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工學博士學位論文

**Synthesis and characterization of linear and
branched high molecular weight
polymethylsilsesquioxane (PMSQ) by
stereoisomer of cyclic siloxane**

입체 환형 실록산 단량체를 이용한 선형
및 가지형 고분자 메틸실세스퀴옥산의
합성 및 이의 특성 분석

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**Synthesis and characterization of linear and branched high
molecular weight polymethylsilsesquioxane (PMSQ) by
stereoisomer of cyclic siloxane**

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Abstract

This study presents the synthesis, characterization, and applications of linear and branched high molecular weight polymethylsilsesquioxane (PMSQ) by stereoisomer of tetra cyclic siloxane. Silsesquioxanes are inorganic-organic hybrid materials that have properties between that of ceramic and organic polymers such as good solubility, easy functionalization, and high thermal stability. However, except cage structured silsesquioxanes, polysilsesquioxanes are almost always applied as a cross-linked structure because of difficulty of synthesis. Therefore, it is hard to achieve functionalization and good solubility after being a cross-linked structure, even before. Moreover, it is known that silsesquioxane easily form a small particles rather than network matrix.

In various silsesquioxanes, methyl functional silsesquioxane is one of the most well studied materials for inter layer dielectric (ILD) application, as they have an intrinsically low polarizability, high thermal stability, and excellent mechanical properties based on rigid silicon oxide framework. In addition, PMSQs are conventionally reported as forming cross-linked structures by the sol-gel method. In construction of cross-linked structure, the properties are severely affected by its synthetic route of hydrolysis-condensation and innumerable synthetic conditions, which have shown to form cage, cage-like, or cyclic structures as mentioned. Moreover, further processing of heat treatment is required to obtain an integrated network PMSQ which leads to a large

amount of shrinkage by secondary condensations that lead to high internal stresses that can crack the films

Due to above mentioned difficulties, researchers have tried to investigate linear high molecular weight polymethylsilsesquioxane. Traditionally, the synthetic route of linear PMSQ is from trichloro- or trialkoxy- silane. This method has greatly depended on the nature of the substituent attached to the silicon atom, as well as the condition of synthesis. As is the case, the use of trifunctional monomers undoubtedly leads to uncertainties in intermediary structures during polymerization.

In order to approach the favorable properties of PMSQ in a reproducible manner, PMSQs were synthesized and characterized as below.

First, by using specific tetra functional cyclic compounds as definitive precursors, PMSQ can be tailored to a ladder structure. Four stereoisomer of tetra cyclic tetraol substituted with methyl groups were successfully synthesized, and then the *cis-trans-cis* isomer from mixture of four stereoisomers isolated. Isolated *cis-trans-cis* Methyl-T4-tetraol was characterized by HPLC, ^1H and ^{29}Si NMR spectra.

Secondly, this isolated unit was directly polymerized to give ladder structured polymethylsilsesquioxane (PMSQ) by hydrogen bond induced ring condensation. Structural analysis of linear PMSQ was conducted by ^1H and ^{29}Si NMR spectra, FT-IR, GPC, MALDI-TOF MS, and solution small angle x-ray scattering.

Third, high molecular weight PMSQs were synthesized by controlling the reaction conditions and these materials applied for ILD. This rigid ladder backbone with high molecular weight would support lower dielectric constants stemming from increase of

inter-molecular space and high mechanical strength, as well as minimizing shrinkage during the ILD process. In addition, as followed end-capped reaction by trimethyl- and triphenyl- moiety, related properties such as modulus and dielectric constant were observed.

Finally, branched high molecular weight PMSQs were introduced by control of four isomer compositions because of induction of material density and viscosity. In a view of ILD process, it was very important to control of material density and viscosity because density was directly related with dielectric constant and viscosity was significantly affected to processibility. Branched PMSQs were analyzed by ^{29}Si NMR, dilute SAX scattering, and static light scattering. Then, their mechanical and electrical properties were also observed.

Key word: PMSQ, stereoisomer, linear and branched polymer, low dielectric material.

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TABLE OF CONTENTS

Abstract	i
List of Figures	v
List of Tables	viii

Chapter 1

Introduction & Motive

1. Introduction	
1.1 Definition and History of Silsesquioxanes	2
1.2. Classes of Silsesquioxane and Their Characteristics	6
1.3. Early Development and Problems of Ladder-like Polysilsesquioxanes	11
1.4 Motivation	15
1.5. References	17

Chapter 2

Synthesis and characterization of Ladder

Polymethylsilsesquioxane by isolation of cyclic stereoisomer

2.1. Introduction	21
2.2. Experimental	23
2.3. Results and Discussion	26
2.4. Conclusion	45
2.5. References	46

Chapter 3

Structural analysis of high molecular weight PMSQs and their related properties for interlayer dielectric (ILD) application

3.1. Introduction	52
3.2. Experimental	54
3.3. Results and Discussion	59
3.4. Conclusion	86
3.5. References	88

Chapter 4

Comparative evaluation of various structural PMSQs from stereo

isomer compositions

4.1. Introduction	91
4.2. Experimental	93
4.3. Results and Discussion	95
4.4. Conclusion	106
4.5. References	107
Abstract in Korean	108

List of Figures

Figure 1.1.	Various structures of silsesquioxane (SiO _{1.5}) _n	4
Figure 1.2.	Structural analysis of siloxane- ‘T’ structures through ²⁹ Si NMR spectrum	5
Figure 1.3.	Preparation steps and drawbacks of 3-D networked silsesquioxane by silicon sol-gel precursor.	8
Figure 1.4.	Typical application methods of polyhedral-oligo-silsesquioxane (POSS).	10
Figure 1.5.	General features and benefits of Ladder-like poly silsesquioxane (LPSQ)	11
Figure 2.1.	¹ H NMR spectrum of MethylT4(A) in CDCl ₃ , four MethylT4-tetraols (B) in DMSO- <i>d</i> ₆ .	27
Figure 2.2.	FT-IR spectrum of MethylT4(A) and four methylT4-tetraols (B)	27
Figure 2.3.	²⁹ Si NMR spectrum of Methyl-T4(A) and four methyl-T4-tetraols (B).	28
Figure 2.4.	Assignment of ESI-TOF MS peaks of four Methyl-T4-tetraol in decreasing order of intensity (Positive ion mode)	29
Figure 2.5.	¹ H NMR spectrum of methyl group (Si- <u>CH</u> ₃) chemical shift of Methyl-T4 and Methyl-T4-OH	30

Figure 2.6.	²⁹ Si NMR spectrum of stereoisomers of MethylT4-tetraol and isolated isomers	31
Figure 2.7.	¹ H NMR spectrum of stereoisomers of MethylT4-tetraol and isolated isomers	32
Figure 2.8.	HPLC results of stereoisomers of MethylT4-tetraol in cyclohexane and ethyl acetate at a rate of 4 to 6	32
Figure 2.9.	HPLC results of stereoisomers of MethylT4-tetraol in cyclohexane and ethyl acetate at a rate of 2 to 8	33
Figure 2.10.	FT-IR spectrum of stretching peak of silicon oxide bond and hydroxide in each stereoisomers	33
Figure 2.11.	Modeling of <i>cis-syndiotactic</i> ladder silsesquioxane structure	35
Figure 2.12.	²⁹ Si NMR spectrum of four stereoisomers of Methyl-T4-tetraol(A) and isolated tetraol-(3) (B) in acetone_d6	36
Figure 2.13.	HPLC (Normal phase, cyclohexane/Ethylacetate = 6/4, 1.6 ml/min) of Methyl-T4-tetraol isomers(A) and isolated tetraol-(3) (B).	36
Figure 2.14.	Size exclusion chromatography (SEC) results of PMSQs, (A) oligoMSQ and (B) PMSQ.	38
Figure 2.15.	¹ H NMR spectrum of OliMSQ(A) and PMSQ(B).	39
Figure 2.16.	²⁹ Si NMR spectrum of PMSQs, (A) oligoMSQ and (B) PMSQ	39
Figure 2.17.	¹ H NMR spectra (A) and ²⁹ Si NMR spectra (B) of end-capped PMSQ	40
Figure 2.18.	MALDI-TOF MS spectrum of PMSQ	41

Figure 2.19.	Proposed PMSQ structure during polymerization	42
Figure 2.20.	Small angle x-ray scattering of dilute PMSQs. (1) the log-log plot of (A) oligoMSQ and (B) PMSQ, (2) Kratky plot of (A) oligoMSQ and (B) PMSQ	43
Figure 2.21.	TGA diagram of oliMSQ (A), and PMSQ (B)	45
Figure 3.1.	(A) Logarithm plot of weight average versus reaction time and three kind of PMSQs. (B) GPC diagram of PMSQs. (a) PL10K (Mw:10K) (b) PL130K (Mw:130K), and (c) PL570K (Mw:570K)	60
Figure 3.2.	FT-IR spectrum of three kind of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K	61
Figure 3.3.	TGA trace of three kinds of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K	63
Figure 3.4.	²⁹ Si NMR spectrum of three kinds of PMSQs (a) PL10K, (b) PL130K, and (c) PL570.	64
Figure 3.5.	Static light scattering (SLS) diagram of (A) PL130K and (B) PL570K	65
Figure 3.6.	Small angle x-ray scattering from dilute solution of three kinds of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K. (A) Log-log plot of the scattered intensity as a function of q and (B) Kratky plot of $q^2I(q)$ versus q .	66

Figure 3.7.	X-ray diffraction of three kinds of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K	69
Figure 3.8.	FT-IR spectrum of PMSQs from various organic solvents. (a)Ethyl acetate, (b)Acetone, (c)Methanol, and (d) DMAC	71
Figure 3.9.	TGA diagram of PMSQs from various organic solvents. (a)PL570k, (b)Acetone, (c)Methanol, and (d) DMA	72
Figure 3.10.	XRD of PMSQs from various organic solvents. (a)PL130k, (b)Acetone, (c)Methanol, and (d) DMAC	73
Figure 3.11.	¹ H NMR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a)PL10k, (b) PL130k, (c) PL750k	75
Figure 3.12.	²⁹ Si NMR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a)PL10k, (b) PL130k, (c) PL750k	76
Figure 3.13.	FT-IR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a)PL10k, (b) PL130k, (c) PL750k	77
Figure 3.14.	FT-IR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a)PL10k, (b) PL130k, (c) PL750k	78
Figure 3.15.	Measurements of surface flatness (Ra) by AFM images. (A) PL10K for 0.364 nm, (B)PL130K for 0.550 nm, and PL570K for 0.502 nm	81
Figure 3.16.	XRR results of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K shifted for clarity	82

Figure 3.17.	Nanoindentation results of (a) PL10k, (b) PL130K, and (c) PL570K	84
Figure 4.1.	¹ H NMR spectrum of four compositions of isomers. (1)PL, (2)PB85 (3)PB55, and (4)PB35	96
Figure 4.2.	HPLC diagram of four compositions of isomers. (1)PL, (2)PB85 (3)PB55, and (4)PB35	97
Figure 4.3.	GPC results of polymerization of four compositions of isomers. (1)PL, (2)PB85 (3)PB55, and (4)PB35	98
Figure 4.4.	FT-IR spectrum of branched PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35	100
Figure 4.5.	²⁹ Si NMR spectrum of branched PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35	101
Figure 4.6.	Dilute SAX scattering of PMSQs in toluene, THF, and methanol. (1)PL, (2)PB85 (3)PB55, and (4)PB35	103
Figure 4.7.	TGA diagram of PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35	104
Figure 4.8.	Degradation venue of methyl group as branched PMSQ	105

List of Scheme

scheme 1.1.	Brown's synthetic route of polysilsesquioxane	12
scheme 1.2.	Zhang's synthetic route of Ladder-like polysilsesquioxane (LPSQ) using template group	14
scheme 2.1.	Schematic diagram of isolation of four Methyl-T4-tetraol. A. 1,3,5,7-tetramethyl-2,4,6,8-tetrahydrido cyclosiloxane (Methyl-T4). B. Four stereoisomers of Methyl-T4-tetraol, C. Isolated four Methyl-T4-tetraol.	23
scheme 2.2.	Synthetic route of PMSQ by ring condensation of isolated tetraol-(3)	37
scheme 3.1.	Synthetic route of PMSQs by <i>cis-trans-cis</i> Methyl-T4-tetraol	54
scheme 3.2.	Schematic diagram of structure transition of PMSQs as a function of reaction time. (a) PL10K (b) PL130K, and (c) PL570K	68
scheme 3.3.	The description of the bulk PMSQs features	70
scheme 3.4.	Introduction of trimethyl and triphenyl moieties by end-capping reaction of PMSQs.	74
scheme 4.1.	Preparation of four different isomer content as 100%, 85%, 55%, and 35% <i>cis-trans-cis</i> isomer,	92
scheme 4.2.	Schematic illustration of branched PMSQ	99

scheme 4.3. Schematic illustration of PMSQs. (1)PL, (2)PB85 (3)PB55, 103
and (4)PB35

List of Tables

Table 2.1.	Contents of four stereoisomers calculated by ^1H NMR spectrum	30
Table 3.1.	Results of Bulk properties of PMSQs	79
Table 3.2.	Atomic compositions of PMSQs calculated by ^{29}Si NMR spectrum	80
Table 3.3.	Results of Bulk properties of end-caped PMSQs	86
Table 4.1.	Four compositions of isomers	95
Table 4.2.	Molecular weight and polymerdispersity of PMSQs	98

Chapter 1

Introduction & Motive

1. Introduction

1.1 Definition and History of Silsesquioxanes

Silsesquioxane is the general IUPAC name for a family of polycyclic compounds consisting of silicon and oxygen (Figure 1). The name of silsesquioxane was derived from *siloxane* (Si-O-Si) and *sesqui* (meaning one and a half), and the general name reflects the ratio of silicon and oxygen atoms in completely condensed silsesquioxanes $[\text{RSiO}_{3/2}]_n$.

The term ‘silsesquioxanes’ was initially coined by Scott and his coworkers in 1946,[1] as he described a completely condensed alkyl-substituted silsesquioxane. Although he was not able to assign the exact structure, he was able to determine that the general formula was $(\text{RSiO}_{3/2})_n$, in which ‘*n*’ was integer.

Twenty years later, various structures of the silsesquioxane were reported by Brown and Vogt.[2] They described the polycondensation of cycloalkyltrichlorosilane in a water mixture solvent. The main products that were formed at the beginning of the reaction were incompletely condensed dimers ($\text{RSi(OH)}_2\text{ORSi(OH)}_2$, R = Cyclohexyl) and higher oligomers, that still contained silanol groups. Many researchers followed this synthetic method to prepared polyorganosilsesquioxanes.[3-6]

Polyphenylsilsesquioxanes (PPSQ), known to have ladder structure, was first introduced by Brown et al in 1964.[7,8] They prepared the polysilsesquioxane through

hydrolytic polycondensation reaction from phenyltrichlorosilane. Furthermore, Obtained PPSQ was characterized by IR and UV spectroscopy, and many isolated incompletely condensed silsesquioxanes are shown in Figure 1.1 These synthetic results were very significant, because of proposed the analytical methods about polysilsesquioxane structures. However, there are still a lot of problems such as uncontrollable structure, difficulty to obtain high molecular weight polymer, low yield, and complicated processes.[9,10] Figure 1.2 shows the analytical technique of silsesquioxane structure through ^{29}Si NMR spectrum.

Polymethylsilsesquioxane(PMSQ) was first introduced in 1978 probably because PMSQ is very easily gelled during the course of its synthesis.[11] Suminoe et al. reported on synthesis of PMSQ by adding water dropwise to methyltrichlorosilane dissolved in a mixture of MIBK(methylisobutylketone) and THF in the presence of triethylamine at 0 °C, followed by heating at 100~110 °C for 4 hrs. However, structural regularity of PMSQ has been few discussed. Despite the past and present interests in PMSQ, their formation process and molecular structure have been still controversial. Although this class of polymers should be a potentially useful material for numerous applications, a general synthetic route which affords rational control over their structure and properties has not yet been developed. Previous synthetic routes have largely relied upon the in situ formation of the silsesquioxane or have utilized conventional

silsesquioxane with unordered structure, low molecular weight, and inconstant functionality.

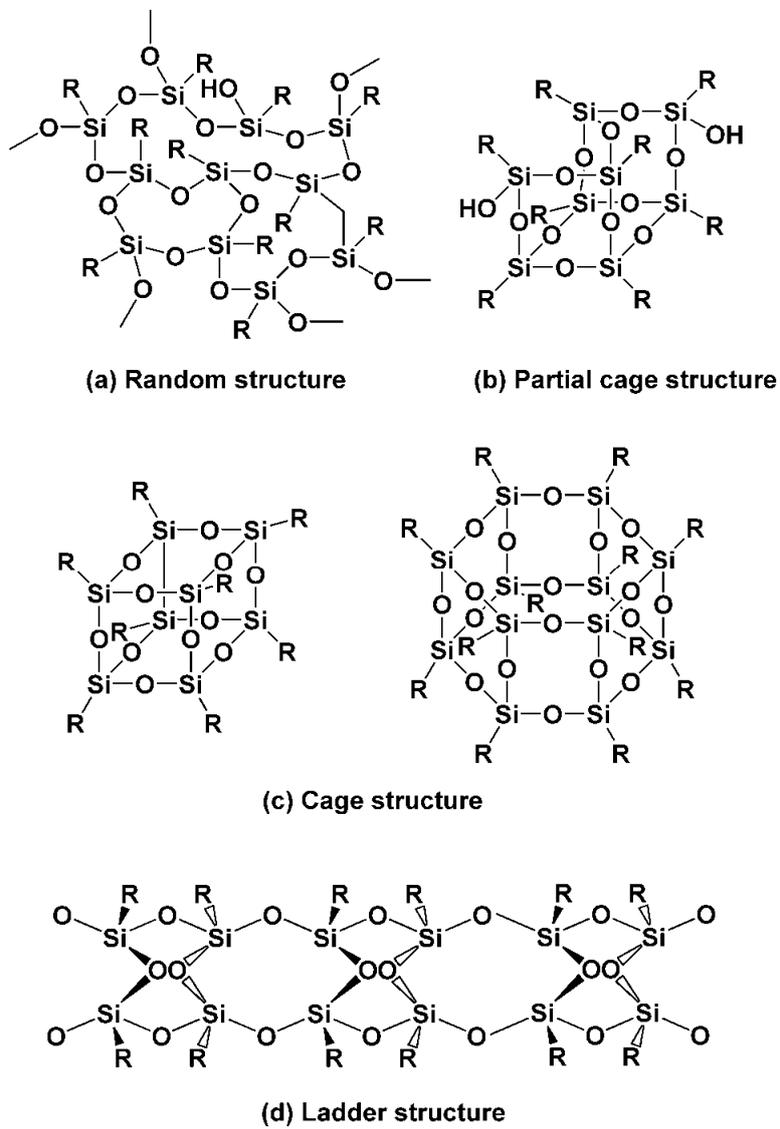


Figure 1.1. Various structures of silsesquioxane ($\text{SiO}_{1.5}$)_n.

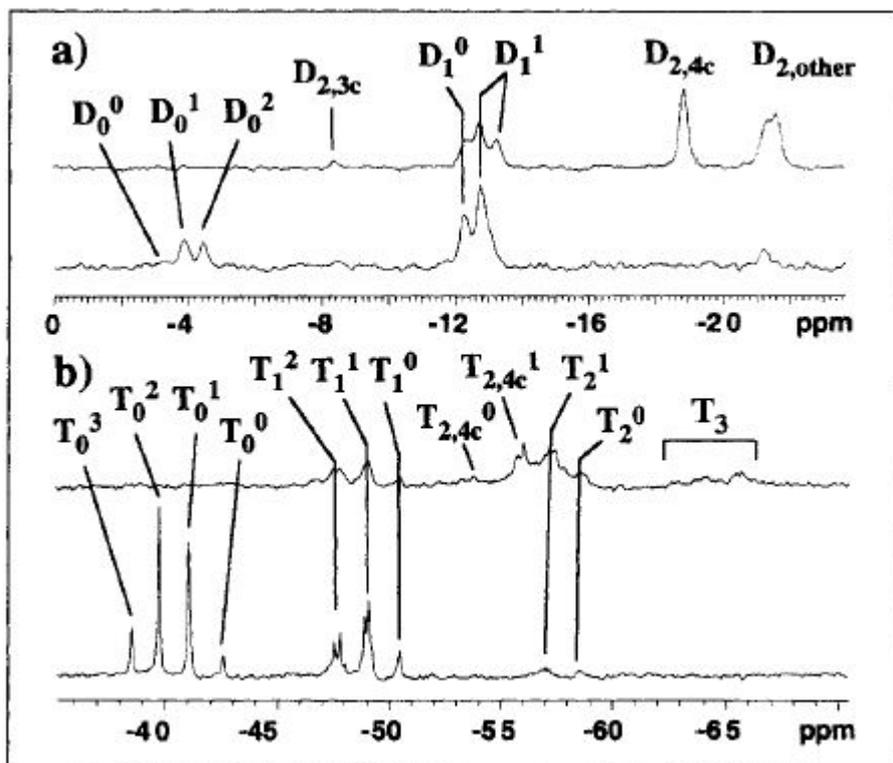


Figure 1.2. Structural analysis of siloxane- 'D and T' structures through ^{29}Si NMR spectrum.

1.2 Classes of Silsesquioxane and Their Characteristics

The structure of silsesquioxanes can be divided into three main classes: random network, cage, and ladder architecture. Of these structural classes, Si-sol precursor of random type as shown in Figure 1(a) was discovered first. Preparation of organosilsesquioxane using the silicon sol-gel method can be summarized in three steps (Figure 3).[12] First, the organic functional groups attached to the silane monomer are hydrolyzed and condensed in acid or basic aqueous solution, with Si-OH groups remaining in the precursor polymer. These precursors are prepared by coating on substrates such as plastic, silicon wafer, or glass, followed by a thermal treatment process to necessitate the further condensation of the remaining Si-OH groups. Finally, fully condensed silsesquioxane product as a 3D-network siloxane (Si-O-Si) can be obtained by sintering at the high temperatures (over 300°C).

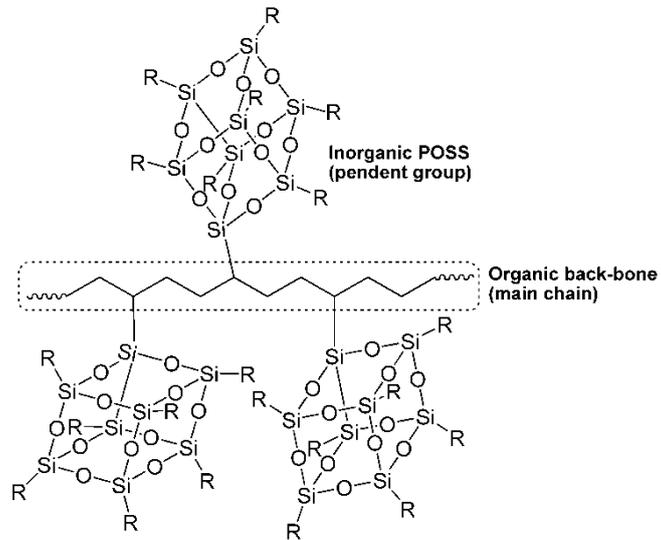
Compared to the organic polymer resins, silicon sol-gel derived materials exhibited superior surface hardness and thermal stability.[13] However, the thermal sintering at temperatures exceeding 300°C required for secondary thermal condensations between the many uncondensed Si-OH groups or Si-OR leads to a great amount of shrinkage is one of the significant drawbacks of the above mentioned sol-gel derived materials.

