Electronic Supplementary Information

Caterpillar-shaped polysilsesquioxanes

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EXPERIMENTAL

Materials

DDSQ was prepared according to the literature.[1] Dichloromethylsilane (analytical grade), dichlorodimethylsilane (analytical grade), pyridine (analytical grade), triethylamine (analytical grade), and tris(pentafluorophenyl)borane (99%) were purchased from J & K Scientific Co. Ltd (Shanghai, China) and used as received. Tetrahydrofuran (THF) and toluene were dried by refluxing with sodium-benzophenone under dried air and collected by distillation.

Characterization

Matrix-assisted laser desorption/ionization time of flight mass spectra (MALDI TOF MS) measurements were carried out with a Bruker microflex MALDI-TOF mass spectrometer equipped with a nitrogen laser emitting at 337 nm. THF solutions of 2,5-dihydroxybenzoic acid (0.078 mg/mL) and sodium trifluoroacetate (0.068 mg/mL) were mixed in the ratio of 1/1 (v/v) was chosen as the matrix solution. Matrix solution was mixed with each sample solution (10 mg/mL in THF) in the ratio of 7/1(v/v). The samples were dried in air for at least 30 min, and the measurements were performed in the linear mode. Gel permeation chromatography (GPC) was performed in toluene at a flow rate of 1.0 mL/min on a Waters chromatograph. The system has a light scattering detector (DAWN HELEOS) and in-line viscometer (ViscoStar), calibrated using monodisperse polystyrene standards (Polymer Laboratories). The multi-angle laser light scattering (MALLS) method was used to determine absolute molecular weights of polymers. The polymer solution (ca. 10 mg/mL) was prepared by dissolving the polymer in toluene. For the in-line measurements of intrinsic viscosities and molecular weights, the intrinsic viscosities and molecular weights were measured utilizing a Waters GPC with triple-detection which included a refractive index detector, a light scattering detector and in-line viscometer. The refractive index increment dn/dc was determined for caterpillar-shaped PSSQs. Each set of data points corresponding to η and M_w in Figure S10 were thus measured on an individual slice of the GPC

chromatogram. Fourier transform infrared (FT-IR) spectra were got as KBr discs on a Nicolet 5700 FT-IR spectrometer. ^{1}H nuclear magnetic resonance (NMR) spectra (400 MH_Z) and ^{29}Si NMR spectra (99 MH_Z) were recorded on Bruker UltraShield 400 and Bruker Ascend 500, respectively. Chemical shifts (δ) were given in parts per million (ppm) and tetramethylsilane was used as an internal standard. The samples were coated on slide glass and silicon wafer by spin-coating for the measurements of optical transmittances and refractive indices, respectively. Optical transmittances were measured on a ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu, S-3150). Refractive indices were measured on a spectroscopic ellipsometer (J. A. Woollam, M-2000V) at 25 ^{o}C. Thermal stability was evaluated by measuring thermogravimetric analysis (TGA) thermograms on a Netzsch TG209 under nitrogen and air at a heating rate of 10 ^{o}C/min.

Preparation of partially methyldisiloxyl capped DDSQ 3

At room temperature and under nitrogen, 0.22 g (1.9 mmol) of dichloromethylsilane was slowly dropped into a flask containing 2.0 g (1.9 mmol) of DDSQ, 0.30 g (3.8 mmol) of pyridine and 30 mL of THF. Then the reaction mixture was stirred for 6 hours. After that, 10 mL of deionized water and 10 mL of n-hexane were added into the reaction system. After the water layer was separated out, the organic layer was washed with deionized water to neutral, and dried over anhydrous sodium sulfate. After solvent was removed, a white solid could be found. 5 mL of chloroform was added into the white solid, and the mixture was stirred vigorously for 10 min. Then, the mixture was kept in a freezer (-20 ^{o}C) for 12 hours. After insoluble solid was removed by filtration, a clear solution was obtained. After solvent was removed, a white solid was observed. The white solid was extracted with refluxed n-hexane in a Soxhlet extractor for 6 hours. At last, a white solid was obtained (0.80 g, 40%), after the solvent was moved out.

MALDI TOF MS (m/z): 1133.4 ([M+Na]$^{+}$, cald. 1133.1); ^{1}H-NMR (400 MHz, $CDCl_3$, TMS, δ in ppm): 7.16-7.56 (m, 40H, -C_6H_5), 4.96-4.98 (q, *J*=1.6 Hz, 1H, Si-*H*), 4.69 (s, 2H, Si-O*H*), 0.36 (d, *J*=1.6 Hz, 3H, Si-CH_3); ^{29}Si-NMR (99 MHz, $CDCl_3$, TMS, δ in ppm): -32.84 (s, CH_3-*Si*-H), -68.63 (s, Ph-*Si*-OH), -77.89 [s, (MeHSiO)-*Si*-Ph], -79.06 and -79.25 [s, Ph*Si*$(OSi)_3$]; FT-IR (KBr, cm^{-1}): 3307 (ms, br, ν_{OH}), 3074 (w, ν_{C-H} of Phenyl), 2870 (m, ν_{C-H} of CH_3-), 2174 (ms, ν_{Si-H}), 1978, 1904, 1829, 1777 (w, γ_{C-H} of C_6H_5-), 1594 (m, ν_{Si-C} of Si-CH_3), 1431 (m, ν_{Si-C} of Si-Ph), 1079 (s, br, $\nu_{Si-O-Si}$).

