Supporting Information

Polymethacrylates containing cage-silsesquioxanes in the side chains: effects of cage and linker structures on film properties

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Contents:

1. NMR spectra

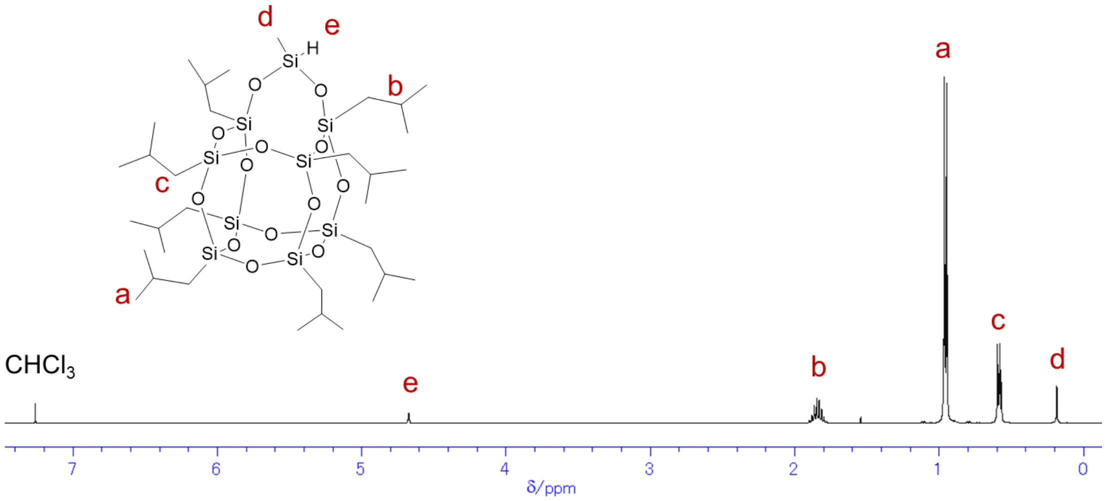


Figure S1. ^{1}H-NMR spectrum (400 MHz) of **2b** in $CDCl_3$.

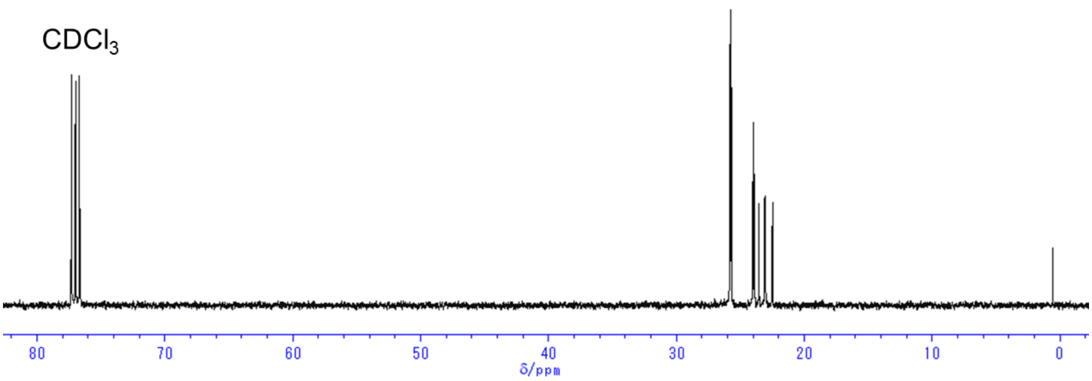


Figure S2. ^{13}C-NMR spectrum (100 MHz) of **2b** in $CDCl_3$.

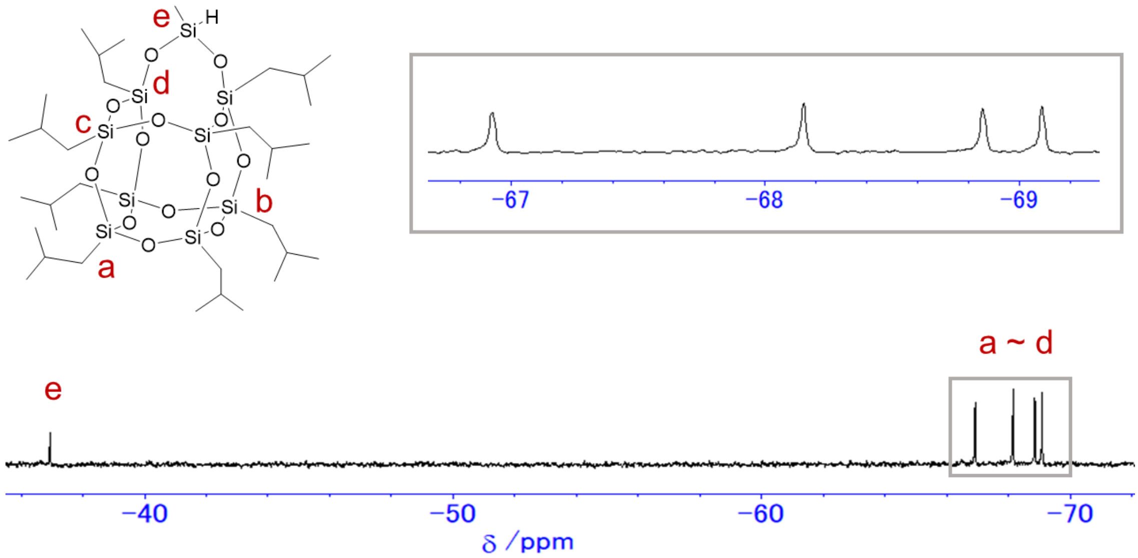


Figure S3. ^{29}Si-NMR spectrum (80 MHz) of **2b** in $CDCl_3$.

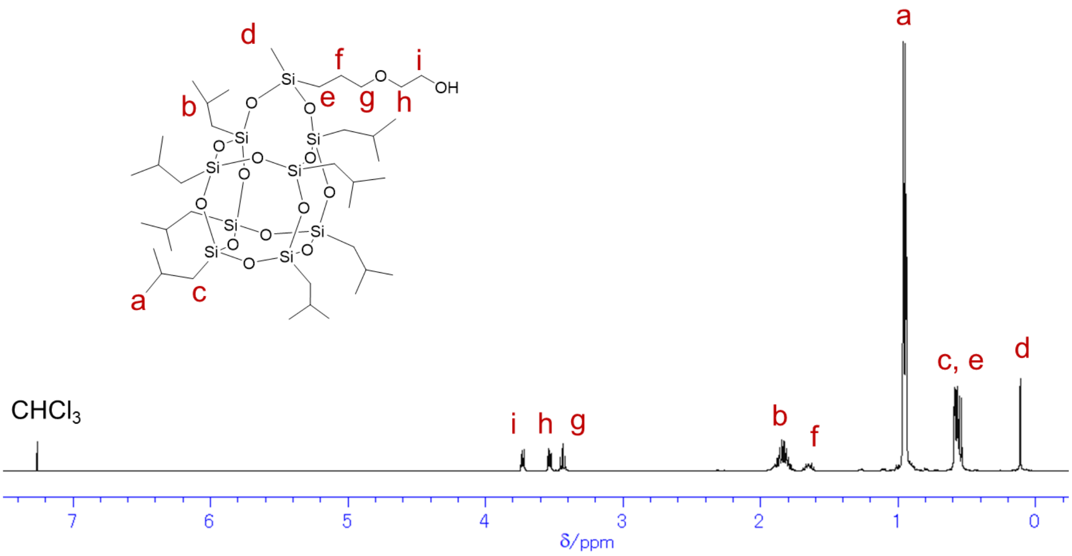


Figure S4. ^{1}H-NMR spectrum (400 MHz) of **3b** in $CDCl_3$.

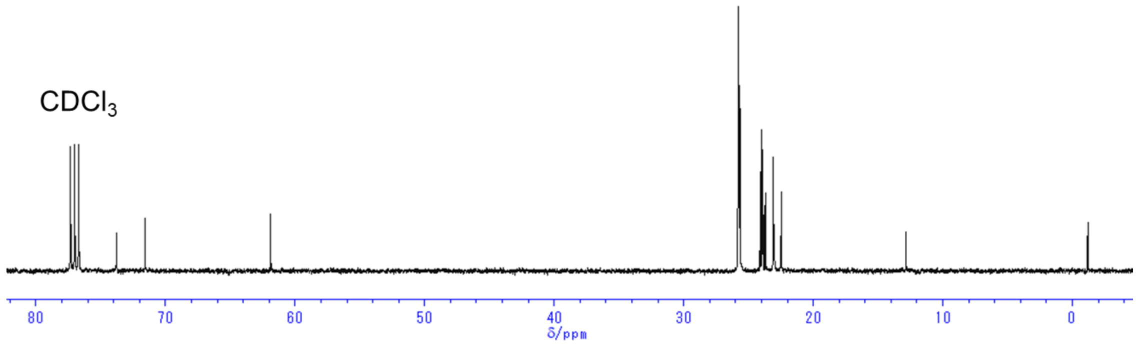


Figure S5. ^{13}C-NMR spectrum (100 MHz) of **3b** in $CDCl_3$.

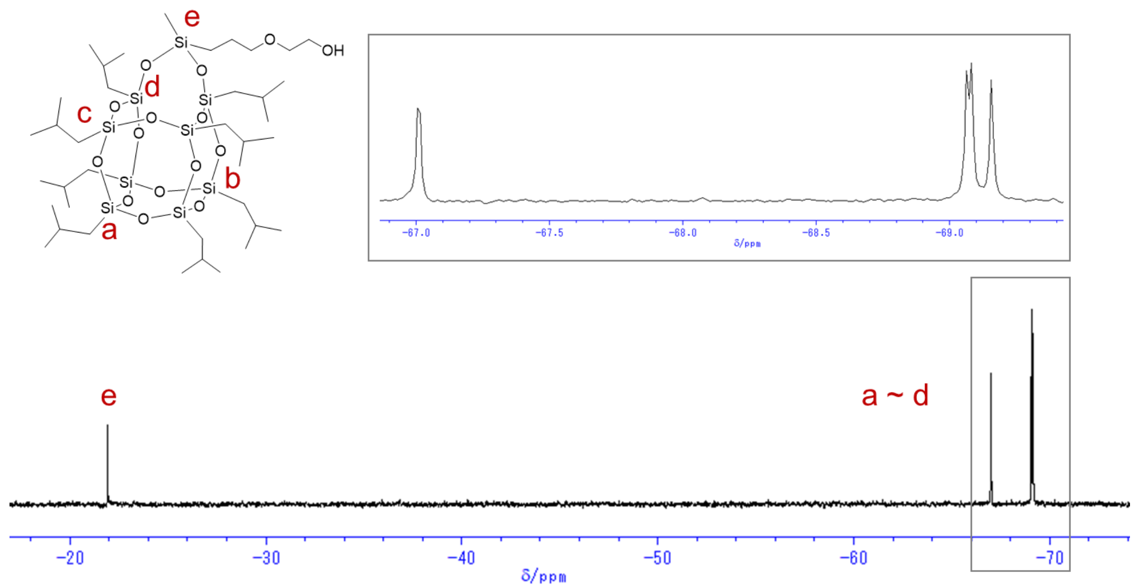


Figure S6. ^{29}Si-NMR spectrum (80 MHz) of **3b** in $CDCl_3$.