In order to overcome the drawbacks of silicon sol-gel resins, structurally well-defined polysilsesquioxanes have been extensively researched.[14,15] Compared to

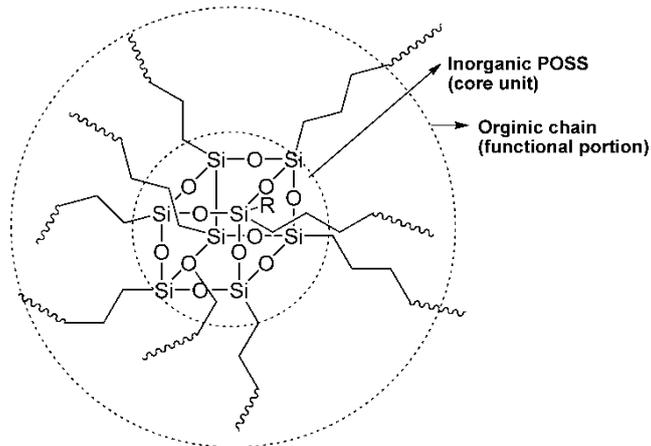
silicon sol-gel derived materials, these structurally sound polysilsesquioxanes can be said to be well-defined in structure, contain very few unstable Si-OH groups, while exhibiting superior properties such as chemical resistance and thermal stability, making them a very appropriate material candidate as organic-inorganic hybrid polymers. These well-defined polysilsesquioxanes are be divided into two major groups, Polyhedraloligosilsesquioxanes (POSS) (Figure 1.1(c)) and Ladder-like Polysilsesquioxanes (LPSQ) (Figure 1(d)). POSS compounds are oligomers with molecular weight between 1K ~ 3K and have a closed cage structure consisting of Si-O-Si bonds with the R functionality located on the vertices of the polyhedron.[16] LPSQ compounds are polymeric in nature with molecular weight exceeding 10K, and consist of a double stranded siloxane bond structure.[17]

Currently, there have been innumerable studies using POSS compounds either by having the organic functional moiety on each vertex of the cage, or by having POSS as a pendant moiety on an organic polymer (Figure 1.4).[18] Both of these strategies have shown to have enhanced the targeted properties. However, POSS being an oligomer, requires additional modification for use as the functional hybrid materials, and has only been studied as an additive or matrix within an organic framework.[19,20]

On the other hand, double stranded LPSQ not only can be used as a matrix by itself, but can also replicate or surpass the performance of POSS compounds.(Figure 1.5) Such advantages notwithstanding, LPSQs have been overlooked due to their difficult syntheses.



a) Application of POSS as a pendent group



b) Application of POSS as a core unit

Figure 1.4. Typical application methods of polyhedral-oligo-silsesquioxane (POSS).

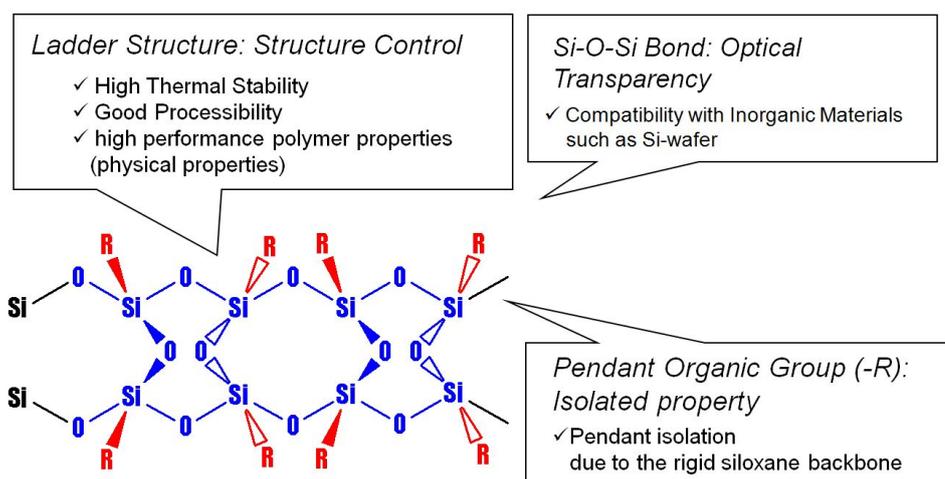
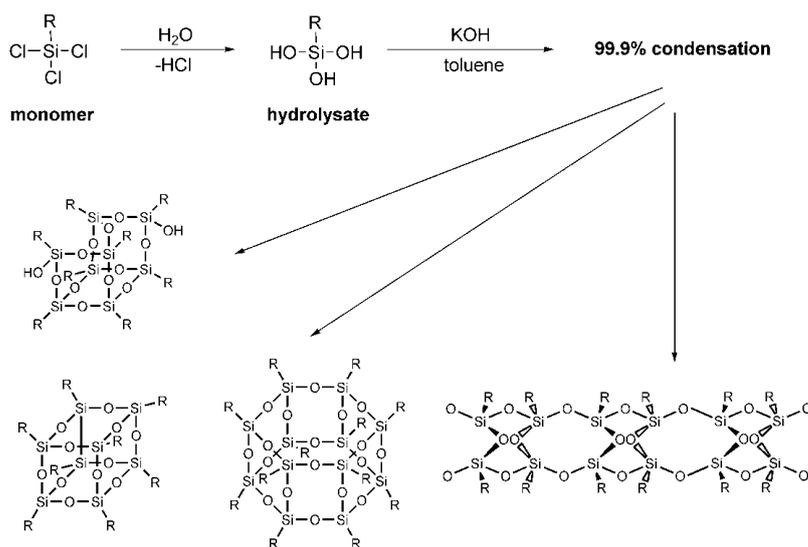


Figure 1.5. General features and benefits of Ladder-like poly silsesquioxane (LPSQ).

1.3 Early Development and Problems of Ladder-like Polysilsesquioxanes

As early as 1960, Brown et al.[7,8] first reported the synthesis of a soluble ladder-like polyphenylsilsesquioxane(LPPSQ) via ‘equilibration polymerization’ using a trichlorosilane monomer and potassium hydroxide (KOH) catalyst at high temperature over 200°C conditions (Scheme 1.1). Many researchers followed this method to prepare LPSQ. Andrianov et al. [21], Pavlova et al.[22] and Lee et al.[23] also researched LPSQ

in various solvents and under different reaction conditions. They employed this ‘equilibration method’ and developed their own synthesis of LPSQ. However, synthetic LPSQ using the ‘equilibration method’ and other ‘modified methods’ have had drawbacks of producing LPSQs with insecure chemical structure and unstable gelation properties in atmospheric environments, as well as complicated synthetic methods.[24] These problems arose from difficult control of unstable hydrolyzed oligomers with remaining alkoxy or Si-hydroxyl groups. Therefore, synthetic LPSQ using the ‘equilibration method’ have had the disadvantage that it is difficult to distinguish from the general sol-gel materials.

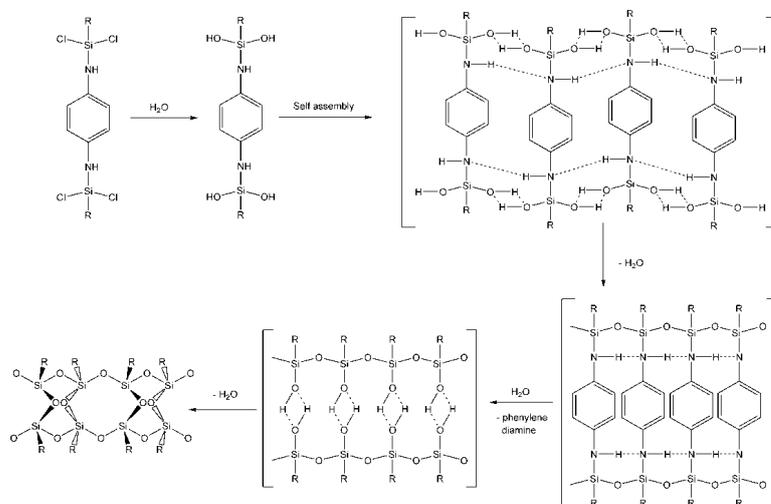


Scheme 1.1. Brown’s synthetic route of polysilsesquioxane.

In the past decade, in order to overcome these synthetic difficulties of well-defined LPSQ, many researchers have developed various analysis methods and synthesis techniques.

The most representative example of this is the works of Zhang and his coworkers. They studied the preparation of ladder polyphenylsilsesquioxane (LPPSQ) under various conditions, and preparation of LPPSQ was carried out in various combinations of organic solvents such as benzene, toluene, tetrahydronaphthalene using potassium hydroxide (KOH) at 250°C. Later on, Zhang and his coworkers synthesized polyorganosilsesquioxane with perfect ladder structure through a ‘template method’[25] and ‘new-three steps approach’[26] as shown Scheme 2. The chemical structure was investigated thoroughly.

According to these results, the aforementioned references make up the modern accepted structural analysis of LPSQ. While this novel method gave well-defined information of the LPSQ, several cumbersome synthetic steps were necessary to prepare alkoxy silane monomers with templating groups such as amine derivatives. Furthermore, introduction of functional group (-R) into LPSQ was not easy in this method, because the -R group of the alkoxy silane monomer worked as a template, not as a functional group. Therefore this synthetic method of utilizing a templating group has had limitations in industry.



Scheme 1.2. Zhang's synthetic route of Ladder-like polysilsesquioxane (LPSQ) using template group.

1.4 Motivation

High molecular weight polysilsesquioxanes as hybrid materials are expected to show unique properties compared with organic polymers. Among them, it is most advantageous to attain harmony of two structural factors. One is that silsesquioxane main chain showing the features of ceramics, while the functional group side chains revealing their own organic property.

Moreover, the brittleness of ceramics would be reduced by chain entanglement of polysilsesquioxane, while the weak thermal properties of the organic polymer would become stronger by the silicon oxide bond. In order to achieve them, the structure of silsesquioxane is preferred to form linear structure comparing than network random structure.

Despite various benefits of them, ladder polysilsesquioxanes have been rarely studied, with the exception of polyphenylsilsesquioxane[PPSQ] because of the notoriously tedious synthetic scheme. One reason is that organic group of starting unit affects the electric polarizability of silicon atom, which leads to variable reactivity. Therefore, synthetic route of ladder silsesquioxane is highly dependent in which organic functional group selected.

Especially, PolyMethylsilsesquioxane [PMSQ] having methyl functional side group is known to be very difficult to build a ladder structure. The ladder structure from trialkoxy- or trichloro- as a starting monomer was hardly formed because there are no secondary

interactions or any induced forces helping growth to be a regular intermediate. It may be for this reason, PMSQ has only been derived by conventional sol-gel methods, albeit its applicability as a low dielectric material. Such sol-gel methods have had problems such as preparation of precursor, process temperature, and shrinkage after curing, which are critical issues when applied to practical applications as reliability tests.

As a matter of fact, ladder structured PMSQ was directly able to be introduced without any curing process. In addition, it was expected to have good compatibility with analogous polymer or monomers. In a point of dielectrics, it also takes advantage of decreasing polymer density by increasing free volume from steric hindrance in each polymer.

Concerning a particular silsesquioxane polymer, branched structure becomes an effective approach to control of material density without chemical substitution in polymer. Moreover, branched polymers would exhibit lower viscosity in solution or bulk state when compared to linear structure, leading to good coating properties. Therefore, all of these motives were fulfilled by controlling various structures of polysilsesquioxane, such as ladder and branched structure from four cyclic stereoisomers.

1.4. References

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Chapter 2

Synthesis and characterization of Ladder Polymethylsilsesquioxane by isolation of cyclic stereoisomer

2. Introduction

In the past four decades, many researchers have tried to investigate various types of polysilsesquioxanes because of their unique properties. However, due to their strong tendency to form mixed structures after polymerization, control of well defined structure has been notoriously difficult [1,2]. Despite the structural uncertainty of polysilsesquioxanes, ladder type polysilsesquioxanes have attracted considerable interest in connection with their valuable properties due to their structural peculiarities, notably the controlled and double-stranded structure of the macromolecules [3-5]. Such polymers possess solubility, enhanced thermal stability, strength, and inertness towards corrosive media [6,7].

Although several synthetic studies with ladder polysilsesquioxanes have been reported, molecular structure and shape had been controversial [8]. Amid dispute, J. F. Browne et al. and K. A. Andrianov et al. exclaimed their results about synthesis of ladder polysilsesquioxane. They proposed the intermediate form of tetraphenyl tetrahydroxy cyclosiloxane in synthesizing ladder polyphenylsilsesquioxanes from the monomer, trichlorophenylsilane [9,10]. They proved the regularity of ladder silsesquioxane by light scattering and rheological methods [11-13].

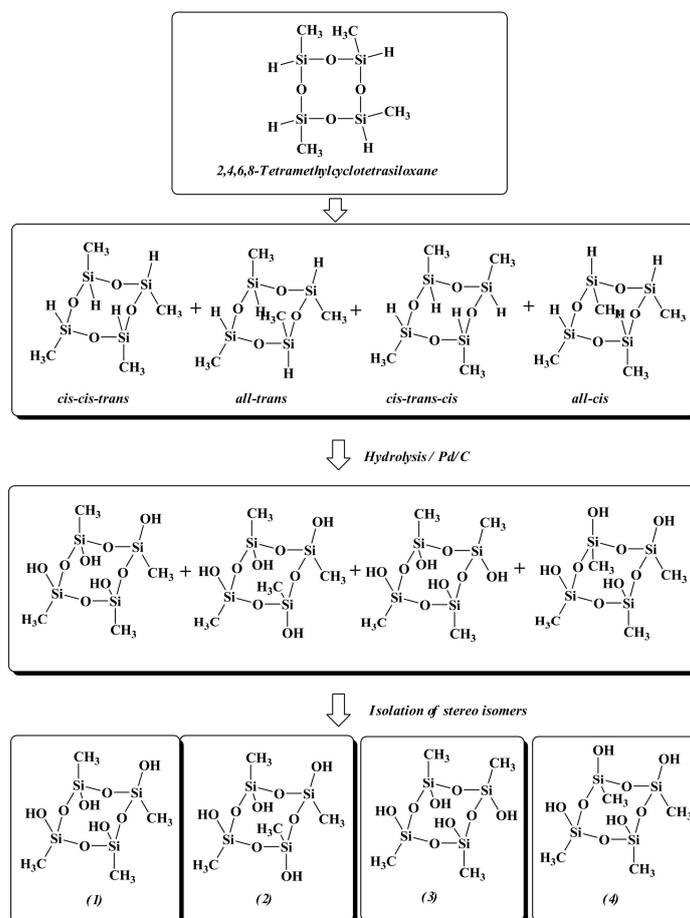
However, synthesis of various organic substituted ladder polysilsesquioxanes by trifunctional compounds has greatly depended on the nature of the substituent attached to the silicon atom, as well as the condition of synthesis [14,15]. As is the case, the use of trifunctional monomers undoubtedly leads to uncertainties in intermediary structures during polymerization.

Therefore, by using specific tetra functional cyclic compounds as definitive precursors, polysilsesquioxanes can be tailored to ladder structure. Studies by Yoshimoto abe et al.[16,17] and Masafumi unno et al.[18,19] have synthesized representative ladder structured silsesquioxane controlled by the stereoisomer of cyclic siloxane precursors. In these works, definite proof of ladder silsesquioxanes was derived from their unique stereoisomers.

However, these studies had the difficulties in maintaining consistent configuration of polymer structure during each step reaction with each fractionated species, constituting a tedious isolation procedure with limitations of obtaining a high molecular weight structure.

On the basis of these studies, condensation polymerization between cyclic tetraol rings with *all-cis* or *cis-trans-cis* isomer was stipulated as the preferred approach to attain polymer regularity, underlain by the linearity and tacticity [20].

In this study, we successfully synthesized four stereo-cyclic hydroxyl substituted siloxane compounds with methyl groups. We successfully isolated *cis-trans-cis* isomer (2) from mixture of four stereoisomers (Scheme 2.1). Isolated *cis-trans-cis* Methyl-T4-tetraol was characterized by HPLC, ^1H and ^{29}Si NMR spectra. In addition, this isolated unit (2) was directly polymerized to give ladder-structured polymethylsilsesquioxane (PMSQ) by hydrogen bond induced ring condensation. Structural analysis of PMSQ was conducted by ^1H and ^{29}Si NMR spectra, FT-IR, GPC, MALDI-TOF MS, and solution small angle x-ray scattering.



Scheme 2.1. Schematic diagram of isolation of four Methyl-T4-tetraol. A. 1,3,5,7-tetramethyl-2,4,6,8-tetrahydro cyclosiloxane (Methyl-T4). B. Four stereoisomers of Methyl-T4-tetraol, C. Isolated four Methyl-T4-tetraol.

2.2 Experimental Section

2.2.1 Materials

95% 1,3,5,7-tetramethyl-2,4,6,8-tetrahydro cyclosiloxane (Methyl-T4) was purchased from Gelest, and distilled to remove the stabilizer and di- or tri-mer. Tetrahydrofuran was dried over sodium. Pd/C (10% activated) was purchased from Across. Distilled water was used for hydrolysis of Methyl-T4. Potassium carbonate was of commercial grade and used without further purification.

2.2.2 *Synthesis of four stereoisomer 1,3,5,7-tetramethyl 1,3,5,7-tetrahydroxyl cyclosiloxane mixture (Methyl-T4-tetraol)*

In a 500 ml round-bottomed flask, hydrolysis of the hydride of Methyl-T4 (19 ml, 0.078 mol) was carried out with water (6.4 ml, 0.355 mol) and Pd/C (10% activated) (0.8 g, 0.75 mmol) for 2 hr in THF (220 ml) at 10 °C. Excess water and Pd/C were removed by MgSO₄ and cellite. The substitution of hydride to hydroxide was confirmed by ¹H NMR (200 MHz, ppm): 0.15 ~ - 0.19 [m, 12H, -CH₃], 6.49 [s, 4H, -OH] in DMSO-*d*₆, and 0.075 ~ 0.047 [m, 12H, -CH₃], 5.46 [s, 2.2H, -OH] in acetone-*d*₆.

2.2.3 *Isolation of four stereoisomer of 1,3,5,7-tetramethyl 1,3,5,7-tetrahydroxyl cyclosiloxane (Methyl-T4-tetraol)*

Isolation of cis-cis-trans Methyl-T4-tetraol(1) ; After filtering, the solution was kept in -15°C for 14 days, and sheet shape crystals obtained. There were mainly collected as cis-cis-trans Methyl-T4-tetraol with minor portion of cis-trans-cis Methyl-T4-tetraol. obtained powder was solute in ether, and recrystallize at -15°C for 1 day. Then, cis-cis-trans Methyl-T4-tetraol was obtained yielding to 20%. ¹H NMR (200 MHz, ppm): 0.0361, 0.001, 0.0077 [s, 12H, -CH₃], 6.486 [s, 4H, -OH] in DMSO-*d*₆

Isolation of all-trans Methyl-T4-tetraol(2) ; the main solution of methylene chloride and THF were continuously used as recrystallization solution for obtaining all-trans methyl-T4-tetraol. Actually, some of cis-cis-trans methyl-T4-tetraol was obtained after 14 days. Therefore, one or two times crystal filterations were required to increase purity of all-trans isomer. In this time, cis-cis-trans isomer and all-trans isomer were obtained with changing of portion of each isomer. Finally, all-trans isomer was obtained after 24 days yielding with 5%. ¹H NMR (200 MHz, ppm): 0.0224 [s, 12H, -CH₃], 6.475 [s, 4H, -OH] in DMSO-*d*₆

Isolation of cis-trans-cis Methyl-T4-tetraol(3) ; After hydrolysis, it was found that cis-trans-cis tetrol-(2) was isolated from four stereoisomers (150 ml in THF) by recrystallization using methylene chloride (1000 ml) and THF (50 ml) co-solvent for 1

hr at 4 °C. ¹H NMR (200 MHz, ppm): 0.014 [s, 12H, -CH₃], 6.49 [s, 4H, -OH] in DMSO-*d*₆, and 0.063 [s, 12H, -CH₃], 5.46 [s, 3H, -OH] in acetone-*d*₆.

Isolation of all-cis Methyl-T4-tetraol(4) ; all-cis isomer is a unstable isomer because of high hydrogen bond interactions. Careful treatment was necessary to obtain it without condensed monomer. After hydrolysis, mixture isomers were precipitated to cyclohexane as much as over nine times of volume. The precipitation were obtained with mixed four stereoisomers, filtering solution was kept at room temperature for 1 month. Needle-shaped crystal was obtained with all-cis Methyl-T4-tetraol. ¹H NMR (200 MHz, ppm): -0.0163 [s, 12H, -CH₃], 6.519 [s, 4H, -OH] in DMSO-*d*₆

2.2.4 Polymerization of cis-trans-cis 1,3,5,7-tetramethyl 1,3,5,7-tetrahydroxyl cyclosiloxane

Isolated tetraol-(3) (2 g) was directly polymerized by systematic ring condensation with potassium carbonate (2 mg) in THF (60 ml) at room temperature for 72 h. The polymerized tetraol-(3) (oligoMSQ) was extracted with methylene chloride and water to remove the catalyst. After drying and evaporating methylene chloride, glassy powder (1.5 g) was obtained. Further reaction was carried out in refluxing toluene (30 ml) without any catalyst, equipped with a dean-stark apparatus for 12 hr. The PMSQ (1 g) was precipitated as white powder in hexane.

2.2.5 Measurement and Techniques

Waters HPLC system was used to certify the purity of isolated tetraol-(3). It was accomplished at arbitrary temperature in a normal-phase mode using normal phase Si100 column (Merk). The HPLC mobile phases consisted of 60% cyclohexane and 40% ethyl acetate. A gradient program was used for the HPLC separation with a flow rate of 1.6 ml/min. Each run time was 40 min and Evaporative light scattering detectors (ELSD) used. The number average molecular weight (*M_n*) and molecular weight distributions (*M_w/M_n*) of the polymers were measured by JASCO PU-2080 plus SEC

system equipped with RI-2031 plus refractive index detector and a UV-2075 plus UV detector (254 nm detection wavelength) using THF as the mobile phase at 40 °C and a flow rate of 1 ml/min. The samples were separated through four Shodex-GPC KF-802, KF-803, KF-804, KF-805. ¹H NMR and ²⁹Si-NMR spectra were recorded in DMSO-*d*₆, Acetone-*d*₆, and CDCl₃ at 25 °C on a Varian Unity INOVA 200MHz for ¹H NMR spectra and Varian NMR System 500MHz for ²⁹Si NMR spectra(²⁹Si: 99.4MHz). The X-ray scattering was examined at the beam-line 4C1 of Pohang light source (PLS) in the Pohang Accelerator Laboratory (PAL) using Cu-K α radiation [21].

2.3. Results and Discussion

2.3.1 Synthesis of four stereoisomers of Hydroxyl-Substituted Methylcyclotetrasiloxane

For preparing ladder-like PMSQ, a hydroxyl substituted cyclotetrasiloxane was synthesized by hydrolysis of Methyl-T4 consisting of four stereoisomers. Hydrolysis of Methyl-T4 was found to give relatively stable, four cyclic stereoisomeric products. Other studies utilizing a cyclic unit to obtain a ladder PMSQ have used various tetracyclic stereoisomers having an activated site such as chloride or bromide, making them extremely unstable [22].

