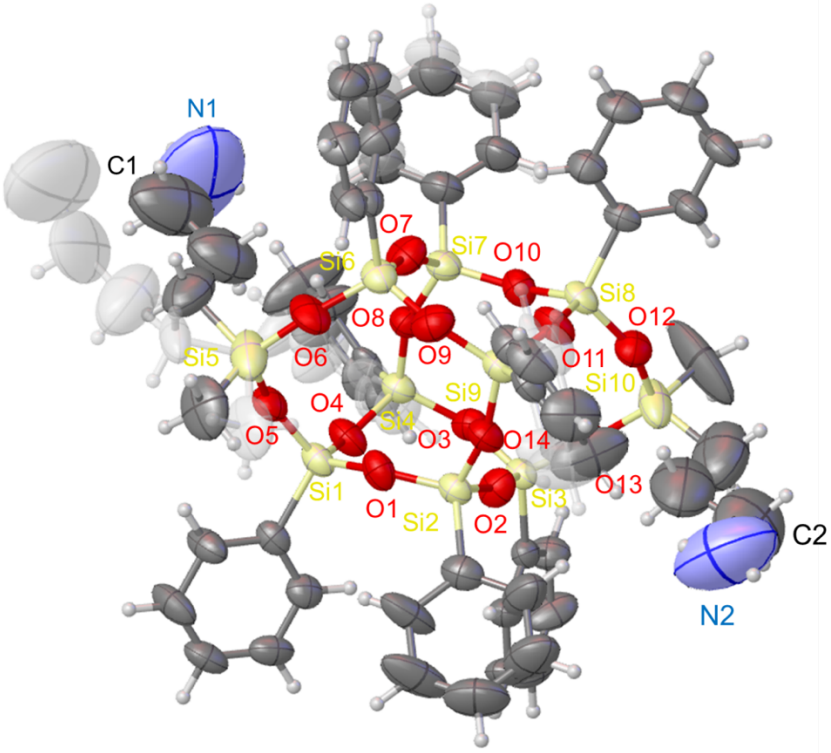
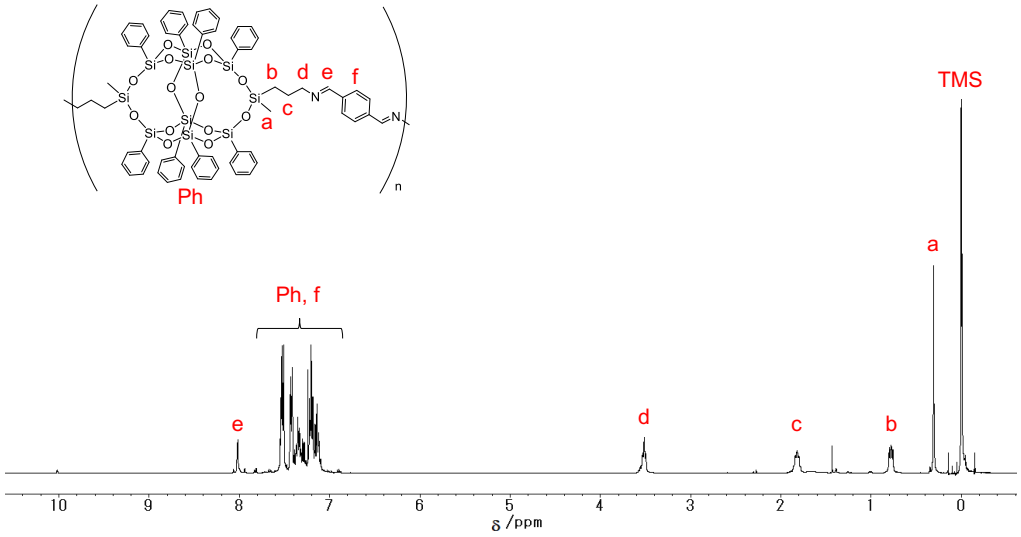
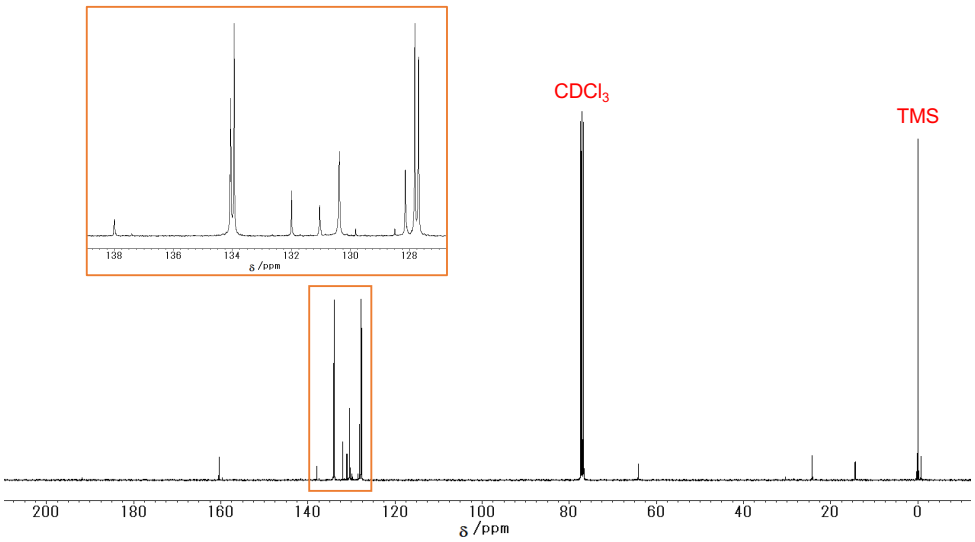