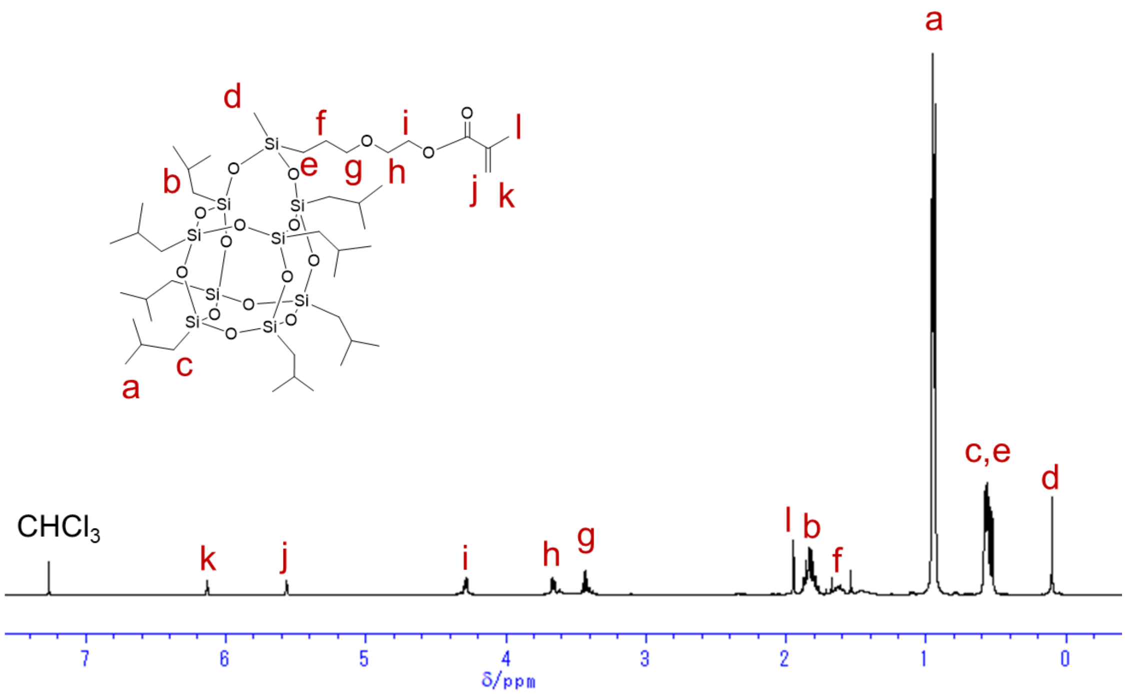


Figure S7. ^{1}H-NMR spectrum (400 MHz) of **4b** in $CDCl_3$.

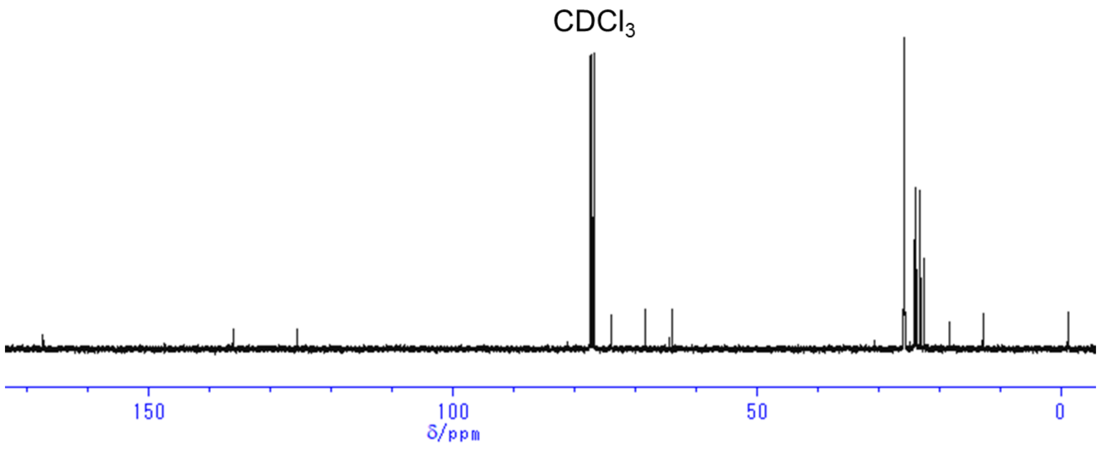


Figure S8. ^{13}C-NMR spectrum (100 MHz) of **4b** in $CDCl_3$.

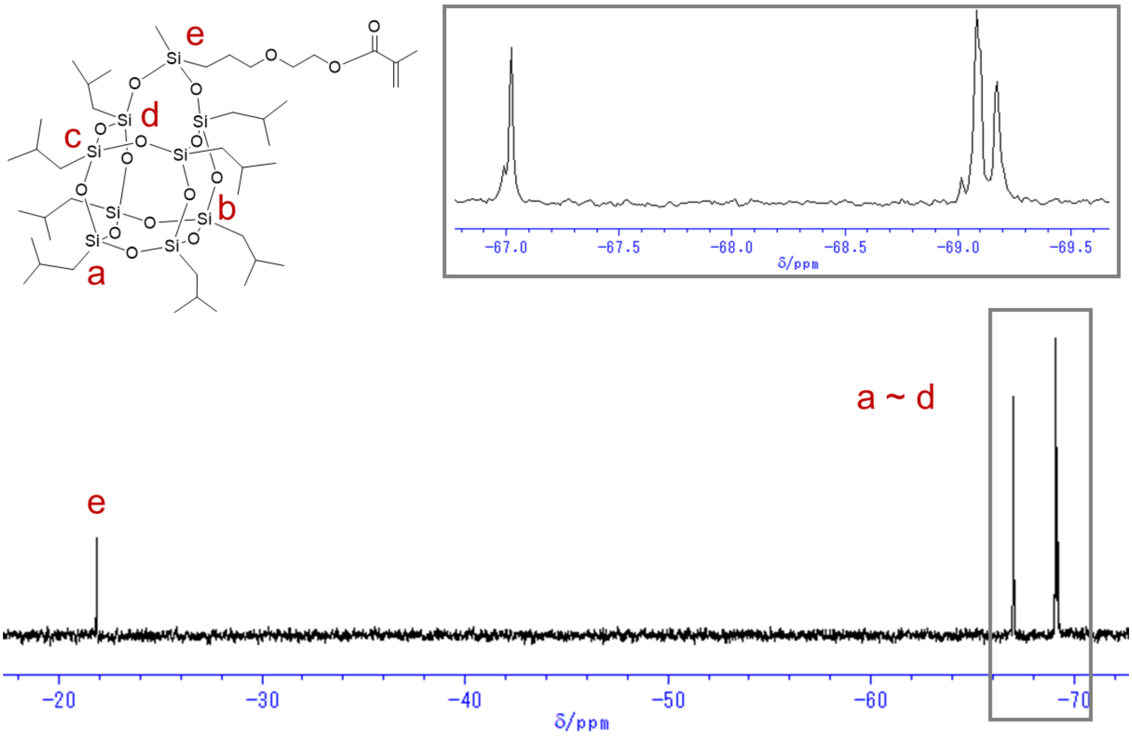


Figure S9. ^{29}Si-NMR spectrum (80 MHz) of **4b** in $CDCl_3$.

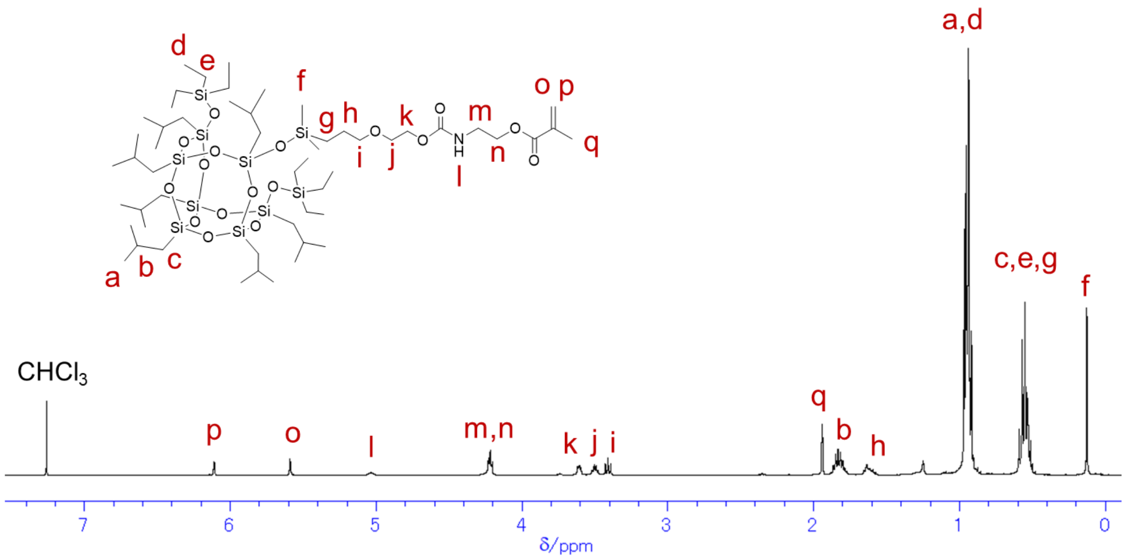


Figure S10. ^{1}H-NMR spectrum (400 MHz) of **5a** in $CDCl_3$.

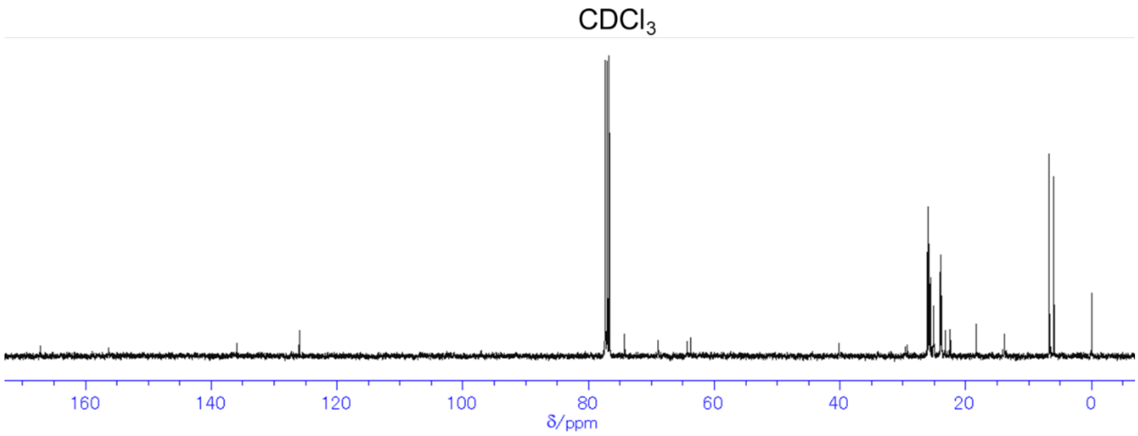


Figure S11. ^{13}C-NMR spectrum (100 MHz) of **5a** in $CDCl_3$.