It was found that hydrolysis of Methyl-T4 with Pd/C and water resulted in the closest approach to neutral conditions giving the highest yield of Methyl-T4-tetraol without any condensation of substituted hydroxide groups (Figure 2.1(B)) as described in Scheme 1. [23].

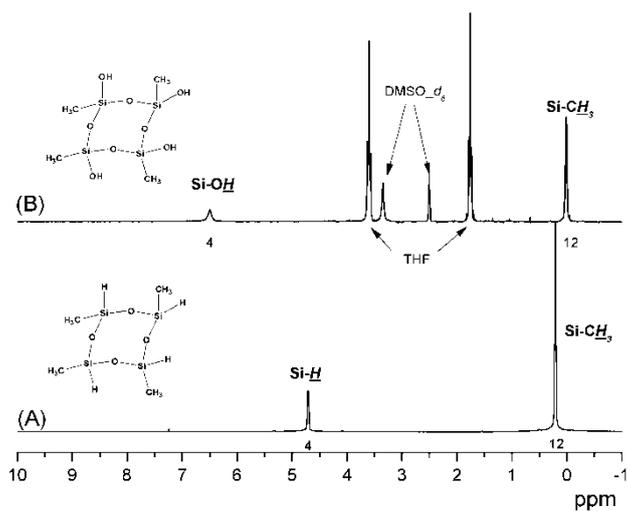


Figure 2.1. ^1H NMR spectrum of MethylT4(A) in CDCl_3 , four MethylT4-tetraols (B) in $\text{DMSO-}d_6$.

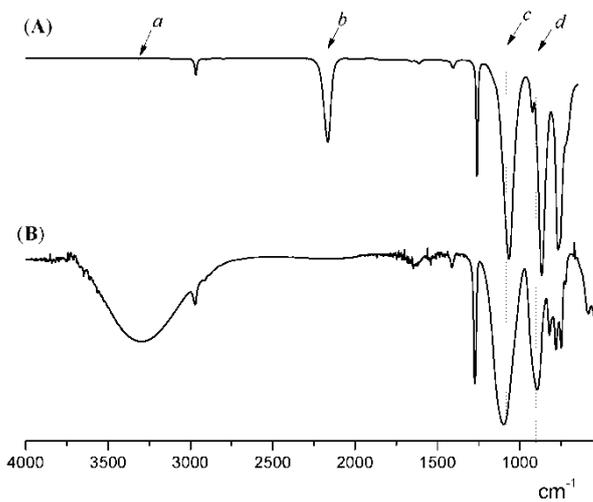


Figure 2.2. FT-IR spectrum of MethylT4(A) and four methylT4-tetraols (B).

Careful temperature control at 10 °C and appropriate solution density during hydrolysis and purification was found to be crucial to obtain Methyl-T4-tetraol because the hydroxyl substituted siloxane $[\text{MeSi}(\text{OH})\text{O}]_4$ was able to be self-condense even in neutral conditions.

After hydrolysis, characteristic peaks of the four stereoisomers, stemming from Methyl-T4 were assigned by the peak position of methyl group in ^1H NMR spectra, with the chemical shift of methyl group by hydroxide displacement showing retention of the four stereoisomers (figure 2.1) [24,25]. According to hydrolysis of hydrido group at 2200cm^{-1} , characteristic peak of hydroxide was shown to 3300cm^{-1} and 980cm^{-1} in FT-IR spectrum (Figure 2.2). In ^{29}Si NMR spectrum (figure 2.3), it was significantly appeared to substitution of hydroxyl group by chemical shift -32.4 ppm to about -56 ppm . Through LC/MS/MS, four stereoisomers were indicated two components as monomer and degradation of one hydroxyl group of monomer (figure 2.4). The major component as Methyl-T4-tetraol was exactly matched to Dalton of 322 which it was plus sodium ion of 18.

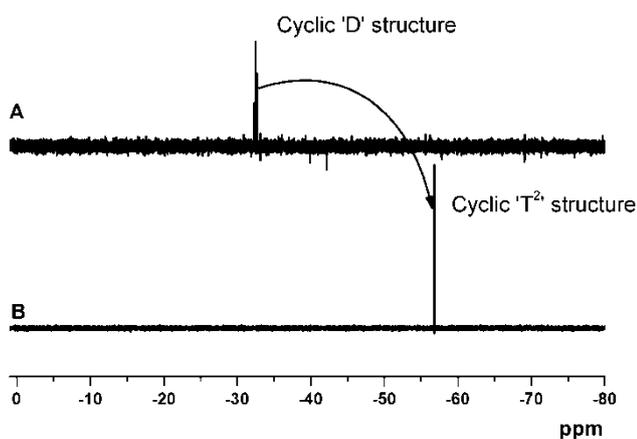


Figure 2.3. ^{29}Si NMR spectrum of Methyl-T4(A) and four methyl-T4-tetraols (B).

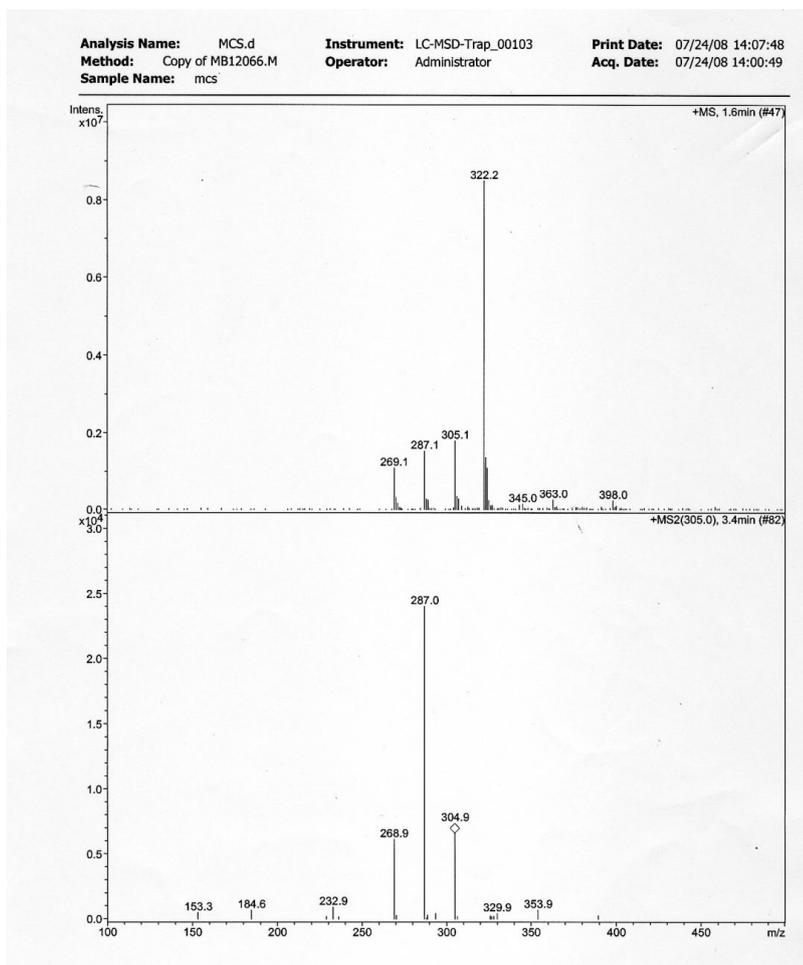


Figure 2.4. Assignment of ESI-TOF MS peaks of four Methyl-T4-tetraol in decreasing order of intensity (Positive ion mode) .

Exptl. M/z	Z	Intensity(x 10 ⁶)	Assignment	Predicted (M+zNH ₄ ⁺)
<i>cis-trans-cis</i>	304	1	C ₄ H ₁₆ O ₈ Si ₄	322
Methyl-T4- tetraol	287	0	C ₄ H ₁₅ O ₇ Si ₄	287

2.3.2 Isolation of four stereoisomer of Hydroxyl-Substituted Methylcyclotetrasiloxane

Form starting monomer as tetramethyl tetrahydrido cyclosilane(Methyl-T4), the contents of four stereoisomers were listed as table 1. To confirm the change of portion of stereoisomer, integration ratio of methyl functional groups were measured by ^1H NMR spectrum. It also proved that the isomers originated from Methyl-T4 as reactant (Figure 5)

Table 2.1. Contents of four stereoisomers calculated by ^1H NMR spectrum

Ppeak #	stereoisomer	Integration (%)
1	All-trans	18.44
2	Cis-trans-cis	17.01
3	Cis-cis-trans	59.27
4	All-cis	5.28

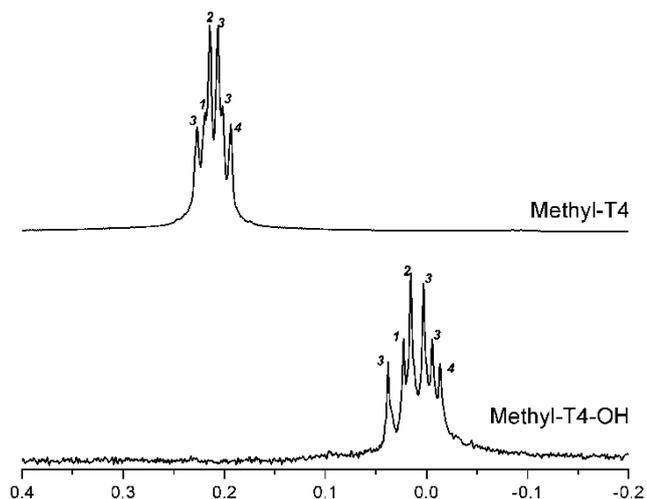


Figure 2.5. ^1H NMR spectrum of methyl group (Si-CH_3) chemical shift of Methyl-T4 and Methyl-T4-OH

After hydrolysis, Four stereoisomers were separated by recrystallization using

various solvent conditions. Therefore, the yields were not reached about 5 to 10 % except cis-trans-cis(3) isomer(50%) as mentioned in experimental section. This study is continually going to try how to obtain specific isomer well. Based on separated isomer, there were successfully analyzed by ^1H NMR, ^{29}Si NMR, FT-IR spectrum, and HPLC diagrams.

Firstly, figure 2.5 showed mixed MethylT4-tetraol and each separated isomers. These spectrums were well matched with reported results by simulation. Secondly, ^{29}Si NMR spectrum was shown to isolated four stereoisomers(figure 2.6). The orders of isomer peaks were a little different from mix four stereoisomers. These results were similar to reference about tetraphenyl tetrahydroxide cyclosilane. Therefore, it was hard to understand a configuration of isolated isomer only using ^{29}Si NMR spectrum.

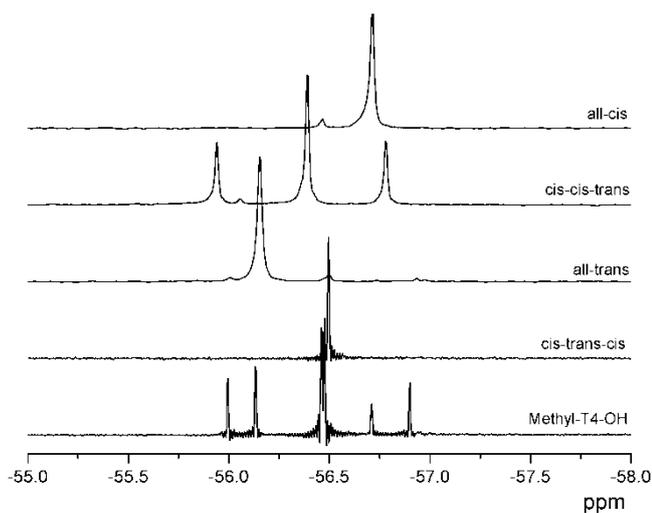


Figure 2.6. ^{29}Si NMR spectrum of stereoisomers of MethylT4-tetraol and isolated isomers

In addition, figure 2.8 also indicated MethylT4-tetraol and isolated isomers as HPLC which eluent condition was cyclohexane and ethyl acetate of 6 : 4 from normal phase Si100 column product of Merck®. However, its condition was not able to detect all-cis isomer because of solubility problem of eluent condition.

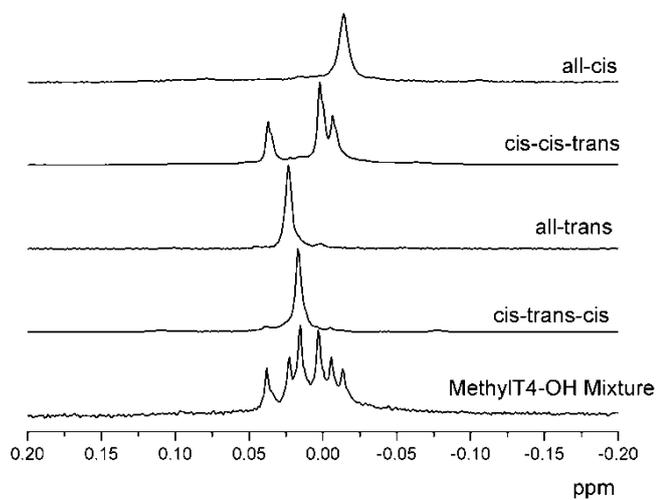


Figure 2.7. ^1H NMR spectrum of stereoisomers of MethylT4-tetraol and isolated isomers

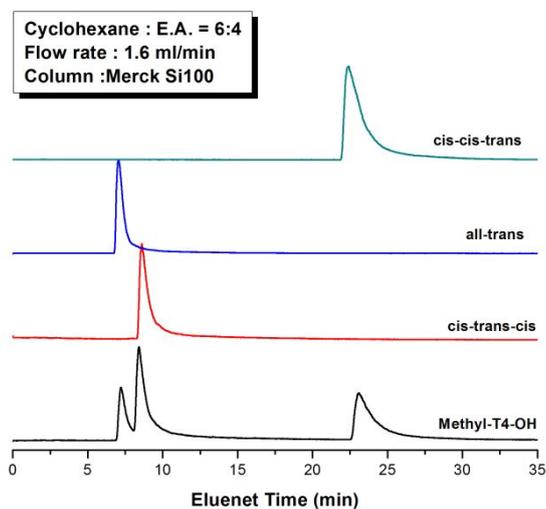


Figure 2.8. HPLC results of stereoisomers of MethylT4-tetraol in cyclohexane and ethyl acetate at a rate of 4 to 6.

In reason, eluent condition was changed to ratio of cyclohexane and ethyl acetate of 8 to 2 to solve all-cis isomer. This eluent condition showed all-cis isomer comparably late time by relatively high polarizable property (figure2. 9).

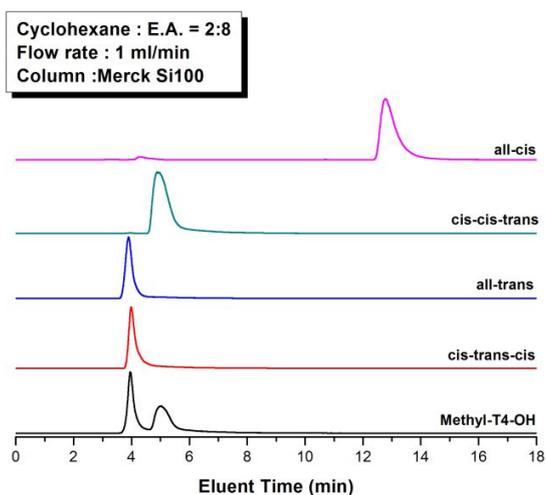


Figure 2.9. HPLC results of stereoisomers of MethylT4-tetraol in cyclohexane and ethyl acetate at a rate of 2 to 8.

Four stereoisomers had significant isomeric properties except to polarizability. In FT-IR spectrum, they had particular angle of siloxane and hydroxide. Figure 2.10 showed characteristic peaks of stretched silicon oxide and hydroxide. According reference about relationship of silicone oxide bond angle and spectrum, all-cis isomer had most bended Si-O-Si angle and cis-cis-trans isomer was expected to be flat structure.

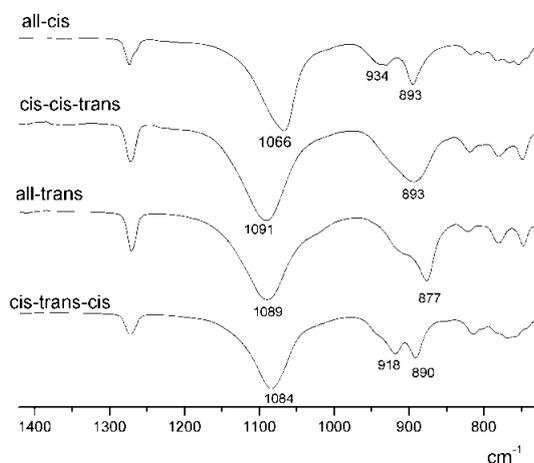


Figure 2.10. FT-IR spectrum of stretching peak of silicon oxide bond and hydroxide in each stereoisomers

2.3.3 Polymerization of *cis-trans-cis* Hydroxyl-Substituted Methylcyclotetrasiloxane(3)

Among four stereoisomers of tetracyclic siloxane, *cis-trans-cis* isomer(3) was proposed to be the most proper intermediate structure for the ladder polysilsesquioxanes due to its thermodynamical stability and isomeric preference towards a ladder structure [16]. In detail, polycondensation of tetraol-(4) in the chair form by condensation of the 1,2-hydroxyls of one ring with the 4,3-hydroxyls of another ring should produce a *cis-syndiotactic* ladder structure (Figure 2.11) [20].

On the basis of them, *cis-trans-cis* tetraol-(3) was isolated by careful recrystallization in M.C/THF. Isolated tetraol-(3) was effectively separated with yields over 50 % as white powder. High yield of this isomer was explained by the polarity deviation and the centrosymmetric molecular structure.

Furthermore, ^{29}Si NMR spectra of isolated tetraol-(3) gave the same peak order as in ^1H NMR spectra as a single signal at -56.49 ppm ranging from six characteristic peaks centered at -56.02, -56.16, -56.49, -56.51, -56.74, -56.93 ppm of cyclic T^2 region by four stereoisomers (Figure 2.12).

The purity of *cis-trans-cis* tetraol-(3) was confirmed by HPLC. With the exception of *all-cis* tetraol-(4) isomer, three Methyl-T4-tetraol isomers were shown as *all-trans* tetraol-(1) (19%), *cis-trans-cis* tetraol-(3) (33%), and *cis-cis-trans* tetraol-(3) (47%) by preparative HPLC (Figure 2.13(A)). Product obtained through fractionation of second peak and the recrystallized product was identical and confirmed as the isolated tetraol-(3). ^1H NMR spectra and HPLC showed that isolated isomer was certified with being of high purity over 99% (Figure 2.3(B)).

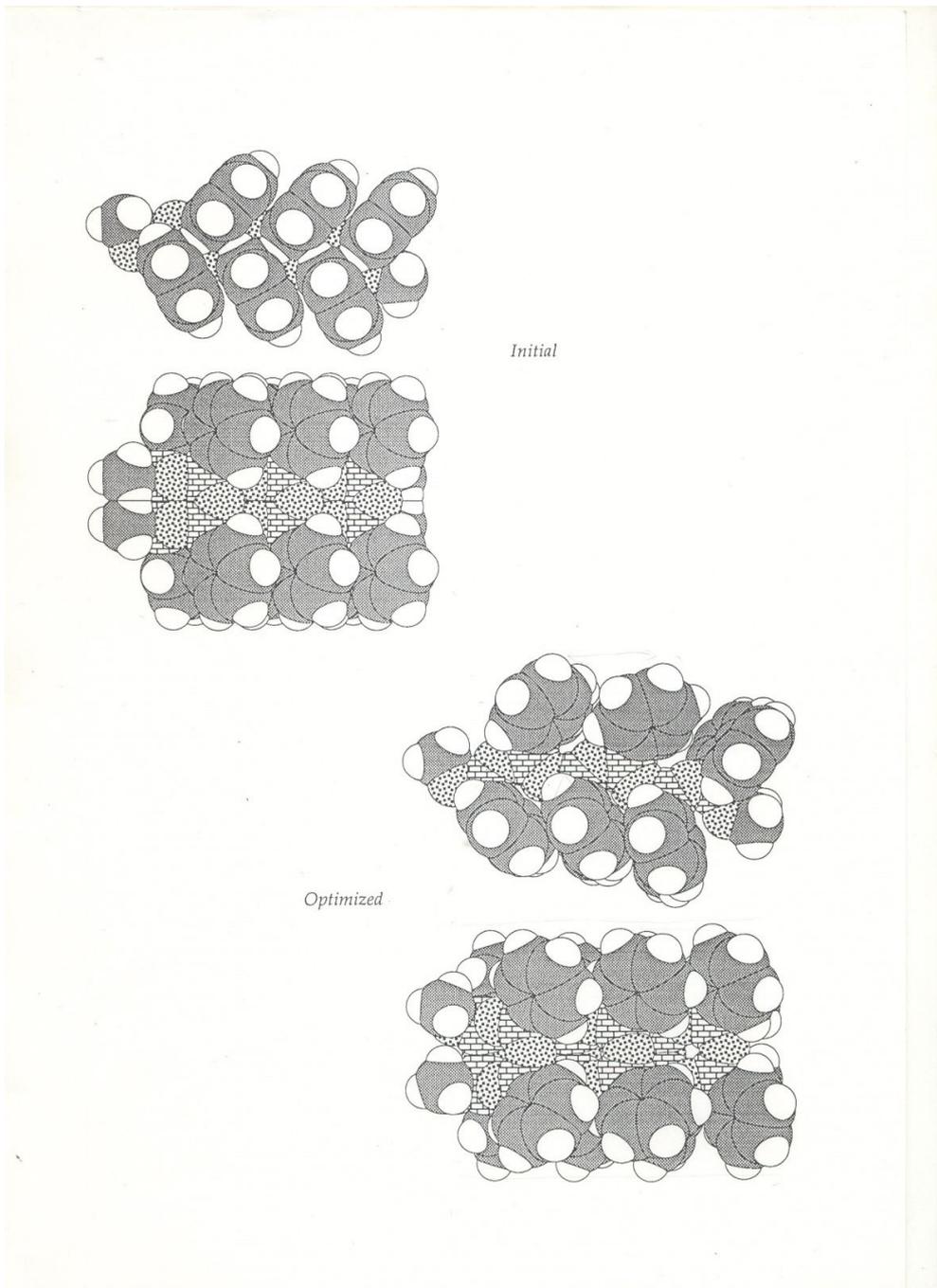


Figure 2.11. Modeling of *cis-syndiotactic* ladder silsesquioxane structure

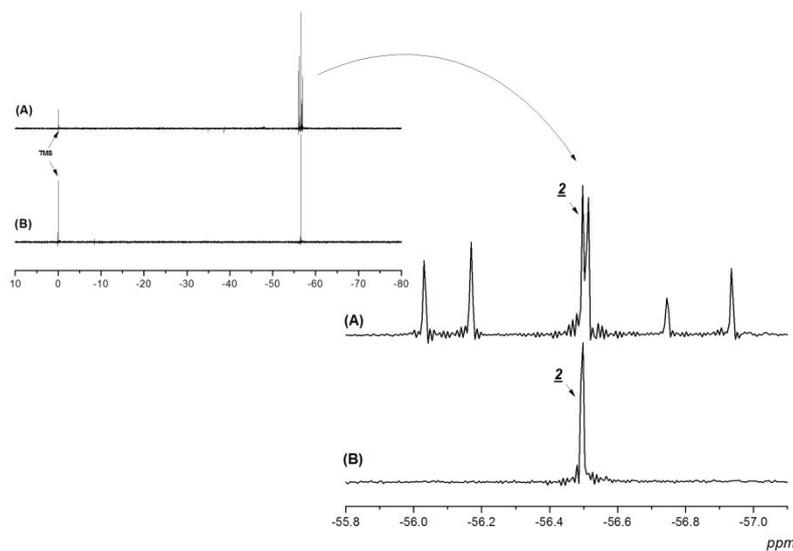


Figure 2.12. ^{29}Si NMR spectrum of four stereoisomers of Methyl-T4-tetraol(A) and isolated tetraol-(3) (B) in acetone- d_6 .

