Polysiloxanes with Periodically Distributed Isomeric Double-Decker Silsesquioxane in the Main Chain

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ABSTRACT: [(2-Methylpropyl)hydroxysilyl]-bridged double-decker silsesquioxane was synthesized, and its stereoisomers were obtained by fractional precipitation followed by silica gel column chromatography, and their structures were confirmed by ^{1}H and ^{29}Si NMR and single crystal X-RD. The pure *cis*, *trans* and mix isomer were polymerized with silane-terminated octamethyltetrasiloxane via cross-dehydrocoupling polycondensation catalyzed by tris(pentafluorophenyl)borane to give completely alternating structure of the double decker silsesquioxane, and linear octamethyltetrasiloxane. All the polymers showed significantly increased glass transition temperature, compared with linear poly(dimethylsiloxane). Excellently transparent organo-soluble polymers gave self-supporting film by simple casting method.

Introduction

It is generally accepted that many of the properties of polysiloxanes are a consequence of the static and dynamic nature of the siloxane backbone.[1] Linear poly(dimethylsiloxane)s have been well-known to show particular characteristics such low glass transition temperature (T_g), thermo-stability, stability against oxidation originating from a strong and flexible main chain, and physiological inertness, with a hydrophobicity based on a mainly methyl side chain.[2,3] However, low T_g and easy cleavage of Si−O−Si bonds under acidic or basic condition,[2,3] or by thermal treatment often limits their applications. Introduction of bulky and rigid moieties like phenylene, naphthylene, anthrylene, phenanthrylene or adamantylene moieties in the main chain increases T_g and thermal stability of the polysiloxanes.[4−7] These polymers, especially, poly(arylene−dimethylsiloxane)s are a kind of good candidates for high-temperature elastomers because of the property originated from flexible Si−O−Si backbone and increased thermal stability given by the presence of arylene moiety, which can be also the origin of good dielectric and surface properties, and so on.[8−10]

Although the introduction of bulky and rigid organic moieties improves some expected properties, it breaks the continuity of Si−O−Si backbone in polymer. If double-decker silsesquioxane consisting of only siloxane bonding was introduced into the polysiloxane backbone instead of the organic counterpart, the resulting polymer would be expected to exhibit further higher T_g and better thermo-stability compared with the case with organic moieties, because of the stronger siloxane bonds. In addition, the 3D silsesquioxane part might introduce toughness and enhanced gas permeability to polymer through loose packing, leaving some free volumes, and also reduce its dielectric constant because of the low polarity of cage silsesquioxane.[11−14]

From these points of view, we report here the synthesis and separation of isomers of [(2-methylpropyl)hydroxysilyl]-bridged double-decker silsesquioxane, DDS(MP)(OH), and construction of a new polysiloxane backbone structure using these compounds as monomers. The effects of the structure on thermal and optical properties were also investigated.

Experimental Section

Materials. Phenyltrimethoxysilane and (2-methylpropyl)trichlorosilane were purchased form Shin-Etsu Chemicals, Japan. Tris(pentafluorophenyl)borane, B(C_6F_5)$_3$ (95% purity), sodium hydroxide and sodium sulfate were purchased from Sigma Aldrich. Triethylamine (TEA) was purchased from Wako Pure Chemical Industries Ltd., Japan. All the chemicals were used as received. Tetrahydrofuran (THF), toluene, chloroform, hexane, and 2-propanol were used after drying by distillation.

Instrumental Analysis. ^{1}H (300 MHz) and ^{29}Si (99.5 MHz, decoupled from H) NMR spectra were obtained on Varian Gemini 2000 and Unity Inova in $CDCl_3$, respectively. Chemical shifts are given in ppm relative to internal $CHCl_3$ (7.26) for ^{1}H and tetramethylsilane (0.00) for ^{29}Si. For MALDI−TOF MS (Voyager-DE RP) analysis, the matrix 2,5-dihydroxybenzoic acid was dissolved in THF (10 mg/ml), and 0.2 μL of sample solution (100 μmol in THF) was mixed with matrix (1:1 v/v ratio). The resultant solution was deposited on a stainless steel sample plate and dried. The measurement was done in linear mode with UV laser (337 nm), and positive mode with an accelerating voltage of 20 kV. The spectra were calibrated by using the sample of angiotensin I with the matrix of α-cyano-4-hydroxycinnamic acid. All the data was collected by laser intensity 1901 (3.0 Hz) with accumulation of laser shots 50/spectra. Size exclusion chromatography (SEC) was performed on a JASCO high speed liquid chromatograph, model Gulliver 900 with combination of Shodex KF-801 (exclusion limit: polystyrene, 1.5×10^3 Da) and KF-802 (exclusion limit: polystyrene, 5×10^3 Da) for monomers and KF-804 (exclusion limit: polystyrene, 4×10^5 Da) and KF-805 L (exclusion limit: polystyrene, 4×10^6 Da) for polymers using THF as an eluent. In single crystal X-ray analysis, a colorless needle crystal of DDS(MP)(OH) having approximate dimensions of 0.20 × 0.04 × 0.03 mm was mounted in a loop. All measurements were made on a Rigaku RAXIS-RAPID imaging plate area detector with graphite monochromated Cu Kα radiation ($\lambda = 1.54187$ Å). The data were collected at a temperature of -180 ± 1 °C. The structure was solved by direct method (SHELXL97) and expanded using Fourier techniques (DIRDIF99). Thermal stabilities of polymers were investigated by SEIKO SSC/5200H TGA under nitrogen at a heating rate of 10 °C/min. T_g measurements were done by SEIKO SSC model 6200 differential scanning calorimeter equipped with a liquid nitrogen cooling accessory at the heating and cooling rate of 30 °C/min. Thermo-mechanical analysis (TMA) was conducted with a Bruker AXS TMA 4000 SA at a scan rate of 10 °C/min with a compression probe of 8 mm diameter. The softening temperature (T_s) was taken as the inflection point of the displacement curve from the baseline.

