Synthesis of Polysilsesquioxanes with Double-Decker Silsesquioxane Repeating Units

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Abstract

Polysilsesquioxanes were synthesized with end functional double-decker silsesquioxanes (DDSQ) and the polymers were characterized with ^{1}H NMR, ^{29}Si NMR and size exclusion chromatography (SEC). Polysilsesquioxane containing *iso*-butyl end capped DDSQ showed better solubility compared to that of methyl end capped DDSQ. Thermal properties investigated with TGA showed that the polymers exhibited exceptionally high stabilities in the range of 470-530°C even in both nitrogen and air atmosphere. The average residual weights of the polymers at 760°C were around 80% in the nitrogen atmosphere.

1. Introduction

Linear polysiloxanes have been well-known to show particular characteristics such as flexibility of the main chain, low glass transition temperature, thermo-stability, stability against oxidation, and physiological inertness [1-2]. This polysiloxane is also a kind of good candidates as high-temperature elastomer because of the property originated from flexible and heat-resistant Si–O–Si backbone [3-6]. For the expanded and high temperature application of polysiloxane, glass transition temperature T_g and thermal stability must be improved.

Introduction of bulky and rigid moieties like phenylene, naphthylene, anthrylene, phenanthrylene and adamantyl moieties in main chain exhibits high T_g and good thermal

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stabilities of the polysiloxanes [7-11]. However, this introduction of organic moieties breaks the continuity of Si-O-Si backbone in the chemical structure of the formed polymer.

There are few attempts to improve the physical properties by the introduction of polyhedral oligomeric silsesquioxane (POSS) unit in main chain of polysiloxane in place of the bulky and rigid organic moieties [12-14]. Moreover, incorporation of POSS unit in backbone of the linear step-condensed polymer in definite structure was quite difficult as the polycondensation of POSS having multiple reactive sites of equivalent reactivity with di-functional monomers typically generates insoluble cross-linked products [15-18]. The problems caused by the multi-functionality of POSS could be readily eradicated by replacing POSS with double-decker silsesquioxane (DDSQ) having two definite polymerizable functional groups. Recently some researchers synthesized polysilsesquioxane having DDSQ units in the main chain [19-20]. They used bi-functional DDSQ unit having organic spacers. In those cases, they obtained high molecular weight polymers having alternative silsesquioxane unit and organic unit giving -Si-O-Si-C-backbone. Hoque *et al*. [21] introduced DDSQ units as bulky and rigid moiety groups instead of organic moieties in the backbone to produce the copolymers with linear tetrasiloxane retaining continuous Si-O-Si backbone. This polymer consists of DDSQ and linear Si-O-Si linker showed significant improvement in thermal stability.

If a polymer was synthesized with only DDSQ units without any single chain siloxane linker which is susceptible to acid or basic medium [1-2] would further increase the mechanical dimension, thermal stability and resistivity to acidic or basic medium of the polymer. So far the knowledge of the author, no any author has reported polysilsesquioxane having only DDSQ unit in the main chain.

In this study, we preliminarily report the synthesis of a new polymer consisting of only bi-functional DDSQ's as monomers. Formation of polymeric backbone was examined with proton and silicon NMR. The effect of cage type building block (DDSQ) on thermal property was investigated.

2. Experimental

2.1. *Materials*

Phenyltrimethoxysilane, methyldichlorosilane, methyltrichlorosilane, and isobutyltrichlorosilane were purchased from 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 these chemicals were used as received. Tetrahydrofurn, toluene, chloroform, hexane, methanol and *i*-propanol were used after drying by distillation.

2.2. *Instrumental analysis*

^{1}H (300 MHz) and ^{29}Si (99.5 MHz) 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 Shodex KF-804 (exclusion limit: polystyrene 4×10^5 Da) and KF-805 (exclusion limit: polystyrene 4×10^6 Da) for polymers using THF as eluent. The thermal stabilities of polymers were investigated by SEIKO SSC/5200H TGA under nitrogen at a heating rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were obtained with KBr disc on a JASCO VALOR-III (resolution of 4 cm^{-1}, 400-4000 cm^{-1}) at room temperature.