Figure S11 ORTEP drawing (ellipsoids at 50% probability) of bis(3-aminopropyl)-DDSQ (**6**) measured at -180 °C.

(a)



(b)



(c)

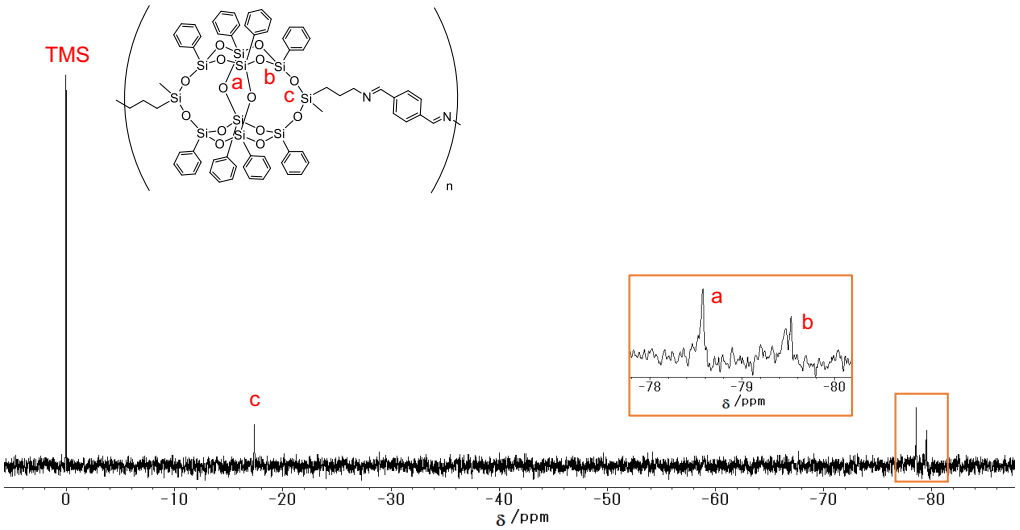
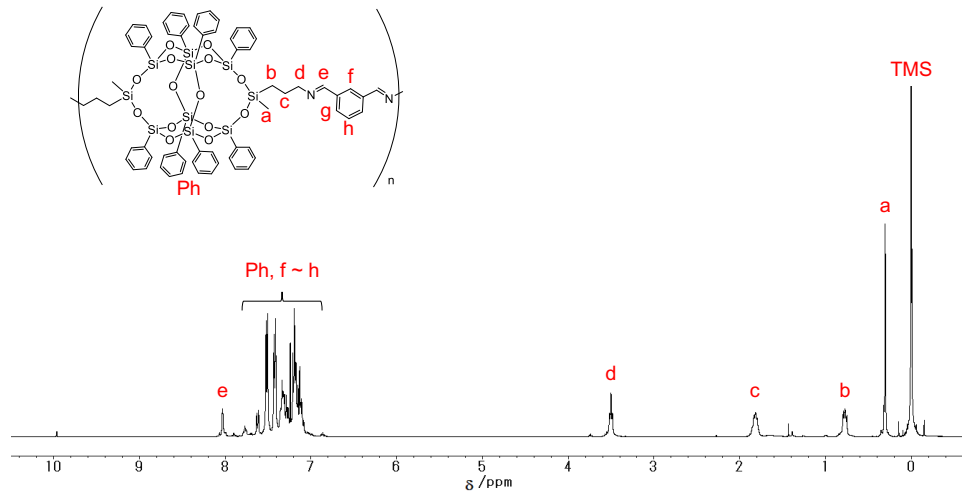
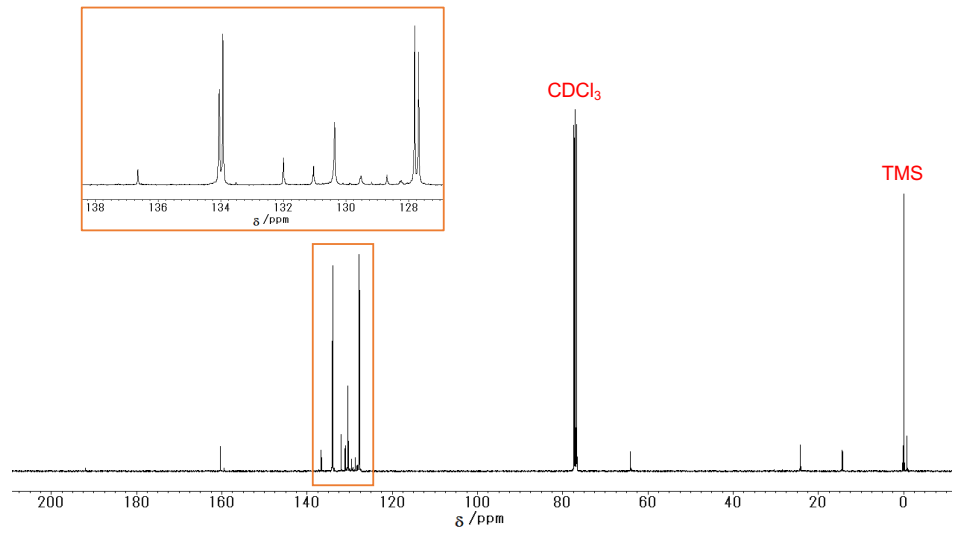


Figure 12 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **7a** in $CDCl_3$.

(a)



(b)



(c)