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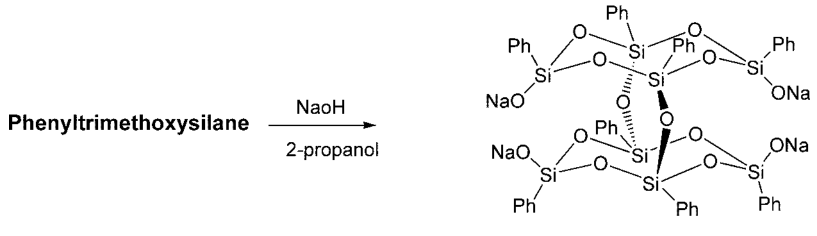
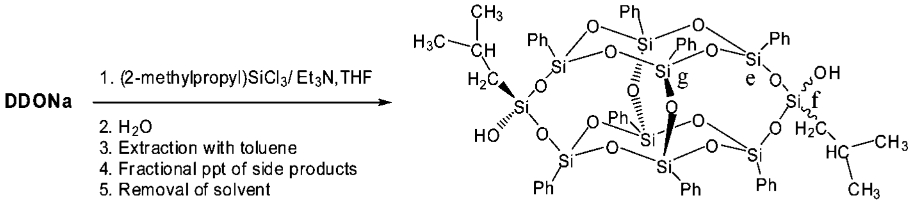
Scheme 1. Synthesis of Tetrasodium Salt of Double Decker Phenylsilsesquioxane



DDONa

Scheme 2. Capping of DDONa with (2-Methylpropyl)trichlorosilane



DDS(MP)(OH)

Synthesis and Separation. *Tetrasodium Salt of Double-Decker Phenylsilsesquioxane (DDONa).*[15] The structure and synthetic route to sodium salt of double decker phenylsilsesquioxane (DDONa) is shown in Scheme 1.

Phenyltrimethoxysilane (48 g, 0.24 mol) was added dropwise to a solution of sodium hydroxide (6.4 g, 0.16 mol) in deionized water (5 g, 0.28 mol) and 2-propanol (240 mL) at room temperature for about 15 min under nitrogen atmosphere. The reaction mixture was heated to reflux for 4 h, and the solution was cooled to ambient temperature, and left standing for about 15 h. After filtration, the formed precipitate was washed once with 2-propanol and dried at 70 °C for 5 h in vacuum oven to obtain 23.9 g of colorless powder, 68% yield.

[(2-Methylpropyl)hydroxysilyl]-Bridged Double Decker Phenylsilsesquioxane, DDS(MP)(OH). The synthetic route to DDS(MP)(OH) is shown in Scheme 2.

In a two-neck 100 mL flask equipped with a reflux condenser were placed DDONa (3 g, 2.59 mmol), THF (30 mL), and TEA (0.78 g, 7.78 mmol), and the reaction system was sealed with a dry nitrogen stream. (2-Methylpropyl)trichlorosilane (1.5 g, 7.78 mmol) was added to the system dropwise with a syringe at room temperature while stirring by means of a magnetic stirrer, and the solution was stirred at room temperature for 12 h. Water (13 mL) was added to the reaction mixture under ice bath, and the system was stirred for 20 min to hydrolyze excess trichlorosilane and the formed chloro-derivative to hydroxy derivative, DDS(MP)(OH), and to dissolve sodium chloride formed during the reaction. Toluene (70 mL) was added to extract soluble products, and the organic layer was separated and washed repeatedly with ion-exchanged water until it became neutral. The organic layer was dried with anhydrous sodium sulfate and the volume of toluene was reduced to around 15 mL to start precipitation of less soluble products. The solution was kept at 0 °C for overnight and the precipitation was filtered off. The clear filtrate was dried on a rotary evaporator to obtain isomeric mixture of DDS(MP)(OH) as colorless solid (1.4 g, 43% yield).

^{1}H: 0.80, 0.81 (two d, $J = 7.0$ Hz, 4H, SiCH_2), 0.90, 0.91 (two d, $J = 6.6$ Hz, 12H, CH_3), 1.81−2.00 (m, 4H, CH), 2.59 (s, 2H, SiOH), 7.19−7.57 (m, 80 H, Ph). ^{29}Si: −79.32, −79.28, −79.19, −78.90, −55.95. MALDI−TOF (m/z): 1292.35 ($M^+ + Na^+$); calcd, 1291.16. GPC: $M_w = 1330$, $M_n = 1320$.