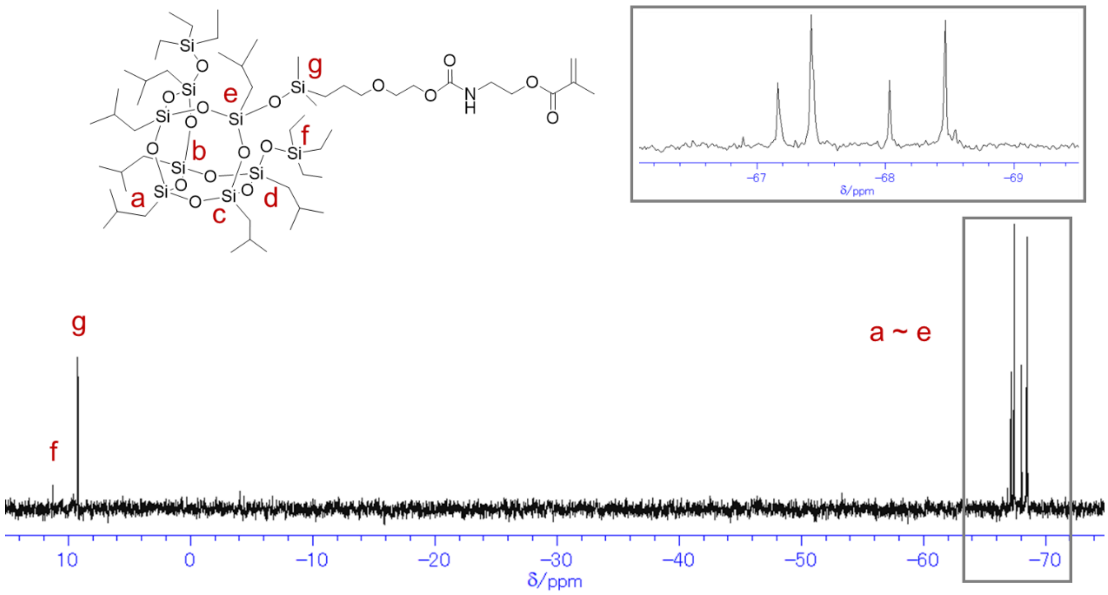


Figure S12. ^{29}Si-NMR spectrum (80 MHz) of **5a** in $CDCl_3$.

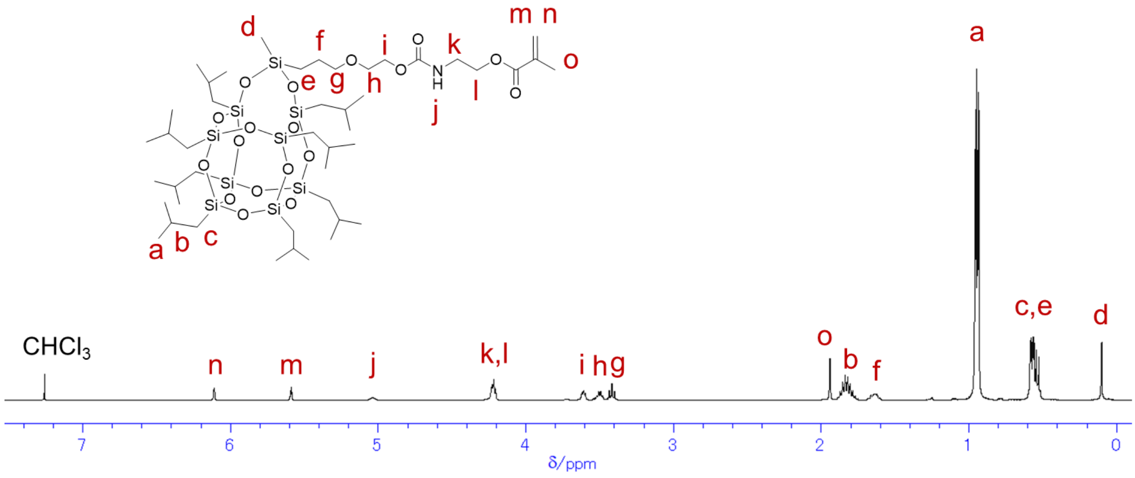


Figure S13. ^{1}H-NMR spectrum (400 MHz) of **5b** in $CDCl_3$.

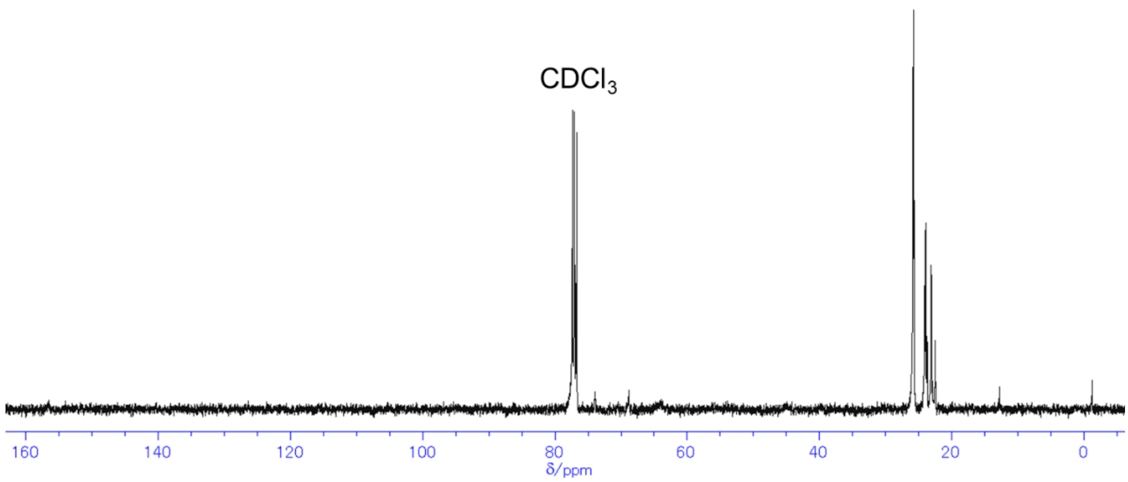


Figure S14. ^{13}C-NMR spectrum (100 MHz) of **5b** in $CDCl_3$.

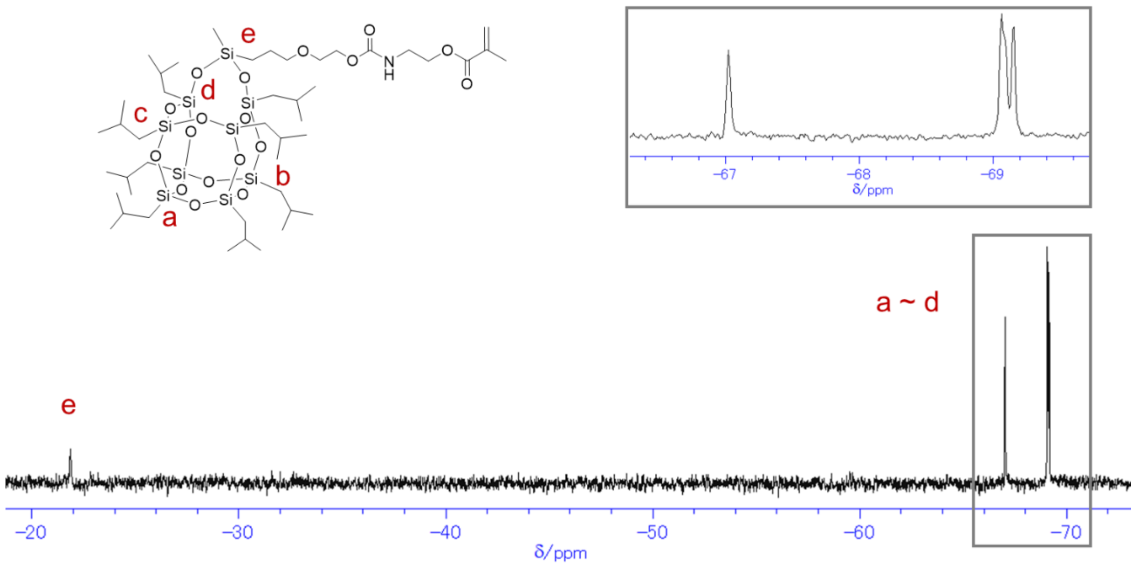


Figure S15. ^{29}Si-NMR spectrum (80 MHz) of **5b** in $CDCl_3$.

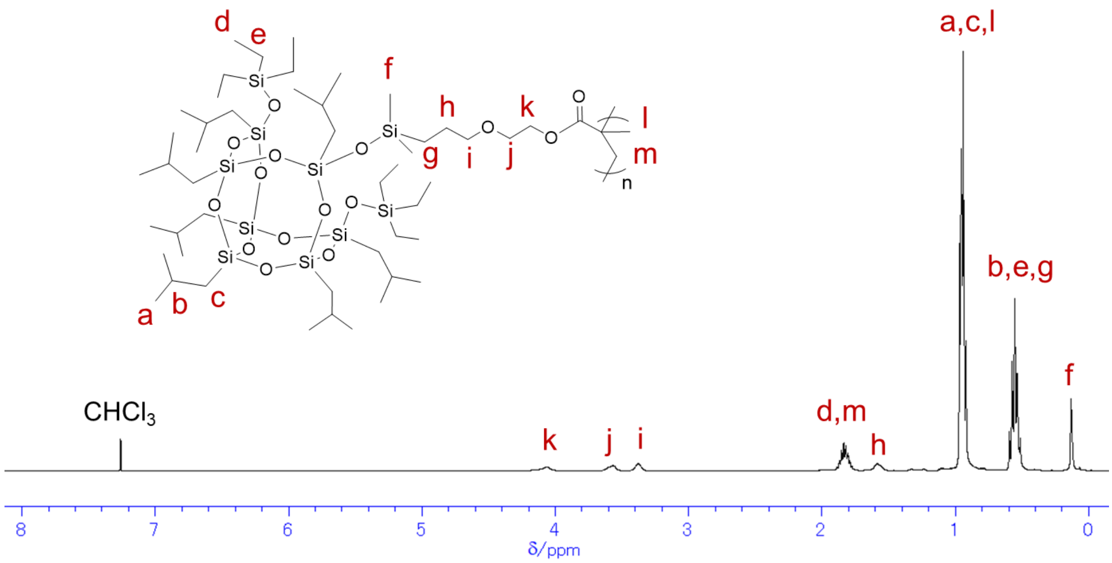


Figure S16. ^{1}H-NMR spectrum (400 MHz) of **6a** in $CDCl_3$.

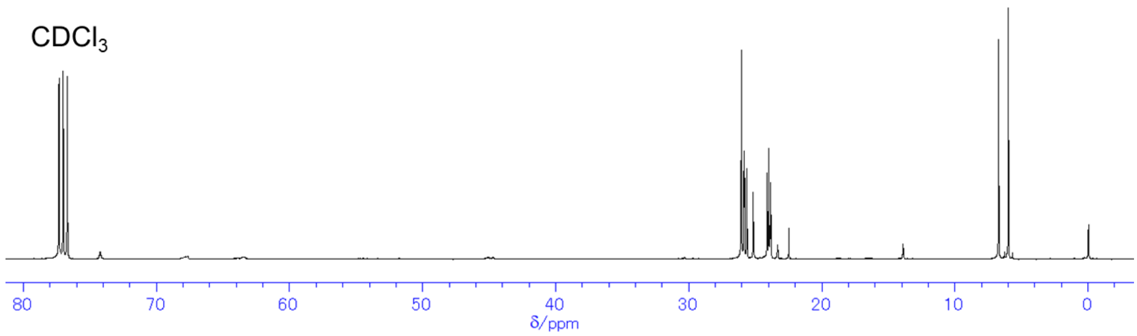


Figure S17. ^{13}C-NMR spectrum (100 MHz) of **6a** in $CDCl_3$.