2.3. *Synthesis of precursor and monomers*

Tetrasodium salt of double-decker silsesquioxane precursor DDSQ(ONa) [22]

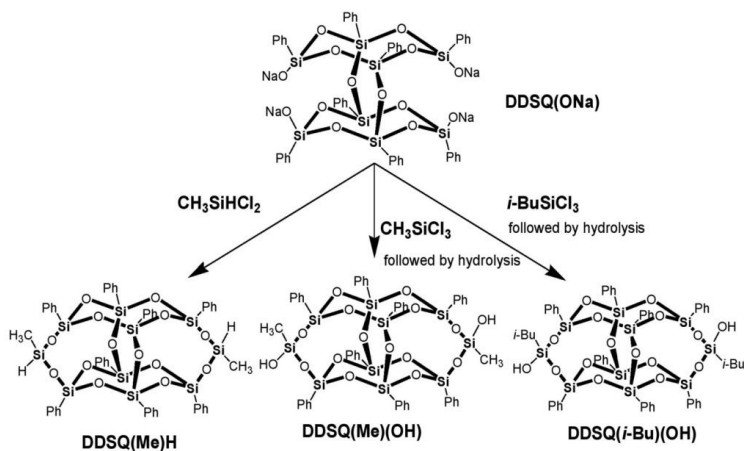**DDSQ(ONa)**

Apparent Mw : 1157 by SEC
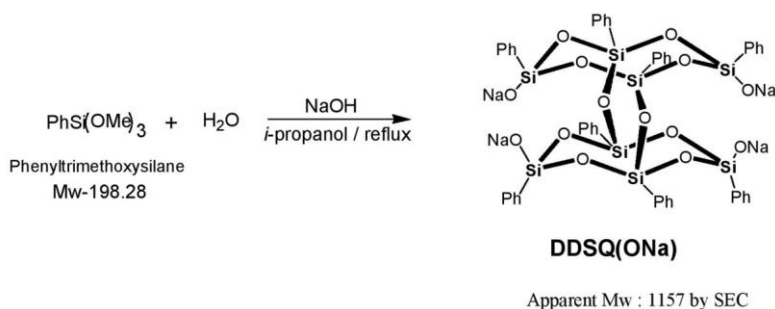
Scheme 1. Synthesis of a double-decker silsesquioxane DDSQ(ONa).

Phenyltrimethoxysilane (48 g, 0.24 mol) was added drop-wise to a solution of sodium hydroxide (6.4 g, 0.16 mol) in *i*-propanol (240 mL) and deionized water (5 g, 0.28 mol) at room temperature for about 15 min. The reaction mixture was heated to reflux for 4 hrs under nitrogen. The solution was cooled to ambient temperature, and left standing for

about 15 h. After filtration, the precipitate was washed with *i*-propanol and dried at 70 °C for 5 h in a vacuum oven to obtain 23.9 g of colorless powder of DDSQ(ONa), 68.2% yield. IR (KBr): 1430, 1600 (Si-Ph) cm^{-1}, 1200 ~ 950 (Si-O-Si) cm^{-1}; One peak in SEC.

Synthesis scheme of double-decker monomers are shown in Scheme 2.

Scheme 2. Synthesis of DDSQ(Me)H, DDSQD(Me)(OH) and DDSQ(*i*-Bu) monomers.