Isomers of DDS(MP)(OH) were separated by fractional crystallization and column chromatography. To a solution of isomeric mixture of DDSQ(MP)(OH) (2 g) dissolved in chloroform (10 mL), hexane (25 mL) was added dropwise, and the solution was kept in a refrigerator at 0 °C for overnight to induce formation of solid. The solid formed was separated by filtration, which contained a mixture of isomers with intensity of 8:2 (isomer-1:isomer-2). To the filtrate, hexane (15 mL) was added dropwise and kept at −30 °C for 24 h to induce further precipitation containing isomeric ratio of about 2: 8 (isomer-1:isomer-2).

The solid fraction {1 g of isomeric mixture of ratio 8: 2 (isomer-1:isomer-2)} was developed on a silica gel column using toluene as solvent. The isomers were successfully separated as two fractions [isomer-1, $R_f = 0.29$, 0.72 g (80%), + isomer-2, $R_f = 0.23$, 0.18 g (20%)]. Pure isomer-2 was obtained more easily from the mixture having isomeric ratio of 2: 8 in the same manner.

Isomer-1. ^{1}H: 0.80 (d, $J = 7.0$ Hz, 4H, SiCH_2), 0.90 (d, $J = 6.5$ Hz, 12H, CH_3), 1.84−1.97 (m, 2H, CH), 2.58 (s, 2H, SiOH), 7.19−7.57 (m, 40H, Ph). ^{29}Si: −79.30, −78.93, −55.96.

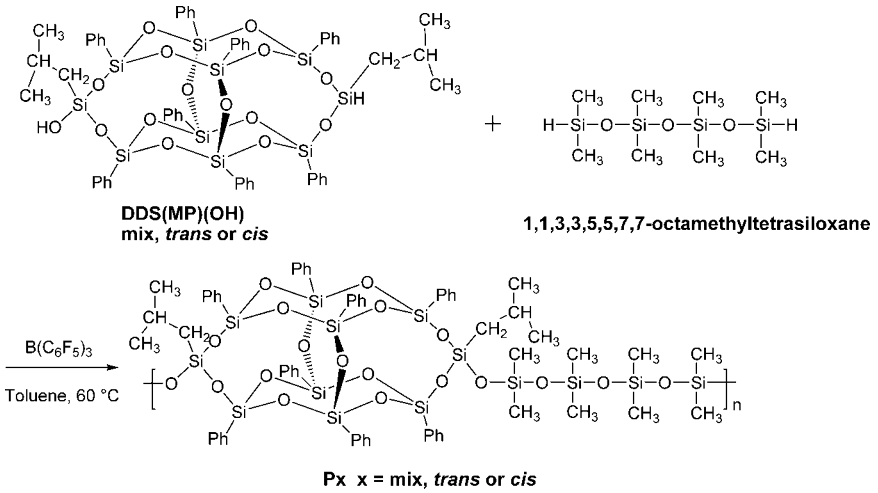
Isomer-2. ^{1}H: 0.81 (d, $J = 7.1$ Hz, 4H, SiCH_2), 0.91 (d, $J = 6.6$ Hz, 12H, CH_3), 1.85−1.99 (m, 2H, CH), 2.57 (s, 2H, SiOH), 7.18−7.58 (m, 40H, Ph). ^{29}Si: −79.34, −79.21, −78.91, −55.96.

Single Crystal X-RD of Isomer-2. Fine crystals suitable for X-ray crystallography were obtained by slow evaporation of a 10 wt % $CHCl_3$/benzene (1:2) solution of isomer-2 of DDS(MP)(OH). Details of the X-ray crystal determination are as follows: empirical formula = $C_{56}H_{60}O_{16}Si_{10}$; formula weight = 1269.94; crystal color and habit = colorless, needle; crystal system, monoclinic; space group, $P2_1/n$; $a = 16.4294(3)$ Å, $b = 35.0539(6)$ Å, $c = 21.4251(7)$ Å, $V = 12318.3(5)$ Å^3, and $\beta = 93.3280(7)°$; reflections collected = 89384; final wR2 value, 0.2600 (all reflections). Additional crystallographic data of isomer-2 of DDS(MP)(OH) (CCDC694555) can be obtained free of charge via www.ccdc.cam.au.uk/data-request/cif.

Polymerization. The procedure to obtain polymer P_x from DDS(MP)(OH) (*cis*, *trans*, and mix isomers) and 1,1,3,3,5,5,7,7-octamethyltetrasiloxane (1:1 molar ratio) is illustrated in Scheme 3.

Into a 30 mL of two-neck flask were placed *cis*, *trans*, or mixture of isomers of DDS(MP)(OH) (0.4 g, 0.32 mmol) and $B(C_6F_5)_3$ (0.0033 g, 2 mol %). After drying, the flask was sealed with an argon atmosphere, and 2.5 mL of toluene (dried with sodium metal) was added. Equimolar octamethyltetrasiloxane as a linear monomer (0.091 g, 0.32 mmol) was added slowly and the mixture was stirred at 60 °C. After few minutes of stirring, the DDS(MP)(OH) went into the solution with hydrogen bubbling (collected in a balloon attached to the flask), which confirmed the progress of reaction. The reacting solution was further stirred for 12 h and then the mixture was poured into methanol to give the precipitation which was dried in vacuum to get 0.45, 0.43, or 0.42 g (92%, 87%, or

Scheme 3. Cross-Dehydrocoupling Polycondensation of DDS(MP)(OH) and 1,1,3,3,5,5,7,7-Octamethyltetrasiloxane To Obtain Polymer P_{cis}, P_{trans}, and P_{mix}



86% yield) of the polymer P_{cis}, P_{trans}, and P_{mix} respectively. The crude polymers were purified by repeated reprecipitation from THF into methanol.