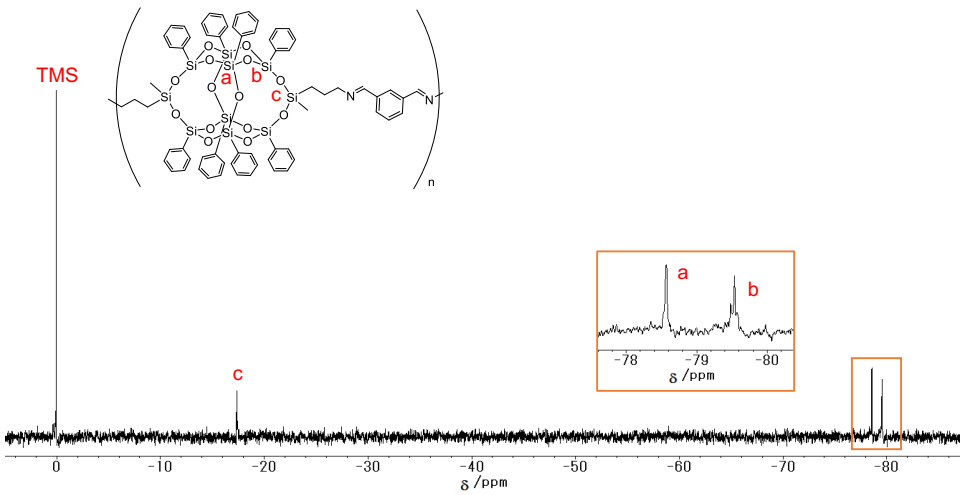
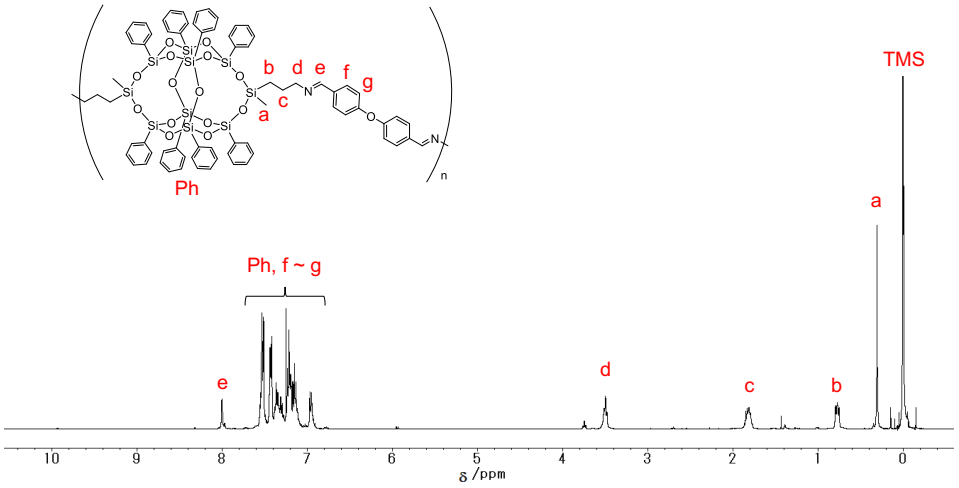
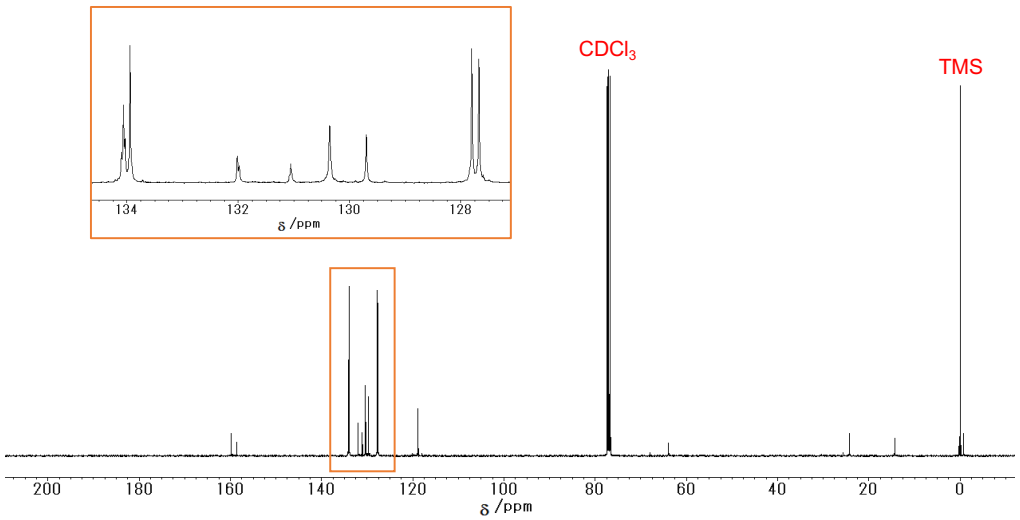


Figure S13 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **7b** in $CDCl_3$.