DDSQ(Me)H [23]

DDSQ(ONa) (11.6 g, 10.0 mmol) was vacuum dried at elevated temperature in a 300 mL round bottom two neck flask. Triethylamine (30 mL, 3.0 g) and THF (100 mL) were then added to DDSQ(ONa) under nitrogen. To the flask, methyldichlorosilane (30 mmol, 3.4 g) was added dropwise and the mixture was stirred at room temperature for 2 hrs. The formed salts (NaCl and Et$_3$NHCl) were removed by filtration. The solution was then subjected to rotary evaporation to remove the unreacted methyldichlorosilane, solvent and Et$_3$N. Drying was commenced to find white residue which was re-dissolved in THF and re-precipitated in 400 mL toluene. Re-precipitation was done twice, and the product was dried in vacuum for 8 hrs. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 0.37 (d, 6H, SiCH$_3$), 4.98 (q, 2H, SiH), 7.18-7.56 (m, 40H, Ph); ^{29}Si NMR (99.5 MHz, CDCl$_3$): δ (ppm) -79.32 (t, 4Si), -77.83 (s, 4Si), -32.77 (s, 2Si); MALDI-TOF (m/z): 1175.95 (M$^+$ + Na$^+$), *calc*: 1175.06; One peak in SEC.

DDSQ(Me)(OH) [23]

A 300 mL three neck flask equipped with a dropping funnel, a reflux condenser and a thermometer was charged with the compound DDSQ(ONa) (11.6 gm, 10 mmol), THF (100 gm) and triethylamine (3.0 g, 30 mmol), and it was sealed with dry nitrogen.

Methyltrichlorosilane (4.5 g, 30 mmol) was added drop-wise thereto at room temperature while stirring by means of a magnetic stirrer. Then, the solution was stirred at room temperature for 3 h. Water (50 g) was added to the reaction mixture and stirred for 30 min to dissolve sodium chloride formed and to hydrolyze un-reacted methyltrichlorosilane. The reaction mixture thus obtained was subjected to extraction with toluene (150 mL), and the organic layer was washed once with 1N HCl acid and once again with the saturated solution of sodium hydrogen carbonate. It was further washed repeatedly three times with ion-exchanged water. The organic layer obtained was dried on anhydrous magnesium sulfate, filtrate and then solvent was removed under reduced pressure by the rotary evaporator to obtain 7.1 gm of white powdery solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 0.36 (s, 6H, SiCH$_3$), 2.66 (s, 2H, SiOH), 7.17-7.57 (m, 40H, Ph); ^{29}Si NMR (99.5 MHz, CDCl$_3$): δ (ppm) -79.17 (t, 4Si), -78.61 (s, 4Si), -53.91 (s, 2Si); MALDI-TOF (m/z): 1207.22 (M$^+$ + Na$^+$) calc: 1207.05; One peak in SEC; FT-IR: 3450, 3070, 2971, 1594, 1430, 1270, 1088, 909, 730 cm^{-1}.
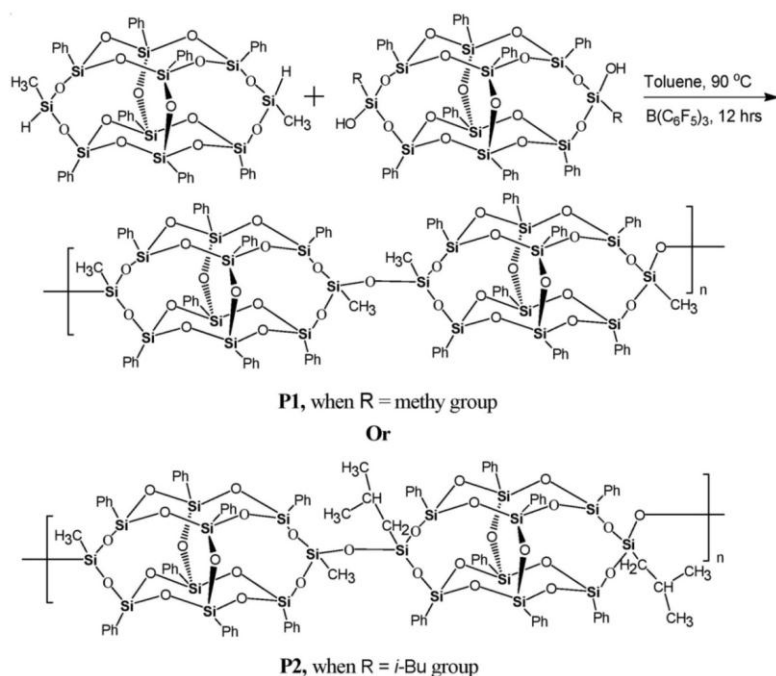
DDSQ(i-Bu)(OH) [21]

