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博士論文

ハロゲン化シランの塩基付加体を経由したオリ
ゴラダーフェニルシルセスキオキサンの合成と
フォトリソグラフィへの応用に関する研究

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Abstract

The organic-inorganic hybrid materials have received considerable interest in the past decades because of their prospects in developing materials with unique optical, thermal and electronic properties. Recently, silsesquioxanes (SQ) have been noticed as organic-inorganic hybrid material in the field of Flat Panel Displays. Especially, SQ's with high regularity structures like a ladder is expected to give superb properties such as high thermal resistance, high transparency, low dielectric constant, and high cracking threshold as compared to SQ with a low regularity structure.

Here, I found new synthesis methods for oligo-ladder PPSQ via silicon-amine adducts using phenyltrichlorosilane (TCP) as monomers by one-pot synthesis at an aqueous-organic boundary (*n*-propylacetate (nPA) /water). Furthermore, I also showed the possibility of photosensitive material formulation using oligo-ladder PPSQ to be applied to a photo-patternable dielectric layer in TFT (Thin Film Transistor)s.

In Chapter 2, silicon-amine(alkali ligand) adducts which affect the hydrolysis of TCP was described. The liquid boundary reaction which has a slow kinetic rate of homo-condensation is limited by the reaction area at the nPA-water liquid boundary. This leads to a thermodynamically stable ladder structure. The direct synthesis of ladder SQ using silicon-amine adduct at water-nPA liquid boundary has not been reported yet. Several amines such as pyridine, TMEDA(tetramethylethylenediamine), PMDETA(pentamethyldiethylenetriamine) were tested. These amines have a lone electron-pair initiates formation of interaction compounds with TCP via d_{π} - p_{π} overlap. The oligo-ladder PPSQ was formed in all types of amines (ligand), but best results were obtained by TMEDA. The developed methods are based on simple one-step reaction, which will open possibility for low cost ladder SQ production for industrial use. Moreover, reaction mechanism was studied using simulation techniques for the density of pyridine-complex by MP6 and MALDI-TOF/TOF MS. In the synthesis of ladder structure, most important process was formation of phenyltrisilanol ($\text{PhSi}(\text{OH})_3$). The condensation scheme for this ladder structure was proposed as sequential reaction based on $\text{PhSi}(\text{OH})_3$. Amine-ligands are effective in controlling the hydrolysis reaction and homo-condensation of silanol.

Chapter 3 described positive-/negative-tone photosensitive oligo-ladder PPSQ based on Novolak resin's photoresist formulations. The pattern resolution was about $3\mu\text{m}$ in L/S. This value is also acceptable for dielectric layer in the display region. The silanol (-Si-OH) has its acidity higher than phenol in Novolak resin. Then negative-tone system with photo acid generator showed high resolution and high sensitivity for photon energies of $20\text{ mJ}/\text{cm}^2$. The basic reaction in this case is also controlled by the homo-condensation of silanol.

On the other hand, electrical properties exhibit superior characteristics for application in optical and electrical field. Optical transmittance was over 98% at 400nm, this value is enough for optical devices. Dielectric constant was between 3.1 - 3.2. Our SQ showed characteristics similar to low-k materials. Furthermore, TGA analysis showed high thermal stability with a 5% weight loss at temperature 500°C and ceramics yield of 80% at 800°C .

Consequently, I found out new synthesis scheme for oligo-ladder PPSQ via silicon-amine (mono-, bi-, tri- ligand) adducts. TMEDA (bi-ligand amine compound) was most superior in term of the yield and reaction controllability. The photosensitive SQ was also investigated. It was shown that lithography is highly possible using synthesized oligo-ladder PPSQ. I believe that my research will open new pathway for mass production of ladder SQ and will be applicable to new architecture of display in near future.

Key words: silsesquioxane, ladder structure, amine-ligand, pyridine, TMEDA, PMDETA, photosensitive.

Acknowledgment

I have strived hard to fulfill this degree in my multiple roles as a company employee as well as a student. Usually according to University standards it takes 3 years to obtain this degree, but to date I took more than five years to complete this work.

During this time, I could continue to work due to the kind support of Professor Ebitani. I am really grateful to him for his guidance as a teacher as well as a mentor.

In particular, I would like to mention that I really appreciate all the advice and guidance from Professor Ebitani in all aspects of life including professional and philosophical areas helped me to stand at this goal. In addition, I would like to thank the JAIST technical advisor Dr. Miyazato who would always had come up with a good advice and suggestion. I would also like to thank Dr. Ninad Shinde who is my company colleague.

Here, I would like to express my deep gratitude to my family, especially to my wife whose extraordinary support in all those good times and bad times was my source of energy to overcome all the difficulties in achieving my goals.

On the other hand, as a student at JAIST I was able to get acquainted with many other teachers and academic staff, who were always friendly with me. Interestingly, with the help of these good relationships here, I could generate a joint research between my

company and JAIST. In future, as a company employee I will continue to strive to obtain the fusion of advanced technology of JAIST with our industrial business. I believe our abilities and interests will continue to build a deeper relationship for times to come.

Yuji Tashiro

September, 2015

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Chapter 1

1. Introduction

1.1 Basic Chemistry of Si

Silicon is a well-known element as the main constituent for glasses and silicones. Also, silicon is the most abundant element in the lithosphere; Clarke Number precise quantification of abundance shows that oxygen makes up about 49.5 and silicon is 25.8. Interestingly, there are no natural organic silicon compounds; all of them have been created by researchers in a chemical laboratory. However, it is this element that we humans can much effectively use from the point of view of chemical specialties and natural abundance. Table 1.1.1 shows Clark number of some elements.

Table 1.1.1 Clarke Number of Main Elements

O	Si	Al	Fe	Ca	Na	K	Mg	C	N
49.5	25.8	7.56	4.70	3.29	2.63	2.40	1.93	0.08	0.03

Also, for similar 4th valency element like carbon, the electron negativity of silicon is different. (For C it is 2.55 and for Si it is 1.9).

Various product lines for large-scale manufacturing such as of the hetero-chemistry in the modern organic-chemical industry, fine chemicals such as medicines, an

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agrochemical industry, wherein all these products are basically based on carbon chemistry.

Silicon is in the IVa group, same as for carbon, and it can thus theoretically form compounds which are similar to the organic compounds. Consequently, molecular designs and functions using similar tools are possible. Furthermore, organic chemistry-like handling of silicon is possible unlike many other inorganic elements, which are difficult to handle and without a concept of 'molecules' even silicon is a typical inorganic element. Also, the new functions or the advancement of the existing functions which cannot be realized in the carbon system could be expected based on the following characteristics of silicon unlike carbon.