(a)



(b)



(c)

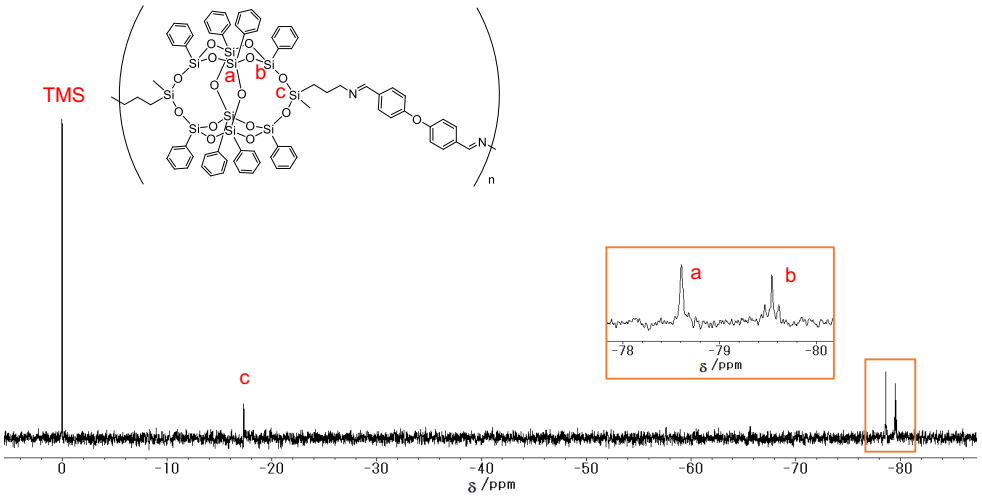


Figure S14 (a) ^{1}H-, (b) ^{13}C-, and (c) ^{29}Si-NMR