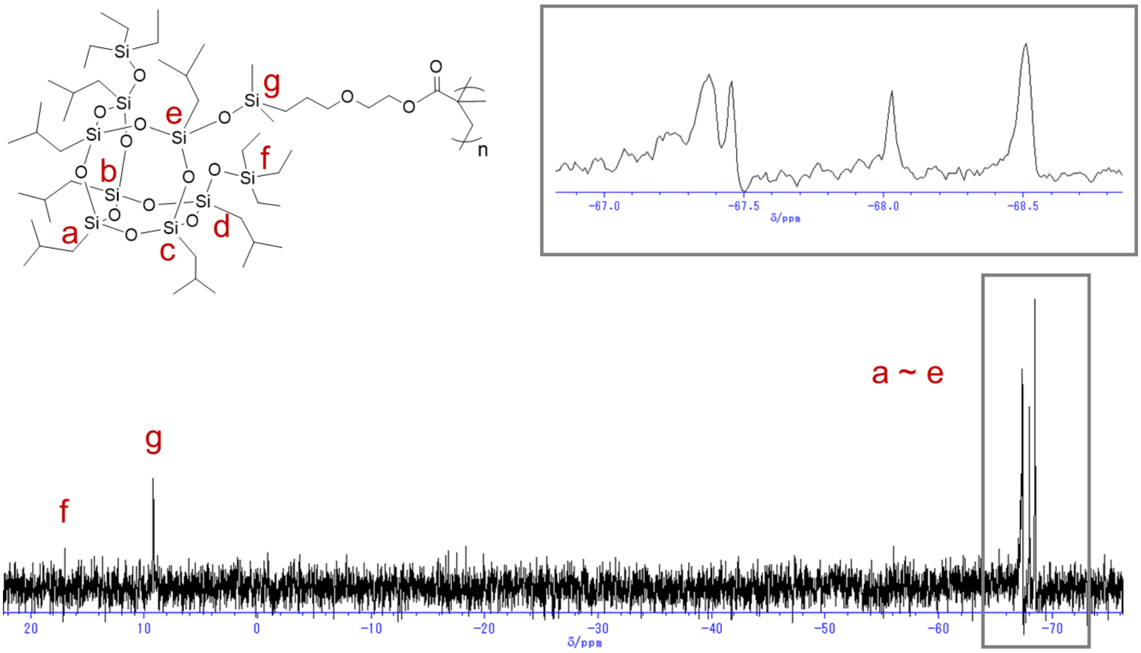


Figure S18. ^{29}Si-NMR spectrum (80 MHz) of **6a** in $CDCl_3$.

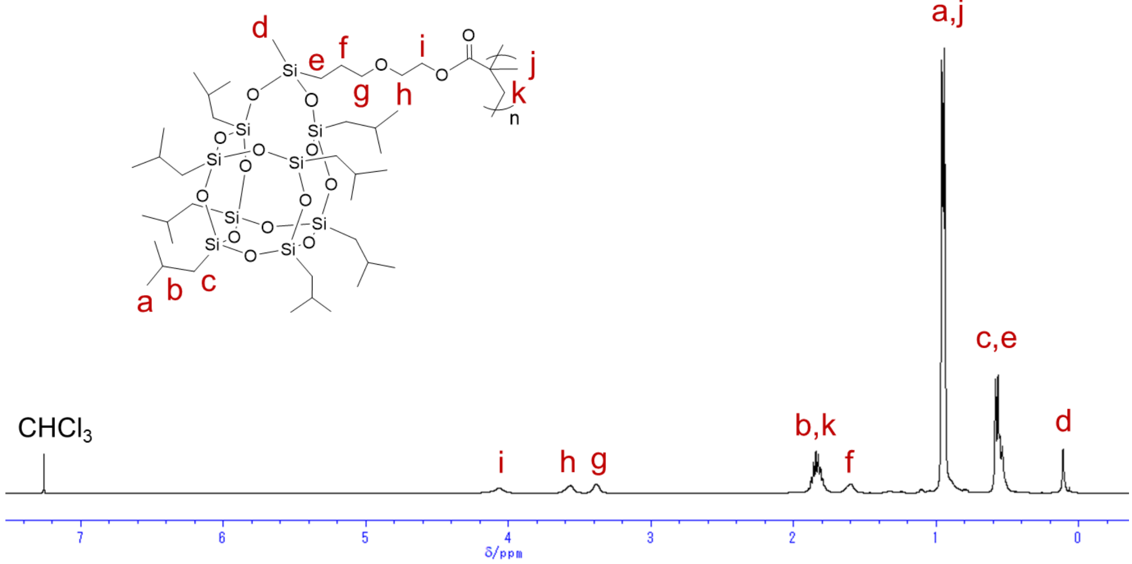


Figure S19. ^{1}H-NMR spectrum (400 MHz) of **6b** in $CDCl_3$.

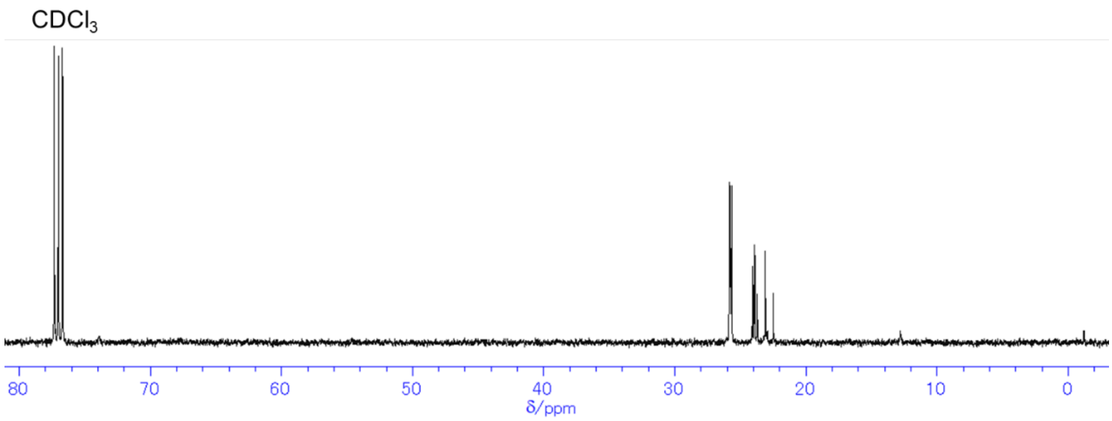


Figure S20. ^{13}C-NMR spectrum (100 MHz) of **6b** in $CDCl_3$.

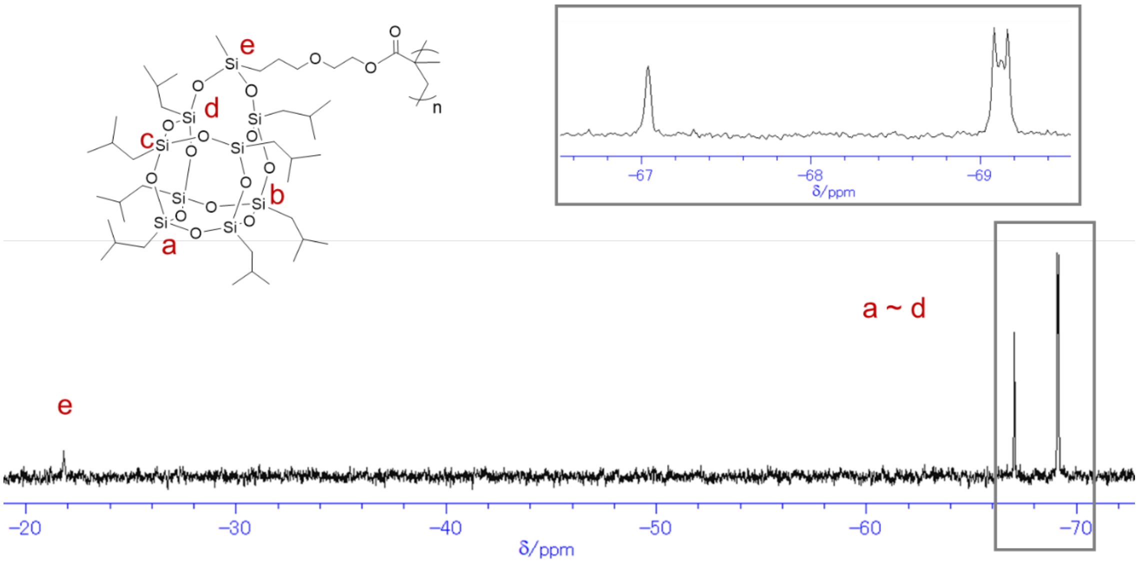


Figure S21. ^{29}Si-NMR spectrum (80 MHz) of **6b** in $CDCl_3$.

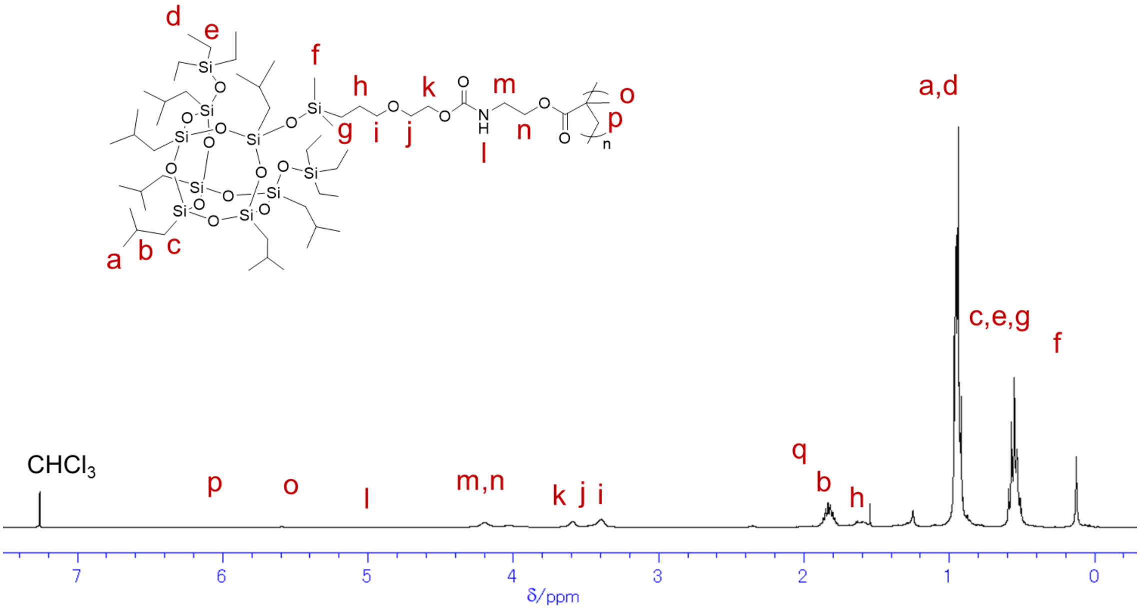


Figure S22. ^{1}H-NMR spectrum (400 MHz) of **7a** in $CDCl_3$.