Preparation of caterpillar-shaped PSSQs 2

At room temperature and under nitrogen, 18 mL of mixture of toluene and THF ($v_{toluene}/v_{THF}$=4/1) was added into a Schlenk flask containing 0.55 g (0.49 mmol) of **4**. After **4** was dissolved, 0.50 mL toluene solution containing 20 mg (0.039 mmol) of $B(C_6F_5)_3$ was added into the reaction system. Then the reaction mixture was stirred for 5 days. After solvent was removed, a white solid could be found. The solid was washed with n-hexane to remove the catalyst. Then the product was dissolved in 5 mL of toluene, and 30 mL of methanol was dropped into the solution. After the mixture stands for 8 hours, the product was taken out over a centrifuge. At last, a colorless film solid was obtained (0.50 g, 91%), after the solvent was moved out.
^{1}H-NMR (400 MHz, CD_3COCD_3, TMS, δ in ppm): 6.93-7.67 (m, 739H, -C_6H_5), 5.03-5.04 (m, 1H, Si-*H*), 0.45 (d, *J*=1.6 Hz, 3H, H-Si-CH_3), 0.13-0.40 (50H, O-Si-CH_3); ^{29}Si-NMR (99 MHz, $CDCl_3$, TMS, δ in ppm): -33.00 (m, Me-*Si*-H), -55.80 (m), -57.16 (m), -62.39 (s), -62.54 (s), -64.46 (m) [Me*Si*$(OSi)_3$], -69.51, -69.60 (s, Ph-*Si*-OH), -75.44 (s), -75.48 (s), -78.33~-79.67 [m, Ph*Si*$(OSi)_3$]; FT-IR (KBr, cm^{-1}): 3307(ms, br, ν_{OH}), 3074 (w, ν_{C-H} of Phenyl), 2178 (w, ν_{Si-H}), 1978, 1904, 1829, 1777 (w, γ_{C-H} of C_6H_5-), 1594 (m, ν_{Si-C} of Si-CH_3), 1430 (m, ν_{Si-C} of Si-Ph), 1081 (s, br, $\nu_{Si-O-Si}$); GPC: M_n=11.7 kDa, M_w/M_n=1.98.

Preparation of 4

At room temperature and under nitrogen, 0.10 g (0.78 mmol) of dichlorodimethylsilane was slowly dropped into a flask containing 0.14 g (0.13 mmol, calulated as one repeating unit) of **2**, 0.15 g (1.5 mmol) of triethylamine and 10 mL of THF. Then the reaction mixture was stirred for 18 hours. After that, 10 mL of deionized water and 20 mL of toluene were added into the reaction system. After the water layer was separated out, the organic layer was washed with deionized water to neutral, and dried over anhydrous sodium sulfate. After solvent was removed, a brown solid could be found. 10 mL of toluene was added into the solid, and a transparent solution could be found. Then, the solution was poured into 50 mL methanol, and some precipitation was observed. After filtration, and the solvent was removed under vacuum, a white solid was obtained (0.14 g, 93%).
^{29}Si-NMR (99 MHz, $CDCl_3$, TMS, δ in ppm): -8.80~-9.26 [m, Me_2Si(-O-)OH], -16.71~-16.74[m, Me_2Si(-O-)$_2$], -62.70 (s), -62.78 (s) [Me*Si*$(OSi)_3$], -75.43~-80.76 [m, Ph*Si*$(OSi)_3$].