spectra of **7c** in $CDCl_3$.

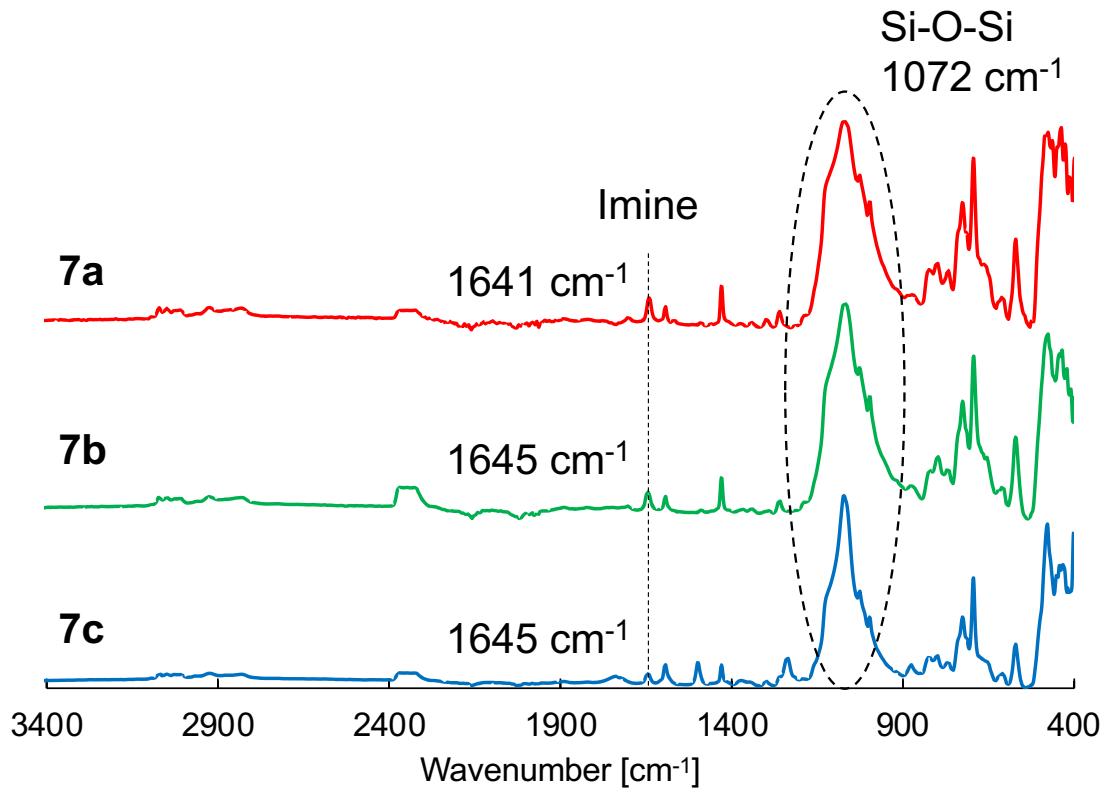
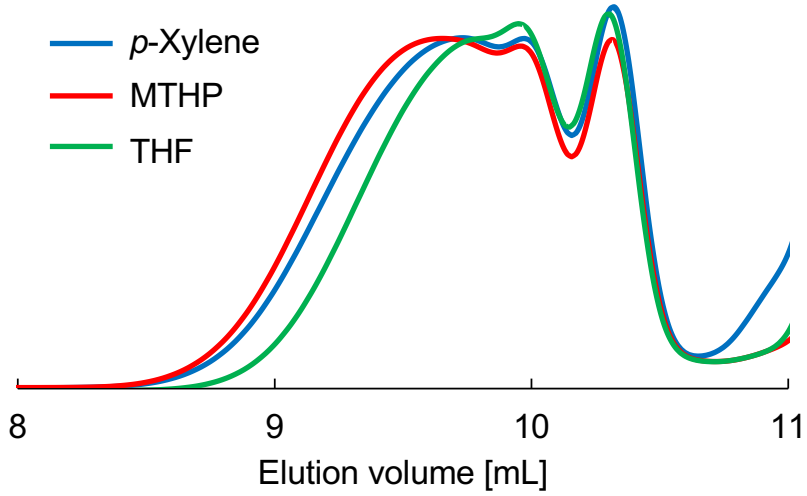