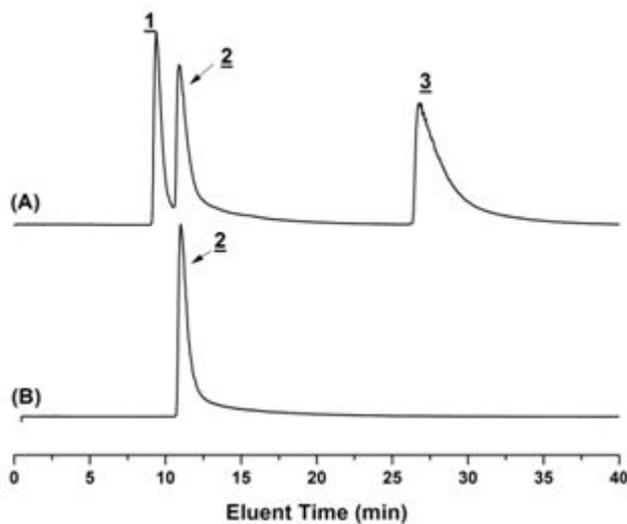
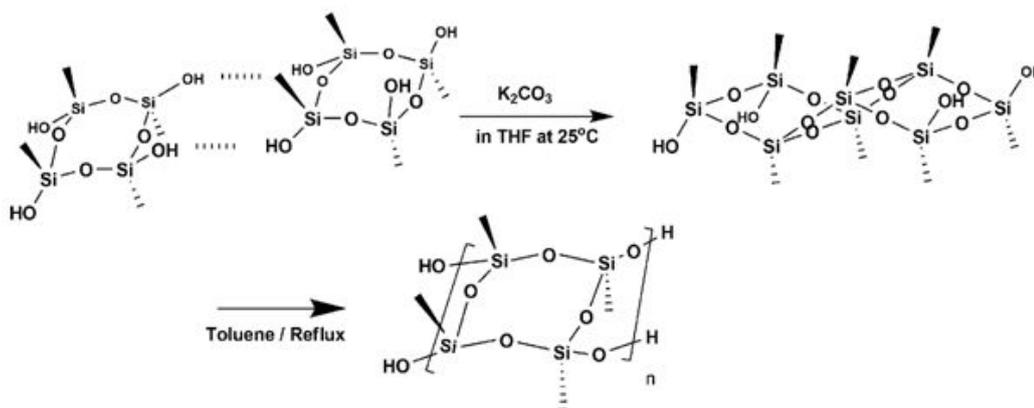


Figure 2.13. HPLC (Normal phase, cyclohexane/Ethylacetate = 6/4, 1.6 ml/min) of Methyl-T4-tetraol isomers(A) and isolated tetraol-(3) (B).

Through a two step reaction, PMSQ was synthesized by systematic ring condensation from the isolated *cis-trans-cis* tetraol-(3). As polymerization progressed, the molecular structure of PMSQ was speculated to grow in the form diagrammed in Scheme 2.2.



Scheme 2.2. Synthetic route of PMSQ by ring condensation of isolated tetraol-(3)

Polymerization carried out in THF at $25^\circ C$ with K_2CO_3 gave an oligomeric ladder PMSQ. It was found that the molecules did not increase in molecular weight after 3 days as monitored by GPC. After removing the base catalyst, the oligoMSQ was obtained with 5,400 M_w (630 M_n in polystyrene standard) (Figure 14(A)) and 87% T^3 area by ^{29}Si NMR spectra (Figure 16(A)).

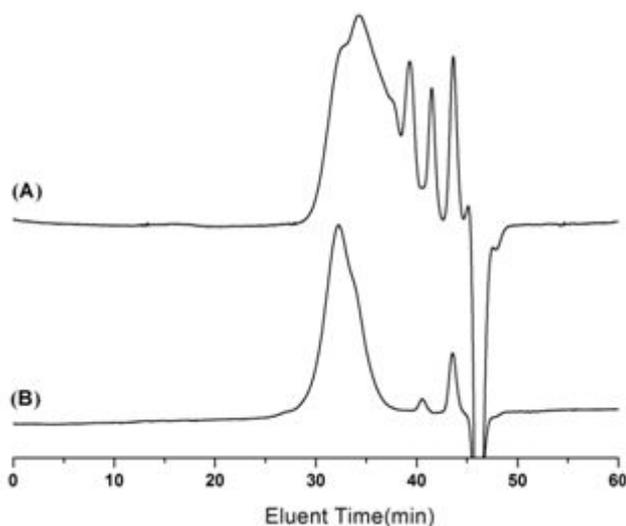


Figure 2.14. Size exclusion chromatography (SEC) results of PMSQs, (A) oligoMSQ and (B) PMSQ.

Subsequent polymerization in refluxing toluene was carried out not only for increasing molecular weight but also to close the uncondensed hydroxides within main chain. After precipitation in hexane, PMSQ was found to have a M_n of 7,400 and M_w of 16,410 with a polydispersity of 2.2 by GPC (Figure 2.14(B)).

In ^1H NMR spectrum (figure 2.15), they were only showed to methyl group as $-\text{CH}_3$ about 0 ppm. It meant that large amount of hydroxyl groups were disappeared by condensation reaction, and it showed a possibility to build a molecule of ladder structure.

In order to confirm the condensation progress, ^{29}Si NMR spectrum was observed by T^2 and T^3 ratio of oligomer and polymer. As a result, PMSQ showed 89% T^3 area which correlated to a number-average molecular weight of 2,590 (9 tetraol-(3) units) from 87% T^3 area of oliMSQ(Figure 2.16(B)). Besides hydroxyl contents, they showed that sharp split of peaks by small molecules in OliMSQ were disappeared as increasing the molecular weight.

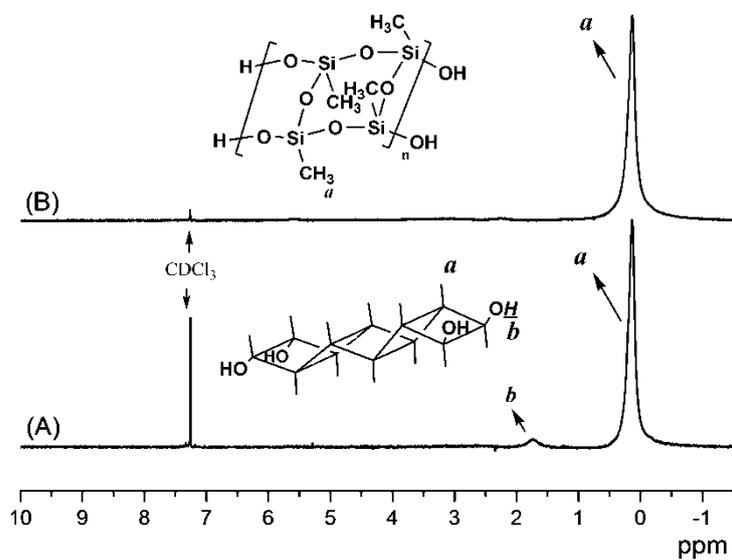


Figure 2.15. ^1H NMR spectrum of OliMSQ(A) and PMSQ(B).

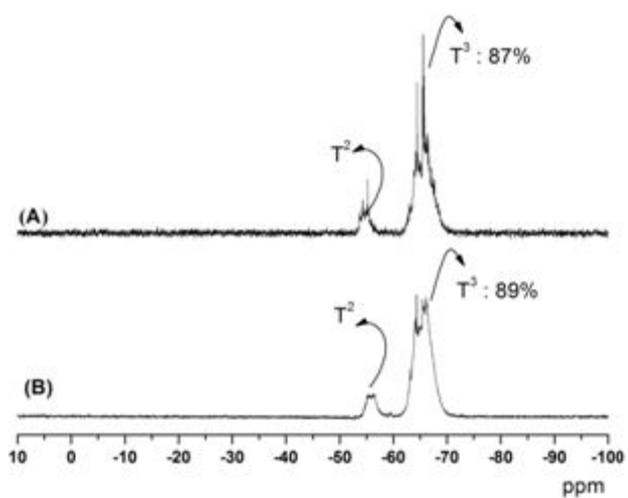


Figure 2.16. ^{29}Si NMR spectrum of PMSQs, (A) oligoMSQ and (B) PMSQ.

The number of uncondensed hydroxides was confirmed by a capping reaction using dimethylphenylchlorosilane. According to the integration ratio of phenyl and methyl, four phenyl moieties have about nine to ten repeat units. This was found to be an analogous result with the molecular weight calculation by ^{29}Si NMR spectra (Figure 2.17).

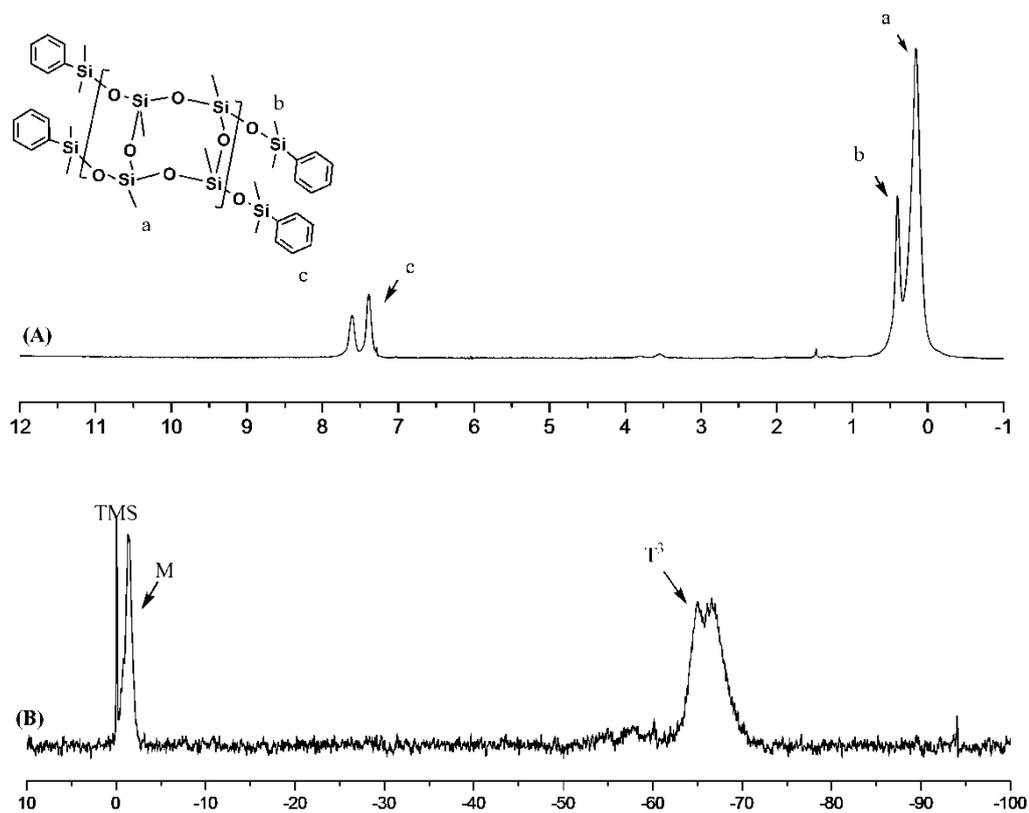


Figure 2.17. ^1H NMR spectra (A) and ^{29}Si NMR spectra (B) of end-capped PMSQ

2.3.4 Structural analysis of synthesized PMSQ

Calculation of the molecular weight of the capped PMSQs using ^{29}Si NMR and GPC analyses gave a discrepancy as large as three-fold. This was explained by two factors.

First, when the calculation the molecular weight of PMSQ is carried out using ^{29}Si NMR, the T^2 sites can only be assumed to exist on the ends of the polymer chain, as a perfect ladder structure. However, this calculation of the number of repeating units is inaccurate for when main chain hydroxides exists. For the same relative number of T^2 sites per T^3 sites, calculation of the number of repeating units results in a vastly small number for those PMSQs with main chain hydroxide groups. The second factor is the effect of hydrodynamic volume. Obtained PMSQ, with its double stranded backbone is considerably stiffer than polystyrene, and thus GPC calculations of molecular weight are invariably an overestimate of the absolute molecular weight.

For these reasons, we carried out the MALDI-TOF MS to approximate the number of uncondensed hydroxide, indicated by ^{29}Si NMR. According to the MALDI-TOF mass, PMSQ gave a *Mn* of 4150 (16 repeating units (64 Si atoms)) (Figure 2.18). When the PMSQ having *Mn* of 4150 with 89% T^3 ratio (56 T^3 Si atoms) was analyzed, the linear PMSQ was stipulated to have two cyclolinear points (uncondensed site) which were not composed of double chain structure.

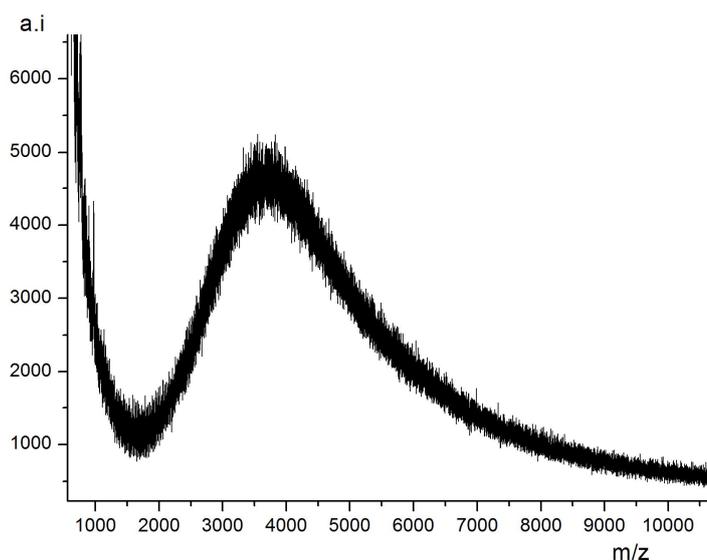


Figure 2.18. MALDI-TOF MS spectrum of PMSQ

It can be presumed that the reactivity of condensed MSQ with 5 to 6 repeating units precipitously decreases, and just one among the four hydroxyl group reacts with other one in this condition. In other words, PMSQ had not only four T² Si atoms at the chain end but also four T² Si atoms at the middle of chain (Figure 2.19). For this reason, even though the molecular weight of PMSQ increased 5,400 Mw to 16,400 Mw as threefold after further reaction, the T³ ratio increased only 2%.

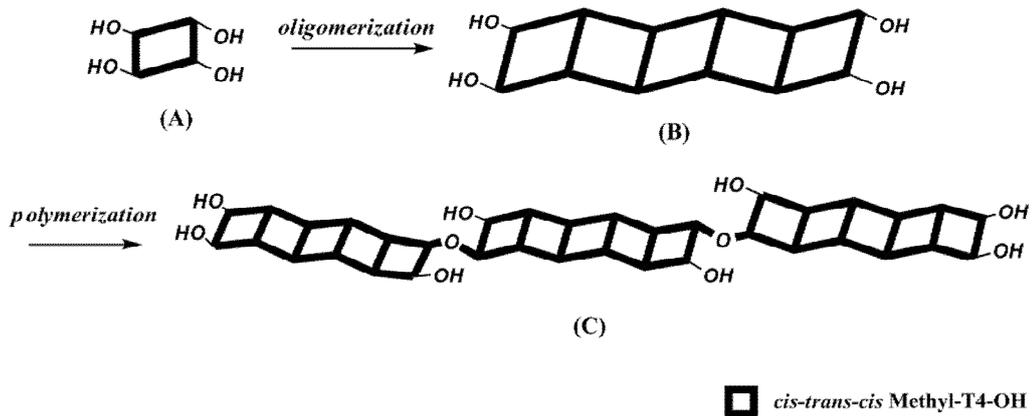


Figure 19. Proposed PMSQ structure during polymerization

Due to difficulties in defining a certain molecular structure through ²⁹Si NMR, GPC, and MALDI-TOF MS analyses, PMSQ's detailed molecular structure was investigated using small x-ray scattering. According to X-ray scattering, it was possible to calculate the molecular shape for the whole range of q without making any approximations [26]. The amplitude A(q) of scattering from a single particle is calculated from :

$$A(q) = \int \rho(r) e^{-iqr} dr$$

where $\rho(r)$ is the scattering length density distribution. The calculated intensity was overlaid with experiment intensity to verify the particle structure. Obtained intensity was analyzed by means of Porod law, as related to the scattering angle, θ , by the

equation:

$$q = (4\pi/\lambda) (\sin \theta/2)$$

which depended on the geometric structure of the scattering entities. For example, in a log-log plot of scattered intensity versus the scattering vector, q , the slope in Porod region is predicted to equal -1 for a thin rod shape, and -2 for a thin disk shape.

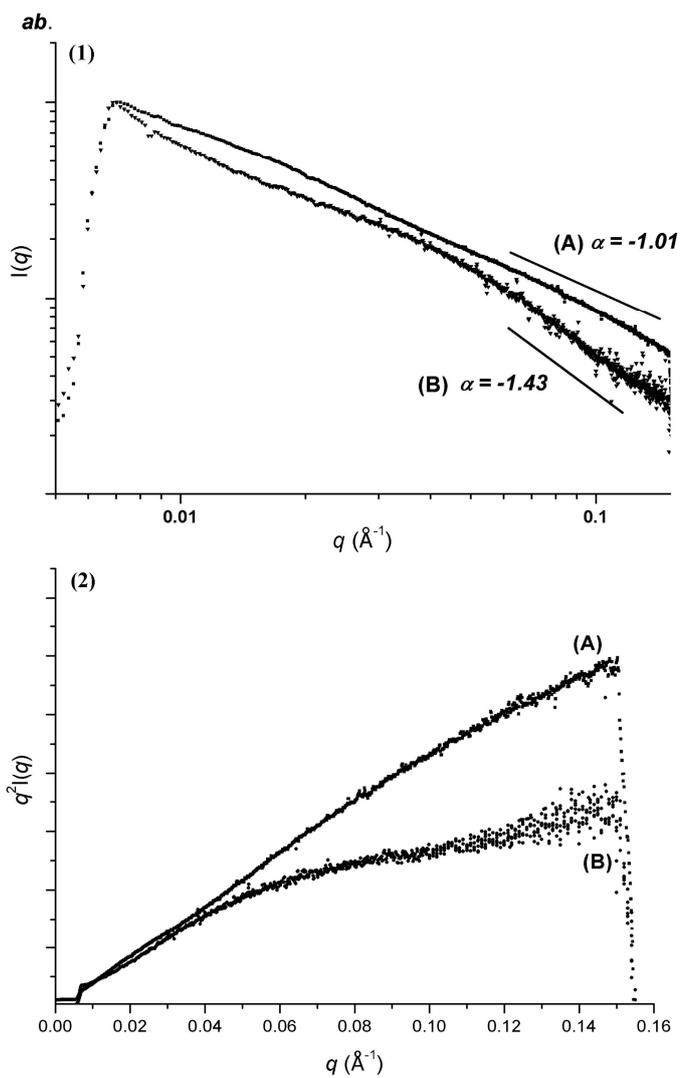


Figure 2.20. Small angle x-ray scattering of dilute PMSQs. (1) the log-log plot of (A) oligoMSQ and (B) PMSQ, (2) Kratky plot of (A) oligoMSQ and (B) PMSQ

Dilute oligoMSQ (3 mg/ml in THF) and PMSQ (1 mg/ml in toluene) was scattered by x-ray (Figure 20). OligoMSQ indicated a thin rod molecular conformation explained by calculated slope of $\alpha = -1.01$ using log-log plot in Porod region (Figure 2.20(1A)). Furthermore, when the scattering curve of oligoMSQ corresponded with Kratky plot where $q^2I(q)$ was plotted as a function of q , the scattering curve representing a straight line was interpreted as a clear indication for a linear molecular conformation (Figure 2.20(2A)) [27]. This linear conformation would be formed by the strong, multiple hydrogen bonding between two cyclic tetraols, which led to perfect ring condensation.

Meanwhile, evaluation of the slope of PMSQ scattering curve in Porod region (Figure 2.20(1B)) gave the value of -1.43. Concerning the large hydrodynamic volume and Kratky plot, it could be proposed that the PMSQ may have become distorted and entangled by the polymer chains (Figure 2.20(2B)). These conformations occurred at the cyclolinear sites, which contributed to increased molecular movement, leading to improved solubility [28]. These results corresponded well with the presumed structure of molecular growth of MSQ mentioned previously.

Comparison of the results from ^{29}Si NMR, MALDI-TOF mass, and X-ray scattering, synthesized PMSQ was found to be of ladder-like structure. Furthermore, the enhanced thermal stability up to 700°C of obtained PMSQ also supported the supposition of a ladder silsesquioxane frame [29]. (Figure 2.21(B))

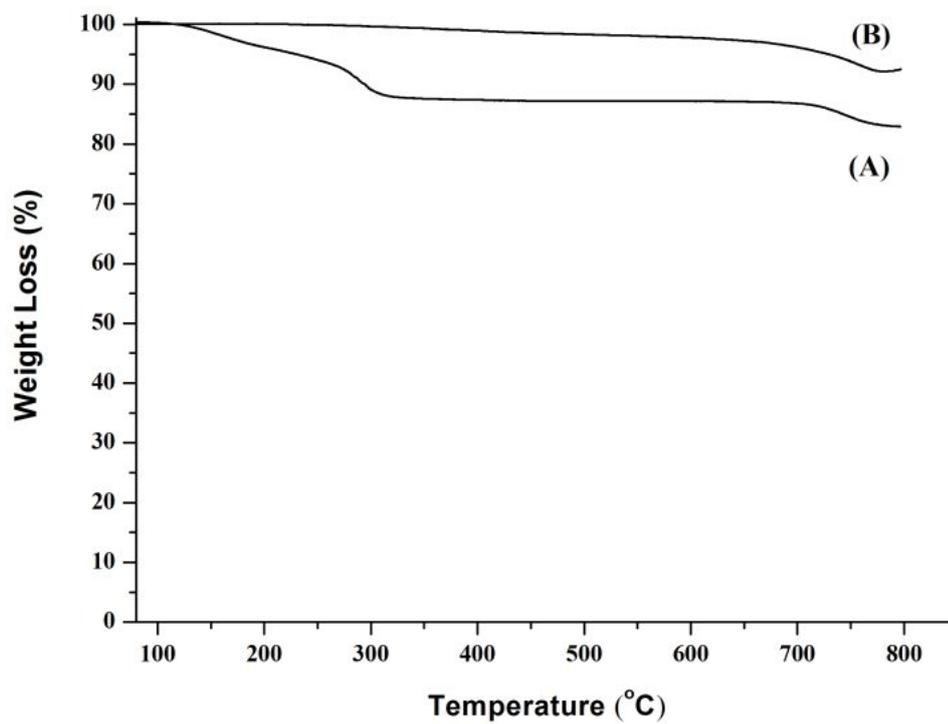


Figure 2.21. TGA diagram of oliMSQ (A), and PMSQ (B)

2.5. Conclusion

Methyl-T4-tetraol with four stereoisomers was synthesized by hydrolysis of the hydride precursor without condensation. The tetraol-(2) was isolated from four stereoisomers in a specific recrystallization condition. Using the isolated tetraol-(3), ladder-like polymethylsilsequioxane was successfully synthesized by systematic ring condensation. Linearity of the polymer was characterized by GPC, MALDI-TOF mass, and diluted small angle x-ray scattering. The ladder-like PMSQ from tetraol-(3) was expected to have *cis-syndiotactic* conformation even a few cycloliner positions existed.