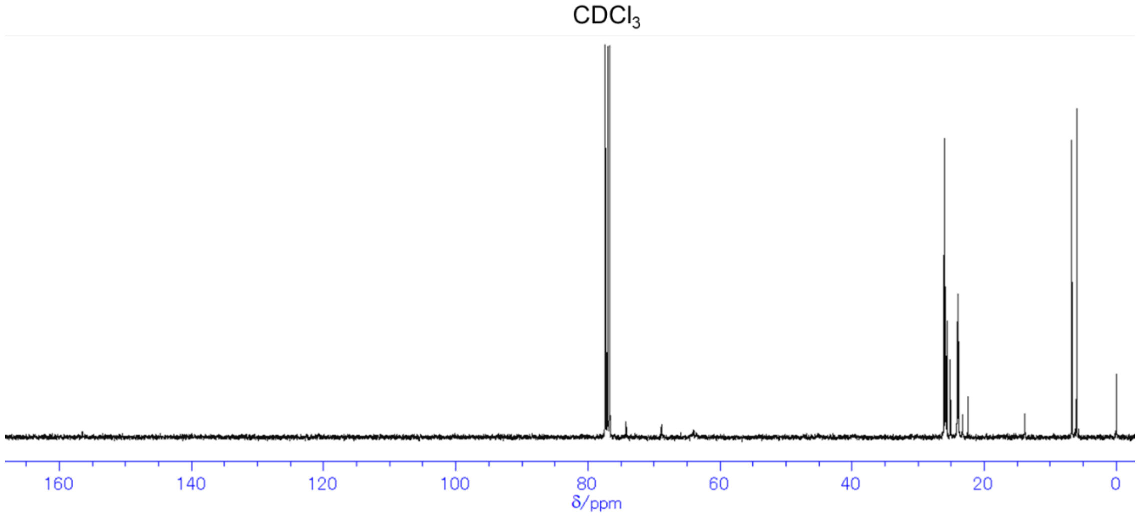


Figure S23. ^{13}C-NMR spectrum (100 MHz) of **7a** in $CDCl_3$.

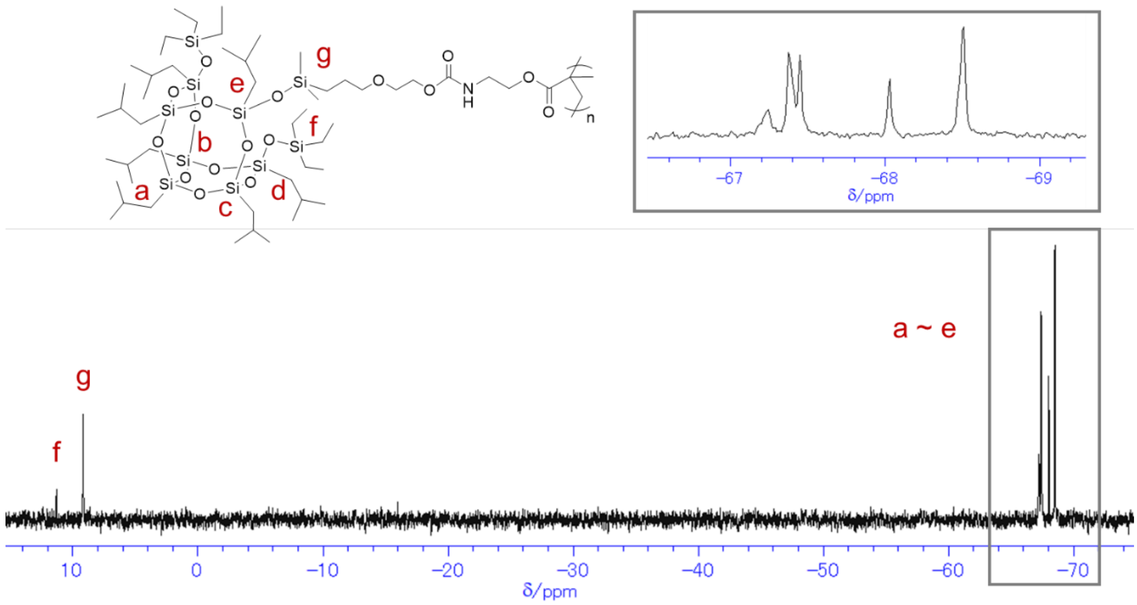


Figure S24. ^{29}Si-NMR spectrum (80 MHz) of **7a** in $CDCl_3$.

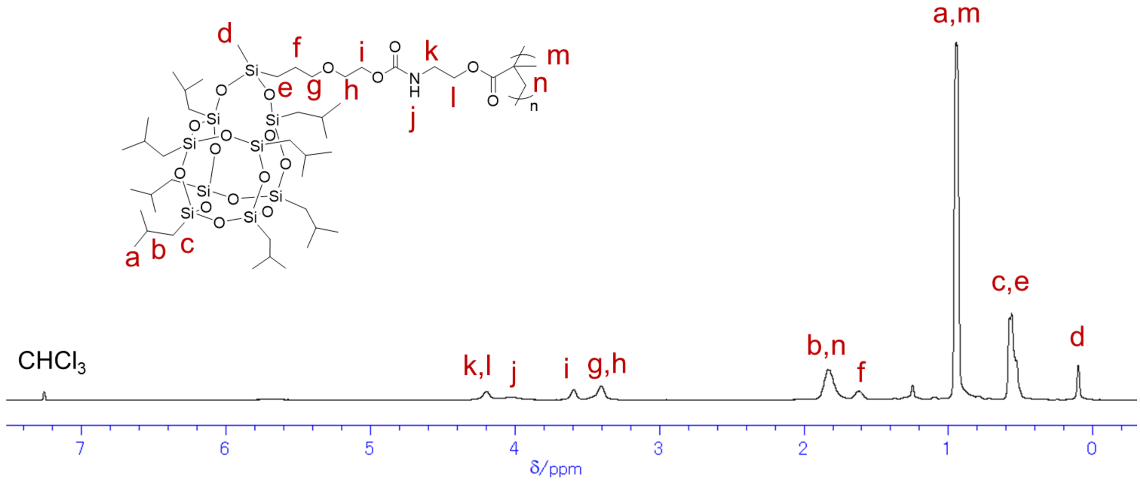


Figure S25. ^{1}H-NMR spectrum (400 MHz) of **7b** in $CDCl_3$.

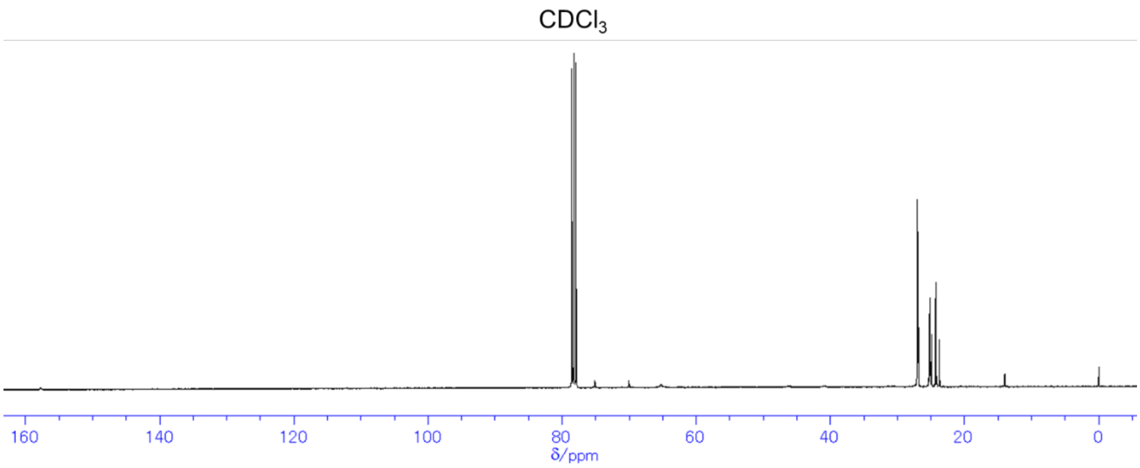


Figure S26. ^{13}C-NMR spectrum (100 MHz) of **7b** in $CDCl_3$.

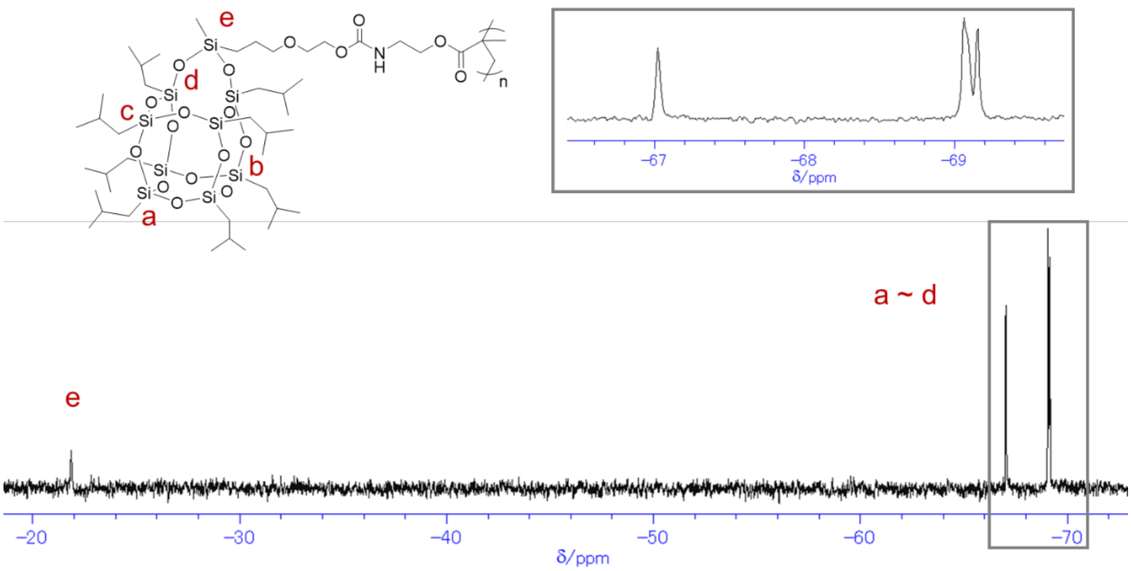


Figure S27. ^{29}Si-NMR spectrum (80 MHz) of **7b** in $CDCl_3$.