- (1) **Formation of a stable sigma bonding:** The sigma bond combination with a variety of elements such as oxygen, halogen and a metal atom is more stable than carbon, therefore it gives a heat resistance that is higher than carbon system. Making of complex compounds by using silicon is possible as it will act as a contact points in the inorganic/organic interface.
- (2) **Highly HOMO Level:** Homo Level of silicon is higher than that of carbon

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in quantum chemistry (188kcal/ mol.). Therefore, silicon is sensitive to the electronic movement, physical perturbation including electronic excitations, the cleavage of sigma-bonding by the light which is not possible in the carbon system, fine processing of even at the submicron order, and higher conductivity than carbon are expected.

- (3) **Large polarization of binding:** There are functional properties such as larger piezoelectric effect than carbon, large magnetization by strong polarization on the binding for hetero-atom with silicon.

- (4) **Large covalent radius:** Silicon can utilize space in the silicide by their large covalent radius as compared to carbon.

Ordinarily, silicon is a typical inorganic element constituting the earth crust, and it is an element which most closely resembles carbon structurally. The properties and behavior of silicon compounds are significantly different as compared with that of carbon's there due to the different electronic state, stereotyped characteristic on the atomic state. Therefore, silicon can be assumed to possess a harmonized character with organic / inorganic or it is expected to manage new functions and advanced properties which cannot be invented by carbon-based organic chemistry.

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1.2 Hetero Polymer Chemistry

Studies on silicon (silicon compounds) which are expected to possess unique properties were initially started in the field of organic chemistry from synthesized organic-silicon compounds. In 1863, Friedel and Craft had first synthesized organosilane compounds¹.

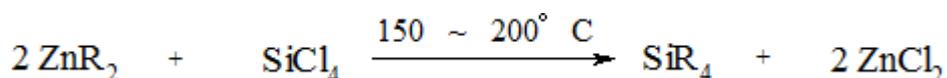


Figure 1.2.1 Synthesis Scheme of Organosilane Compounds

After which, polysiloxane, or silicone which are composed of $-\text{R}_2\text{SiO}-$ as repeating unit was synthesized from hydrolysis of dialkylchlorosilane using Grignard reagent by Kipping² in 1912.

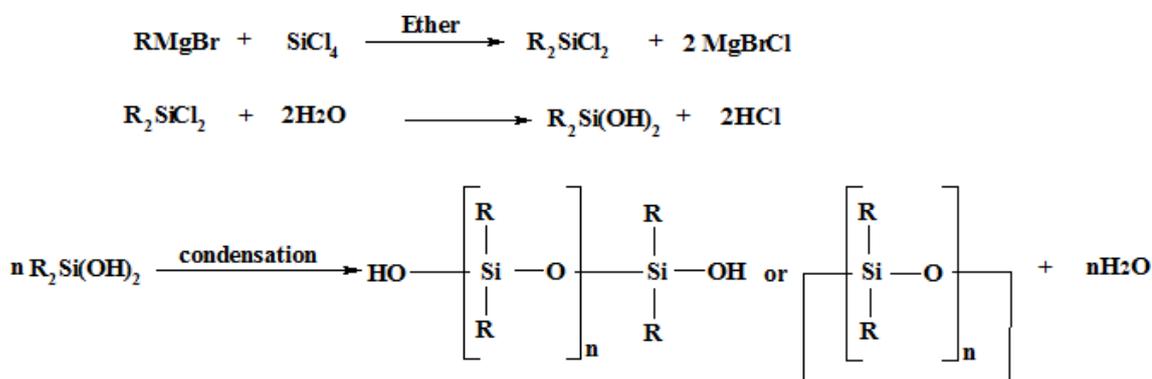


Figure 1.2.2 Synthesis Scheme of Organosiloxane by Grignard Reagents

In 1940, Rochow³ found out direct synthesis method of organo-halosilane from

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halo-carbon with silicon using copper-catalyst. By this time the organo-silicon chemistry had developed in an extremely advanced science. Since then, various organo-silicon compounds can be synthesized even at the industrial level scales.

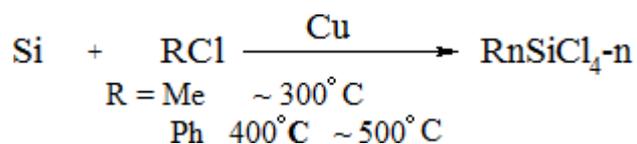


Figure 1.2.3 Direct Synthesis of Organohalosilane Compounds

After this, the synthesis of various silicon containing polymers using organo-silicon compound as a starting monomer and their applications to make polymers were carried out. The main purpose of those syntheses was expectation of high thermal stability, electric properties and optical properties based on unique character of hetero-bonding (Si-N, Si-C, Si-Si, Si-O, etc.). Here, I focus on the hetero-bonding silicon polymers from the point of view of synthesis and their applications in order to clear positioning of my study.

1.2.1 Si-N Polymer (Polysilazane , Polyaminosilazane)

The main chain is consisting of Si-N, and Si-N binding is easy to be hydrolyzed. It was initially thought that they had poor stability in atmosphere. At first, their applications were almost considered to be as high thermal durability ceramics which were in turn

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derived from the conversion of Si-N polymer. The study of organo-polysilazane such as methyl, vinyl polysilazane, and cyclic silazane etc. was mainly focused from the point of view of ceramics ($\text{Si}_x\text{N}_y\text{C}_z$) fiber applications⁴⁻¹⁰. Penn et al. had obtained $\text{Si}_x\text{N}_x\text{C}_z$ fiber form dry spinning of N-methyl polysilazane as shown in following scheme.



Figure 1.2.4 Synthesis Scheme of N-methylpolysilazane

Nicholas D in 1949 studied some polysilazane through ammonolysis reaction and its condensation as shown in Fig.1.2.5. This polymer was synthesized using as organosilane such as $\text{R}_x\text{SiH}_{4-x}$. (US Patent 2,579,418 Nicholas D. polymeric resinous products containing repeating unit of Silicon linked to Nitrogen and Process for Making Some)

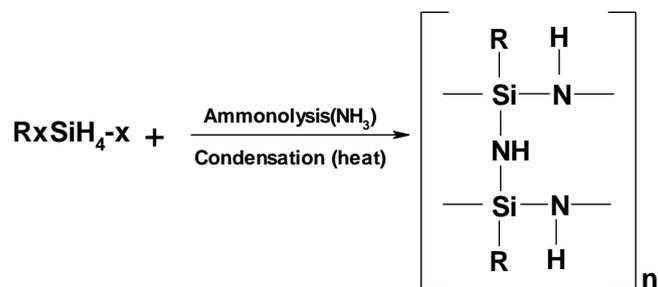


Figure 1.2.5 Synthesis Scheme of Organopolysilazane

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Rochow¹¹ had synthesized a ladder-like polymer containing Si-N bonding from

Me_2SiCl_2 and ethylenediamine using CuCl_2 catalyst as shown in Figure 1.2.6 in 1960.