P_{cis}. ^{1}H: −0.06 {s, 12H, DD−O−Si(CH_3)$_2$}, 0.02 {s, 12H, O−Si−O−Si(CH_3)$_2$}, 0.78 (d, J = 7.1 Hz, 4H, −SiCH_2), 0.94 (d, J = 6.6 Hz, 12H, CH_3), 1.84−2.03 (m, 2*H*, C*H*), 7.15−7.60 (m, 40H, Ph). ^{29}Si: −79.97, −79.70, −79.40, −67.31, −21.26, −20.69.

P_{trans}. ^{1}H: −0.11, −0.03, 0.71, 0.87, 1.75−1.99, 7.11−7.55. ^{29}Si: −79.68, −67.34, −21.25, −20.72.

P_{mix}. This showed overlapped signals.

Results and Discussion

Synthesis of DDS(MP)(OH). The capping of DDONa with 2-methylpropyltrichlorosilane takes longer time (12 h) compared with methyltrichlorosilane (1 h). Steric-hindrance of bulky 2-methylpropyl group renders longer reaction time. Moreover, the synthesized DDS(MP)(OH) was not the only product. Incompletely capped double-decker silsesquioxanes were the side products. Comparatively less polar DDS(MP)(OH) was more soluble in toluene forming insoluble products on reducing the volume of toluene. Drying the solvent from the clear filtrate gave colorless solid DDS(MP)(OH) as product.

The molecular weight of product measured with MALDI-TOF mass spectrometer is well coincided with the calculated value as shown in Figure 1a.

Three ^{29}Si at −55.95 (marked as **f**), −78.90 (**e**) and −79.28 (center) (**g**) ppm for DDS(MP)(OH) in Scheme 2 can be seen in Figure 1b. The signal g has split into three peaks, which suggested the existence of isomeric structures for DDS(MP)(OH) as shown in Figure 2.

Contrary to that the g signal of trans isomer should appear as one signal, that of *cis* isomer could appear as two signals (g_1 and g_2), as shown in Figure 2.

Existence of two doublets at 0.81 (CH_2) and another two doublets at 0.91 (CH_3)$_2$ ppm in ^{1}H shown in Figure 3c strongly suggests the existence of isomers for DDS(MP)(OH).

The slight difference in solubility was utilized to separate them from their mixture. Before final separation of isomers by silica gel column, fractional precipitation was performed to

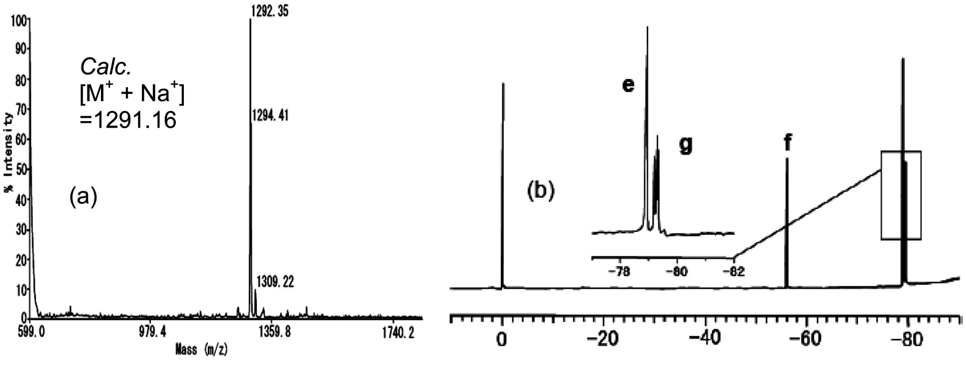


Figure 1. (a) MALDI−TOF mass and (b) ^{29}Si NMR of isomeric mixture of DDS(MP)(OH).

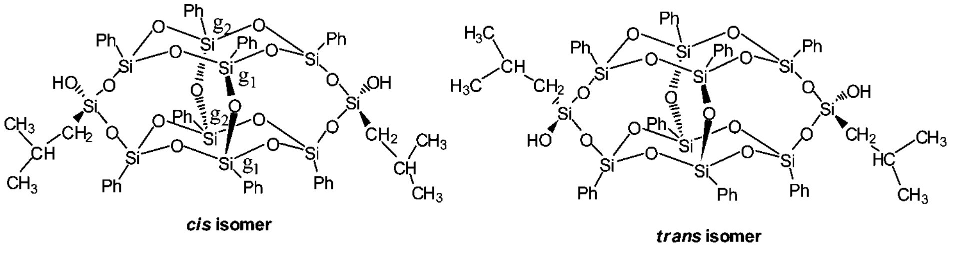


Figure 2. *cis* and *trans* configuration of DDS(MP)(OH).