2. MALDI-TOFMS

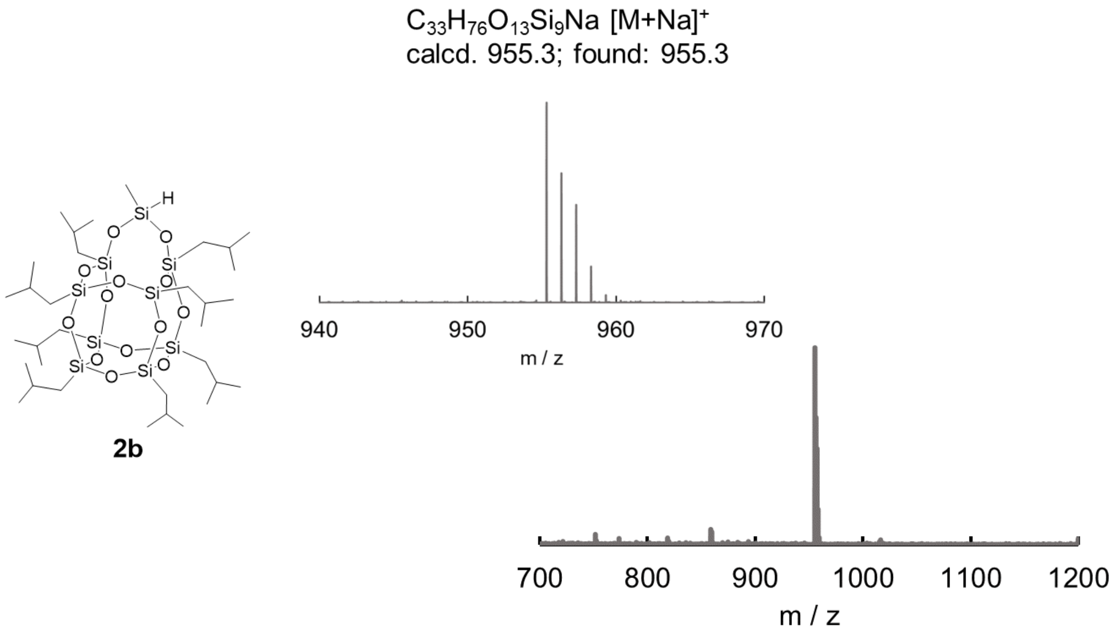


Figure S28. MALDI-TOFMS spectrum (full spectrum and expanded view) of **2b**. Matrix: DCTB (20 mg/mL in $CHCl_3$), cationizing agents: TFANa (1 mg/mL in THF).

3. Nanoindentation

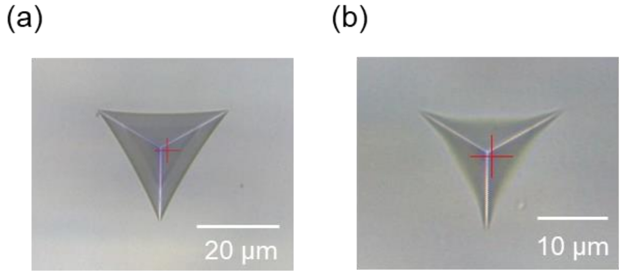


Figure S29. Indentation images of (a) **7a-1** and (b) **7b-1** for dynamic ultra-micro-hardness tests.

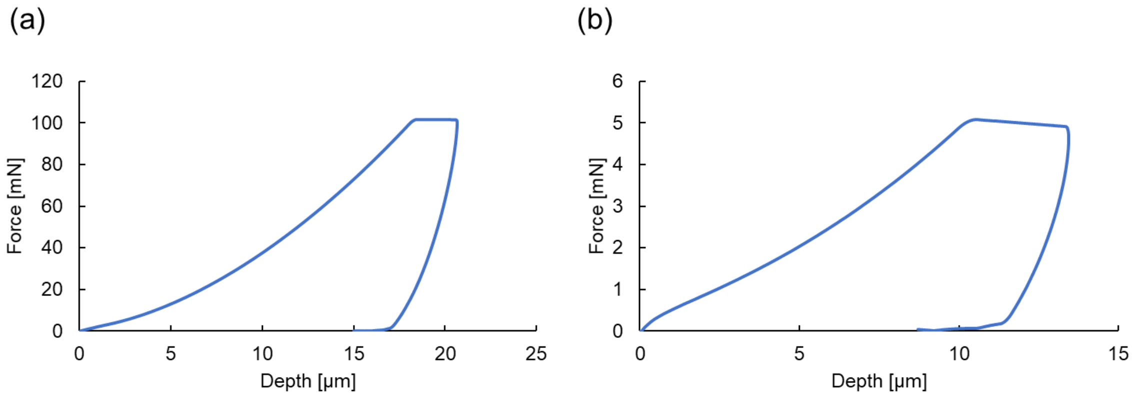


Figure S30. Load-depth nanoindentation curves of (a) **7a-1** and (b) **7b-1** for dynamic ultra-micro-hardness tests.

4. Solubility test

Table S1. Results of solubility test for **2a** and **2b**

	2a	**2b**
n-Hexane	P	P
Diethyl ether	P	P
p-Xylene	P	P
Toluene	P	P
Ethyl acetate	P	P
Chloroform	P	P
THF	P	P

	2a	**2b**
Acetone	P	P
Acetonitrile	F	F
DMF	F	F
DMSO	F	F
Ethanol	F+	F
Methanol	F	F

P: Complete dissolution within 2 min

F+: Significant but incomplete dissolution occurred

F: Little or no dissolution was observed

5. IR spectra

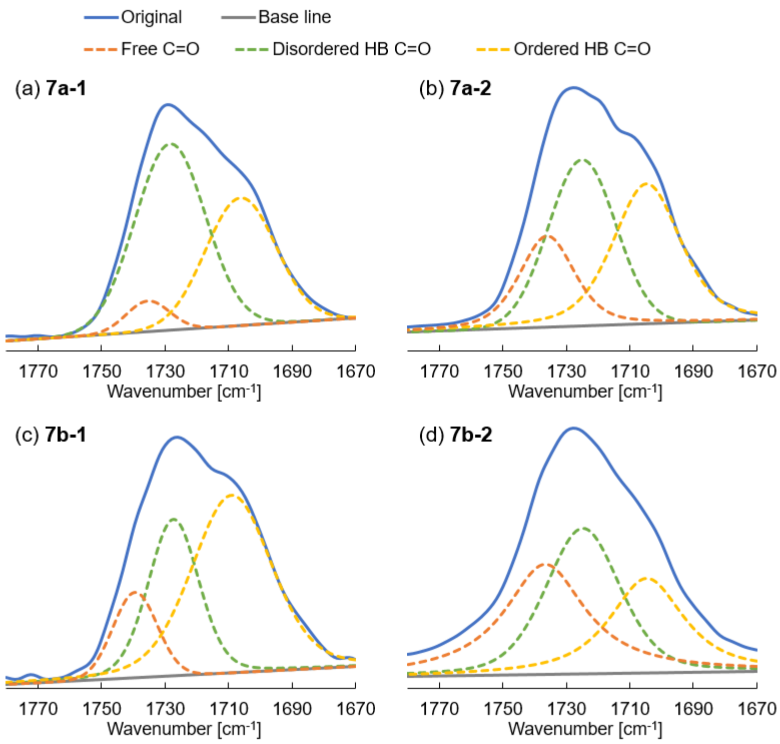


Figure S31. IR spectra of (a) **7a-1**, (b) **7a-2**, (c) **7b-1**, and (d) **7b-2** around the signals due to the C=O groups.

6. Thermal analyses

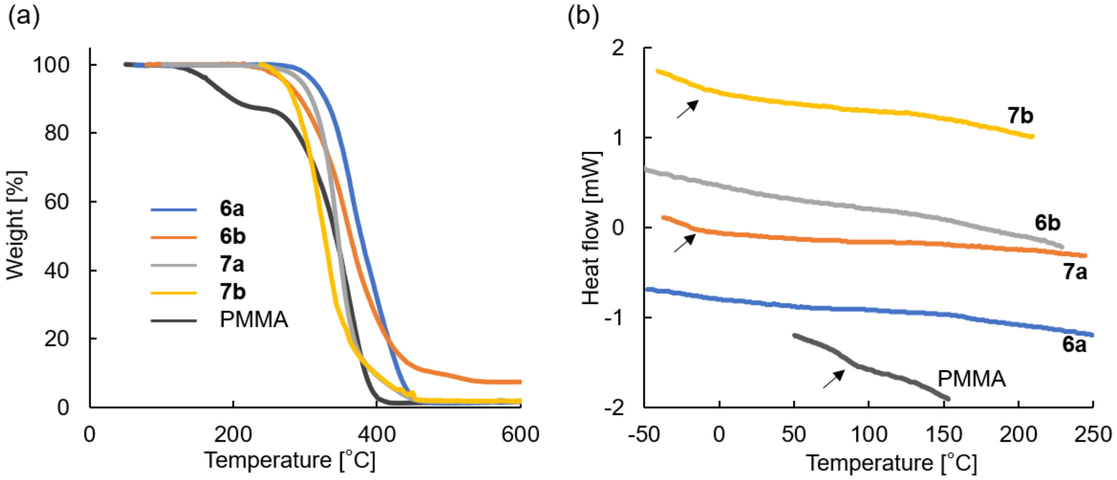


Figure S32. (a) TGA thermograms and (b) DSC curves (second scan) of **6a**, **6b**, **7a**, **7b**, and PMMA (under N_2, 10 °C/min).

7. SEC traces

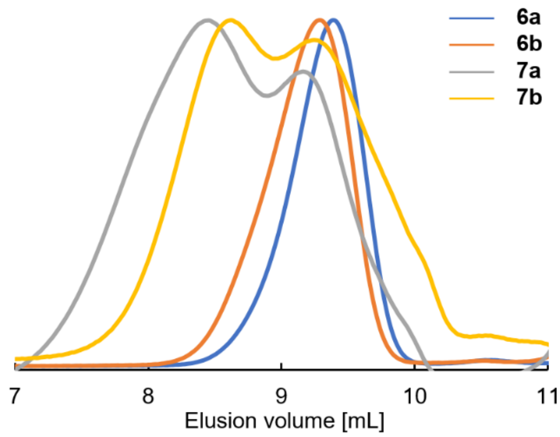
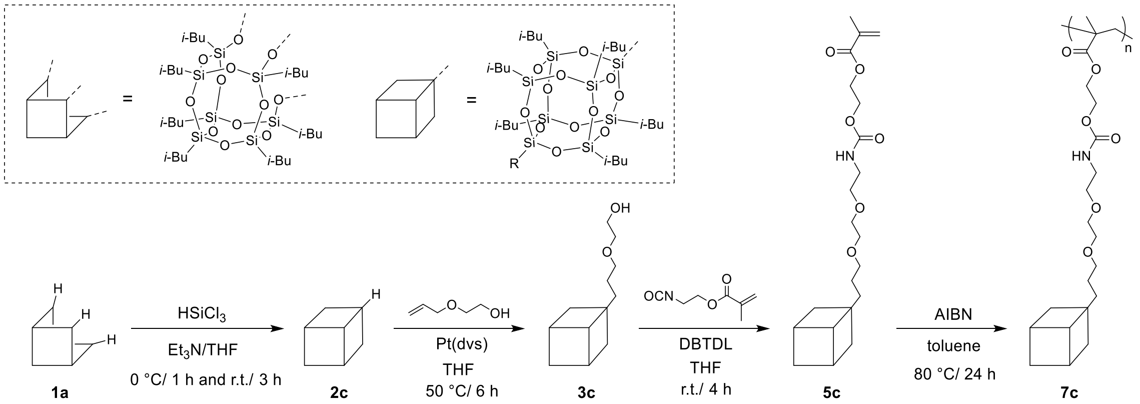


Figure S33. SEC traces (1 mL/min in THF, RI detector) of **6a**, **6b**, **7a**, and **7b**.

8. Cubic POSS-tethering polymer

A polymer having conventional cubic POSSs (**7c**) in the side chain was synthesized as shown in Scheme S1.