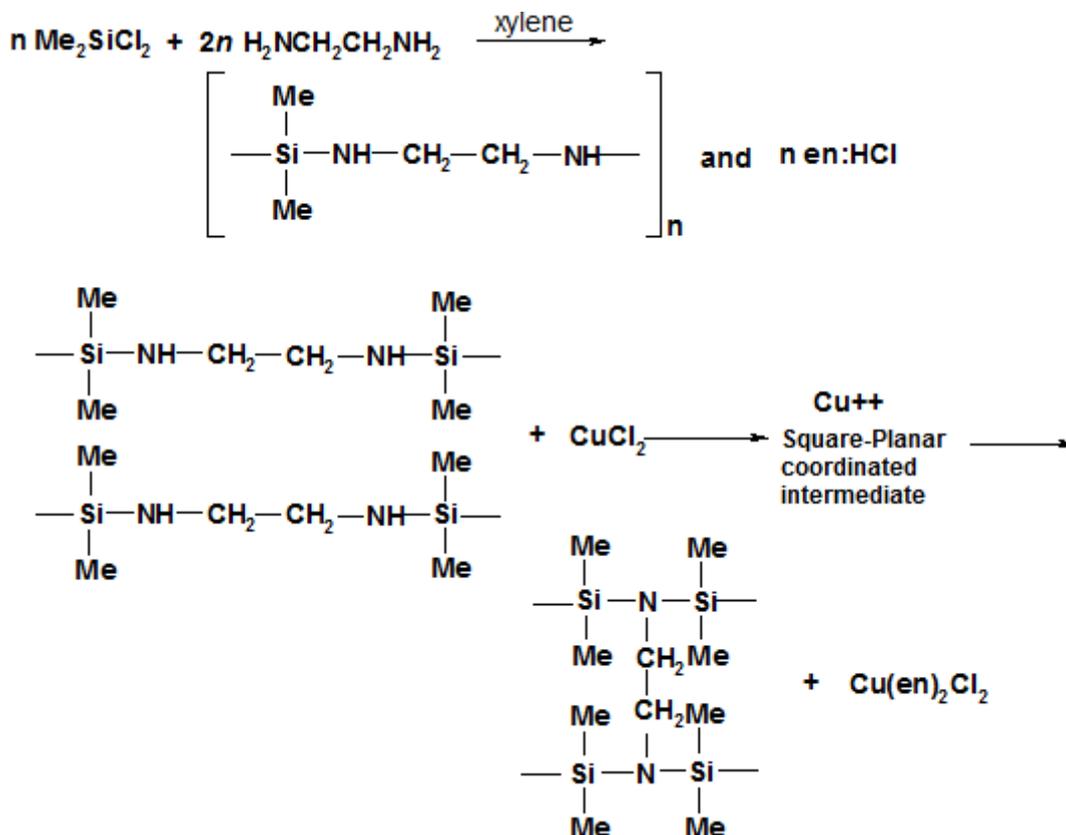


Figure 1.2.6 Synthesis Scheme of Ladder-like Organopolysilazane

Even though, many studies on organopolysilazane were carried out from the point of view of ceramics pre-cursors. However, there was little progress because these materials could not show superiority properties as compared to those existing ceramics, and thus did not find any suitable applications and were almost found no used in the industry until today. However, pre-ceramics precursor method is the only one method for making

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ceramics fibers. This, it is hoped that organosilazane could help to find out new pathway in the future.

On the other hand, perhydropolysilazane which is a form of completely inorganic silazane consisting of Si, N and H is a useful pre-ceramics polymer of pure Si₃N₄ (silicon Nitride). Only this polymer has successfully found applications as dielectric layer, STI (Shallow Trench Isolation) in IC (Integrated Circuit) region and industrial functional coating through Merck PMI.

Stock first synthesized perhydropolysilazane from dichlorosilane / ammonia into toluene at -70° C in 1921¹². The obtained polymer was a low viscosity liquid and polymer character was unclear.(Figure 1.2.7)

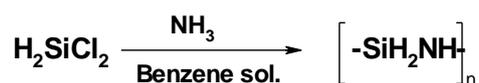


Figure 1.2.7 Synthesis Scheme of Perhydropolysilazane

Seyferth et al. had reported, synthesis of polysilazane from H₂SiCl₂¹²⁻¹³, as first he synthesized a high viscosity perhydropolysilazane using DHCD (dehydrocyclodimerization) reaction using KH catalyst in 1984 as shown in following figure. This polymer included a 4-ring structure as shown in Figure 1.2.8. And

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furthermore, studied by Seyferth on the synthesis of various polysilazane based through this DHCD reaction ¹⁴⁻¹⁵.

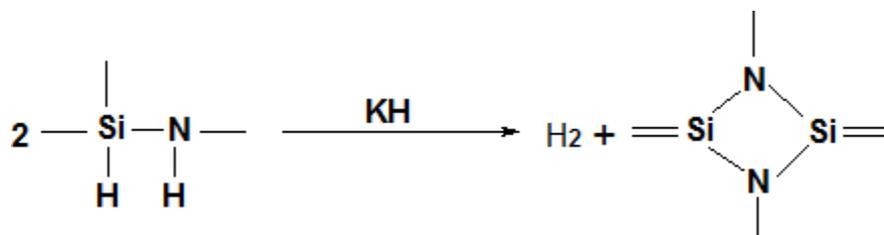


Figure 1.2.8 Dehydrocyclodimerization of Si-NH bonding

Aylett had studied synthesis of an aminopolysilazane in n-hexane solvent as shown in Figure 1.2.9; the obtained polymer was white and the unit number was about 20 in case of methylamine. Further, he estimated the Si-N stability based on d π - p π overlap ¹⁷.



Figure 1.2.9 Synthesis of aminopolysilazane

Isoda et al. synthesized a high molecular polysilazane from ammonolysis of dichlorosilane-pyridine adducts as shown in Figure 1.2.10¹⁸⁻¹⁹. This polymer had a molecular weight of 1390 and SiH₃/(SiH+SiH₂) ratio to be 2.5.

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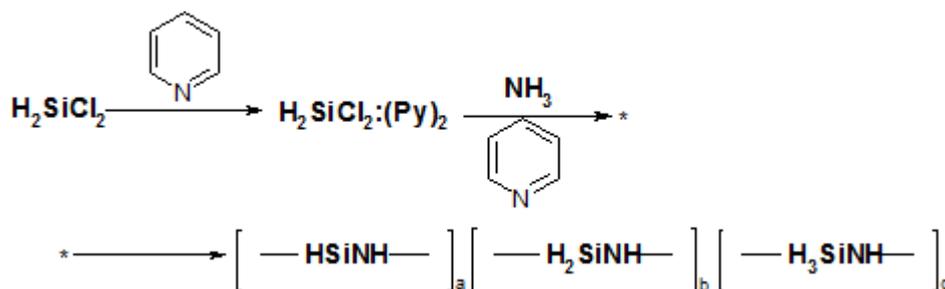


Figure 1.2.10 Synthesis scheme of perhydropolysilazane via pyridine adduct

Furthermore, the ammonia modification and the thermal polymerization of obtained polymer found to further increase the molecular weight, controlling the elemental components²⁰. These polymers were solid after solvent removal and showed good properties as a Si₃N₄ pre-ceramic precursor²¹⁻²³. They were the first to obtain a polymer in solid state by solvent removal. The structure of this polymer is composed of 8-ring-structure, 6-ring structure and a linear chain as shown in following figure.