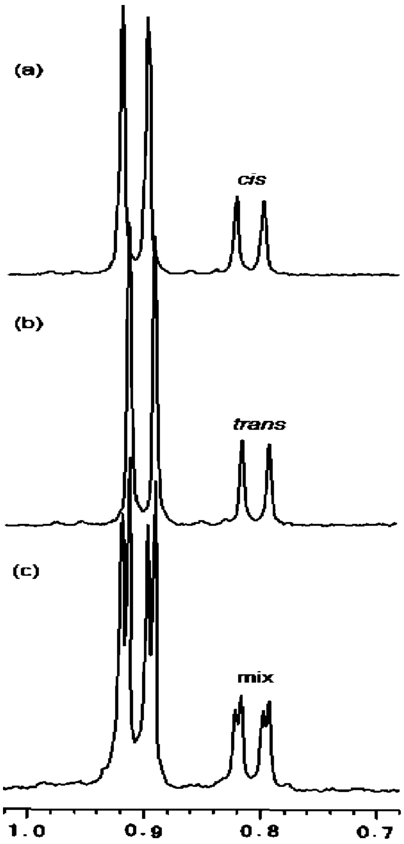


Figure 3. Chemical shifts of mixture and separated isomers of DDS(MP)(OH). (a) *cis* isomer (b) *trans* isomer and (c) mix isomer.

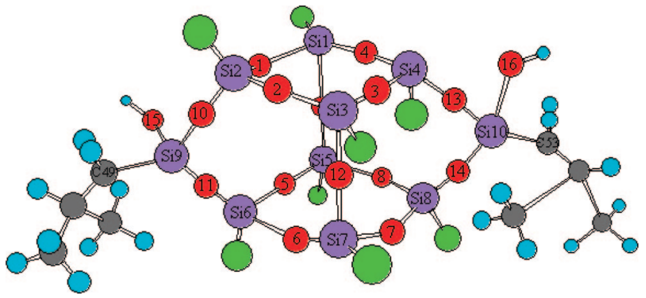


Figure 4. Simplified configurational illustration of isomer-2 based on the analysis of single crystal X-RD.

create the difference of isomeric ratio in the mixture. The relatively long column was used for the better efficiency. ^{1}H NMR of the separated isomers gave very clear peaks confirming the successful separation as shown in Figure 3. Combined with ^{29}Si NMR, the fraction with $R_f = 0.23$ was tentatively assigned as *cis* isomer.

Even though the ^{1}H and ^{29}Si NMR and MALDI-TOF MS well support the structural architecture of DDS(MP)(OH), the analysis of separated isomer-2 with single crystal X-RD will definitely confirm the structural arrangement of the isomers.

Simplified structure of the *cis* isomer is shown in Figure 4.

Selected bond distances and angles for actual determination are collected in Table 1.

Silicon−oxygen bond length (1.60~1.61 Å) and silicon−oxygen–silicon bond angles (~150°) are close to typical values. The bond angles O10−Si9−C49, O13−Si10−C53 and O11−Si9−C49, O14−Si10−C53 are 111.6, 111.8 Å and 110.0, 110.3 Å, respectively, a fact which strongly supports the *cis* configuration of isomer-2. Furthermore, it can be seen from Table 1, Si−O−Si bond angles for the upper and lower decks are not same. The *cis* isomeric configuration causes steric-hindrance on the lower deck which results in some contraction of bond angles. Some discrepancies may have resulted due to the relatively low quality of the crystals. Nevertheless, isomer-2 was confirmed as the *cis* isomer as shown in Figure 4, which implies that isomer-1 is the *trans* isomer.

Table 1. Selected Bond Angles (deg) and Bond Distances (Å) for DDS(MP)(OH)

bond angles O−Si−O		bond lengths Si−O	
Si1−O1−Si2	155.4[6]	Si6−O11	1.597[9]
Si7−O7−Si8	149.6[6]	Si6−O6	1.616[8]
O10−Si9−O11	108.7[4]	Si7−O6	1.602[9]
O10−Si9−C49	111.6[5]	Si1−O4	1.615[9]
O11−Si9−C49	110.0[5]	Si4−O4	1.600[9]
O13−Si10−O14	107.2[4]	Si9−O11	1.578[9]
O13−Si10−C53	111.8[5]	Si9−C49	1.829[11]
O14−Si10−C53	110.3[5]	Si10−O14	1.593[8]
O10−Si9−O15	108.9[4]	Si10−C53	1.828[11]
O11−Si9−O15	106.9[4]	Si9−O10	1.609[9]
O15−Si9−C49	110.6[5]	Si9−O15	1.637[9]
O13−Si10−O16	108.2[4]	Si10−O13	1.603[9]
O14−Si10−O16	110.2[4]	Si10−O16	1.634[9]
O16−Si10−C53	109.1[5]		

This result demonstrates that the comparatively less soluble DDS(MP)(OH) is *trans* isomer. X-RD analysis also reveals that the *cis* isomer exists as aggregates by the intermolecular hydrogen bonding. The melting point's of the monomers are summarized in Table 2.

Polymerization of *cis*, *trans*, and Mix Isomers of DDS(MP)(OH) with Tetrasiloxane. The cross-dehydrocoupling polycondensation of DDS(MP)(OH) with tetrasiloxane were performed to synthesize the polymers P_{cis}, P_{trans}, and P_{mix} under the same conditions described in Scheme 3. The results of the polymerization and thermal properties are summarized in Table 2.

Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ as a catalyst has been used in a number of organic and polymerization reaction.[16] Normally this catalyst is very active at room temperature to facilitate a number of reactions such as the silylation of alcohol[17] and hydrosilylation of carbonyls[18] and thiocarbonyls.[19] In this study, we used $B(C_6F_5)_3$ catalyst for the polycondensation of hydroxy functional double-decker silsesquioxane and tetrasiloxane at 60 °C because at room temperature the *trans* isomer of DDS(MP)(OH) was limitedly soluble in toluene and could give only low molecular weight product.

In the ^{1}H spectrum of P_{mix} in Figure 5, the concomitant disappearance of Si*H* at $\delta = 4.71$ ppm of siloxane monomer with hydroxyl hydrogen of the DDS(MP)(OH) at $\delta = 2.59$ ppm confirms the formation of polycondensation product. Further, the appearance of two new proton signals ($\delta = -0.06$ to -0.10 and 0.03 to -0.03 ppm) are due to DDOSi(CH_3)$_2$ and OSiOSi(CH_3)$_2$, respectively, which verifies the connection of tetrasiloxane to DDS unit. 2-Methylpropyl group chemical shifts at $\delta = 0.76$ (d, $J = 7.0$ Hz)$_{trans,}$ 0.77 (d, $J = 7.1$ Hz)$_{cis}$ and 0.92 (d, $J = 6.5$ Hz)$_{trans,}$ 0.93 (d, $J = 6.6$ Hz)$_{cis}$, and 1.94 ppm (m) are assigned to CH_2, CH_3, and C*H*, respectively, which confirms the isomeric DDS(MP)(OH) present in polymeric backbone.

The *cis* and *trans* isomers of DDS(MP)(OH) were also polymerized with the same tetrasiloxane to obtain P_{cis} and P_{trans}. ^{1}H NMR of polymers showed clearly separated peaks at 0.71 (d, $J = 7.0$ Hz, CH_2) and 0.87 (d, $J = 6.5$ Hz, CH_3) for P_{trans} and at 0.78 (d, $J = 7.1$ Hz, CH_2) and 0.94 (d, $J = 6.6$ Hz, CH_3) ppm for P_{cis}, which demonstrate the presence of the only *trans* and *cis* isomeric unit in P_{trans} and P_{cis}, respectively.

Figure 6 shows the ^{29}Si NMR of polymers. The peak at around −55.95 ppm assigned to the T_2-structured silicon O_2*Si*(MP)(OH) completely disappeared and a new signal at

Table 2. Polymerization of DDS(MP)(OH) with Octamethyltetrasiloxane with Feed Ratio 1:1 Catalyzed by $B(C_6F_5)_3$ at 60 °C and Thermal Properties of the Formed Polymers

DDS(MP)(OH)		Polymers							
						T_{d5},[d] (°C)		residual (wt %)	
structure	T_m[a] (°C)		(M_w/M_n)[b] × 10^{-3}	T_g[a] (°C)	T_s[c] (°C)	N_2	air	N_2	air
cis	304	P_{cis}	50/29	~30	~39	500	470	77	52
trans	357	P_{trans}	64/39	~35	~82	500	460	79	53
mix	295	P_{mix}	42/27	~34	~45	450	400	71	53

[a] Determined by DSC (30 °C/min). [b] By GPC with polystyrene standard. [c] By TMA (10 °C/min). [d] 5% weight loss by TGA (10 °C/min).

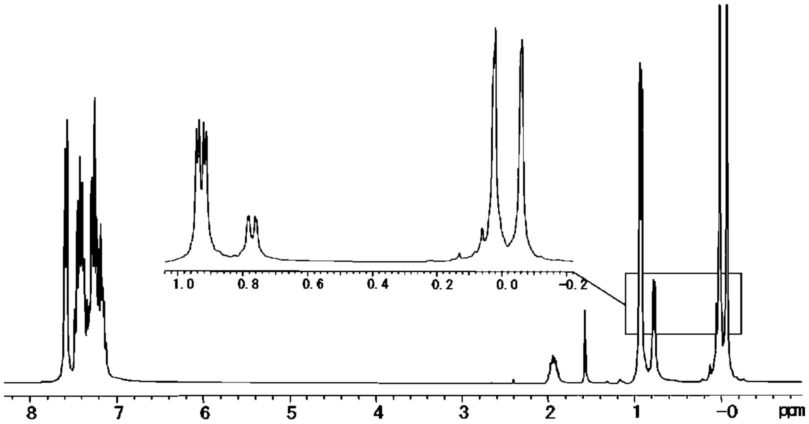


Figure 5. ^{1}H NMR of P_{mix}.