Figure S15 FT-IR spectra of **7**.



Polymerization solvent	M_n	M_w	M_w/M_n
p-Xylene	2,300	4,700	2.07
MTHP	2,400	5,100	2.13
THF	2,100	3,900	1.83

Figure S16 SEC traces of the polymerization solutions of **3a** in *p*-xylene, THF, and MTHP using THF as an eluent with UV detection at 254 nm.

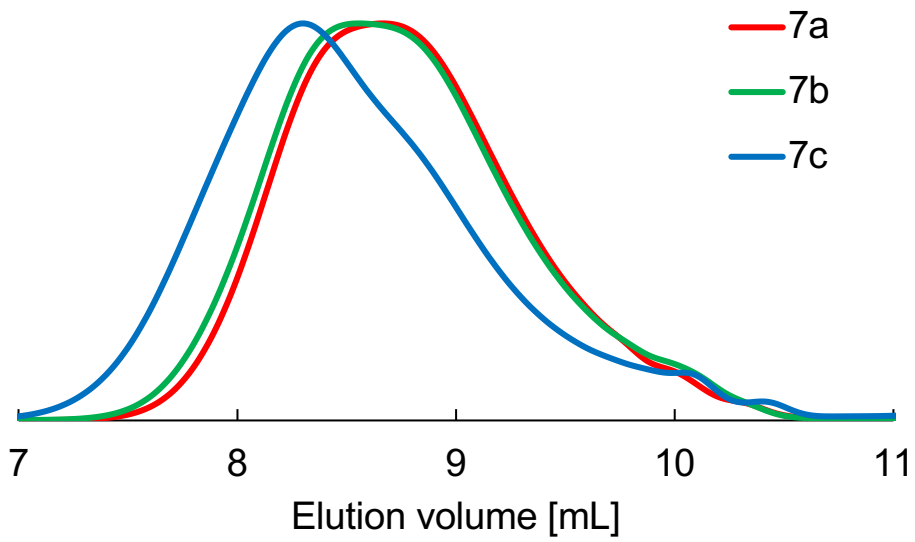
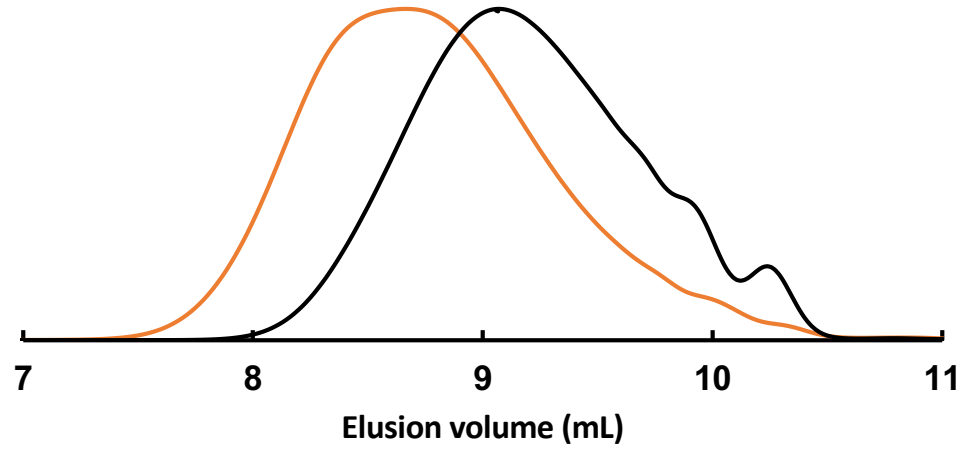