Interestingly, they obtained Si₃N₄ fibers via NH₃ gas treatment of perhydropolysilazane fibers which were in turn obtained by dry-spinning methods²³⁻²⁴. The mechanical properties of these fibers were measured and further tested in applications as fiber for reinforcement of ceramics²⁴. Further, various precursors based on perhydropolysilazane such as polyaluminosilazane, polyborosilazane were synthesized in order to obtain Si-Al-O-N, Si-N-B-O ceramics which were expected for increasing thermal resistance^{20,22}.

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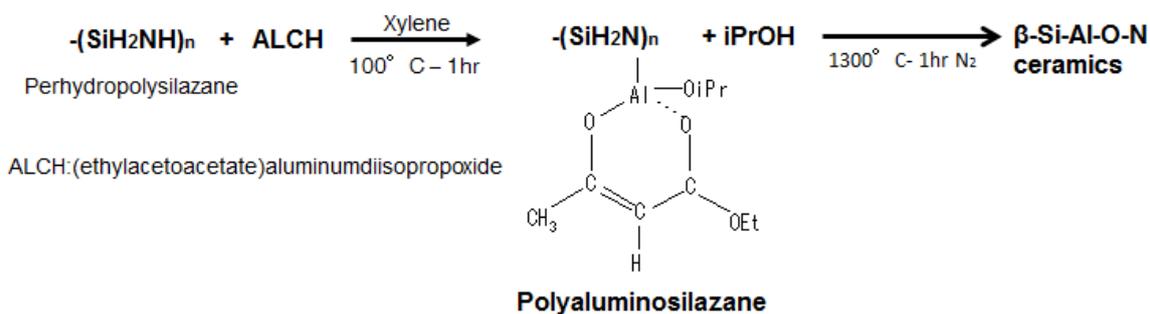


Figure 1.2.11 Synthesis of polyaluminosilazane

Further studies by Tonen Co. Ltd. showed that, perhydropolysilazane could be coated on silicon wafers. When these wafers were treated in steam at 850° C, high quality quartz-like films with very high purity SiO₂ were obtained and SiO₂ conversion scheme was shown as shown in Figure 1.2.12.

In the semiconductor industry, SiO₂ dielectric layers can be deposited using even the CVD (Chemical vapor deposition) process. However, with the more high-end devices where-in the line and spaces get halved every now and then, it has become very difficult for the CVD process to fill those narrow trenches. In this case, perhydro-polysilazane can be spin-coated to achieve better gap fill. This wet process is used in DRAM, NAND-Flash and Logic devices²⁶⁻²⁸.

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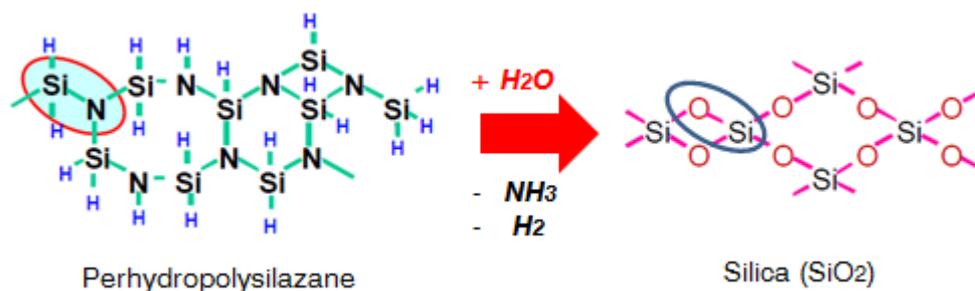


Figure 1.2.12 Conversion to Pure SiO₂ from Perhydropolysilazane

Moreover, recently Shinde et al. prepared thin Silicon-Nitride like films from perhydropolysilazane by 172nm excimer lamp irradiation as shown in Figure 1.2.13.

This shows further advancement of research activities in the field of electronic materials

29.

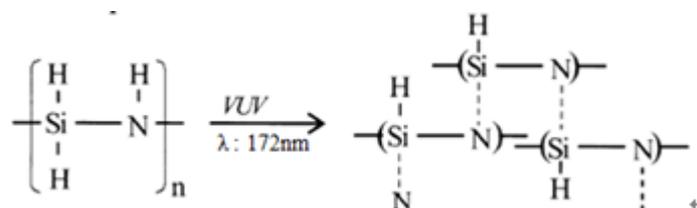


Figure 1.2.13 Polymerization of Perhydropolysilazane by VUV

1.2.2 Si-C polymer (polycarbosilane)

Polycarbosilane, which is composed of -Si-C- main chain and polycarbosilane polymer; is a pre-ceramic precursor for Silicon Carbide (SiC) ceramics. SiC ceramics has some unique properties such as electrical conductivity, semiconductor nature, high

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temperature stability and superb oxidation resistance. There are many reports about the properties of SiC, synthesis and fiber like fabrications. Lately, SiC is studied in point of view of high temperature semiconductor in the fields of vehicles and space travel.

In 1980, Yajima first successfully synthesized polycarbosilane from polydimethylsilane by thermal transfer reaction³¹⁻³⁶.

Polydimethylsilane is obtained by the de-chlorination condensation reaction of dimethyldichlorosilane with sodium metal. It is so known as Wurtz reaction. The chemical structure of polydimethylsilane is shown in Figure 1.2.14. Finally, polycarbosilane is also obtained from thermal transfer reaction of polydimethylsilane, the reaction mechanism is shown in Figure.1.2.15.

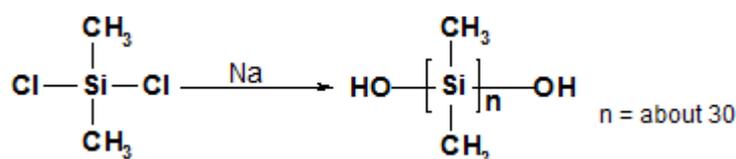


Figure 1.2.14 Synthesis of Polydimethylsilane by Wurtz reaction

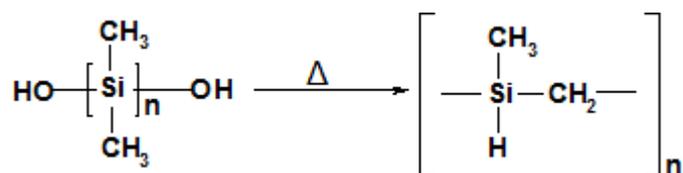


Figure 1.2.15 Synthesis of polycarbosilane by thermal transfer reaction at 350° C

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And further, Yajima and Okamura obtained polycarbosilane fiber through dry spinning of polycarbosilane polymer via ozone treatment for unit-melting. The silicon-carbide fiber (SiC fiber) was prepared by heat treatment of polycarbosilane fiber at 1300° C in inert gas ambient. Now, these SiC fibers (so called NICALON) are provided by Nihon Carbon Co. Ltd.