Scheme S1. Synthesis of cubic POSS-tethering polymer **7c**

CC-POSS derivatives **2c** and **3c** were prepared according to the literature procedure.[1]

5c: A THF solution (13.5 mL) of **3c** (1.35 g, 1.47 mmol), 2-isocyanatoethyl methacrylate (0.21 mL, 1.47 mmol), and catalytic amounts of dibutyltin(IV) dilaurate (five drops) were stirred at room temperature for 4 h under N_2 atmosphere. The volatiles were removed *in vacuo* to obtain **5c** (1.48 g, 1.38 mmol, 94%) as colorless liquid. ^{1}H-NMR (in $CDCl_3$, 400 MHz): δ 6.11 (s, 1H), 5.59 (s, 1H), 5.13-4.97 (br, 1H), 4.29-4.14 (m, 4H), 3.66-3.56 (m, 2H), 3.54-3.46 (m, 2H), 3.45-3.38 (t, J = 14.0 Hz, 2H), 1.94 (s, 3H), 1.91-1.75 (m, 7H), 1.74-1.58 (m, 2H), 1.08-0.83 (m, 42H), 0.72-0.47 (m, 16H), 0.11 (s, 3H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 167.21, 156.33, 135.95, 126.00, 77.35, 77.03, 76.71, 73.51, 68.84, 64.29, 64.15, 63.74, 40.15, 29.60, 29.49, 29.27, 25.69, 23.88, 23.86, 22.75, 22.50, 22.47, 18.29, 8.16 ppm. ^{29}Si-NMR (in $CDCl_3$, 80 MHz): δ -67.38, -67.65, -67.85 ppm.

7c: A toluene solution (0.50 mL) of **5c** (0.60 g, 0.56 mmol) and AIBN (9 mg, 0.05 mmol) was stirred at 80 °C for 24 h under N_2 atmosphere. After the volatiles were removed *in vacuo*, the residue was dissolved in $CHCl_3$ to be subjected to reprecipitation into acetone. The precipitates were collected by centrifugation to obtain **7c** (0.30 g, 0.28 mmol, 50%) as colorless liquid. ^{1}H-NMR (in $CDCl_3$, 400 MHz): δ 4.60-4.14 (br, 4H), 4.14-3.80 (br, 1H), 3.67–3.53 (br, 2H), 3.53-3.18 (br, 4H), 1.99-1.73 (m, 9H), 1.72-1.58 (br, 2H), 1.09-0.83 (d, 45H), 0.71-0.47 (d, 16H) ppm. ^{13}C-NMR ($CDCl_3$, 100 MHz) δ 156.54, 73.44, 68.74, 63.94, 63.90, 44.95, 39.63, 30.33, 29.35, 28.30, 25.70, 23.86, 23.84, 23.04, 22.70, 22.50, 22.46, 21.97, 8.18 ppm. ^{29}Si-NMR (in $CDCl_3$, 80 MHz): δ -67.40, -67.67, -67.89 ppm. SEC (I mL/min in THF, polystyrene standards): M_n = 27,100, M_w/M_n = 2.88.

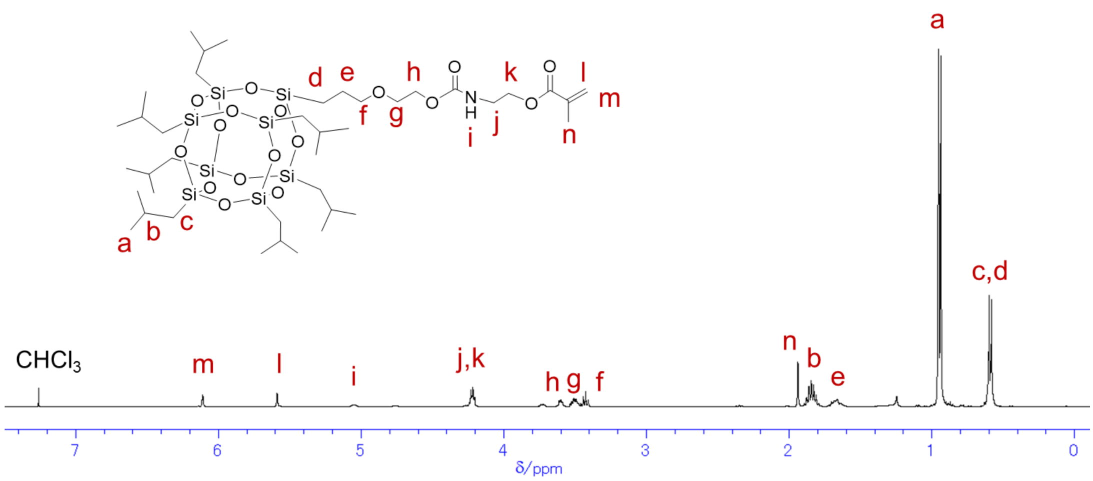


Figure S34. ^{1}H-NMR spectrum (400 MHz) of **5c** in $CDCl_3$.

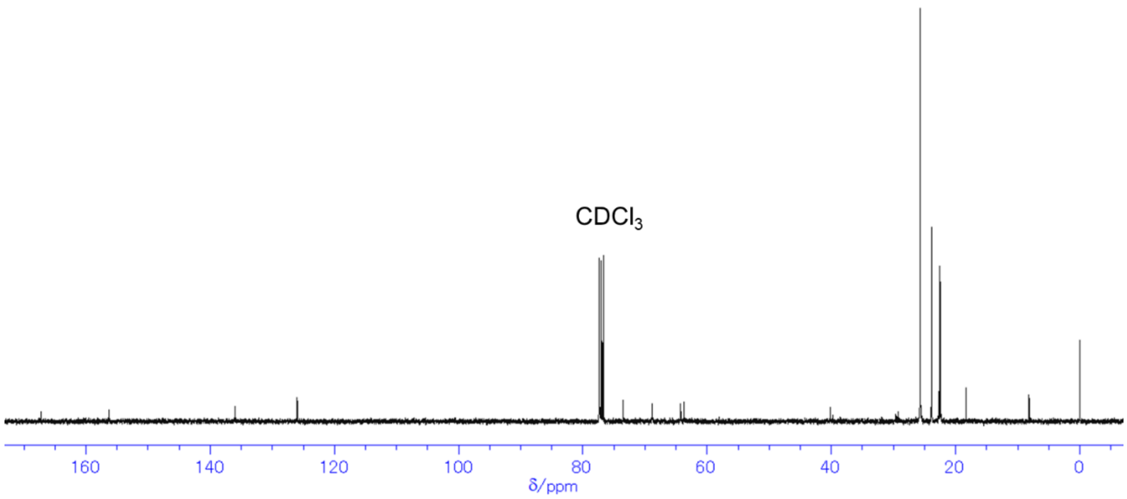


Figure S35. ^{13}C-NMR spectrum (100 MHz) of **5c** in $CDCl_3$.

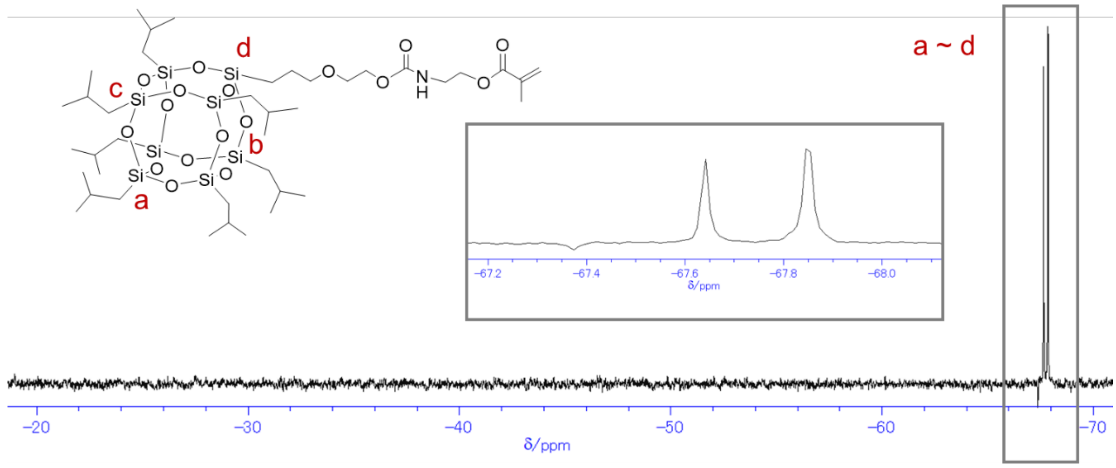


Figure S36. ^{29}Si-NMR spectrum (80 MHz) of **5c** in $CDCl_3$.

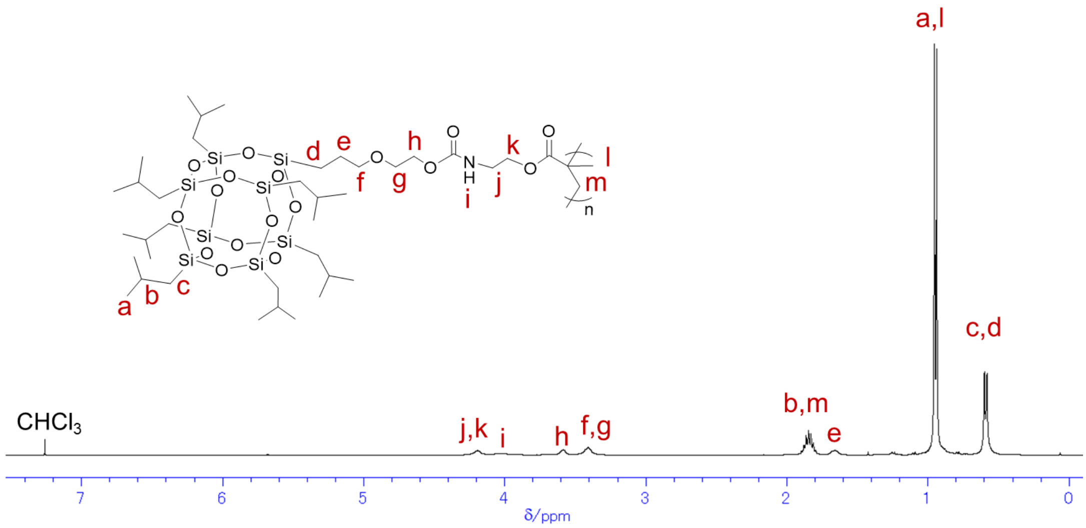


Figure S37. ^{1}H-NMR spectrum (400 MHz) of **7c** in $CDCl_3$.

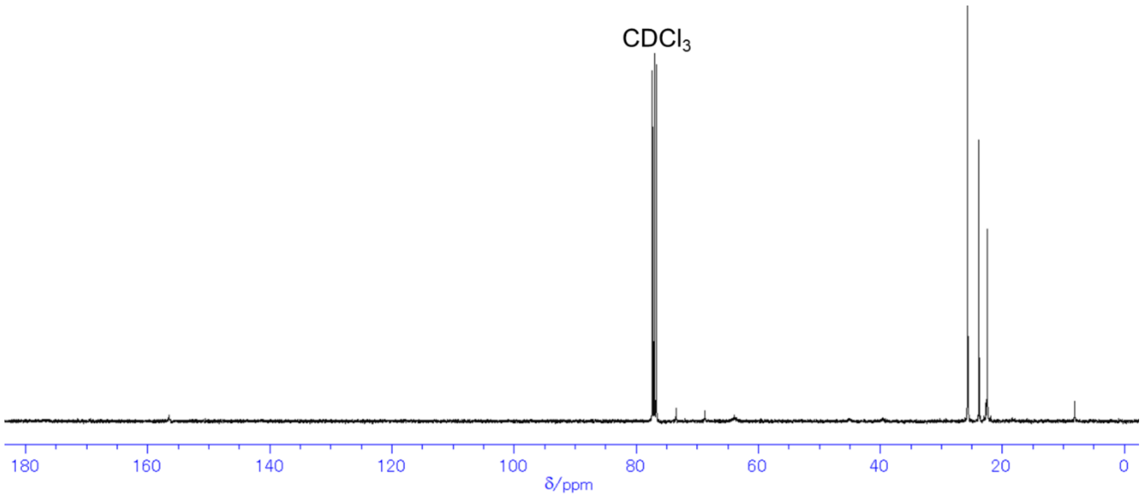


Figure S38. ^{13}C-NMR spectrum (100 MHz) of **7c** in $CDCl_3$.