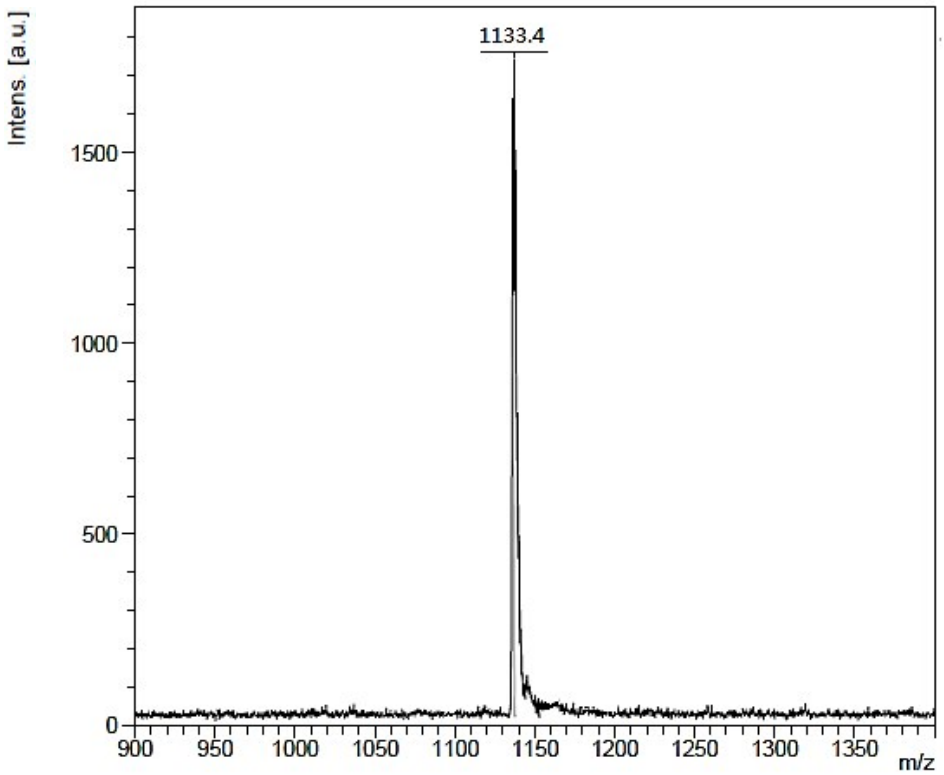

Figure S1 MALDI TOF MS of **3**

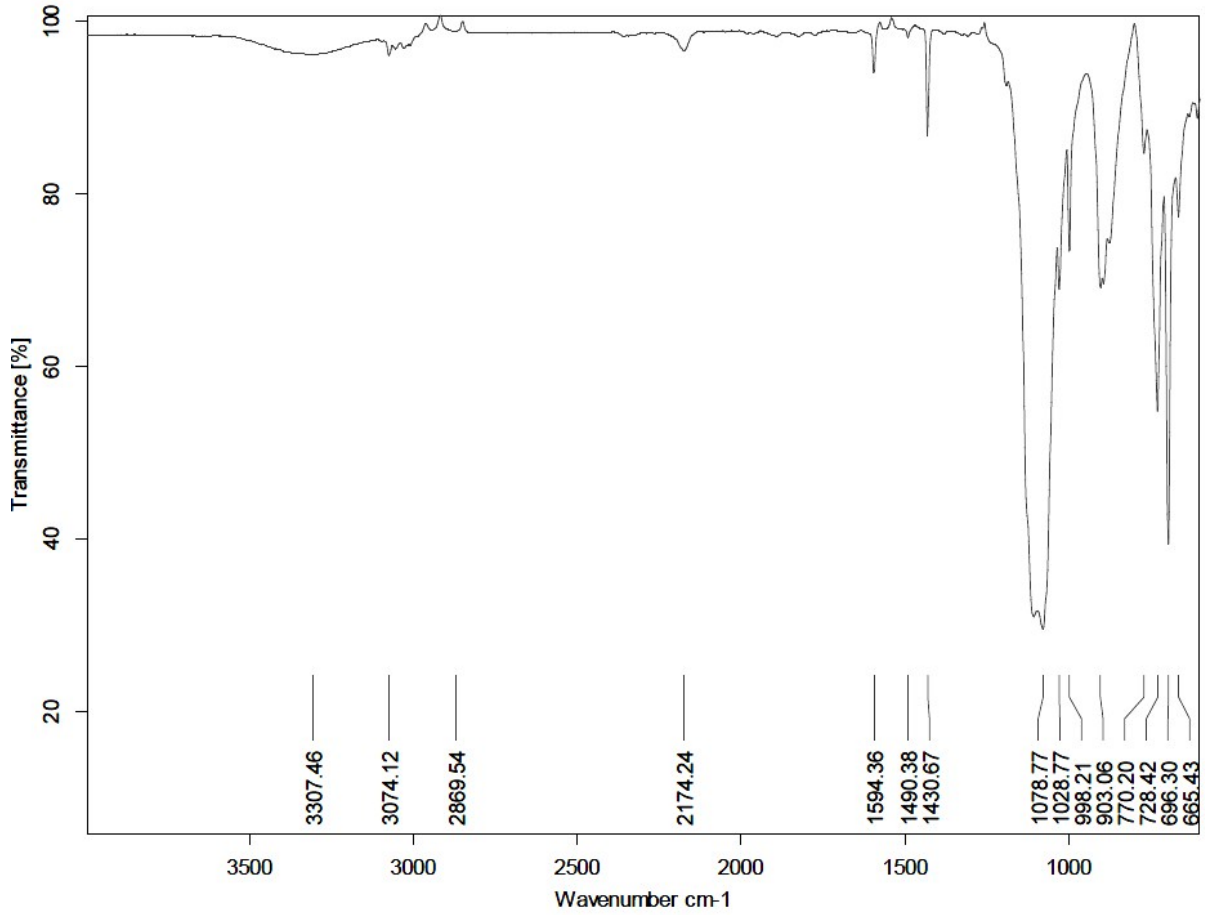

Figure S2 IR spectrum of **3**

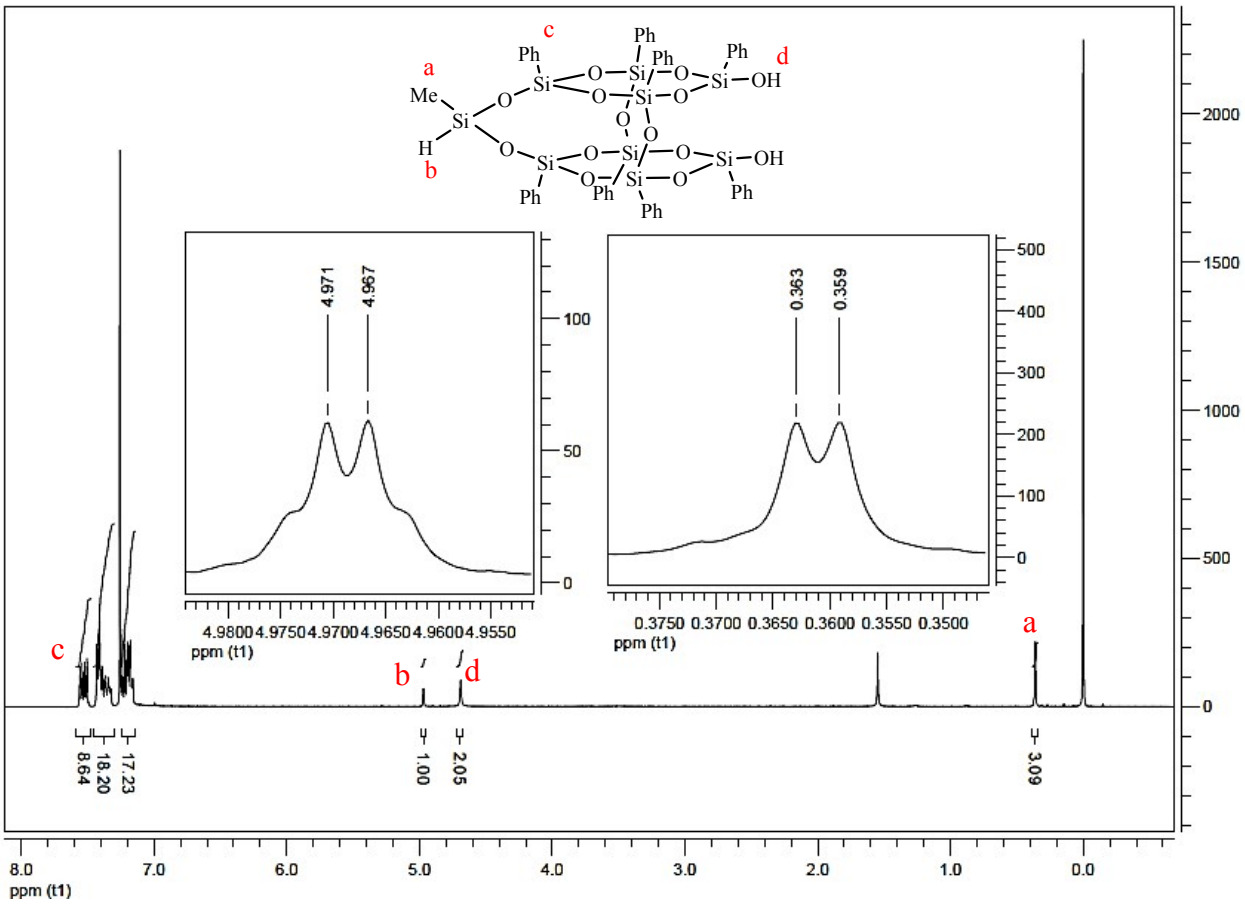