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Chapter 3

Structural analysis of high molecular weight PMSQs and their related properties for interlayer dielectric (ILD) application

3.1 Introduction

As integrated circuit (IC) dimensions continue to decrease, materials with lower dielectric constant are constantly being required as interlayer dielectrics (ILD) and low resistivity conductors such as copper. These materials should be combined with good thermal and mechanical stability to adapt the ILD process. Generally, the types of chemical structures that impart structural stability are those having strong individual bonds and a high density of such bonds. However, the strongest bonds often are the most polarizable, and increasing the bond density gives corresponding increase in polarization [1].

Many researchers have tried to overcome these limits through synthesizing new polymers. Among them, rigid organic polymers often have implemented because of having lower density, high thermal stability and good mechanical properties [2,3]. However, these materials tend to have elevated dielectric constants and decreased processability because the main frame of these polymers are composed of aromatics, double, and triple bonds, which were readily polarized.

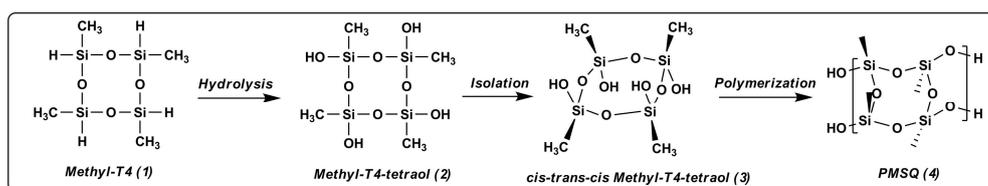
Hybrid polymers, such as methyl silsesquioxane polymers, is one of the most well studied materials for ILD application, as they have an intrinsically low polarizability, high thermal stability, and excellent mechanical properties based on rigid silicon oxide framework [4].

Synthesis of polymethylsilsesquioxanes (PMSQ) have traditionally been through the sol-gel method, as its utility in being able to obtain highly cross-linked structures through acidic and or basic conditions has been well documented [5,6,7]. However, the properties of sol-gel derived products have been known to be severely affected by its synthetic route of hydrolysis-condensation and innumerable synthetic conditions, which have shown to form cage, cage-like, or cyclic structures. [8,9]. Moreover, further processing of heat treatment is required to obtain an integrated network PMSQ which leads to a large amount of shrinkage by secondary condensations that lead to high internal stresses that can crack the films [10].

In order to approach the favorable properties of PMSQ in a reproducible manner, a regular structure with high molecular weight, like ladder-structures, is to be favorable. This rigid ladder backbone with high molecular weight would support lower dielectric constants stemming from increase of inter-molecular space and high mechanical strength, as well as minimizing shrinkage during the ILD process.

In this study, in order to obtain high molecular weight ladder-like structured PMSQs, we polymerized a well-defined intermediate tetraol, cis-trans-cis hydroxyl-substituted methylcyclotetrasiloxane, by varying the condensation time. The molecular structure of the PMSQs were verified by FT-IR, ^{29}Si NMR spectrum, static light scattering (SLS), dilute solution small angle x-ray scattering (SAXS), and x-ray diffraction (XRD). On the basis of these analyses, the related properties for ILD application such as modulus and dielectric constant were analyzed and correlated with their structural type.

In addition, synthesized PMSQs were carried out to end-capped reaction by trimethylchlorosilane and triphenylchlorosilane. Through these further reactions, PMSQs were able to be confirmed to their electrical and physical properties without effect of hydroxyl groups.



Scheme 3.1. Synthetic route of PMSQs by *cis-trans-cis* Methyl-T4-tetraol

3.2 Experimental

3.2.1 Materials

95% 1,3,5,7-tetramethyl-2,4,6,8-tetrahydro cyclosiloxane(MethylT4) was purchased from Gelest, and distilled to remove the stabilizer and di- or tri-mer. Tetrahydrofuran was dried over sodium. Pd/C (10% activated) was purchased from Across. Distilled water was used for hydrolysis of MethylT4. Potassium carbonate was of commercial grade and used without further purification. Chlorotrimethylsilane and chlorotriphenylsilane were purchased from Aldrich with 95%, and used without further purification. Triethylamine as acid salt agent was from TCI with 99%.

3.2.2 Preparation of high molecular weight PMSQs (**4**)

In a 500 mL round-bottomed flask, hydrolysis of the hydride of MethylT4 (**1**) (19 mL, 0.078 mol) was carried out with water (6.4 mL, 0.355 mol) and Pd/C (10% activated) (0.8 g, 0.75 mmol) for 2 h in THF (220 mL) at 10 °C. Excess water and Pd/C were removed by MgSO₄ and cellite. The substitution of hydride to hydroxide was confirmed by ¹H NMR (200 MHz, DMSO, ppm): 0.15 ~ -0.19 [m, 12H, -CH₃], 6.49 [s, 4H, -OH].

After hydrolysis, the tetrol (**3**) was isolated from four stereo isomers (**2**) (150 mL in THF) by recrystallization using methylene chloride (1000 mL) and THF (50 mL) co-solvent for 1 hour at 4 °C. ¹H NMR (200 MHz, DMSO, ppm): 0.014 [s, 12H, -CH₃], 6.49 [s, 4H, -OH].

In a two-necked flask equipped with a reflux condenser, the isolated Methyl-T4-tetraol (**3**) (1.3g) was polymerized with K₂CO₃ as catalyst in THF (40 mL) at 25°C. In same system, PMSQs was synthesized by varying reaction time at 2 h, 16 h, and 72 h.

Afterwards, the three PMSQs were purified by the same procedure. For example, the PMSQ reacted for 2 hours was precipitated in deionizer water, and white powder was obtained. Crude product was dissolved in chloroform for an hour and dried over MgSO₄. The dried chloroform solution was precipitated into hexane to rid of low molecular weight compounds, and white powder (0.8g) was obtained, and dried under vacuum for one day at room temperature.

In addition, the polymerization was also carried out in kinds of organic solvent such as ethyl acetate, acetone, methanol, Dimethylacetamide (DMAC) to understand the effect of polarity. The reaction concentration and amount of catalysts were same as THF. PMSQ from acetone, methanol, and DMAC finally became a non-soluble white powder. This occurred about 6 hours in acetone, 4 hours in MeOH and, 2 hours in DMAC. These PMSQs were precipitated and washed using water to remove the K_2CO_3 , and dried in vacuum at 60°C for 2 days. In case of PMSQ-EA, the polymerization did not proceed for 3 days, because the density of solution might be not sufficient to react each other.

3.2.3 Preparation of endcapped high molecular weight PMSQs

Obtained PMSQs of 10k, 130k, 570k were prepared for endcapping reaction by each trimethyl- and triphenyl moieties. The each polymer was carried as same of PL10K. Representatively, methyl capped PL10k of 1g was dissolved in THF 50ml with 2 wt%, and capping agent (trimethylchlorosilane) put in reaction flask as much as molar contents ratio of monomer. It was calculated as 3.2mmol and TEA was added as same molar ration. The reaction was carried for 6 hr and reaction solution was precipitated in Methanol. White powder (1.2g) was obtained.

3.2.4 Characterization and Measurements

The number average molecular weight (M_n) and molecular weight distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with RI-2031 plus refractive index detector and a UV-2075 plus UV detector (254 nm detection wavelength) using THF as the mobile phase at 40 °C and a flow rate of 1 mL/min. The samples were separated through four Shodex-GPC KF-802, KF-803, KF-804, KF-805. ^1H and ^{29}Si NMR spectrum were recorded in DMSO and CDCl_3 at 25°C on a Varian Unity INOVA 200MHz for ^1H NMR spectrum and Varian NMR Systems 300MHz for ^{29}Si NMR spectrum(^{29}Si : 59.6MHz). IR spectrum of the product was also obtained using Thermo Scientific NICOLET IS10. IR spectrum was acquired on an IR spectrometer at resolution of 4 cm^{-1} . 32 scans were carried out at least and the average was taken as data. The thermal properties of the PMSQs were analyzed by thermo gravimetric analysis (TGA) ranging from 60~800°C with a scanning speed of 10°C/min under N_2 flow, Perkin Elmer TGA7.

3.2.5 Dilute small x-ray scattering (SAXS) and x-ray diffraction (XRD)

Small angle x-ray scattering (SAXS) experiments were conducted at the beam-line 4C1 of Pohang light source (PLS) in the Pohang Accelerator Laboratory (PAL) using Cu-K α radiation. For the SAXS experiments, the PMSQs were dissolved directly in THF (3mg/mL) and filtered using 0.45 μm membrane filter. The details of the measurement are described elsewhere [11]. X-ray diffraction (XRD) of PMSQs was observed by Rigaku

model D/MAX-2500.

3.2.6 Thin film analysis

3.2.6.1 Dielectric constant

Dielectric constant of PMSQs was measured at a frequency at 1MHz with an HP4192a with a metal-insulator-metal (MIM) structure, with a top electrode diameter of 2 mm, and aluminum metal deposited by thermal evaporation. The dielectric layer was prepared to a 150nm thickness. The thickness was measured by Alpa-stepIQ KLA Tencor. All thin films were prepared at 60°C for 1 hour to remove the residual hexane and water.

3.2.6.2 Nanoindentation

Mechanical properties were measured by the Hysitron Inc. TriboIndenter[®]. Measurements of elastic modulus were performed as continuous stiffness measurement technique. With this technique, each indent gives elastic modulus as a continuous function of the indenter's displacement into the samples. Twelve indentations were performed on each sample. Loading was controlled such that the loading rate divided by the load was held constant at 0.5/s. Experiments were terminated at a depth of approximately 50 nm. The tip used for these experiments was a Berkovich diamond tip. As a control, a sample of

fused silica (amorphous SiO₂) was also tested. Samples were approximately 500 nm thick to minimize any effect of the substrate on the measurements.

3.3 Results and discussion

3.3.1 Observation of molecular growth of PMSQ and preparation of high molecular weight PMSQs

The synthetic route and isolation method of cis-trans-cis Methyl-T4-tetraol has been reported in Part 1 along with the linearity of the synthesized PMSQ [12]. In order to prepare high molecular weight PMSQs, the amounts of catalyst and solution density were slightly increased.

As a result, the rate of polycondensation and molecular weight considerably increased (Figure 3.1(A)). The rate of molecular weight growth of PMSQ was expressed through a logarithm plot of weight average versus reaction time. After 72 hours of reaction, polymerization ceased to proceed when a GPC weight average molecular weight of 140k g/mol was attained.

In accordance with the preliminary polymerization, the three different PMSQs were synthesized by varying the reaction time at 2 hours, 16 hours, and 72 hours. Consequently, the molecular weights of obtained PMSQs were 10k for 2 hours (PL10K), 130k for 16 hours (PL130K), and 570k for 72 hours (PL570K) with a broad polydispersity (Figure 3.1(B)). Obtained PMSQs had good solubility in common organic solvents.

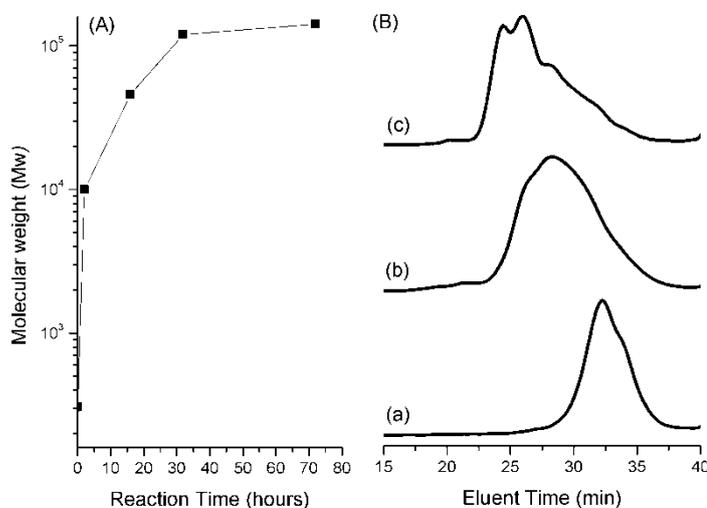


Figure 3.1. (A) Logarithm plot of weight average versus reaction time and three kind of PMSQs. (B) GPC diagram of PMSQs. (a) PL10K (M_w :10K) (b) PL130K (M_w :130K), and (c) PL570K (M_w :570K)

3.3.2 Structural analysis of high molecular PMSQs

A use of ring intermediate can be said to be the most proper intermediate to form ladder polysilsesquioxane structures by the strong, multiple hydrogen bonding interactions which occur when two cyclic tetraols are brought together. (Scheme 3.1) [13]. Furthermore, this strategy also has advantages in obtaining high molecular weight polysilsesquioxane by suppressing molecular cyclization and undergoing an irreversible pathway not being in competition between hydrolysis- condensation rearrangement reactions seen in common sol-gel methods.

FT-IR spectrum: FT-IR analyses of silsesquioxane structures of either ladder-structures or cross-linked structures are conducted by analyses of the characteristic asymmetrical Si-O-Si stretching peaks in the $1000 \sim 1200 \text{ cm}^{-1}$ region, which are unaffected by the nature of the substituent [14].

The FT-IR spectrum of the three PMSQs indicated a highly regulated ladder-like structure indicated by the symmetric mode at 1038 cm^{-1} and asymmetric stretching mode at 1120 cm^{-1} of the Si-O-Si siloxane bonds (Figure 3.2). Moreover, the characteristic hydroxyl peak around 3300 cm^{-1} and 980 cm^{-1} were quantitatively decreased. As the molecular weight increased, the characteristic peaks of ladder-like PMSQs in the $1000 \sim 1200 \text{ cm}^{-1}$ region remained the same. This was evidence that the PMSQs retained the same molecular structure as ladder-like during polymerization.

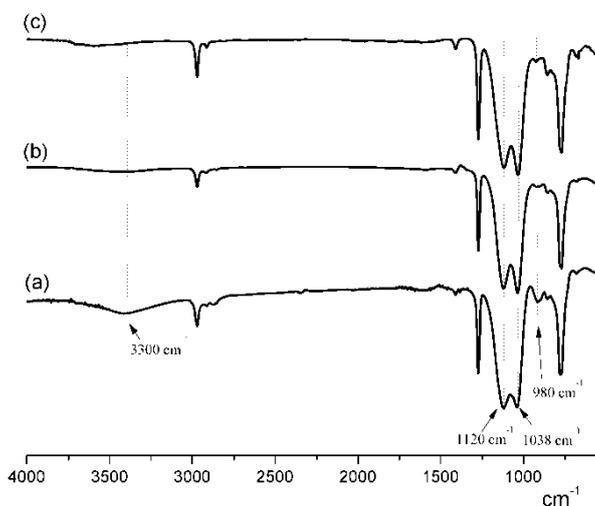


Figure 3.2. FT-IR spectrum of three kind of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K

Thermogravimetric analysis (TGA); A recent study on the thermal degradation dependence on molecular structure of polysilsesquioxanes [15] indicated that two of three synthesized PMSQs with high molecular weight, PL130K and PL570K, had been formed with robust ladder-like structure, having higher thermal stability than reported (Figure 3.3). Although each PMSQ had very similar silsesquioxane structure according to other analytical techniques, however, the patterns of PL10k in TGA curves showed significant differences in thermal degradation.

The weight loss of PL10K from 215°C to 480°C was attributed to the condensed water due to the reaction between end hydroxyl groups. Additional 10 wt% loss by decomposition of the methyl groups in main chain occurred after 480°C. On the other hand, PL130K and PL570K hardly showed any weight loss via end Si-OH groups (<1.5 wt%) up to 700°C. It was presumed that the reason for the enhanced thermal property in the form of increased degradation temperatures is the increase of the molecular weight and high stereo-regularity of PMSQs [16, 17].

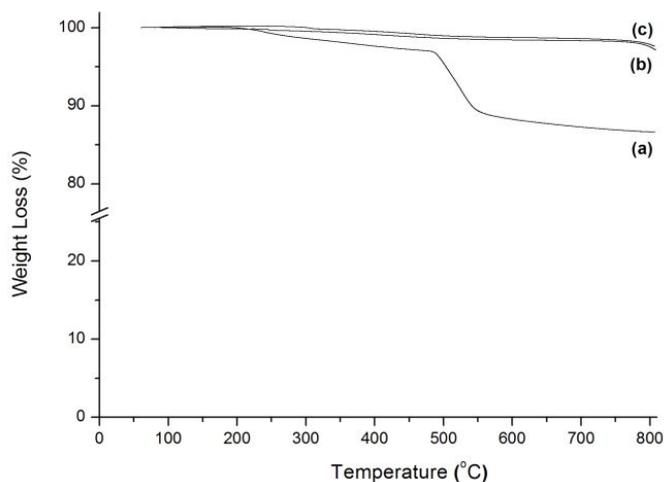


Figure 3.3. TGA trace of three kinds of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K

²⁹Si NMR spectrum; ²⁹Si NMR spectra were taken in order to elucidate the siloxane structure of the obtained PMSQs. A silicon atom bonded to three oxygen atoms through Si-O-Si bonds (T³) showed characteristic peaks ranging from -60 ~ -70 ppm, while a silicon atom bonded to two oxygen atoms through Si-O-Si bonds and one terminal -OH group (T²) show characteristic peaks ranging from -50 ~ -60 ppm. Figure 4 shows the ²⁹Si NMR spectra of the three types of PMSQs, as well the increase in T³ content from 83% for PL10K(a), 91.4% for PL130K(b), and 92.7% for PL570K(c) as the molecular weight increased.

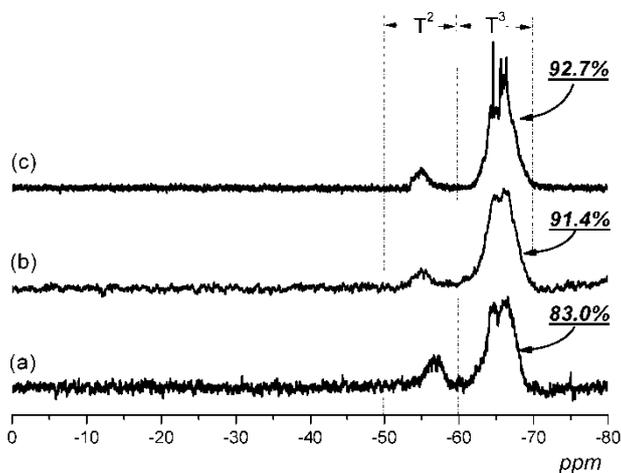
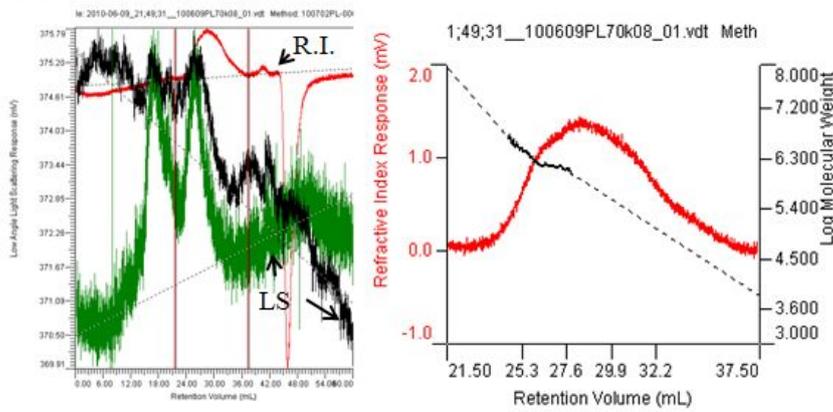


Figure 3.4. ^{29}Si NMR spectrum of three kinds of PMSQs (a) PL10K, (b) PL130K, and (c) PL570K

As the silanol content decreases during the polymerizations of PMSQs, two possibilities exist on how the macromolecule increases in size: to either keep growing linearly or to form a branched polymer. In the former case, condensations occur between hydroxyl end groups of the linear PMSQs, while the latter case can be explained through condensations of residual intra hydroxyl groups.

Light and X-ray scattering; In order to analyze the structural variance between the high molecular weight PMSQs, light scattering and x-ray scattering experiments were conducted. Light scattering experiments were carried out by a triple detection SEC system (light scattering, viscometry, and refractive index detectors) to compare between relative molecular weight and absolute molecular weight (Figure 3.5).

(A) SLS diagram of PL130K



(B) SLS diagram of PL570K

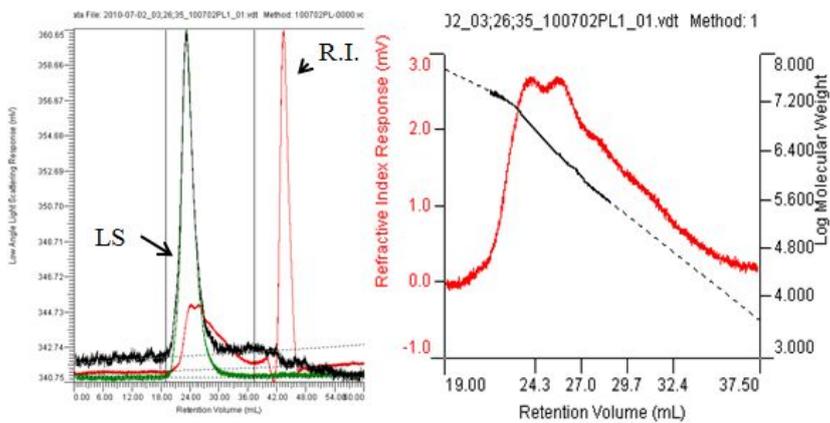


Figure 3.5. Static light scattering (SLS) diagram of (A) PL130K and (B) PL570K

PL10K did not give any light scattering because of its small molecular size. Similarly, the curves of LS detection of PL130K showed very weak signals despite comparatively high molecular weight of 130K, which was calculated by polystyrene standard. This weak light scattering was explained by the relatively large hydrodynamic volume induced by rigid polymer chains. However, PL570K gave a strong light scattering signal in the early

eluent time region with a calculated absolute weight average molecular weight (M_w) of 3600K. The six-fold difference between relative molecular weight and absolute molecular weight meant that PL570K most likely of a branched polymeric structure.