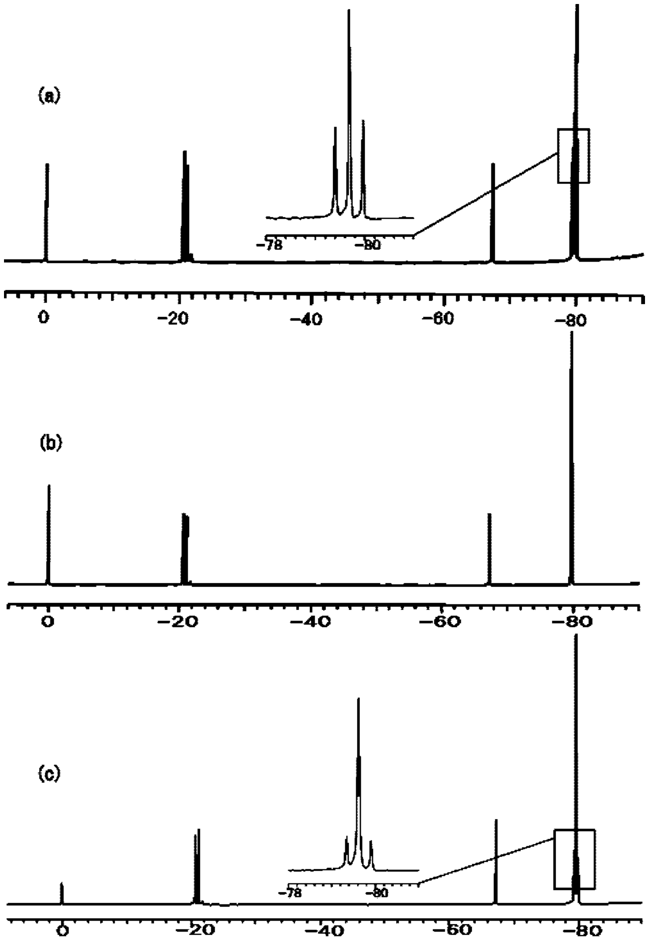


Figure 6. ^{29}Si NMR of Polymer (a) P_{cis}, (b) P_{trans}, and (c) P_{mix}.

approximately −67.3 ppm was observed as T_3-structured silicon atom, which also confirms the condensation between the hydroxyl group of DDS(MP)(OH) and hydrogen atom (HSi) of tetrasiloxane. Furthermore, two new signals at approximately −21.2 and −20.7 ppm in Figure 6a−c are assignable to the silicon chemical shifts of tetrasiloxane. These two signals again support the co-condensation of DDS unit and tetrasiloxane.

Furthermore, chemical shift of Si atoms of DDS(MP)(OH) except capped Si atoms, gave a singlet at −78.90 and a triplet at −79.28 ppm, which after polymerization gave a triplet with an enhanced intensity of the centered signal at −79.63 ppm in Figure 6c.

Cis isomer of DDS(MP)(OH) gave three kinds of singlet (−79.34, −79.21, −78.91 ppm), whereas *trans* isomer gave two kinds of singlet (−79.30, −78.93 ppm) which after polymerization gave three singlets (−79.97, −79.70, −79.40 ppm) and a singlet (−79.68 ppm) were found for P_{cis} and P_{trans} respectively as can be seen in Figure 6a,b.

The above-described polymerization can be applied to oligosiloxanes with different length and substituents. Longer chain lengths gave a softer polymer having lower T_g. The use of phenyl groups in linear siloxane as substitute instead of methyl groups or ologosiloxane shorter than trisiloxane gave insoluble polymer.

Thermal Properties. Thermal properties of polymers P_{cis}, P_{trans}, and P_{mix} were studied by DSC, TGA, and TMA, and results are also summarized in Table 2. As shown in Figure 7, all the polymers exhibit good thermal stability above 450 °C. The high thermal stabilities of these polysiloxane polymers arise due to the presence of double-decker silsesquioxane (DDS) unit in the main chain. It can be seen that 5% weight loss temperature (T_{d5}) for the P_{cis} and P_{trans} are around 500 °C in nitrogen atmosphere while that of P_{mix} is 450 °C. The distinguishable low degradation temperature recorded for P_{mix} compared to that of P_{cis} and P_{trans} might be due to the presence of random *cis* and *trans* sequence of DDS in the backbone. The residual weights at 760 °C for P_{cis}, P_{trans}, and P_{mix} are 77%, 79%, and 71%, respectively, in nitrogen. The residual weights at the same temperature analyzed in air was 53%, which was consistent with the complete removal of only organic moieties from the polymer structure via oxidation, namely as SiO_2 (53%). Apparently, no cleavage of tetrasiloxane or cage component occurred. Accord-

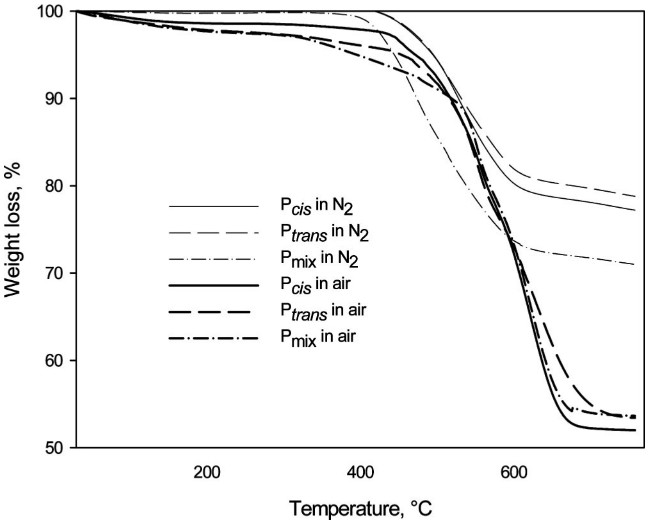


Figure 7. TGA curves of polymer P_{cis}, P_{trans}, and $P_{\rm mix}$ in nitrogen and air with a heating rate of 10 °C/min.

ingly, some of the organic moieties still remain at 760 °C, while maintaining all the siloxane-connected main chain under nitrogen atmosphere.