Figure S3 ^{1}H-NMR spectrum of **3** (in chloroform-*d*)

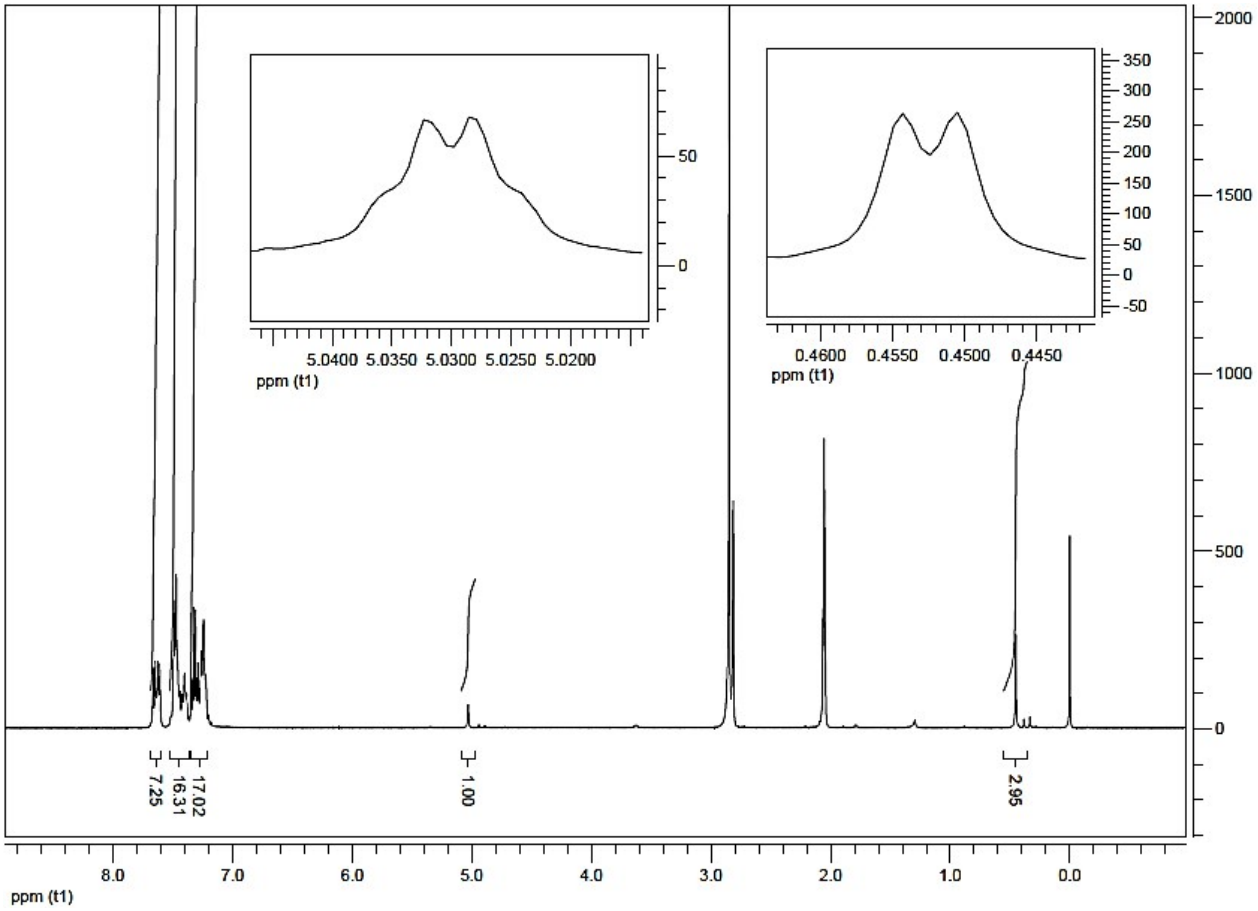

Figure S4 ^{1}H-NMR spectrum of **3** (in acetone-d_6)