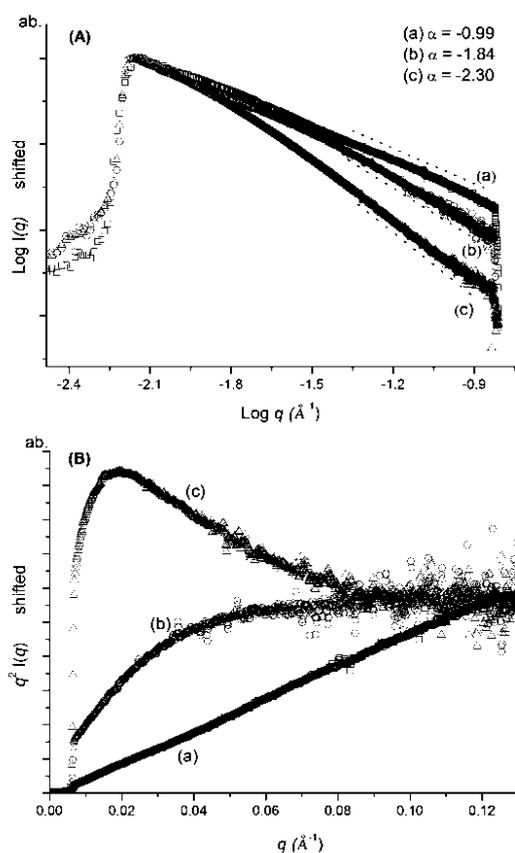


Figure 3.6. Small angle x-ray scattering from dilute solution of three kinds of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K. (A) Log–log plot of the scattered intensity as a function of q and (B) Kratky plot of $q^2 I(q)$ versus q .

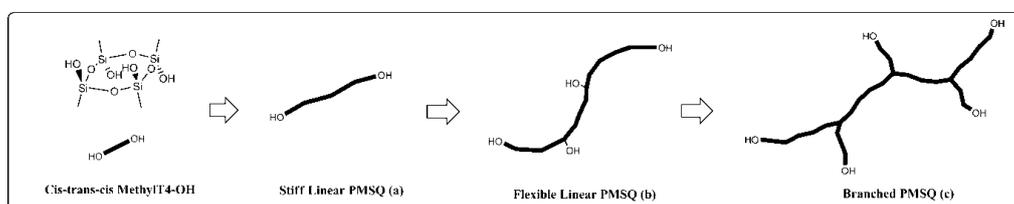
In order to more accurately characterize the high molecule PMSQs, solution small angle x-ray scattering experiments were performed. The solution small angle x-ray scattering experiments helped elucidate the polymer structure at intermediate or high q values, thus easily distinguishing the structural class. These experiments helped explain the major transformation of molecular shape by fractal theory.

For a collection of dilute polymer shape, the scattered intensity $I(q)$ is given by the Porod relation. For examples, in a log-log plot of scattered intensity versus the scattering vector, q , the slope in Porod region is predicted to equal -1 for a rod shape polymer, and -2 for a Gaussian chain polymer.

According to the Porod relation, the log q vs. log $I(q)$ plot of the PMSQs resulted in linear curves with corresponding slopes of 0.99 for PL10K(a), 1.84 for PL130K(b), and 2.30 for PL570K(c) (Figure 3.6(A)). These values explain that there are gradual transitions from PL10K to PL570K. PL10K, which had just tens of repeating units, was revealed to be of rigid, rod shape. As the molecular weight increased, bending of the polymer impedes the q^{-1} dependence of the scattering function. Consequently, PL130K arrays of Gaussian chain assembled at random showed a close dependence on q^{-2} of the scattering intensity. Furthermore, the structure of PL570K is expected to a narrowing of the branch shape that evolves toward a $q^{-2.3}$ power-law behavior.

The Kratky plot of $q^2I(q)$ versus q showed the molecular transition of PMSQs more clearly (Figure 3.6(B)). The most striking feature of the PMSQ scattering factors in this

plot is the appearance of a maximum (Figure 3.6(B)(c)), indicative of branched polymers [18, 19]. This characteristic feature of PL570K being of a branched structure can be explained by the considerations of which positions condensations occur, as described by the hydroxyl group content in ^{29}Si NMR. Consequently, the structural transition of PMSQs was analyzed as a stiff linear chain for PL10K (a), high molecular linear chain for PL130K (b), and high molecular branched polymer (c) for PL570K as Scheme 3.2.



Scheme 3.2. Schematic diagram of structure transition of PMSQs as a function of reaction time. (a) PL10K (b) PL130K, and (c) PL570K

X-ray diffraction; The transition of molecular structure of PMSQs was also shown in bulk state x-ray diffraction (Figure 3.7). X-ray diffraction peaks of the PMSQs showed a structural transition as shown by the broadening and weakening of the characteristic peak of PMSQ at 9~10 degrees assigned to the inter-chain space and isotropic property.

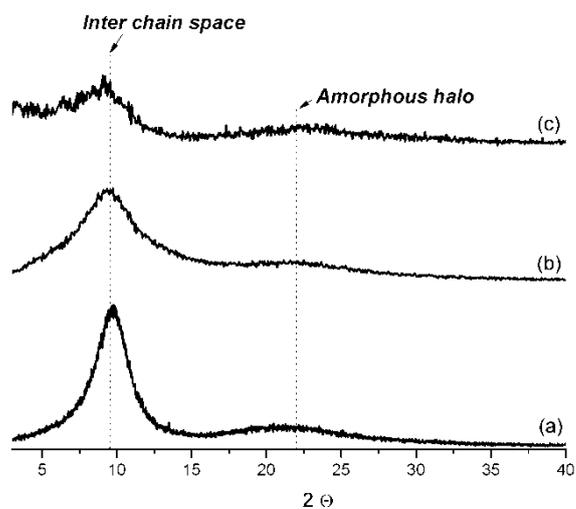
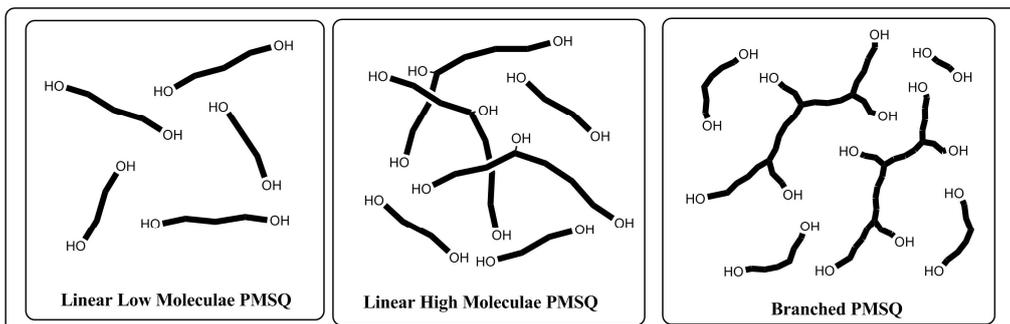


Figure 3.7. X-ray diffraction of three kinds of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K

The FWHM of the inter-chain space peak significantly broadened from PL10K(a) 2.55 degrees, to PL130K(b) 3.75 degrees. This broadening effect of chain entanglement is noticeable when increasing the chain length. Moreover, PL570K(c) gave a very weak diffraction pattern as compared to others because the anisotropic property of the polymer decreased as the branched chains disturbed their chain arrays. The above discussion shows that x-ray scattering and diffraction of prepared PMSQs provide very important information about isotropic property of materials for ILD application. According to the analyzed PMSQs, the bulk state PMSQs were described as Scheme 3.3.



Scheme 3.3. The description of the bulk PMSQs features

3.3.3 Polymerization of *cis-trans-cis* Methyl-T4-tetraol using various organic solvents

To understand solvent effect for polymerization, *cis-trans-cis* Methyl-T4-tetraol was carried out to various organic solvent in which were ethyl acetate (EA), acetone, methanol, and DMAC. In results, there was no reaction in ethyl acetate because of very dilute concentration by poor solubility of isolated tetraol. In other hands, the polymerization was rapidly occurred in acetone, methanol, and DMAC. Consequently, they were precipitated in reacting solution as white powder which had no solubility in other organic solvent kinds of toluene, chloroform, dimethyl chloride etc. therefore, obtained powders were characterized by FT-IR, TGA, and XRD because there were limits to analyze the polymer structure in state of solid.

FT-IR spectrum of PMSQs from various solvents; According to FT-IR spectrum (figure 3.8), PMSQs were shown to be completely polymerized as disappearing of hydroxyl group and silsesquioxane peak ranging from 1000 to 1100 cm^{-1} . However, it was hard to

say that all PMSQ was constructed as same structure because the patterns of silsesquioxane peaks were significantly different in each polymer. Interestingly, hydroxide of PMSQ was substituted to methoxy group which indicated at $2800 \sim 3000 \text{ cm}^{-1}$ during polymerization in methanol. In case of acetone and methanol, increases of molecular weight of them were confirmed by GPC. Therefore, it was assumed that PMSQs were more preferred to form random structure.

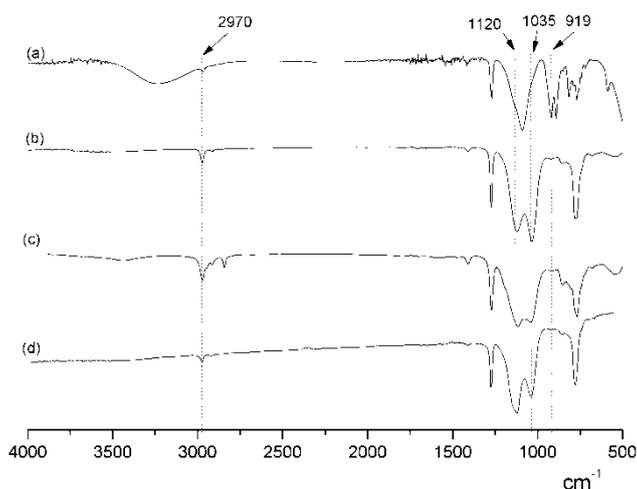


Figure 3.8. FT-IR spectrum of PMSQs from various organic solvents. (a)Ethyl acetate, b)Acetone, (c)Methanol, and (d) DMAC

TGA trace of PMSQs from various solvents; Figure 3.9 showed TGA diagram of PMSQs from various organic solvents. According to degradation temperature, they were able to be characterized as sublimation of POSS structure at 200°C , condensation of methoxy and hydroxyl group from 200°C to 350°C , and degradation of methyl group at 450°C . However, the weight loss over 500°C of (b) and (c) was very curious what

moieties made a reduction of weight because methyl group had about 20% weight over total molecules, quantitatively.

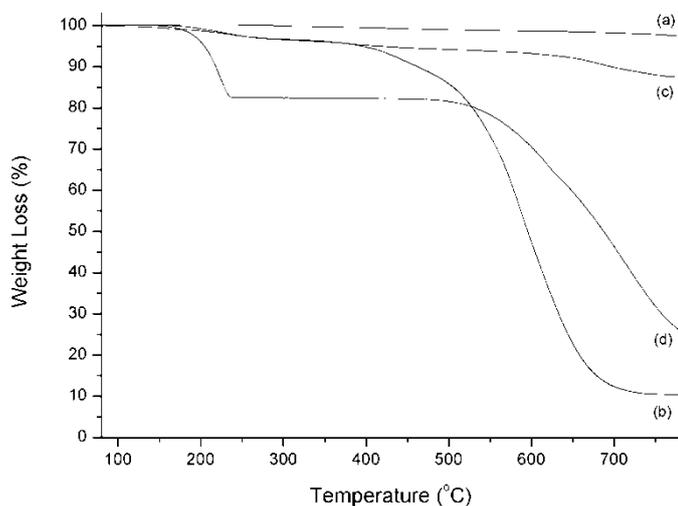


Figure 3.9. FT-IR spectrum of PMSQs from various organic solvents. (a)PL570k, (b)Acetone, (c)Methanol, and (d) DMAC

XRD of PMSQs from various solvents; XRD curves of PMSQ from various solvents definitely showed that there was having different molecular structure (figure 3.10). In comparison with PL570K, the inter-chain distance was closer between molecules, and crystalline peaks were shown to PMSQ from DMAC and methanol. In case of PMSQ from DMAC, the crystalline was related with POSS structure that was occurred to be sublimate at 150°C.

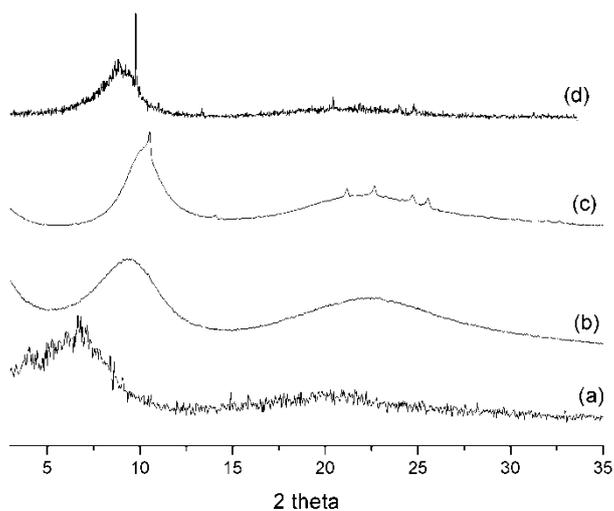


Figure 3.10. XRD of PMSQs from various organic solvents. (a)PL130k, (b)Acetone, (c)Methanol, and (d) DMAC

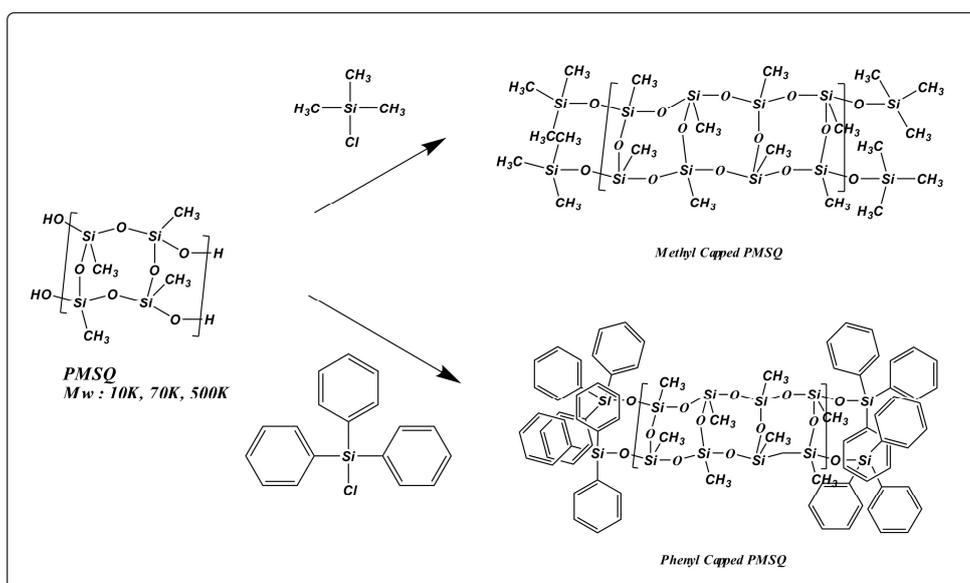
Therefore, solvents severely affect to form PMSQ structure which might have possibility from POSS to ladder structure even using cis-trans-cis Methyl-T4-tetraol. For synthesizing ladder PMSQ, conclusively, it assumed that it was important to keep the secondary interaction between tetraol without disturbances by high polar solvent.

3.3.4 End-capped reaction of PMSQs by triphenyl- and trimethyl- moieties

The perfect ladder PMSQ would have few hydroxyl groups as following to increase molecular weight, the more. Synthesized PMSQs of 10K, 130K, and 570K were considerably well characterized by various analysis tools. Despite increase of molecular weight of PL series, however, they were constructed as similar hydroxyl contents because of forming as branched structure. As results, they had hydroxyl contents about 10% in

molecule even having high molecular weight. This significantly affect on polymer property such as solubility, dielectric constant, and thermal stability at high temperature.

Therefore, next best thing to remove hydroxyl sites was to carry them out end-capping reaction although it compromised silsesquioxane structure by mono substitute siloxane moiety. However, it gives a high thermal stability of molecular structure with function of capping agent. The schematic root of reaction was shown to scheme 3.4.



Scheme 3.4. Introduction of trimethyl and triphenyl moieties by end-capping reaction of PMSQs.

¹H NMR spectrum of end-capped PMSQs; Figure 3.11 showed end-capped PMSQs by trimethyl(1) and triphenyl(2) moieties. In methyl capped PMSQs, they were not shown to significant substituted methyl peak because of same function of backbone. On the other

hands, triphenyl functional groups were shown to characteristic phenyl moieties at 7 to 8 ppm. As increase of molecular weight, the substitution ratio of phenyl group decreased that was calculated as number of repeating unit of tetramethyl cyclic siloxane per four phenyl moieties. According to it, the repeating units were indicated to 16 units of PL10K, 24units of PL130K, 34 units of PL570k.

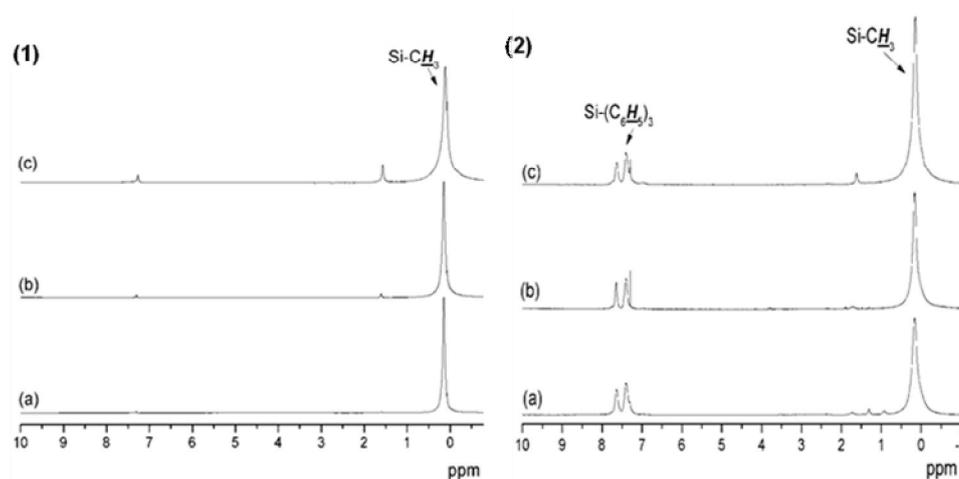


Figure 3.11. ^1H NMR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a) PL10k, (b) PL130k, (c) PL750k

^{29}Si NMR spectrum of end-capped PMSQs; After capping reactions, it was important to confirm that they were completely reacted with residual hydroxide groups. Using ^{29}Si NMR, existence of hydroxide was observed by T^2 region where indicated form -50 ppm to -60 ppm. The methyl capped PMSQs were able to be confirmed to disappearing of T^2 characteristic peaks (figure 3.12(1)). In addition, there quantitatively showed M structure about 10 ppm which explained that capping agents were chemically reacted with PMSQs.

However, the phenyl capped PMSQs rarely showed M structure, and some T² structure also detected in ²⁹Si NMR spectrum (figure 3.12(2)). It was very controversial point whether capping agent of triphenyl silane reacted with PMSQs or not. Apparently, there showed phenyl moieties in ¹H NMR spectrum and also the amount of T² structure was decreased. Therefore, we assumed that the capping agents of triphenyl group were not completely reacted with hydroxyl group because of bulk triphenyl moieties.

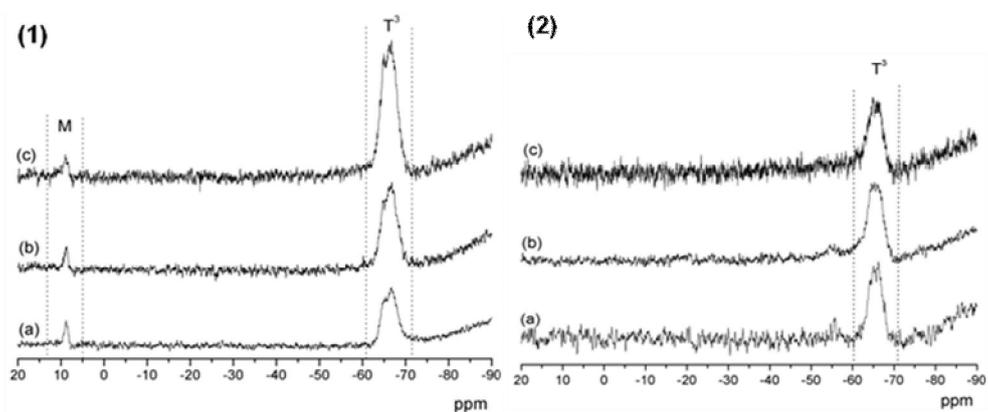


Figure 12. ²⁹Si NMR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a) PL10k, (b) PL130k, (c) PL750k

FT-IR spectrum of end-capped PMSQs; FT-IR is known as very sensitive to hydroxyl group (OH) around at 3000 ~ 3500 cm⁻¹ and silsesquioxane structure. From ambiguous results of substituent possibility in ²⁹Si NMR spectrum, FT-IR was able to give a clue about substitution by characteristic peak of hydroxyl group. Figure 3.13 showed no hydroxyl peaks and characteristic silsesquioxane peak around 1000 ~ 1100 cm⁻¹. When

methyl moiety was reacted to PMSQ, the silsesquioxane peak of Si-O-Si was shown that high angle stretching vibration (1000 cm^{-1}) was stronger than low angle stretching vibration (1100 cm^{-1}). It meant that trimethyl moieties were freely rotated at their position. In case of phenyl moiety (figure 3.13(2)), C-H stretching vibration was weakly observed at 3000 cm^{-1} , and aromatic ring stretching also observed at 1500 cm^{-1} . In comparison with methyl moiety, however, the characteristic peaks of silsesquioxane of phenyl capped PMSQ were almost same as before. It was explained that the bulky triphenyl group disturbed to form high angle formation of Si-O-Si.

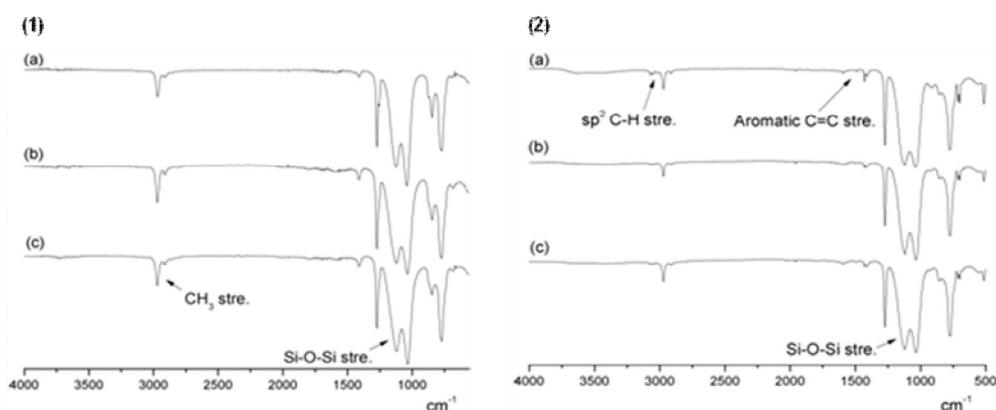


Figure 13. FT-IR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a) PL10k, (b) PL130k, (c) PL750k

TGA trace of end-capped PMSQs; It was interesting that thermal degradation property of end-capped PMSQs were shown to be considerably different from before (Figure 3.14(1)). In case of methyl capped PMSQ, the onset point was shifted to 450°C from 700°C of PL130K as figure 3, and residuals over 800°C were decreased below 70%.

Relatively low thermal stability of siloxane bond compared with silsesquioxane bond was initiated to degradation at low temperature. Therefore, it could be qualitatively confirmed how many capping agents were substituted in PMSQ. In results, the residuals of each methyl capped PMSQs were shown to 53% of PL10K, 58% of PL130K, and 77% of PL570K.