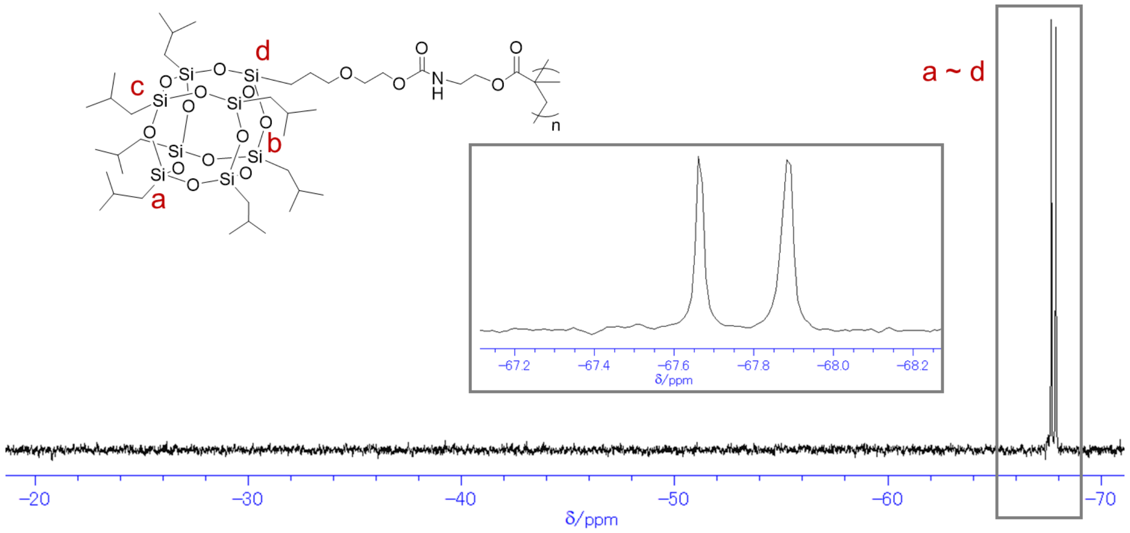


Figure S39. ^{29}Si-NMR spectrum (80 MHz) of **7c** in $CDCl_3$.

Polymer **7c** was dissolved in $CHCl_3$, and the solution was casted onto a glass substrate. The cast film was dried for 24 h under the ambient condition, and the brittle film was obtained (Figure S40a). The PXRD pattern of **7c** indicated the high crystallinity (Figure S40b).

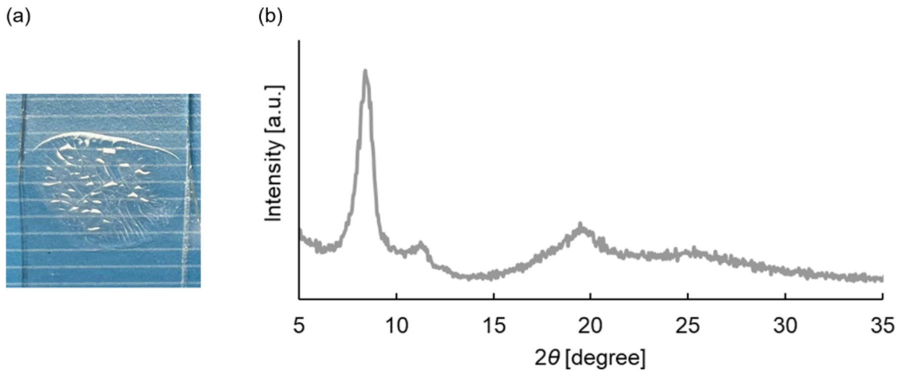


Figure S40. (a) Photograph and (b) PXRD pattern of polymer **7c**

9. Cartesian coordinates in the structures optimized by DFT calculations

2a'

Si	-3.2067	-0.2455	0.7455
Si	4.8818	-0.3866	-1.1503
O	-3.1078	-1.1809	-0.5977
Si	-2.2025	-2.1771	-1.5528
O	-0.6861	-2.3052	-0.9108
Si	0.3074	-2.8192	0.2905
O	-0.441	-2.6328	1.7514
Si	-1.2626	-1.6481	2.7884
O	-2.6187	-1.0699	2.0523
Si	-1.6121	2.4695	1.1299
Si	2.621	-0.8268	1.0623
Si	0.6165	0.904	2.7597
O	-1.0737	3.3678	-0.1231
O	-0.3452	2.0651	2.1106
O	1.6961	0.4227	1.6129
O	3.712	-0.1962	0.0281
C	-3.0342	-3.8418	-1.6468
C	0.7473	-4.6135	0.0645
C	-4.9913	0.1798	1.0528
C	-1.7486	-2.6129	4.299
C	1.4882	1.6049	4.2458
O	1.6724	-1.9037	0.2451
O	-2.2915	1.1021	0.5096
O	-0.291	-0.392	3.2318
O	-2.0871	-1.5504	-3.0544
C	3.4654	-1.6887	2.4893
H	-2.4577	-4.5361	-2.2679
H	-3.1462	-4.2858	-0.651
H	-0.149	-5.2433	0.0784
H	1.413	-4.9579	0.8634
H	-5.1045	0.805	1.9451
H	-5.4107	0.7238	0.1996
H	-0.8657	-3.0152	4.807

H	-2.2894	-1.978	5.0087
H	2.1067	2.4636	3.963
H	2.1386	0.8564	4.7114
H	4.0739	-2.5289	2.1354
H	4.1257	-1.0018	3.0308
C	-2.8602	3.4271	2.1323
H	-2.4119	4.3383	2.5437
H	-3.716	3.7224	1.5153
Si	0.1932	4.2639	-0.755
Si	-1.5016	-0.334	-4.0461
C	5.2141	-2.2257	-1.4125
H	4.2982	-2.7527	-1.7048
H	5.958	-2.3855	-2.203
H	5.5959	-2.7005	-0.5004
C	4.2622	0.4042	-2.7407
H	5.0215	0.3529	-3.5312
H	3.3604	-0.0987	-3.108
H	4.0103	1.4592	-2.5833
C	0.8795	5.3977	0.5882
H	1.714	6.0014	0.2099
H	0.1126	6.0888	0.9583
H	1.2481	4.8179	1.4425
C	-0.5278	5.2775	-2.1692
H	-1.3062	5.9607	-1.8094
H	0.2442	5.8807	-2.6629
H	-0.9808	4.627	-2.9263
C	-2.0749	-0.7527	-5.7913
H	-3.169	-0.7907	-5.8493
H	-1.728	-0.0045	-6.5149
H	-1.6902	-1.7286	-6.1099
C	-2.2091	1.3204	-3.4901
H	-1.8399	2.1379	-4.123
H	-3.3039	1.3222	-3.5528
H	-1.937	1.5473	-2.4528
C	1.5293	3.0923	-1.374
H	1.8888	2.4384	-0.5709

H	2.3895	3.6474	-1.7701
C	0.3803	-0.3259	-3.9478
H	0.7156	-0.1658	-2.9166
H	0.8118	0.4665	-4.5722
H	0.796	-1.2826	-4.2862
H	-2.3986	-3.4524	4.0304
C	6.4378	0.4824	-0.5374
H	6.2442	1.5425	-0.3359
H	7.2448	0.4251	-1.2784
H	6.806	0.0298	0.391
H	2.7335	-2.0862	3.2022
H	1.148	2.4508	-2.177
H	1.2569	-4.7699	-0.8925
H	-4.0333	-3.7484	-2.086
H	0.7665	1.9398	4.9986
H	-3.2355	2.8323	2.9732
H	-5.5855	-0.7286	1.1996

2b’

Si	-2.78543	-1.55996	-0.18975
Si	1.648356	-2.237	-0.46945
O	-1.81024	-2.15676	0.996322
Si	-0.45321	-2.00079	1.919066
O	-0.39948	-0.4875	2.56574
Si	-0.33465	1.1432	2.367258
O	-1.73167	1.680078	1.676736
Si	-2.7581	1.573165	0.390042
O	-3.18219	-0.00064	0.158984
Si	-0.64463	-1.1172	-2.45375
Si	1.68545	2.231035	0.114578
Si	-0.72372	2.026163	-1.9934
O	0.693862	-1.50906	-1.59112
O	-0.68566	0.515238	-2.64364
O	0.668849	2.315096	-1.17265
O	2.996391	1.335603	-0.29062

C	-0.49388	-3.24711	3.295636
C	-0.12336	1.951507	4.027101
C	2.04307	-3.98431	-0.97576
C	-4.32823	-2.58613	-0.30178
C	-4.27705	2.586147	0.72504
C	-0.91522	3.271924	-3.35709
O	0.9313	1.493766	1.380088
O	-1.98488	-1.61478	-1.62997
O	-2.00079	2.144247	-0.95615
O	0.876921	-2.2455	0.986021
C	2.218571	3.953653	0.579056
H	0.409206	-3.17474	3.911021
H	-0.55383	-4.266	2.898447
H	-1.36137	-3.08305	3.943682
H	-0.95441	1.694456	4.692529
H	0.806753	1.624377	4.504051
H	-0.09161	3.042185	3.931085
H	2.683281	-4.47	-0.23131
H	1.129175	-4.5809	-1.07456
H	2.567844	-4.00482	-1.93708
H	-4.88141	-2.5617	0.643045
H	-4.98706	-2.21124	-1.09216
H	-4.08571	-3.62996	-0.52749
H	-4.79905	2.221414	1.615975
H	-4.0153	3.636723	0.889753
H	-4.9711	2.536985	-0.12065
H	-0.95677	4.289417	-2.95411
H	-1.8354	3.091873	-3.92295
H	-0.07116	3.215598	-4.05271
H	2.889955	3.938283	1.444651
H	1.354312	4.578415	0.831131
H	2.748999	4.432524	-0.25122
C	-0.61778	-1.92412	-4.12702
H	0.268143	-1.61466	-4.69178
H	-0.60033	-3.01557	-4.03639
H	-1.50433	-1.64667	-4.70714

O	3.041916	-1.3907	-0.34138
Si	3.916136	-0.0193	-0.02523
C	5.345433	0.037037	-1.23096
C	4.463083	-0.06531	1.76712
H	4.976068	0.074087	-2.2619
H	5.982564	-0.84946	-1.13262
H	5.96952	0.922952	-1.066
H	5.062782	-0.95894	1.975723
H	3.592153	-0.08375	2.432064
H	5.066438	0.813175	2.02499

10. Reference

[1] Y. Sato, H. Imoto, K. Naka, *J. Polym. Sci.* **2020**, *58*, 1456.