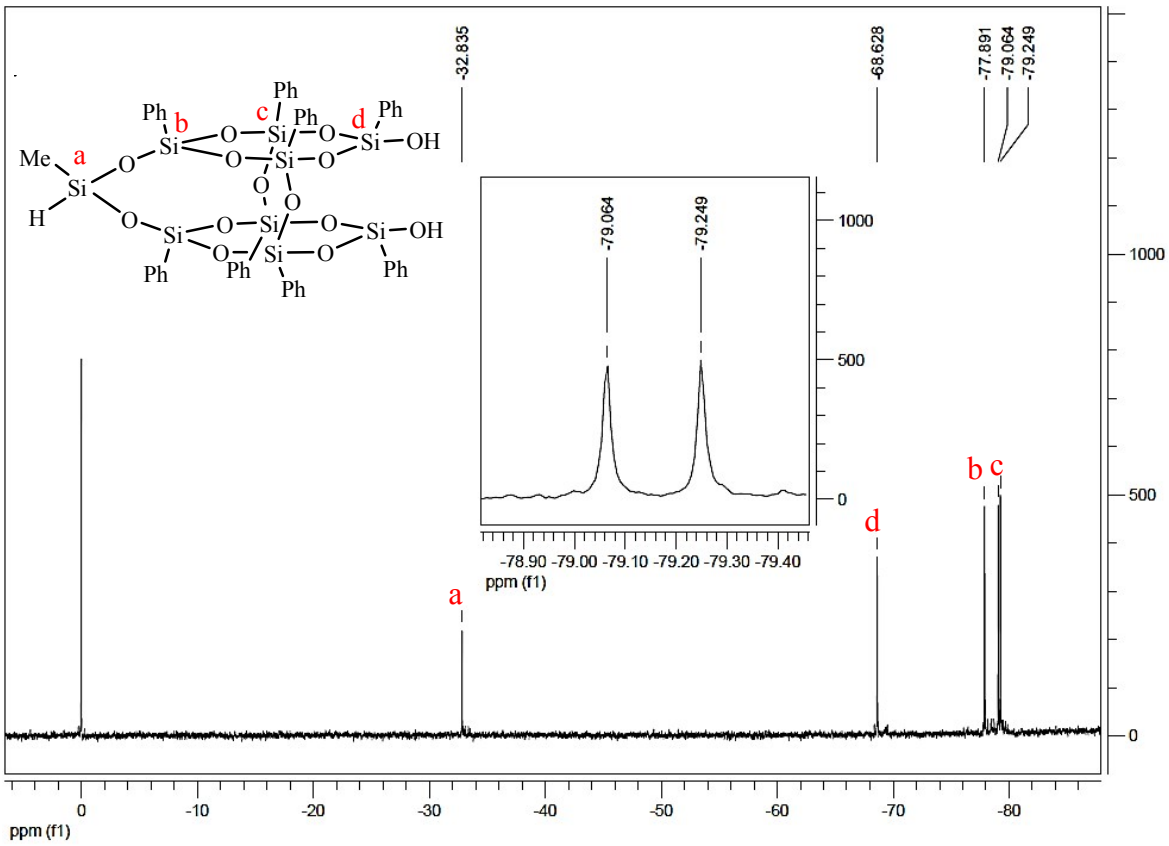

Figure S5 ^{29}Si-NMR spectrum of **3**

Table S1 Reaction conditions performed for the polymerization of **3**

Run	[**3**] (mol L^{-1})	$B(C_6F_5)_3$/**3** (molar ratio)	Solvent	Temperature (^oC)	Time (days)	M_n[a] (kDa)	M_w/M_n[a]	Conversion[a] (%)
1	0.90	0.05/1	THF	25	3	1.9	1.48	65
2	0.90	0.05/1	Toluene/THF= 1/4 (v/v)	25	3	2.6	1.06	64
3	0.90	0.05/1	Toluene/THF =1/2 (v/v)	25	3	2.5	1.10	34
4	0.90	0.05/1	Toluene/THF =1/1 (v/v)	25	3	3.6	1.17	45
5	0.90	0.05/1	Toluene/THF =1/0.5 (v/v)	25	3	4.7	1.25	73
6	0.90	0.05/1	Toluene/THF =1/0.25 (v/v)	25	3	6.4	2.32	94
7	0.90	0.05/1	Toluene	25	3	2.9	1.07	58
8	0.90	0.02/1	Toluene/THF =1/0.25 (v/v)	25	3	4.6	1.72	67
9	0.90	0.04/1	Toluene/THF =1/0.25 (v/v)	25	3	7.8	1.87	69
10	0.90	0.08/1	Toluene/THF =1/0.25 (v/v)	25	3	8.1	1.85	73
11	0.90	0.22/1	Toluene/THF =1/0.25 (v/v)	25	3	5.1	2.11	66
12	0.90	0.08/1	Toluene/THF =1/0.25 (v/v)	0	3	1.0	1.12	0
13	0.90	0.08/1	Toluene/THF =1/0.25 (v/v)	Reflux	3	2.7	1.37	73
14	0.045	0.08/1	Toluene/THF =1/0.25 (v/v)	25	3	5.4	2.25	92
16	0.023	0.08/1	Toluene/THF =1/0.25 (v/v)	25	3	9.9	2.63	90
17	0.018	0.08/1	Toluene/THF =1/0.25 (v/v)	25	3	1.5	1.3	20
18	0.027	0.08/1	Toluene/THF =1/0.25 (v/v)	25	1	2.0	1.17	53
19	0.027	0.08/1	Toluene/THF =1/0.25 (v/v)	25	2	2.8	1.27	66
20	0.027	0.08/1	Toluene/THF =1/0.25 (v/v)	25	3	5.8	1.46	89
21	0.027	0.08/1	Toluene/THF =1/0.25 (v/v)	25	4	7.7	2.21	96
22	0.027	0.08/1	Toluene/THF =1/0.25 (v/v)	25	5	11.7	1.98	91[b]

a. Measured by GPC; b. Isolated yield.