On the other hand, Weyenberg obtained linear dimethylpolycarbosilane from distortional 4-ring organo-silicon compound by Pt catalyst, thermal treatment as shown in Figure 1.2.16.³²

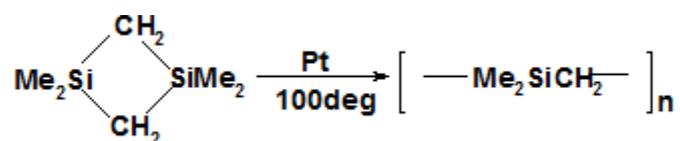


Figure 1.2.16 Synthesis Scheme of linear dimethylpolycarbosilane

After this, many studies were focused on SiC fiber and ceramics formations, for applications such as Si-Ti-O-N fiber (so called TIRANO fiber).³⁴⁻³⁶

Lately, Shimoda announced new pathway to obtain pure SiC ceramics from cyclopentasilane.³⁸ That's method will attract much attention in future.

1.2.3 Si-Si Polymer (polysilane)

Polysilane are compounds whose main chain is composed of -Si-Si- bonds, and they

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are considered as homogeneous polymers similar to -C-C- bonding polymers. This intrinsically generates an interesting property of metamorphism in -Si-Si- polymers, which is not the case of -C-C- polymers. Polysilane is well known for its unique properties arising due to the σ - σ conjugation by Si-Si bonding. Ultra violet (UV) light absorption due to Si-Si bonding is one of them, and λ_{\max} , ϵ of UV absorption correlates to Si-Si chain length was discovered by Gilman. Consequently, main purpose of this study is focused on conductive material, light functional material and lithography material due to σ - σ conjugation.

The synthesis of polysilane advanced after Wesson³⁹ succeeded in the synthesis of organic solvent soluble polymer. Previously, the synthesis of ladder polydisilane was considered using π -electron conjugation of polydisilanophenylene, dehydrogenation coupling synthesis of RSiH_3 , anionic polymerization, Wurtz coupling, etc. In addition, West, Sakurai, Fujiki et al conducted a study of polysilane having an organic group in the side chain. After these discoveries, some polysilanes having various structures such as ladder-like polydisilyne were developed as following.³⁹⁻⁴⁸ Polysilane is thought to applicable as a pre-ceramic precursor or new polymerization catalyst or a photo-polymerization initiator, to assist the development of new materials and functional materials for lithography applications.

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Matumoto had synthesized ladder-like polydisilyne by reduction with Li as shown in

Figure 1.2.17⁴¹.

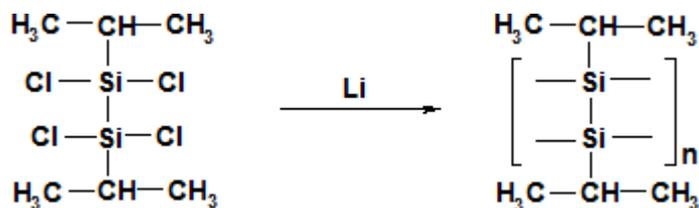


Figure 1.2.17 Synthesis scheme of polydisilyne

Ishikawa had synthesized poly (phenylene-disilanyrene) for p-electron-σ electron conjugation by Wurtz reaction as shown in Figure 1.2.18⁴¹⁻⁴².

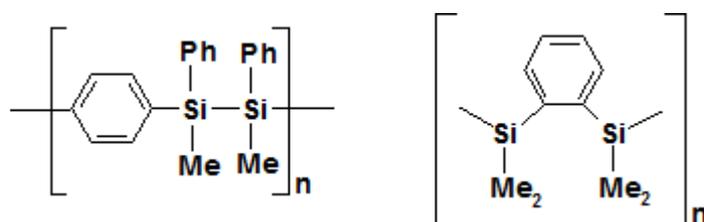


Figure 1.2.18 Synthesis of poly (phenylene-disilanyrene)

Harrod and Tanaka had synthesized polysilane by dehydro-coupling reaction using metallocene such as Titanocene, Zirconocene as shown in Figure 1.2.19.^{44,47}

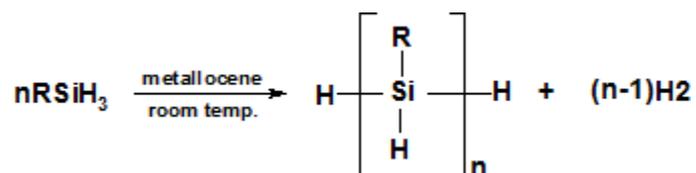


Figure 1.2.19 Synthesis scheme of polysilane by dehydro-coupling reaction

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Sakurai had proposed anionic polymerization of polysilane in 1988 as shown in Figure 1.2.20. Anionic polymerization can be obtained by single dispersible polymer with high yield and it is the epoch-making reaction that has the flexibility of the compound design increase⁴⁶.

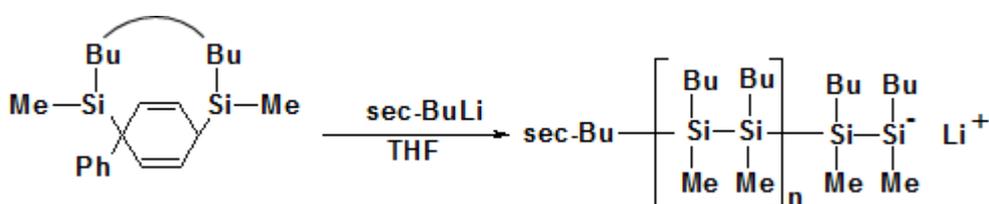


Figure 1.2.20 Synthesis scheme of polysilane by anionic polymerization

Lately, Shimoda, et. al. announced new pathway for the synthesis of perhydropolysilane from ring-opening polymerization by UV exposure using cyclo-silane compound such as cyclopentasilane as shown in Figure 1.2.21. This ring-opening polymer with solvent is also called as Si-ink (silicon ink).