To a 100 mL two neck flask equipped with a reflux condenser, DDSQ(ONa) (3 g, 2.59 mmol), THF (30 mL) and triethylamine (0.78 g, 7.78 mmol) were placed and sealed with dry nitrogen. Isobutyltrichlorosilane (*i*-BuSiCl$_3$, 1.5 g, 7.78 mmol) was added drop-wise thereto with a syringe at room temperature while stirring by means of a magnetic stirrer. Then, the solution was stirred at a room temperature for 12 h. Water (13 mL) was added to the reaction mixture and stirred for 20 min to dissolve sodium chloride formed and hydrolyzed unreacted isobutyltrichlorosilane. The reaction mixture thus obtained was subjected to extraction with toluene (50 mL), and the organic layer was washed repeatedly with ion-exchanged water until it became neutral. The organic layer obtained was dried on anhydrous sodium sulfate and the volume of toluene was reduced to form precipitate of less soluble by-products. The toluene solution containing precipitated by-product was put at 0°C for overnight and then filtered to remove the formed precipitates. Hexane was added drop-wise to the filtrate obtained to induce new precipitation, which was again put at 0°C for overnight. The solid product formed was filtered and collected, and dried to obtain 1 gm of a white solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 0.80, 0.81 (two d, SiCH$_2$), 0.90, 0.91 (two d, 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 NMR (99.5 MHz, CDCl$_3$): δ (ppm) -79.32, -79.28, -79.19, -78.90, -55.95; MALDI-TOF (m/z): 1292.35 (M$^+$ + Na$^+$), calc. 1291.16; One peak in SEC.

2.4. *Synthesis of polymers*

Polymer P1 and P2 were synthesized by the cross-dehydrocoupling polymerization as shown in Scheme 3. To a 10 mL of one-neck round bottom flask, DDSQ(Me)H (0.2 g, 0.173 mmol), DDSQ(Me)(OH) (0.21 g, 0.173 mmol) and B(C$_6$F$_5$)$_3$ (0.0035 g, 2 mol %) were placed for the synthesis of P1 and, DDSQ(Me)H (0.18 g, 0.16 mmol), DDSQ(i-

Bu)(OH) (0.2 g, 0.16 mmol) and $B(C_6F_5)_3$ (0.0035 g, 2 mol%) were placed for the synthesis of P2. After drying, the flask was sealed with argon atmosphere and 1 mL of toluene (dried with sodium metal) was added at 70 °C and reaction mixture was stirred at 90 °C. After few minutes of stirring, the DDSQ monomers went to the solution with hydrogen bubbling, which confirmed the progress of reaction. The reacting solution was further stirred for 12 hours and then the mixture was poured into methanol to give the precipitation which was dried in vacuum to get 0.28 g (68% yield) and 0.29 g (72% yield) of the polymer P1 and P2, respectively. The crude polymers were purified by repeated re-precipitation from THF into methanol.

Scheme 3. Cross-dehydrocoupling polymerization of DDSQ(Me)H and DDSQ(Me)(OH) for the synthesis of polymer P1, DDSQ(Me)H and DDSQ(*i*-Bu)(OH) for the synthesis of polymer P2 using $B(C_6F_5)_3$ as catalyst.