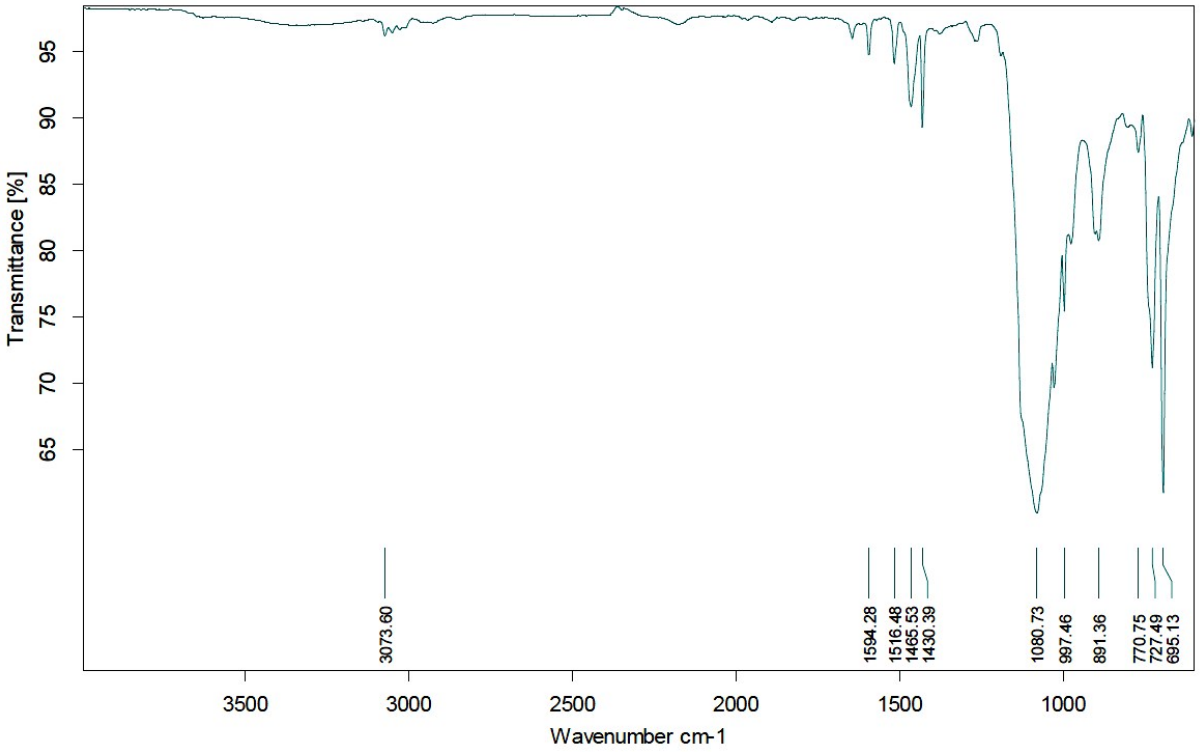

Figure S6 IR spectrum of **2**

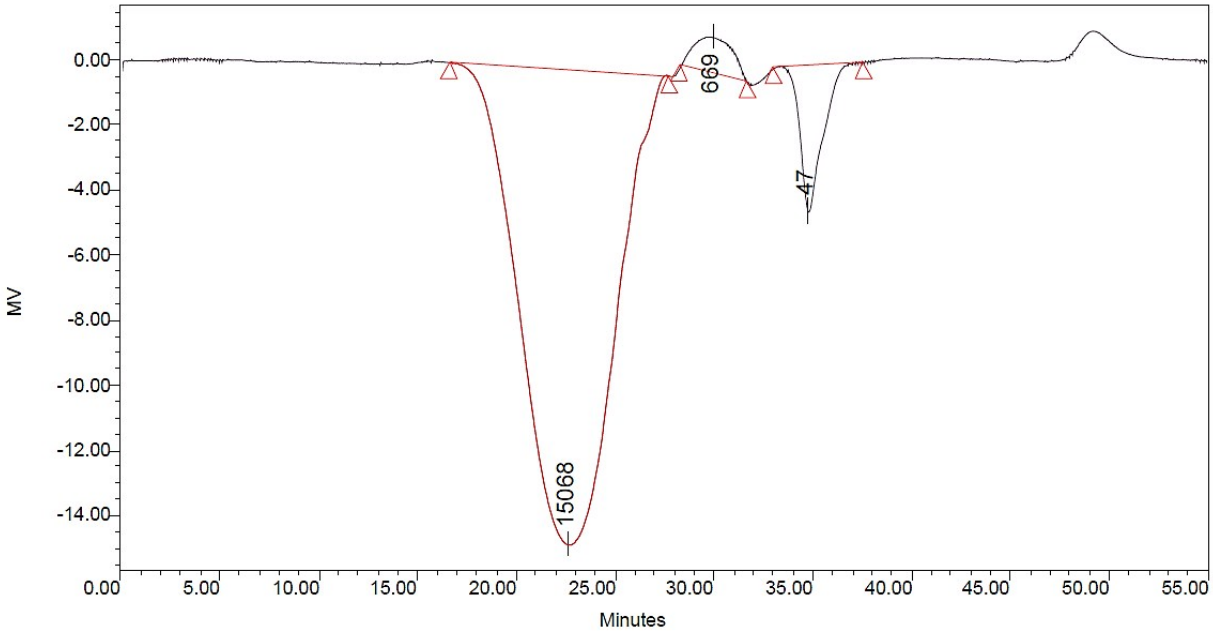

Figure S7 GPC curve of **2**

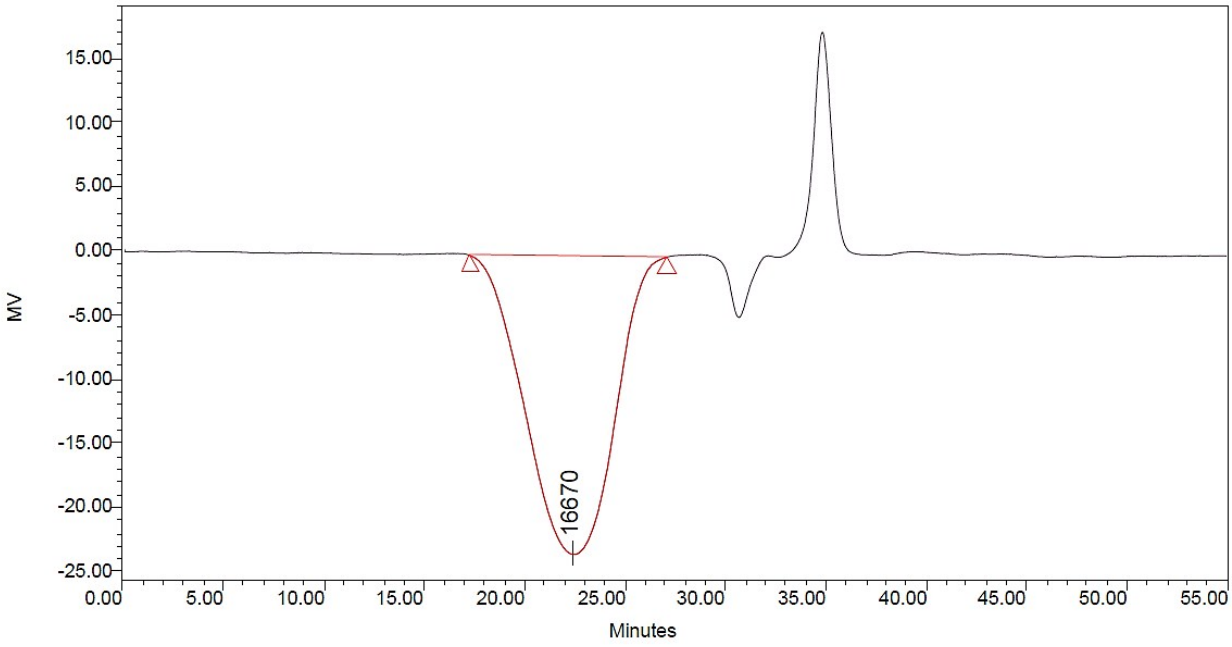

Figure S8 GPC curve of **4**