Figure S17 SEC traces of the polymerization solutions of **5** using THF as an eluent with UV detection at 254 nm.



run	Feed molar ratio, **2a**/**6**	M_n [a]	M_w [a]	M_w/M_n [a]
1	1.0	13,000	34,000	2.6
2	0.9	5,500	13,400	2.5

[a] Determined by SEC (THF 1.0 mL min-1, UV detection.

Figure S18 SEC traces of **7a** obtained from the different feed ratio (**2a**/**6**) in the polymerization using THF as an eluent with UV detection at 254 nm.

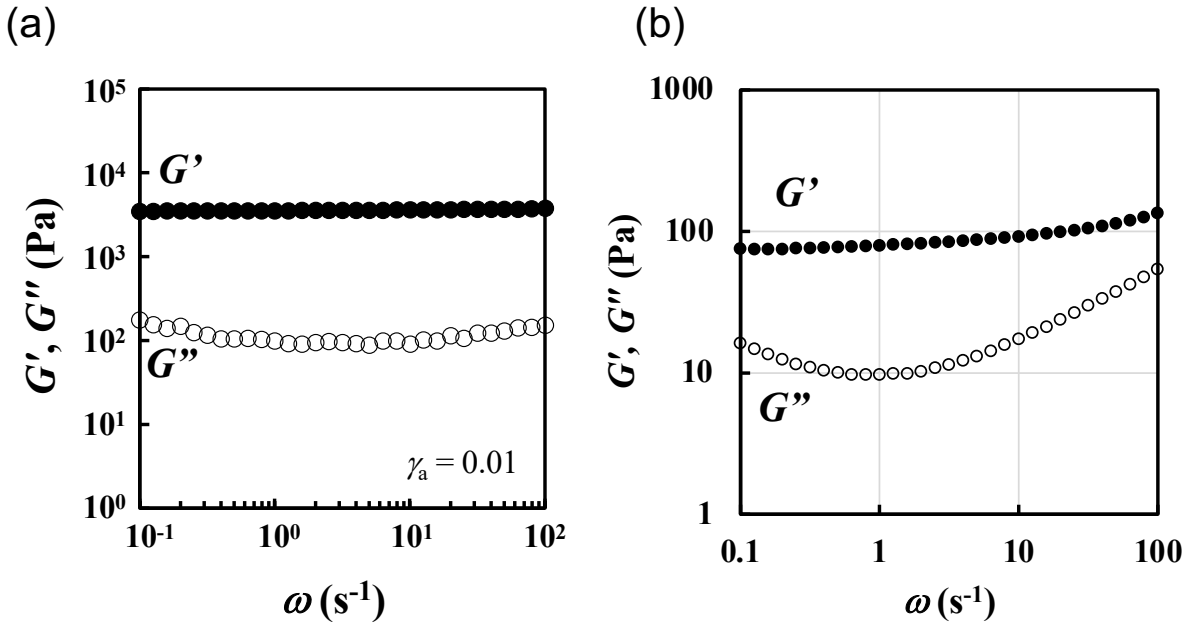


Figure S19 The storage modulus (G') and loss modulus (G'') as a function of angular frequency (ω) for the concentrated solution of **3c** (c = 0.463 g ml^{-1}) (a) and **3b** (c = 0.742 g ml^{-1}) (b).