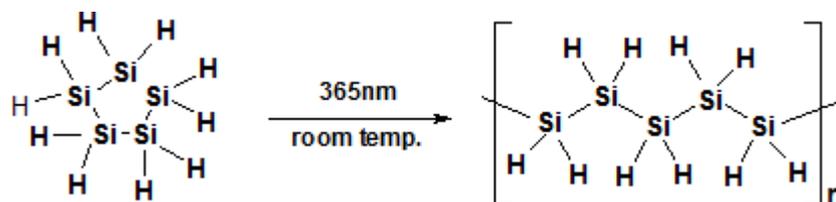


Figure 1.2.21 Synthesis scheme of perhydropolysilane by ring-opening polymerization

Further, Si-ink can be converted into amorphous silicon and silicon carbide by appropriate curing mechanism. This Si-ink material shows a high possibility as the starting material for ceramics or semiconductor materials. In addition, Shimoda et. al. doped Boron, Phosphorous into cyclopentasilane and succeeded in development of the p-type and n-type silicon ink and made the TFT using these.⁴⁸⁻⁵¹

1.2.4 Si-O Polymer (Polysiloxane)

Polysiloxane is composed of -Si-O- bond as the main chain. Also there are compounds in which the polysiloxane polymers having some organic group are called organosiloxane, and they are the most important materials academically, industry as well as practically for various applications. There are many reports about siloxanes and their applications⁵²⁻⁵³. Since, the Si-O bond-length is larger than that of C-C bond, bond rotation between the Si-O bonds occurs easily. For this reason, it is considered that the Si-O bond is more flexible in comparison with C-C bond. For example, dimethylsiloxane which is composed of two functional units these two methyl groups are considered bulky, due to the thermal vibration by methyl-ligand binding. Thus, it is

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difficult for the adjacent molecules to close the neighboring spaces, which in turn reduces the intermolecular forces.

Another interesting effect is that, Si-O binding energy shows large value (106 kcal/mol) in comparison with Si-Si, Si-N, Si-C, C-C, C-O bonds, since the oxygen electron flows into the vacantly d-orbital of Si atom. This in turn shows that why the Si-O bonds are stable at high temperature. And also these Si-O bonds are chemically very stable, thus polysiloxane has some unique properties such as high chemical durability, high thermal stability, and good electrical resistance. Which is a signature of the physical properties of Si-O bonds such as, change in viscosity with temperature is small, the surface tension is small, and has high insulating properties. Polydimethylsiloxane (-SiMe₂O-)_n which is composed of methyl-ligand as a side chain is industrially important and is a daily used compound. It is commonly known as silicone. The siloxane polymers are classified by a functional number as follows⁵².

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Table 1.2.1 Identification of Siloxanes

Structure	$\begin{array}{c} \text{R} \\ \\ \text{R}-\text{Si}-\text{O}- \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{R} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{R} \end{array}$	$\begin{array}{c} \text{R} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \end{array}$	$\begin{array}{c} \text{O} \\ \\ -\text{O}-\text{Si}-\text{O}- \\ \\ \text{O} \end{array}$
unit	$(\text{R}_3\text{SiO}_{1/2})_n$	$(\text{R}_2\text{SiO}_{2/2})_n$	$(\text{RSiO}_{3/2})_n$	$(\text{SiO}_{4/2})_n$
Si-O binding	1	2	3	4
Symbol	M	D	T	Q
Property	-	Oil~Rubber	Resin	Silica

Mono-functional siloxane is a structural unit $\text{R}_3\text{SiO}_{1/2}$, this siloxane structural unit is referred to as M (initials of Mono-functional). And polydimethylsiloxane type di-functional siloxane structural units $\text{R}_2\text{Si}(\text{O}_{1/2})_2$ are represented as D (Di-function). Similarly, the tri-functional siloxane which are $\text{RSi}(\text{O}_{1/2})_3$ and 4 functional siloxane structural units such as $\text{Si}(\text{O}_{1/2})_4$, are each denoted as T (Tri-functional), denoted Q (Quadra-functional).

Polymers which are obtained from the combination of these three structural units are listed as follows.

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a) Linear Siloxane

It is intended termination of the chain-ends by an alkyl group (especially methyl), general formula for which are given below. Silicone oils have this type of backbone.



b) Ring structure Siloxane

The general formula, (especially R = Methyl) is displayed as follows.



These types of polymers are obtained by ring-opening polymerization using appropriate catalyst, and generally consist of high molecular chains. Silicone rubber is made by vulcanizing the ring polymer with appropriate peroxide.

c) Ladder, Cage and 3-dimensional structure siloxane

These are characteristics polymers comprising of a tri-functional or tetra-functional structural units. These structures are randomly arranged, and they are commonly referred to as the silicone resin. The nature of organopolysilane is influenced by the type of R, degree of polymerization and not only the type of structural skeletons.

Although the Si-O-Si bond is synthesized in various forms, most important practical

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reactions are about four as follows.

- a) Silicon-functional monomer hydrolysis and polycondensation
- b) Polycondensation between monomers of 2 different types of functional groups (hetero-functional condensation)
- c) Ring-opening polymerization of cyclic siloxane oligomers by catalysts
- d) Synthesis of Cage, Ladder structure

The basic reaction is the generation of the silanol and their homo-condensation. Especially, siloxanes which are synthesized from the tri-functional group are called silsesquioxane (SQ), and this SQ is a resin. These typically possess characteristics not seen in di-functional siloxane (silicone) such as heat resistance, electrical properties, optical characteristics, etc. Especially the synthesis of highly controlled ladder structure SQ is the theme of this study.

2. Synthesis of polysilsesquioxane and their application

2.1 Polysilsesquioxane (PSQ)

Among the siloxane compounds, particularly a siloxane composed of T structure is

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referred to as silsesquioxane, since 1.5 (Latin for 1.5 is sesqui) units of oxygen in their structure. "Silsesquioxane" is a network polymer having a structure $(\text{RSiO}_{1.5})_n$ resulting by hydrolysis of a tri-functional silane or polyhedral clusters. Each of the silicon is bonded to an average of 1.5 (sesqui) oxygen atom and one hydrocarbon group. Thus, silsesquioxane $(\text{RSiO}_{1.5})$ is stoichiometric intermediate compounds between silica (SiO_2) and silicone (R_2SiO) . Hence, silsesquioxane is a unique nano-material also many times recalled as an "inorganic material with an affinity for organic materials".

Typically, the silsesquioxane is synthesized by hydrolysis and homo-condensation reaction of trialkoxysilane or trihalosilane, acid, an alkali catalyst⁵⁴⁻⁷². These reactions usually are good to obtain polymers with higher linking; however structure control of the obtained polymer is difficult, due to the rearrangement as there are more reactive sites for a tri-functional structure. Among such silsesquioxane compounds, higher-order controlled structure such as a ladder-like silsesquioxane (ladder silsesquioxane) and cage-like silsesquioxane (cage silsesquioxane) is difficulty to synthesis and the control of this composite structure of has been the subject of good research from chemical synthesis. The beauty of chemical structure and function development has been a long perceived activity. In particular, the cage-structured silsesquioxane is relatively easy to synthesis as a dielectric material. It has become the central topic for research and

development.

2.1.1 Synthesis of cage-structured silsesquioxane

Cage-structured silsesquioxane has a three dimensional closed ring structure of siloxane bonds, and is attracting attention due to its unique group of compounds.

Figure 2.1.1 shows a typical cage-structured silsesquioxane⁵⁸. Among them R^T_8 type of structures can easily be synthesized with a relatively high yield, and thus has been extensively studied. R^T_8 is also abbreviated as POSS[®] (Polyoctahedralsilsesquioxane).