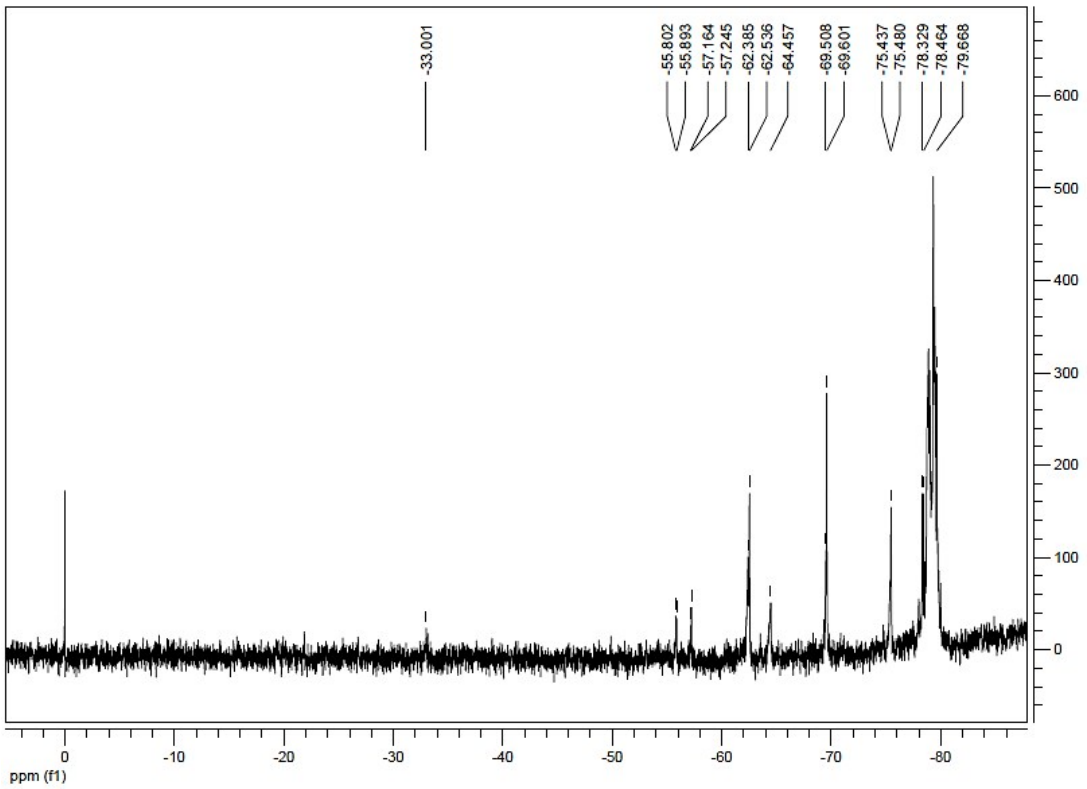

Figure S9 ^{29}Si-NMR spectrum of **2**

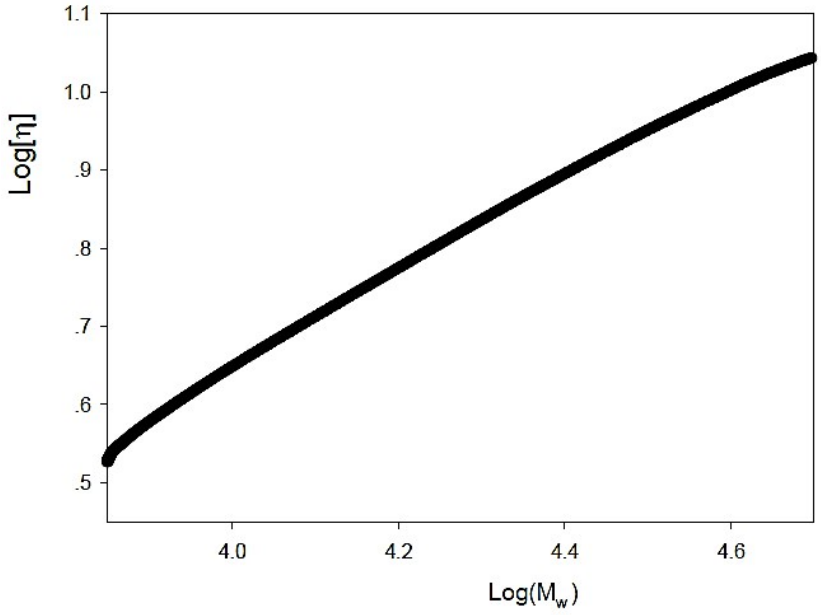

Figure S10 Mark-Houwink plot of intrinsic viscosity [η] as a function of M_w for **2**