For Polymer P1: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.21 (s, 6H, CH_3), 6.91-7.50 (m, 40H, Ph); ^{29}Si NMR (99.5 MHz, $CDCl_3$): δ (ppm) -79.50 (t, 4Si), -79.00 (s, 4Si), -64.44 (s, 2Si); GPC: M_n = 9000, M_w = 23000, M_w/M_n =2.55. For Polymer P2: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.08 (s, 6H, CH_3), 0.22 (4H, isobutyl-CH_2), 0.63 (12H, isobutyl-CH_3), 1.75 (2H, isobutyl-CH), 6.90-7.44 (m, 80H, Ph); ^{29}Si NMR (99.5 MHz, $CDCl_3$): δ (ppm) -79.80 to -79.20 (m), -79.04 (s), -66.73 (s), -64.97 (s); GPC: M_n = 9000, M_w = 24000, M_w/M_n =2.66.

3. Results and Discussion

3.1. *Synthesis of polymers*

Several attempts were made to synthesize polymers from DDSQ(Me)(OH) and DDSQ(*i*-Bu)(H), and DDSQ(*i*-Bu)(OH) and DDSQ(*i*-Bu)H as monomers, prior to the synthesis of P1 from DDSQ(Me)H and DDSQ(Me)(OH) and P2 from DDSQ(Me)H and DDSQ(*i*-Bu)(OH). No reaction proceeded at 100°C for even 72 hrs reaction time in toluene with $B(C_6F_5)_3$ as catalyst.

Table 1. Polymerization of DDSQ monomers with feed ratio 1:1, catalyzed by $B(C_6F_5)_3$ (2 mol%).

Run	DDSQ monomers in toluene		Reaction bath		
	M1	M2	Time (h)	Temp, (°C)	Results
	Molar ratio (1:1)				
1	DDSQ(Me)(OH)	DDSQ(*i*-bu)(H)	72	100	No reaction
2	DDSQ(*i*-bu)(OH)	DDSQ(*i*-bu)H	72	100	No reaction
3	DDSQ(Me)H	DDSQ(Me)(OH)	12	90	P1
4	DDSQ(Me)H	DDSQ(*i*-bu)(OH)	12	90	P2

Reactions were seemed to be prevented due to the strong steric hindrance of *i*-Bu group at SiH site for the accommodation of $B(C_6F_5)_3$ catalyst at the end functional DDSQ units in run 1 and run 2 whereas, run 3 and run 4 allowed the progress of reactions, probably due to the relatively less steric hindrance of methyl group at SiH site as shown in Table 1. Polymer P1 and P2 were obtained according to scheme 3 with the recipes described in run 3 and run 4 in Table 1.

Tris(pentafluorophenyl)borane $B(C_6F_5)_3$ has been used in a number of organic and polymerization reactions, such as silylation of alcohol, hydrosilylation of carbonyls and thiocarbonyls at room temperature as a catalyst [24-27]. In this study, we used $B(C_6F_5)_3$ for the polycondensation of hydroxy end functional double-decker silsesquioxane and hydrogen end functional double-decker silsesquioxane. Although room temperature is sufficient to activate $B(C_6F_5)_3$ catalyst for the cross-dehydrocoupling reaction, we used relatively high temperature (90-100°C) for the better dissolution of the monomers as well as the polymer formed during polymerization . The progress of polymeric reaction was confirmed by the vigorous bubbling of hydrogen by the dehydrocoupling reactions. Although we succeeded in the synthesis of new polymers from double-decker monomers, the molecular weights are rather low, and the polydispersity was rather high. The reason may be in the purity of the monomers. Further efforts to purify the monomers should be made.
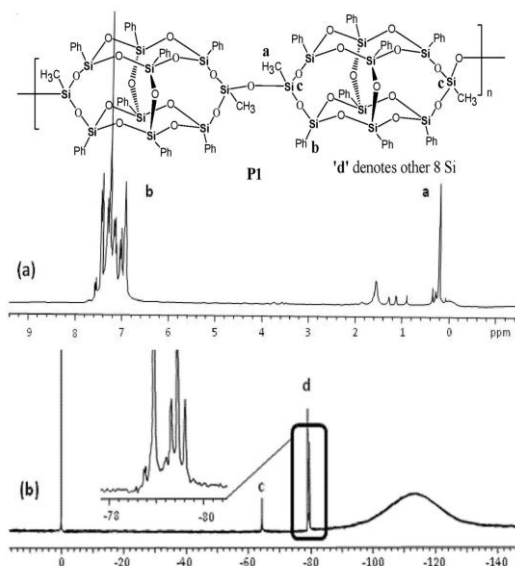
Fig. 1. (a) ^{1}H NMR and (b) ^{29}Si NMR of polymer P1.