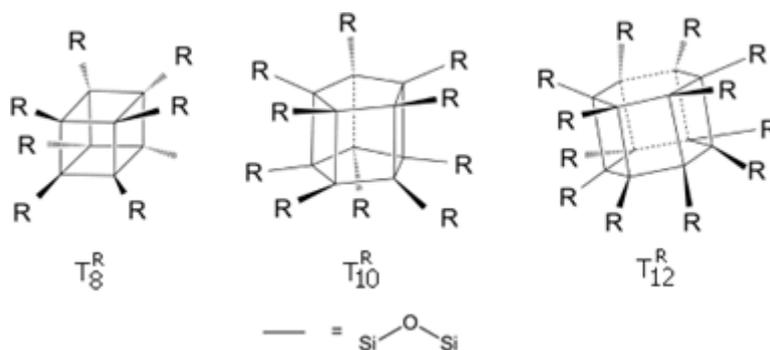


Figure 2.1.1 Representative structure of cage polysilsesquioxanes

Synthetic raw materials for the synthesis of silsesquioxane have been limited to conventional trialkoxysilane or trihalosilane, which undergo hydrolysis and dehydration condensation during synthesis to obtain the appropriate silsesquioxane. However as

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there are 3 reaction points per one molecule, the structure of the products as shown in Figure 3.3.1 are manifold. Thus it is important to correctly choose selectively the synthesis path to obtain the desired product. Since the choice of raw materials is limited, the variation in the type of catalyst and reaction conditions is required to properly synthesize and separate out the product⁶⁰⁻⁷².

The general synthesis method comprises of using trichlorosilane, an organic solvent (acetone, benzene, toluene, THF, methanol) with water is mixed and stirred at room temperature and further allowed to stand to separate the product silsesquioxane as crystals. This simple process has been widely used as a preferred method for large scale synthesis⁶⁵. In this case, the product is different from the size of the substituents groups. In general, bulky substituents tend to generate smaller cage-like structures, and small substituents groups tend to make large cage structures. However, there is a need for improvement in terms of the product yield. In the case of using a trialkoxysilane as the starting material, acid or base catalyst is used for synthesis.

Brown et al. used hydrolyzed halosilane (silanetriol) in pyridine catalyst by performing encapsulation reaction using Me_2SiCl_2 to react to obtain a T^3_8 cage structure. As shown in Figure 2.1.2⁶⁹⁻⁷⁰.

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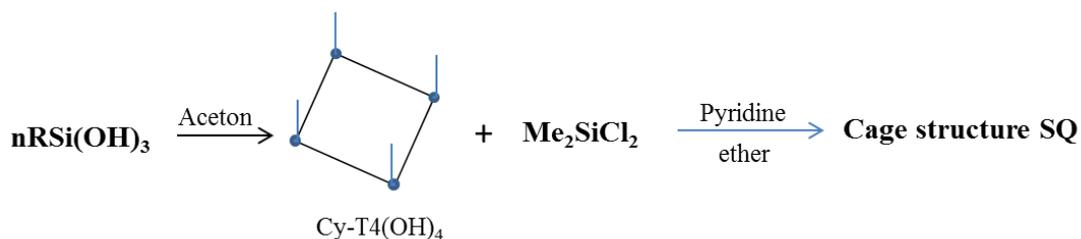


Figure 2.1.2 Synthesis scheme of Cage Silsesquioxane by Brown

Then, Unno et al. diligently isolated the intermediate substituent group of hydrolysis (silanol) in a stable form, and treated this silanol with a condensing agent like KOH, or using DCC (dicyclohexylcarbodiimide) as shown in Figure 2.1.3, a variety of cage type silsesquioxane structures were synthesized in a short period of time than the conventional method⁷¹.

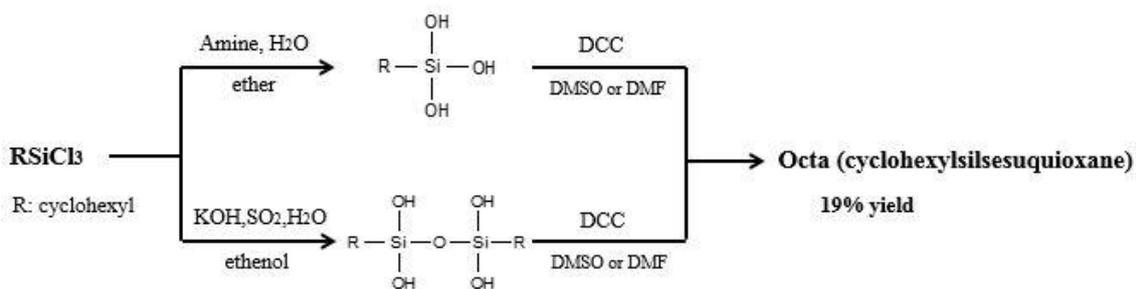


Figure 2.1.3 Synthesis scheme by dehydration using DCC

In addition, recently incomplete cage silsesquioxane has been attracting attention.

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Partial and incomplete removal of atoms or bonds from a perfectly cage-type silsesquioxane is performed to obtain a partial structure, which in fact has become a novel compound. When trimethoxy (phenyl) silane is allowed to undergo hydrolysis during reflux in the presence of sodium hydroxide, then under certain conditions incomplete cage silsesquioxane $T^{Ph}_4D^{Ph}_4(ONa)_4$ can be produced almost quantitatively⁷². A single crystal of the silyl compound of this product is prepared analyzed and shown in Figure 2.1.4. It was found to be a compound possessing the double-decker type structure by linking cyclic tetramer with two siloxane bonds.

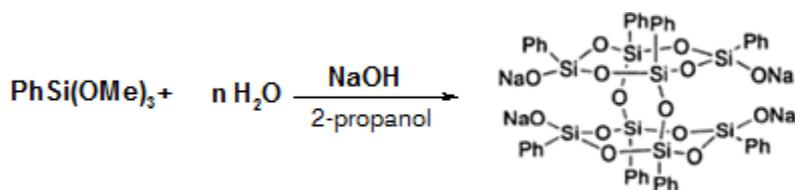


Figure 2.1.4 Configuration of double-decker-type silsesquioxane

2.1.2 Synthesis of ladder-type silsesquioxane

Since the introduction of ladder-type silsesquioxane in 1960 by Brown as shown in Figure 2.1.5, where in their literature gave an example of the polymer structure⁷³, the polymer controlled by as many constituent T structures, has been of particular interest from the viewpoint of heat resistance.