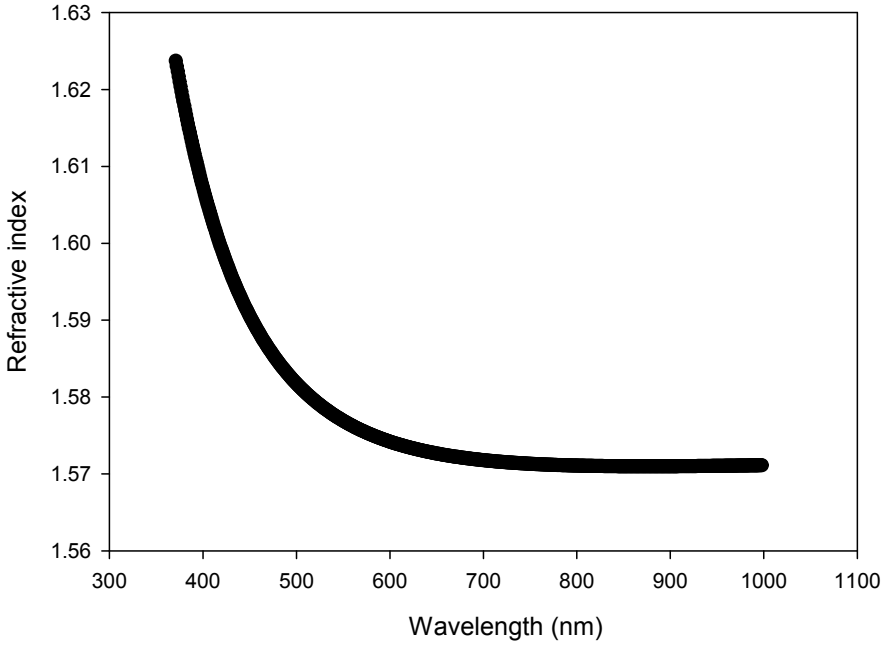

Figure S11 Refractive indices of **2** as a function of wavelength

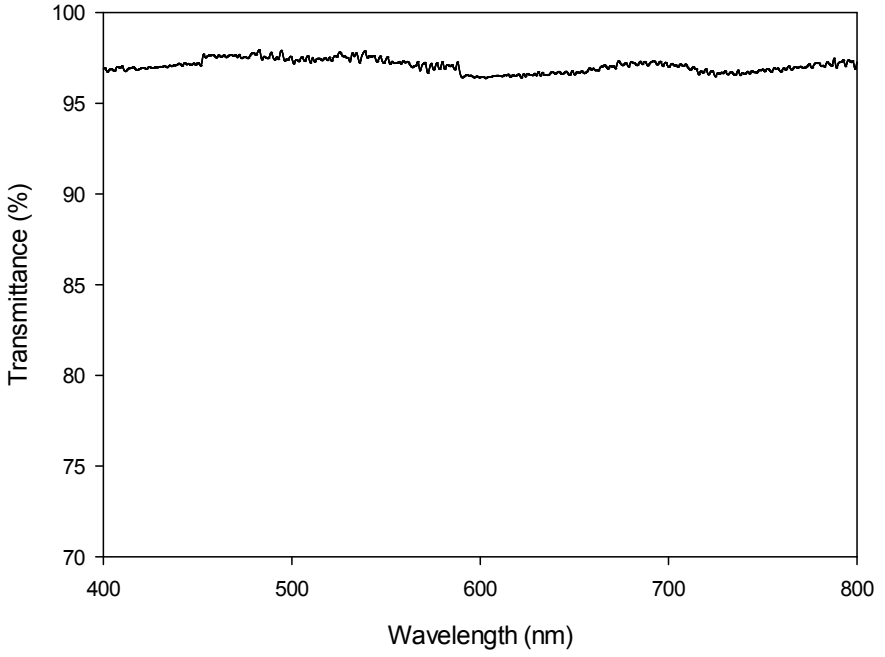

Figure S12 Visible spectrum of **2**

(The thickness of film is 31 μm)

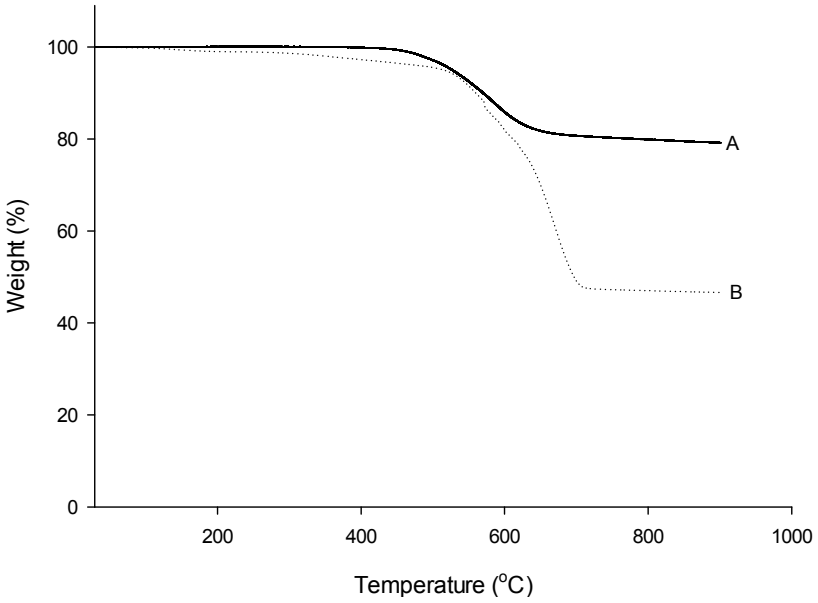

Figure S13 TGA curves of **2**

A. In nitrogen; B. In air.

Reference

(1) D. Lee, Y. Kawakami, *Polym. J.* 2007, **39**, 230.