In the ^{1}H NMR spectrum of P1 in Fig. 1 (a), the concomitant disappearance of SiH at $\delta = 4.98$ ppm of DDSQ(Me)H with hydroxyl hydrogen (Si-OH) of the DDSQ(Me)(OH) at $\delta = 2.66$ ppm confirms the formation of polycondensation product. On the contrary, the appearance of protons chemical shifts of SiCH$_3$ at new position, $\delta = 0.21$ (s, 6H) and SiPh at $\delta = 6.91$-7.50 (m, 40H) also support the formation of P1 polymer. The ^{29}Si NMR of P1 (Fig. 1b) reveals the disappearance of Si(Me)H signal at $\delta = -32.77$ ppm [of DDSQ(Me)H] and Si(Me)(OH) signal at $\delta = -53.91$ ppm [of DDSQ(Me)(OH)] and appearance of single new signal at $\delta = -64.44$ ppm of Si-O-Si bond connecting the DDSQ-DDSQ units strongly supports the formation of polymer P1. The signals of other eight Si atoms are appeared similarly as seen in the double decker monomers.

Fig. 2 (a) and (b) shows the ^{1}H NMR and ^{29}Si NMR spectrum of polymer P2. Similar to the P1, the ^{1}H NMR spectrum of P2 shows the concomitant disappearance of SiH at $\delta = 4.98$ ppm of DDSQ(Me)H monomer with hydroxyl hydrogen (Si-OH) of the DDSQ(i-Bu)(OH) at $\delta = 2.59$ ppm confirms the formation of polycondensation product. On the contrary, the appearance of protons chemical shifts of SiCH$_3$ at new position, $\delta = 0.08$ (s, 6H) of DDSQ(Me)H unit and iso-butyl group chemical shifts at $\delta = 0.22$ (4H), 0.63 (12H) and 1.75 (2H) ppm assignable to CH_2, CH_3, and CH, respectively, confirm the presence of both DDSQ(Me)H and DDSQ(i-Bu)(OH) in the polymer backbone. Again, the phenyl chemical shifts of SiPh are also present at $\delta = 6.90$-7.44 (m, 80H) ppm in the spectrum of polymer P2. The ^{29}Si NMR of P2 (Fig. 2b) reveals the disappearance of *Si*(Me)H signal at $\delta = -32.77$ ppm and Si(i-Bu)(OH) signal at $\delta = -55.95$ ppm of DDSQ(Me)H and DDSQ(i-Bu)(OH), respectively confirms the polycondensation reaction product. At the same time the appearance of new signals at -64.97 and -66.73 ppm

assignable to end capped Si(Me) and Si(*i*-Bu) proves the connection of DDSQ(Me)-DDSQ(-Bu) giving polymer P2. The signals for other sixteen Si atoms are appeared similarly as seen in the double-decker monomers.
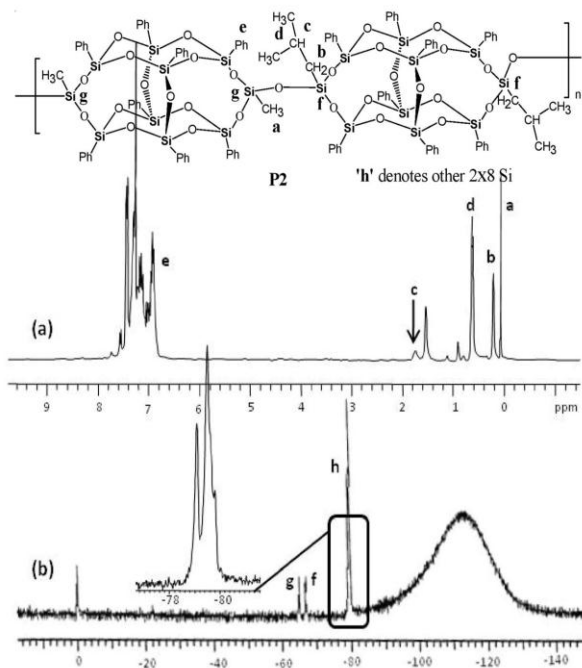