On the other hands, phenyl capped PMSQs were shown to high residual contents compared to methyl capped PMSQ although the onset temperature was almost same as 450°C (Figure 3.14(2)). It assumed that the triphenyl groups were reacted to carbon-carbon linkage by high temperature not to be degradation as small molecules.

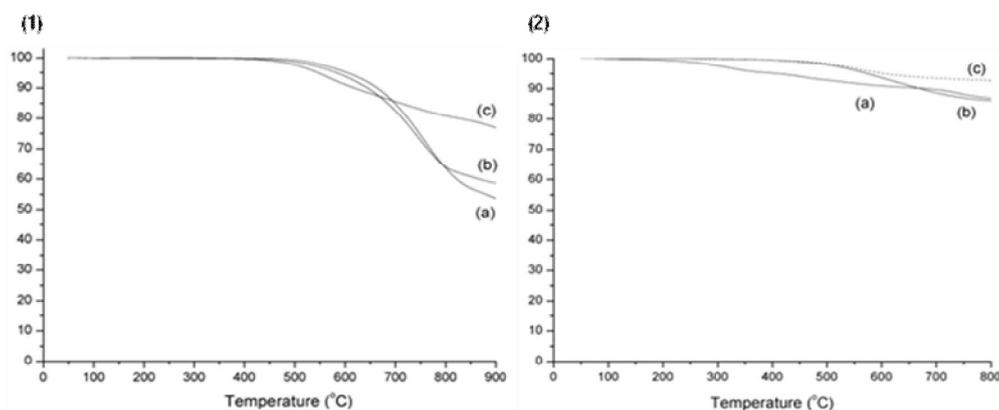


Figure 3.14. FT-IR spectrum of end-capped PMSQ by trimethyl(1) and triphenyl(2) silane. (a)PL10k, (b) PL130k, (c) PL750k

3.3.5 Analysis of bulk PMSQs properties

A particular advantage of characterization of each structure helped predict the different bulk properties. To confirm the correspondence between molecular structure and bulk properties, we have chosen the following properties, and Table (3.1) summarizes the results of them. : Refractive index, density, modulus, dielectric constant. All samples are prepared for thin film having a proper thickness with good flatness on Si wafer as mentioned (Figure 3.15).

Table 3.1. Results of Bulk properties of PMSQs

Sample	Refractive index	Density (g/cm ⁻³)	Modulus (GPa)	Dielectric constant
PL10K	1.407	1.30	3.7	3.13
PL130K	1.409	1.33	6.3	2.93
PL570K	1.375	1.27	5.4	2.74

To understand the bulk PMSQ properties, the refractive index of PMSQs was first measured because it was strongly depending on molar bond refraction of atomic composition and polymer density. According to the *Lorentz-Lorenz equation* and ²⁹Si NMR spectrum, it is approximately able to estimate the tendency of refractive index of PMSQs. Eq.(3) is explained as refractive index [n], polymer density [ρ], molar mass [M], and molecular polarisability [α]. [N_A] and [ε₀] is the Avogadro constant and the permittivity of free space.

As the molecular weight increased, the amount of siloxane group (T³:Si-O-Si) of PMSQs was increased and the hydroxyl group (T²:Si-OH) was decreased. In terms of molar bond refraction per molar mass [α/M], the refractive index of PMSQs might be

expected to decrement with a rise in T³ ratio as calculated by Si-O-Si (0.048 mL/g) and Si-O-H (0.077 mL/g)[20].

$$\frac{n^2-1}{n^2+2} = \frac{N_{AP}}{3\epsilon_0} \frac{\alpha}{M} \quad (3)$$

The refractive index of PL130K was 1.409, which was slightly greater compared to that of PL10K (1.407) even with the decrease of T² structure. After transformation to the branched polymer, the refractive index of PL570K decreased to 1.375. Concerning to the factor of refractive index, the major effect seemed to be bulk polymer density of the molecular transition rather than the molar bond refraction of atomic composition (Table 3.2).

Table 3.2. Atomic compositions of PMSQs calculated by ²⁹Si NMR spectrum

Sample	H (atomic %)	C (atomic %)	O (atomic %)	Si (atomic %)
PL10K	48.1	14.8	22.2	14.8
PL130K	47.2	15.1	22.6	15.0
PL570K	47.0	15.1	22.7	15.1

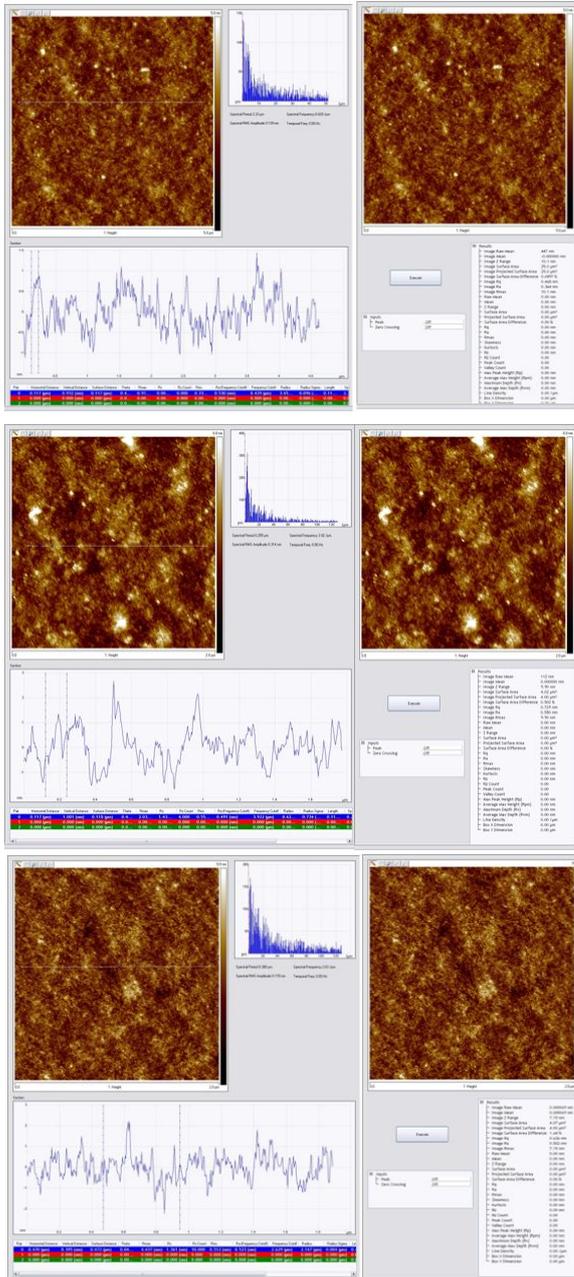


Figure 3.15. Measurements of surface flatness (Ra) by AFM images. (A) PL10K for 0.364 nm, (B) PL130K for 0.550 nm, and PL570K for 0.502 nm

Polymer density of PMSQs was measured by x-ray reflectivity, as calculating the critical angle which is directly related to the average electron density [21]. Figure 3.16 shows that the critical angles of the PMSQs. In case of PL10K and PL130K, the critical angle is slightly shifted to the q_z region at 0.0239 \AA^{-1} for PL130K from 0.0237 \AA^{-1} for PL10K. However, the critical angle of PL570K clearly shifted to the lower q_z region at 0.0232 \AA^{-1} on account of decreasing the film density by the branched side chain. Corresponding to the tendency of PMSQs' density toward structure dependence, the change of refractive index was also taken into account what is shown to the similar trace with it.

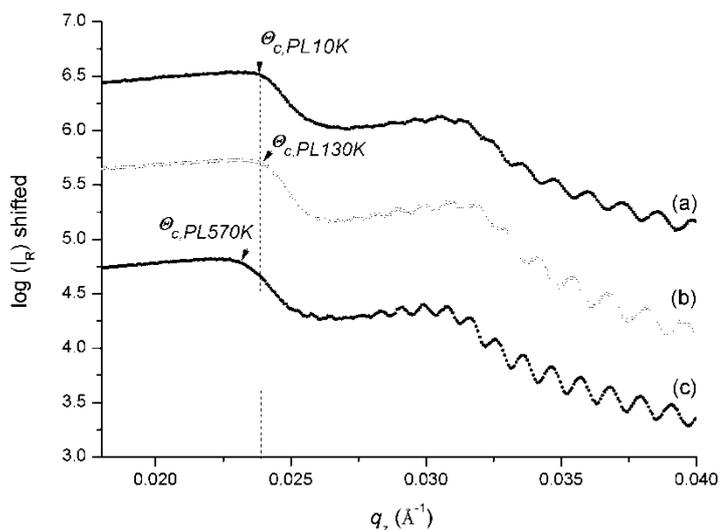


Figure 3.16. XRR results of PMSQs. (a) PL10K, (b) PL130K, and (c) PL570K shifted for clarity

The dielectric constant was measured to confirm the electric property of PMSQs. According to the *Clausius-Mosotti relation* Eq.(4), Dielectric constant [ϵ] can be expressed as such:

$$\frac{\epsilon - 1}{\epsilon + 2} \frac{M}{\rho} = \frac{N_A \alpha}{3\epsilon_0} \quad (4)$$

The PL10K gave a relatively high dielectric value of 3.13 because of the effect of hydroxyl group (T^2) which induced the strong dipolar polarization. In spite of increasing the polymer density, the value of dielectric constant of PL130K was reduced to 2.93 because regarding to the decrease of T^2 ratio, the molecular polarizability rising from electronic and dipolar polarization was decreased.

In addition, the PL570k gave a further depreciated dielectric constant value of 2.74. This depreciation in dielectric constant value was not only due to the reduced bulk polymer density but also rearrangement of the permanent dipoles by transformation to the branched structure.

Moreover, the modulus of PMSQs was shown to the characteristic property as transition of molecular structure. In case of linear polymer, it was usually described that the modulus of the polymer increased with increasing molecular weight. In the same manner, the modulus of PL130K was significantly increased to 6.3 GPa from 3.7 GPa (figure 3.17). Despite increasing the molecular weight several times, on the other hand, PL570K which has branched chains was decreased to 5.4 GPa. This is explained by the

random length and atactic short chains in branched polymer may reduce polymer strength due to disruption of organization [22].

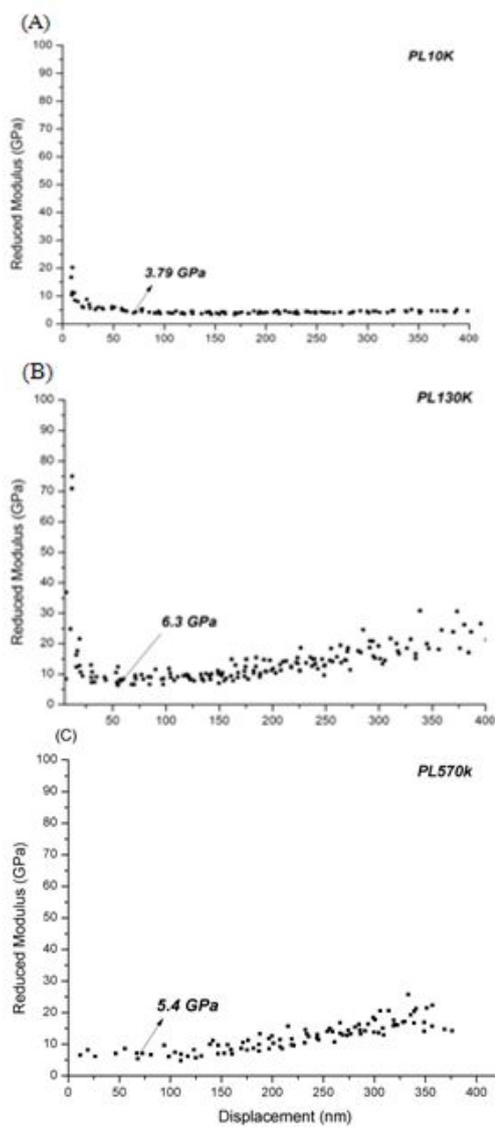


Figure 3.17. Nanoindentation results of (a) PL10k, (b) PL130K, and (c) PL570K

3.3.6 Film properties of end-capped PMSQs

It was considered that the physical property of capped PMSQ would be weakened by mono substituted moiety of siloxane bond and reduced the dielectric property by remove of secondary dipole moment. Therefore, the capping agents having two different features were introduced in each PMSQ. Chlorotrimethylsilane (CTMS) was representatively produced to low dielectric property becoming low polarizability, but it intrinsically had flexible and soft character. On the other hands, chlorotriphenylsilane (CTPS) had a role of relatively low dielectric property by hydroxyl termination, and compensated for weakening of mechanical property by their hard segments.

Table 3.3 showed refractive index, surface modulus, and dielectric constant. The most effective factor by hydroxyl termination was decrease of dielectric constant. Using any capping agents, that was shown under original value. Especially, dielectric constant of capped PL570 dramatically decreased as indicated at 1.95 from 2.79 by CTMS. In an aspect of mechanical property, it was shown to be lowering by CTMS and increasing by CTPS as expected.

Table 3.3. Results of Bulk properties of end-caped PMSQs

Sample	Capping agent	Refractive index	Modulus (Gpa)	Dielectric constant
	-	1.407	3.7	<u>3.13</u>
PL10K	CTMS	1.389	3.56	2.35
	CTPS	1.463	6.2	2.78
	-	1.409	6.3	<u>2.93</u>
PL130K	CTMS	1.391	6.1	2.08
	CTPS	1.449	7.2	2.38
	-	1.375	5.4	<u>2.79</u>
PL570K	CTMS	1.398	5.0	1.95
	CTPS	1.44	6.6	2.37

3.4 Conclusion

We successfully synthesized a series of high molecular weight PMSQs by polycondensation of tetraol, hydroxyl-substituted methylcyclotetrasiloxane. The structure of polymers was considerably well defined using x-ray scattering, ²⁹Si NMR, GPC, and FT-IR. Through structural analyses, a series of high molecular weight PMSQs were confirmed to be a structurally, highly regular polymer, such as ladder-like structure. By controlling the molecular weight, the transformation of molecular structure was examined

from stiff linear to branched. Moreover, the effect of the transition from linear to branched PMSQs was corresponded with the bulk properties for application as an interlayer dielectrics.

3.5 Reference

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Chapter 4

Comparative evaluation of various structural PMSQs from stereo isomer compositions

4.1 Introduction

Polymers can be classified as linear, branched, or crosslinked polymers for their structure. Even their chemical compositions were similar, physical, mechanical, and thermal properties are significantly different. Therefore, as their structural feature, they are properly implemented in industry.

Representatively, linear polymer has most well defined because the monomer molecules have been linked together in one continuous length to form the polymer molecule. This linearity gives good processibility such as melting and solution process by chain relaxation [1-3].

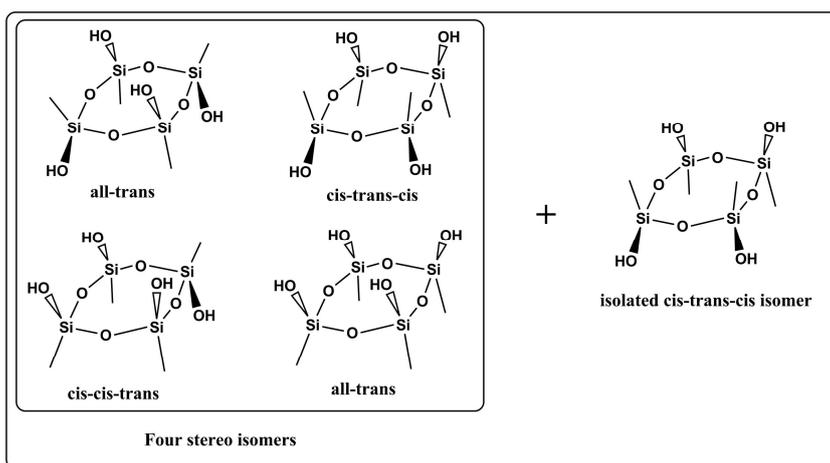
Based on linear polymer, branched and crosslinked polymer were designed as concerning in which side chains were functionalized and how many linkages connected by polymer ends. Moreover, polymer branching induces a lower profile of material density. Because of it, many researchers have investigated polymer geometries such as graft and hyper branched structure.

In aspects of them, silsesquioxane which was composed as organic/inorganic hybrid polymer $[R(SiO_{3/2})]$ was mostly reported as crosslinked polymer by so-called 'sol-gel' method because of more than three reacting sites in mono molecules[4-6]. Despite difficulties of polymerization of linear structural silsesquioxane and branched silsesquioxane, a numerous researchers said the great advantage of linear

polysilsesquioxane such as solubility, enhanced thermal stability, strength, and inertness towards corrosive media [7].

Recently, Hwang et al reported about polymerization of ladder methylsilsesquioxane using isolation of stereo isomer [8]. They introduced the four stereo isomers having four hydroxyl groups for polycondensation and separated cis-trans-cis isomer. In spite of four reacting sites, isolated isomer was induced to form linear structure by hydrogen bond interactions.

On the basis of it, through the addition of isolated isomer from solution of four mixed isomers, we controlled isomer ratio to form branched polymer (Scheme 4.1). Among the four stereo isomers, cis-cis-trans isomer would become a major role of branching points.



Scheme 4.1 Preparation of four different isomer content as 100%, 85%, 55%, and 35% cis-trans-cis isomer,

It was successfully synthesized to branched PMSQ from 35, 55, 85, and 100 % of cis-trans-cis isomer. Controlled isomers were characterized by ^1H NMR, HPLC, and branched polymers were also characterized by FT-IR, ^{29}Si NMR, TGA, solution small angle x-ray scattering. Besides, physical properties such as dielectric constant and surface modulus were measured to analyze the relationship of molecular structure and physical properties.

4.2. Experimental Section

4.2.1 Materials

95% 1,3,5,7-tetramethyl-2,4,6,8-tetrahydro cyclosiloxane (Methyl-T4) was purchased from Gelest, and distilled to remove the stabilizer and di- or tri-mer. Tetrahydrofuran was dried over sodium. Pd/C (10% activated) was purchased from Across. Distilled water was used for hydrolysis of Methyl-T4. Potassium carbonate was of commercial grade and used without further purification.

4.2.2 Preparation of four compositions of isomer from cis-trans-cis 1,3,5,7-tetramethyl 1,3,5,7-tetrahydroxyl cyclosiloxane (Methyl-T4-tetraol)

In a 500 ml round-bottomed flask, hydrolysis of the hydride of Methyl-T4 (19 ml, 0.078 mol) was carried out with water (6.4 ml, 0.355 mol) and Pd/C (10% activated) (0.8 g, 0.75 mmol) for 2 hr in THF (220 ml) at 10 $^{\circ}\text{C}$. Excess water and Pd/C were removed by MgSO_4 and cellite. The substitution of hydride to hydroxide (23.7g) was confirmed by ^1H NMR (200 MHz, ppm): 0.15 ~ - 0.19 [m, 12H, $-\text{CH}_3$], 6.49 [s, 4H, $-\text{OH}$] in $\text{DMSO-}d_6$.

After hydrolysis, it was found that cis-trans-cis tetrol (2g) was isolated from four stereoisomers (150 ml in THF) by recrystallization using methylene chloride (1000 ml) and THF (50 ml) co-solvent for 1 hr at 4 °C. ¹H NMR (200 MHz, ppm): 0.014 [s, 12H, -CH₃], 6.49 [s, 4H, -OH] in DMSO-*d*₆.

After confirming cis-trans-cis isomer, four compositions of 35, 55, 85, and 100% as cis-trans-cis isomer contents were prepared by Methyl-T4-tetraol solution (0.126 g/ml) and isolated isomer. For example, contents of 85% cis-trans-cis isomer were prepared by mixing with 2.9g isolated isomer and 4 ml Methyl-T4-tetraol solution. Finally, cis-trans-cis isomer 2.9g per total isomer 3.4g was prepared.

4.2.3 Polymerization of four compositions of isomers

Each concentration of Methyl-T4-solution was prepared to 10% in THF. In case of 85% composition, 30 ml THF was added in controlled isomer. To obtain similar molecular weights, prepared solutions were carried out to reaction for 12h of 35% (PB35), 24 h of 55% (PB55), 48h of 85% (PB85), and 72 h of 100% (PL) with 0.1wt% K₂CO₃. After polymerization, each solution was precipitated in water, and filtered. They were dried by MgSO₄ in methylene chloride. Dried solutions were precipitated in hexane, again. In case of PB85, white powder (1.9g) was obtained

4.2.4 Measurement and Techniques

Waters HPLC system was used to certify the purity of isolated tetraol. It was accomplished at arbitrary temperature in a normal-phase mode using normal phase Si100 column (Merk). The HPLC mobile phases consisted of 60% cyclohexane and 40% ethyl acetate. A gradient program was used for the HPLC separation with a flow rate of 1.6 ml/min. Each run time was 40 min and Evaporative light scattering detectors (ELSD) used. The number average molecular weight (*M_n*) and molecular weight

distributions (M_w/M_n) of the polymers were measured by JASCO PU-2080 plus SEC system equipped with RI-2031 plus refractive index detector and a UV-2075 plus UV detector (254 nm detection wavelength) using THF as the mobile phase at 40 °C and a flow rate of 1 ml/min. The samples were separated through four Shodex-GPC KF-802, KF-803, KF-804, KF-805. ^1H NMR and ^{29}Si -NMR spectra were recorded in DMSO- d_6 , Acetone- d_6 , and CDCl_3 at 25 °C on a Varian Unity INOVA 200MHz for ^1H NMR spectra and Varian NMR System 500MHz for ^{29}Si NMR spectra (^{29}Si : 99.4MHz). The X-ray scattering was examined at the beam-line 4C1 of Pohang light source (PLS) in the Pohang Accelerator Laboratory (PAL) using Cu-K α radiation [9].

4.3. Result and Discussion

4.3.1 Preparation of four isomers compositions

The branchness was qualitatively controlled by isomer composition of cis-trans-cis isomer which had feature to become linearly polymerize. Table 1 showed each isomer compositions. According to Table 1, cis-cis-trans isomer would be became to major component for forming branched polymer.

Table 4.1 Four compositions of isomers

<i>Abbr.</i>	cis-trans-cis	others		
		All-trans	Cis-cis-trans	All-cis
PL	100	0	0	0
PB85	85	3.3	10.6	1.0
PB55	55	9.9	32.0	3.1
PB35	35	14.3	46.2	4.5

Each composition was confirmed by ^1H NMR and HPLC. As decreasing the amount of cis-trans-cis isomer, the peak area of other isomers was increased shown in figure 4.1 and figure 4.2. In ^1H NMR spectrum, chemical shift of each isomers' methyl group (Si-CH_3) was indicated at (s, 0.019ppm) of cis-trans-cis isomer, (s, 0.026ppm) of all-trans isomer, (triplet, 0.041, 0.0065, and 0.002ppm) of cis-cis-trans isomer, (s,-0.01ppm) of all-cis isomer.