Although clear $T_{\rm g}$‘s could not be seen for all the polymers at the heating or cooling rate slower than 30 °C/min, they might be in the range of 30 to 35 °C, even with tetrasiloxane as connecting unit. Since the $T_{\rm g}$ analysis did not give clear difference among the polymers, a detailed information was obtained by thermo-mechanical analysis on film samples. It is interesting to point out that the P_{trans} showed considerably higher softening temperature than P_{cis} or $P_{\rm mix}$. These $T_{\rm g}$ or softening temperatures are extremely higher than those of linear polydimethylsiloxane (−123 °C). Poly(arylene−disiloxane)s with disiloxane as connecting unit showed $T_{\rm g}$ in the range of −20 to +60 °C.[4,5] The present value is even comparable with these data. The improved $T_{\rm g}$ of polymer P_{cis}, P_{trans}, and $P_{\rm mix}$ are due to the presence of bulky and rigid double-decker silsesquioxane unit in main chain. The double-decker silsesquioxane unit is comparatively bulkier and more rigid than organic moieties. Glass transition temperature of the polymer synthesized from DDS(MP)(OH) and oligosiloxane [$\mathrm{HSi(CH_3)_2{-}O{-}\{Si(CH_3)_2{-}O\}_{\mathit{n}}{-}Si(CH_3)_2H}$), average $n = 14$ determined by ^{1}H NMR] was found at around −80 °C. Although Zhu et al. commented on the toughening effect of short and long polydimethylsiloxane chains in polysilsesquioxane network,[20] detailed discussion on the effects of the incorporation of oligodimethylsiloxane chain in the molecular structure of the polymer backbone could not be made.

Optical Properties of Polymers. Although polymers P_{cis}, P_{trans}, and $P_{\rm mix}$ were made of high content of double-decker silsesquioxane (82 wt %), they provide excellent film qualities with high transparency. Films with thickness 50−85 μm were prepared. The optical transparency of polymer can be compared by the photograph of silsesquioxane symbol taken through polymer as shown in Figure 8 for P_{cis}.

More quantitative data were obtained by UV−vis spectra as shown in Figure 9. All the polymers exhibited cutoffs at 274 nm and transmittance over 80% at 400 nm with the film thickness of 53 μm. A cutoff wavelength is defined here as the point where the transmittance becomes less than 1% in the spectrum.

The different thickness of the films resulted in the differences in the UV−vis transmittances. This cutoff wavelength (274 nm) of these polymers is due to the absorption of phenyl group, and lower than those of siloxane-containing polyimides (289 nm)[21] and double-decker silsesquioxane containing polyimides (320 nm).[22]

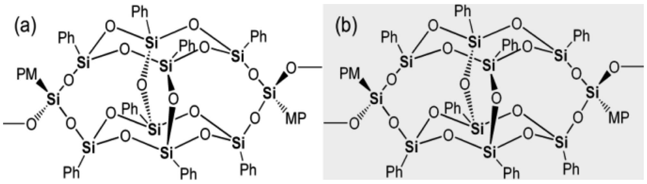


Figure 8. Photographs of silsesquioxane symbol on a white paper, (a) taken directly or (b) taken through a thick film (83 μm) of P_{cis}.

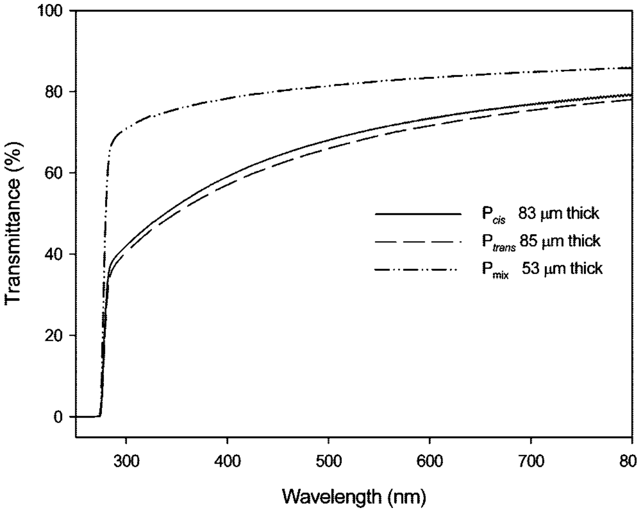


Figure 9. UV−vis spectra of the self-supporting films of polymers P_{cis}, P_{trans}, and $P_{\rm mix}$.

Conclusion

[(2-Methylpropyl)hydroxysilyl]-bridged double decker silsesquioxane was synthesized. Unlike methyl group, presence of bulky 2-methylpropyl group in the bridge of double-decker silsesquioxane DDS(MP)(OH) shows some differences in property of its isomers promoting easy separation by fractional precipitation and silica gel column chromatography. Separated pure stereoisomers were used to synthesize new polysiloxanes with periodically distributed double decker cage in the main chain. The polymers $P_{cis,}$ P_{trans}, and $P_{\rm mix}$ synthesized from pure *cis*, *trans*, and mix isomers show outstanding thermal stability up to 500 °C and significantly increased in $T_{\rm g}$ (30−35 °C), and in $T_{\rm s}$ for P_{trans}. Polymers also exhibit excellent optical transparency with low cutoff wavelength (274 nm).

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