Fig. 2. (a) ^{1}H NMR and (b) ^{29}Si NMR of polymer P2.

3.2. *Thermal properties*

Thermal properties of polymers P1 and P2 were studied by thermogravimetric analysis (TGA) method and the thermal stabilities are shown as graphical representation in Fig. 3. From Fig. 3, it is seen that both the polymers exhibit good thermal stability in the range of 470-530°C. The high thermal stabilities of these polymers arise due to the presence of double-decker silsesquioxane (DDSQ) unit in the main chain and phenyl substituent in the silsesquioxane structure [28]. Comparatively low thermal stabilities of both the P1 and P2 polymers in air are due to the early oxidative degradation of methyl and isobutyl substituent in the side chain at elevated temperature. It can be seen that 5% weight loss temperature (T_{d5}) for the P1 and P2 are around 470°C and 530°C, respectively in nitrogen atmosphere and that are 470°C and 510°C respectively, in air atmosphere.
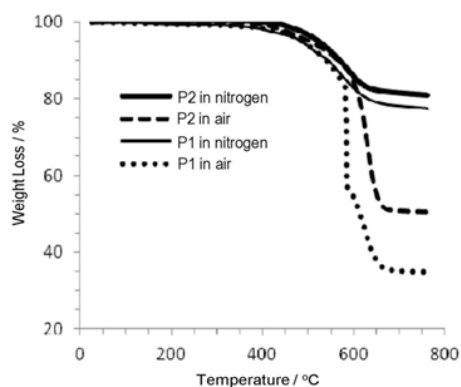
Fig. 3. TG analysis of P1 and P2 in nitrogen and air with the heating rate of 10°C/min.

The distinguishable low degradable temperature (T_{d5}) for P1 (470°C) compare to that of P2 (530-510°C) is assumed for the low packing density which arise from the isomeric irregular conformation of DDSQ(Me)-DDSQ(Me) unit in the polymer backbone. The residual weights for P1 and P2 are 78% and 81% in nitrogen and 36% and 51%   in air, respectively. The high residual weight in nitrogen atmosphere suggests that P1 and P2 merely lost organic moieties from the backbone persisting siloxane/silsesquioxane backbone or slightly cleavage of backbone at 760°C, whereas, in air atmosphere, the polymers were completely oxidized (form SiO_2) with the complete cleavage of the backbone at 760°C [21].

4. Conclusions

Polymers with highly thermal stabilities were synthesized with the alternating incorporation of two different double-decker silsesquioxane units, (DDSQ)(Me)H and (DDSQ)(Me)(OH), or (DDSQ)(Me)H and DDSQ(*i*-Bu)(OH) in the backbone. Characterization with ^{1}H NMR, ^{29}Si NMR and SEC proved the formation of polysilsesquioxane. High thermal stability of DDSQ units resulted exceptional thermal stability of polysilsesquioxane up to 500 °C with no weight loss. Poor solubility as well as process ability of polysilsesquioxane containing methyl functional end capped double-decker silsesquioxane poly(DDSQ(Me)) was improved by replacing methyl group with *iso*-butyl group as DDSQ(*i*-Bu). Good process-ability, high thermal stabilities and chemical inertness of siloxane bond of these polymers would expand their applications to the adverse atmospheres.

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