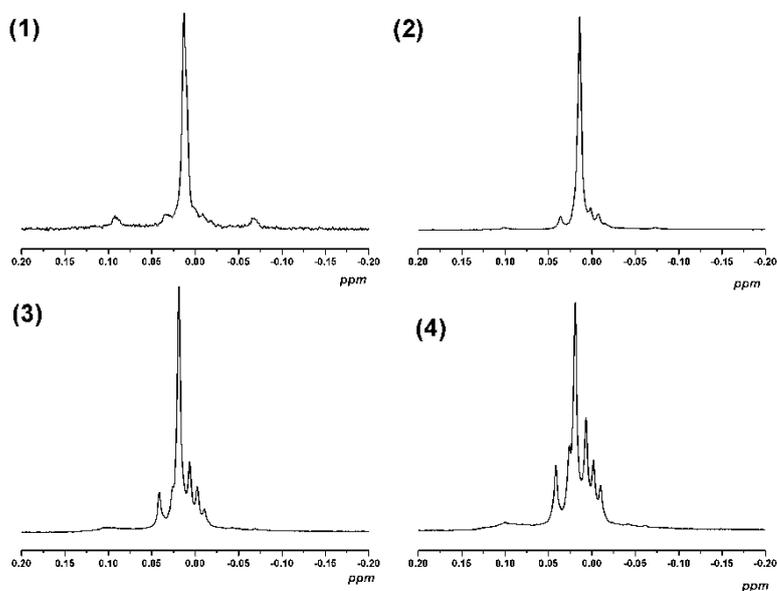


Figure 4.1. ^1H NMR spectrum of four compositions of isomers. (1)PL, (2)PB85 (3)PB55, and (4)PB35

In case of HPLC, there was carried out to cyclohexane and ethyl acetate as eluent solvent ratio of 6 : 4. In this condition, the compositions of isomers were able to be confirmed, clearly. In diagram (figure 4.2), each peaks was indicated as all-trans isomer at

11 min, cis-trans-cis isomer at 13 min, and cis-cis-trans isomer at 35min.

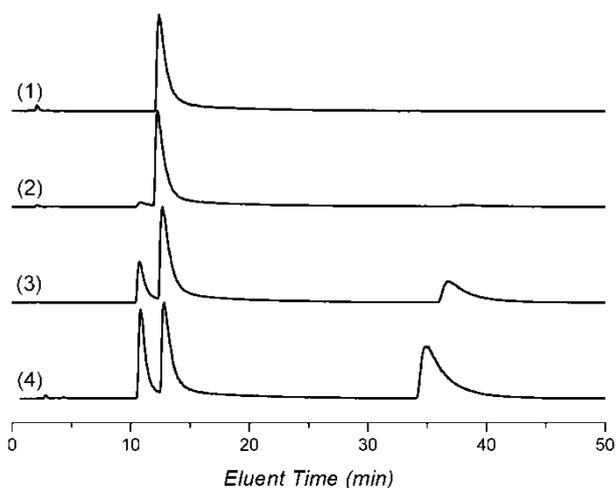


Figure 4.2. HPLC diagram of four compositions of isomers. (1)PL, (2)PB85 (3)PB55, and (4)PB35

4.3.2 Characterization of PMSQs from four compositions of isomers

GPC Results ; The prepared compositions were polymerized by same concentration and catalyst (figure 4.3). As increasing cis-cis-trans isomer, molecular weight was rapidly increased compared than PL silsesquioxane in same reaction time because of giving more reaction sites (scheme 4.2). In results, although number average molecular weight of PMSQs was similar as 20k, the weight average molecular weight was considerably shown to be different over ten times.

Moreover, polydispersity was significantly broadened as polymerization with including four stereo isomers. It was assumed that the reactivity of each stereo isomer was unequal.

The reaction time was manipulated to give a similar molecular weight in each polymer.

Molecular weight and polydispersity was listed in Table 4.2.

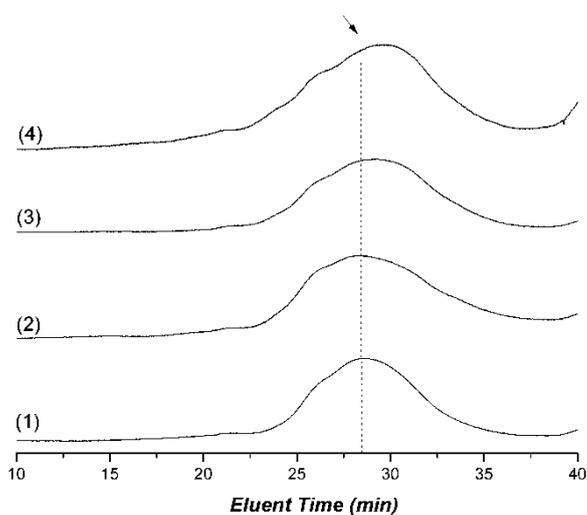
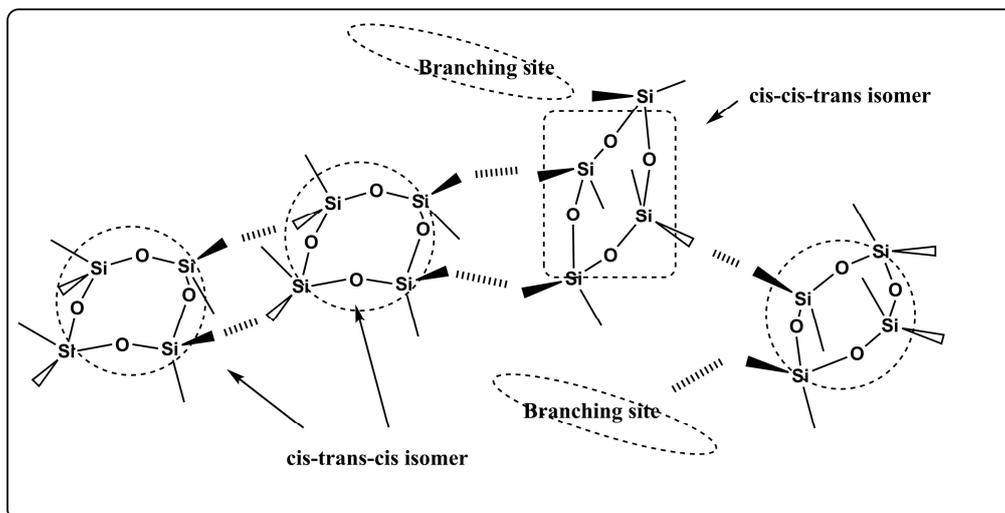


Figure 4.3. GPC results of polymerization of four compositions of isomers. (1)PL, (2)PB85 (3)PB55, and (4)PB35

Table 4.2. Molecular weight and polymerdispersity of PMSQs

<i>Abbr.</i>	Mn/Mw	PDI	T ³ ratio
PL	19,200 /420,000	21.8	91%
PB85	19,000/810,000	42.6	91%
PB55	19,500/772,000	39.5	93%
PB35	22,000/7.6 x 10⁶	345.4	92%



Scheme 4.2. Schematic illustration of branched PMSQ.

FT-IR & ^{29}Si NMR spectrum ; Figure 4.4 showed FT-IR spectrum of PMSQs from four isomer compositions. Actually, there was no different characteristic peak by branched structure. It was very interesting because many published works said that two split peak of silsesquioxane usually implied their molecular structure such as network, cage, or ladder [10]. According to published work about FT-IR spectrum, these four PMSQs were evaluated to high regulated ladder structure.

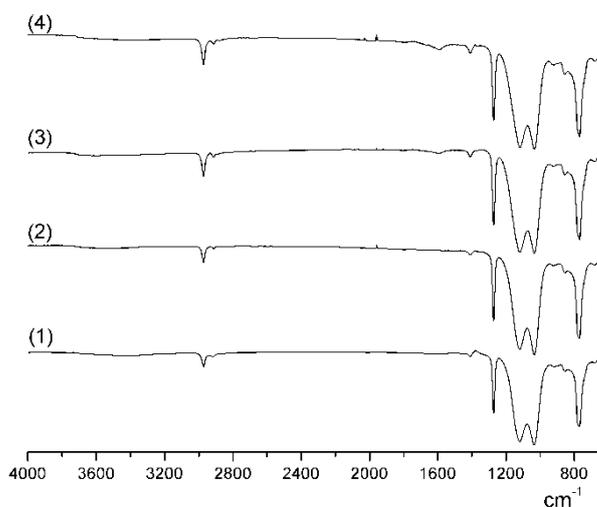


Figure 4.4. FT-IR spectrum of branched PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35

However, it was hard to understand that isomers were transitioned to their conformation during polymerization which was preferred to ladder structure. ^{29}Si NMR was carried out to confirm molecular structure of PMSQs.

If they were formed to ladder structure The T^2 resin which was hydroxyl group attached silicon atom was rarely shown in ^{29}Si NMR spectrum (theoretical value of 90% T^3 was 2,700 Mn, and 97% T^3 was 10k Mn). In results, figure 4.5 showed quantitative T^2 and T^3 integration ratio. Their integration values of them were shown to be similar to each other about $92\% \pm 1$ although branched PMSQs was expected to have more T^2 site as increase of end hydroxyl sites by increase of cis-cis-trans isomer (Table 4.2). It was explained that hydroxyl group of T^2 sites were positioned not only at chain end but also intra molecules of uncondensed hydroxyl group which was also evaluated as T^2 structure [8]. Therefore, it was not certain that PMSQs were branched or not by ^{29}Si NMR

spectrum.

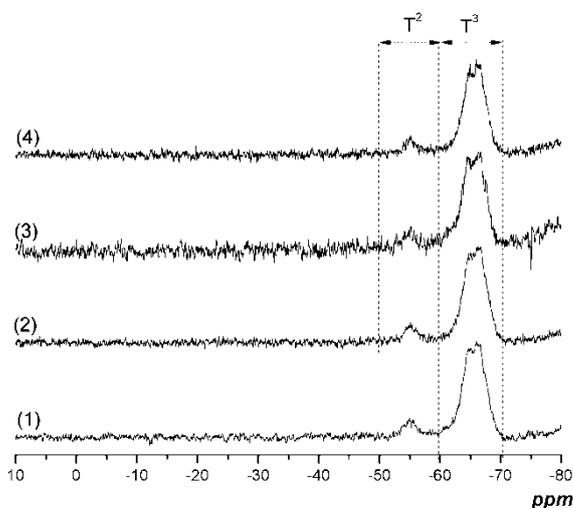


Figure 4.5. ^{29}Si NMR spectrum of branched PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35

Dilute SAX scattering ; Due to difficulties in defining a certain molecular structure through GPC, ^{29}Si NMR, and FT-IR analyses, PMSQ's detailed molecular structure was investigated using small x-ray scattering. The solution small angle x-ray scattering experiments helped elucidate the polymer structure at intermediate or high q values, thus easily distinguishing the structural class. These experiments helped explain the major transformation of molecular shape by fractal theory.

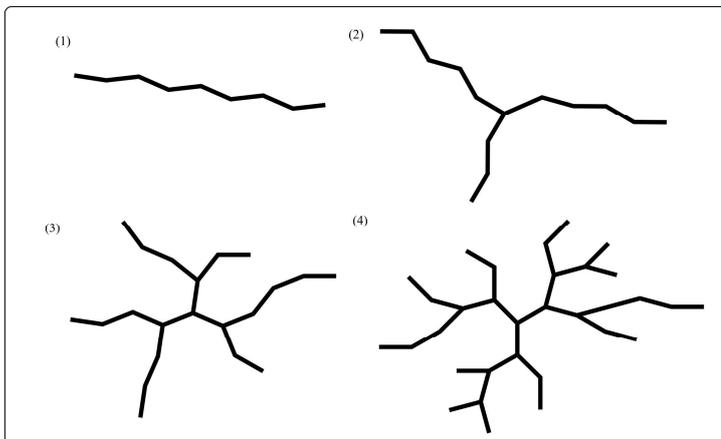
The Kratky plot of $q^2I(q)$ versus q showed the molecular transition of PMSQs more clearly (Figure 4.6). Each PMSQ was characterized in toluene, THF, and methanol solvent. These three kinds of solvent having various polarity indices from 2.4 to 5.1 would be able to say the polymer structure in detail. Excepting PL polymer, the most

striking feature of branched PMSQ scattering factors in this plot is the appearance of a maximum [11,12].

In comparison with calculated fit of rigid linear polymer, PB85 was shown to linear polymer structure at high q region in THF solvent so called Kuhn segments which meant that cis-trans-cis isomer was polymerized. However, it didn't show upturn point in methanol because it was not sufficient comparability with methanol to loosen chain entanglements by relatively high polarity.

In case of PB55 and PB 35, there showed linear segments in methanol at high q region after upturn position. This meant that they were more easily dissolved in high polar solvent. It was assumed that these PMSQs had amphiphilic property compared than PL and PB85 due to hydroxyl group located at end site in branched polymer.

As a comprehensive analysis of molecular structure of PMSQs, their structures were described as scheme 4.3. PMSQs were formed to having more branched segments by cis-cis-trans, all-trans, and all-cis isomer. Among them, cis-cis-trans isomer severely affected to form branched structure comparing than others. Conclusively, molecular structure of PMSQs showed more likely hyper branched structure rather than comb branched shape.



Scheme 4.3. Schematic illustration of PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35

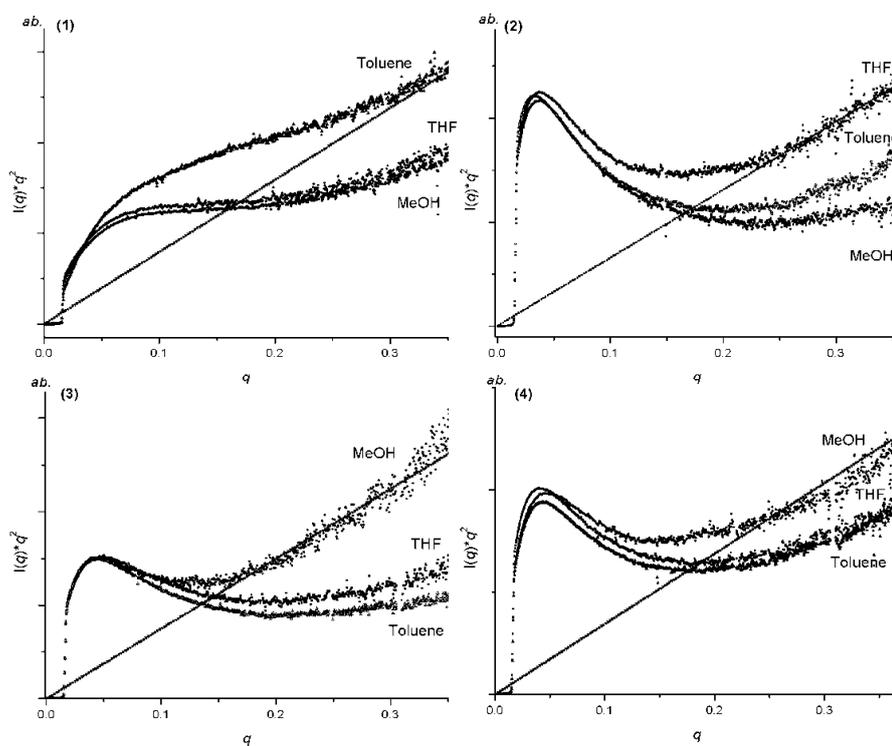


Figure 4.6. Dilute SAX scattering of PMSQs in toluene, THF, and methanol. (1)PL, (2)PB85 (3)PB55, and (4)PB35

TGA diagram ; The most particular phenomenon of branched PMSQs was degradation property by heat. According to isomer composition, degradation temperature was observed in different temperature. 2~3% weight loss in beginning of degradation over 200°C was usually water by condensation of hydroxyl group. After then, methyl group was decomposed as described in figure 4.7. Despite same silsesquioxane bond as $(\text{CH}_3\text{SiO}_{3/2})_n$, the onset temperatures of methyl group of PMSQs were dramatically shifted from 450°C to 750°C. This was explained that the branching venue would be formed to singular bond like siloxane (Si-O-Si), and nearby methyl group became degradation earlier than others.

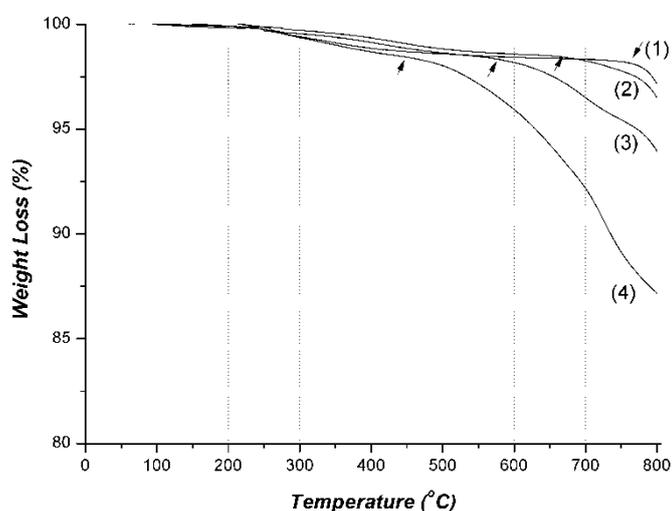


Figure 4.7. TGA diagram of PMSQs. (1)PL, (2)PB85 (3)PB55, and (4)PB35

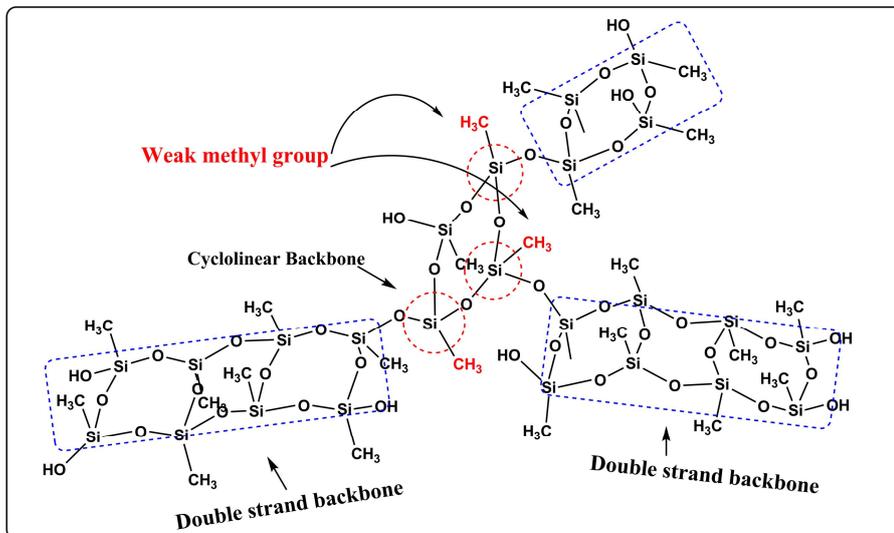


Figure 4.8. Degradation venue of methyl group as branched PMSQ

Dielectric constant and surface modulus ; Dielectric constant were measured to understand electric property of branched PMSQs because it was directly related with molecular polarizability. Concerning their chain movement in dilute solution, it was expected to have similar arrangement in bulk state.

They showed different dielectric values as 2.93 of PL, 3.18 of PB85, 3.21 of PB55, and 3.37 of PB35 although PMSQs were indicated to analogue hydroxyl group by ^{29}Si NMR spectrum. In results, it was shown that molecular structure of branched PMSQs affected to dielectric constants.

In addition, moduli of PMSQs were measured by nanoindentation as prepared in thin film on wafer. They also showed increase modulus as increase of branchness for 6.3 GPa of PL, 6.88 GPa of PB85, 7.19 GPa of PB55, and 7.26 GPa of PB35. It was carefully

explained. One is that they were polymerized to more dense structure by hyperbranched structure, and other was possibility of inter-crosslink between polymers. Previous one was more preferred when they were considered with several analysis results.

4.4. Conclusion

Branched PMSQs were successfully prepared by using four stereo isomers. It was polymerized in same conditions to confirm the degree of branch relatively. Four compositions of 100, 85, 55, and 35% were prepared as increasing cis-trans-cis isomer. After polymerization, molecular structure of PMSQs was found out that they have branching sites, and their structure were closely related with electrical and mechanical properties.

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논문 요약

본 연구는 4환형 입체이성체를 이용한 쇄상 및 가지형 고분자 폴리메틸실세스퀴옥산의 중합 및 이의 특성에 관한 연구이다. 실세스퀴옥산은 일반적으로 세라믹과 유기 고분자의 장점을 동시에 가지는 물질로서, 특히 세라믹의 내열특성과 유기 고분자의 고기능성 및 매우 좋은 가공성을 가지고 있다. 하지만 새장 구조의 실세스퀴옥산을 제외하고는 실세스퀴옥산을 졸-겔 방법을 이용한 망상구조로 응용 되고 있다. 더욱이 망상구조의 처리시 실세스퀴옥산의 구조 특성으로 인하여 미세한 파티클로 형성되는 특성을 가지는 것으로 보고 되어 있다.

이러한 여러가지 실세스퀴옥산 중에서, 매틸관능기를 가지는 실세스퀴옥산은 저유전 물질로서 잘 알려져 있으며, 그리고 여러 연구자들을 통하여 그 특성이 잘 알려져 있다. 특성들 중에는 저유전 특성 이외의 높은 열안정성 및 상당이 좋은 기계적 특성도 가지고 있는것으로 알려져 있다. 하지만 매틸실세스퀴옥산을 응용하기 위하여, 이 또한 졸-겔 방식을 통한 망상형으로 구성하여 사용되고 있으며, 이러한 구조 특성으로 인하여 앞서 언급한 문제 이외에 중합 방식 및 후 처리 공정에 의한 물성 조절이 매우 상이하게 나타는 것이 보고 되고 있다. 더욱이 열처리 공정에 의한 물질의 수축현상에 대하여 그 대책이 미미한 실정이다.

이러한 문제를 해결하기 위하여 쇄상 구조의 사다리형 실세스퀴옥산의 개발이 필요하다는 보고가 있으며, 이를 위하여 많은 연구자들의 연구가

있었다. 이 중 쇄상 구조를 얻기 위하여 trichlorosilane 계열의 모노머를 이용한 연구가 가장 활발 하였으나, 그 결과가 매우 부족한 실정이다. 이러한 이유는 3개의 관능성을 통한 사다리형 구조를 유도하기 위한 중간체의 형태가 일정하게 유지 되지 못하기 때문인 것으로 알려져 있다.

그리하여, 본 연구에서는 일정한 규칙성을 가지는 중간체인 4환형 구조 이성질체로부터 특정 구조를 분리하여 쇄상 구조의 실세스퀴옥산의 중합에 관한 내용을 기술하였다.

이를 위하여 아래와 같은 순서로 실험 내용을 기술한다.

첫째, 4환형 이성질체를 물질의 변질 없이 안정하게 수산기로 치환 시키는 단계 및 치환된 이성질체 중 특정 이성질체를 분리하는 과정을 설명하였다.

둘째로 이렇게 분리된 이성질체를 이용하여 쇄상 고분자를 중합 하였으며, 이의 구조를 분석하는 과정을 설명한다.

셋째로 분리된 이성질체를 이용하여 분자량을 조절하여 고분자량의 쇄상 구조를 얻어 내는 과정 및 저유전 특성에 관하여 설명한다.

마지막으로 4가지 입체 구조 이성질체의 조성을 조절하여 가지형으로 분자 구조를 유도 하였으며, 중합된 고분자의 구조를 분석하는 단계를 설명한다.

본 연구를 통하여 쇄상 구조 및 가지형 구조의 실세스퀴옥산의 중합이 성공적으로 이루어 졌음을 알 수 있었으며, 또한 이렇게 중합된 구조에 따른 유전 특성 및 기계적 특성등을 확인 할 수 있었다.

주요어 : 선형 고분자, 가지형 고분자, 실세스퀴옥산, 저유전 물질
입체이성질체

학 번 : 2006-30865