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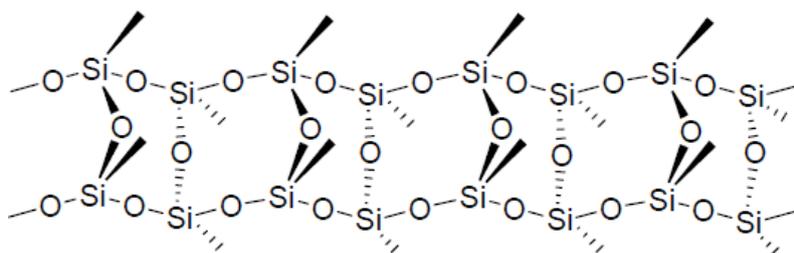


Figure 2.1.5 Configuration of cis-syndiotactic ladder structure (Brown)

The pre-polymer was synthesized by refluxing the hydrolyzed phenyltrichlorosilane (PhSiCl_3) with 0.1% KOH in toluene. The pre-polymer had an intrinsic-viscosity (η) of 0.12dL/g, a number of average molecular weight (M_n) of 1.4×10^4 , and a weight average molecular weight (M_w) of 2.6×10^4 . The degree of the silanol condensation was approximately 99.9%. Soluble high molecular weight was prepared from the pre-polymer by an alkaline equilibration method. The (η) was 4.0dL/g and the M_w was 4.1×10^6 .

Many researchers reported various methods include this equilibration reaction scheme to prepare polyphenylsilsesquioxane⁷⁴⁻⁹⁴. (Figure 2.1.6)

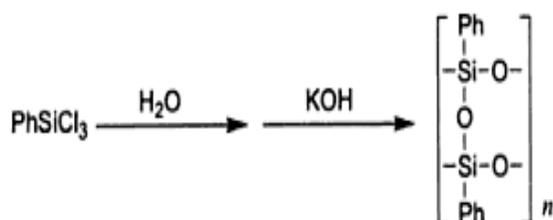


Figure 2.1.6 Synthesis of ladder SQ by Alkali equilibrium reaction (Brown)

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Lee and Kimura obtained a more distinctive result from stepwise synthesis of polyphenylsilsesquioxane⁷⁶. The hydrolysis of phenyltrichlorosilane was carried out in toluene/water solvent. A low molecular weight hydrolyzate consisting mainly of phenylsilanetriol was crystallized from the aqueous layer. When this hydrolyzate was subjected to KOH-catalyzed poly-condensation in toluene, polyphenylsilsesquioxane with a highly order ladder structure was obtained as shown in Figure 2.1.7.

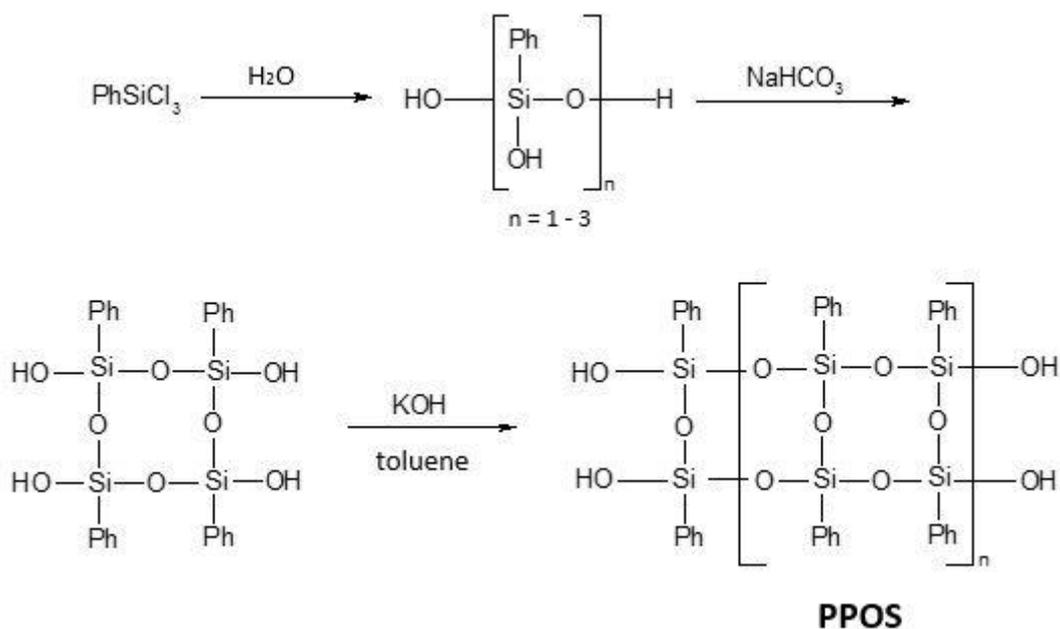


Figure 2.1.7 Synthesis scheme of ladder PPQS

Xie and Zhang et al. reported a polyphenylsilsesquioxane with ladder-like structure synthesized by diamine (primary amine), followed by hydrolysis and polycondensation

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Meanwhile Unno carried out precision synthesis of first order single ladder structure by bypassing the condensation reaction of the silanols⁸³. They reacted cyclo tetra isopropyl tetra silanol and 1,4 dichloride and phenyl isopropyl disiloxane in pyridine, so that trimer of hydrogen chloride and aluminium chloride were obtained so that de-phenyl reduction and dechlorination gave trimers terminated with silanols. This reaction was performed repetitively to obtain a 5-ring ladder SQ^{84, 86}.

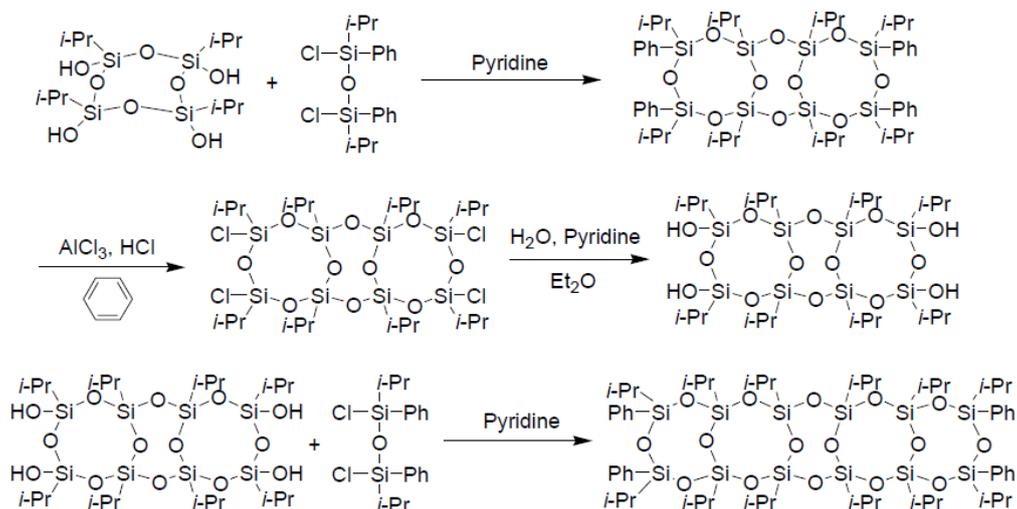


Figure 2.1.9 Synthesis scheme of 5-ring ladder SQ

Also, Gunji et al. approach consists of using reactive isolable stable isocyanate group in siloxanes, thereby obtaining a ladder SQ structure⁸⁹.

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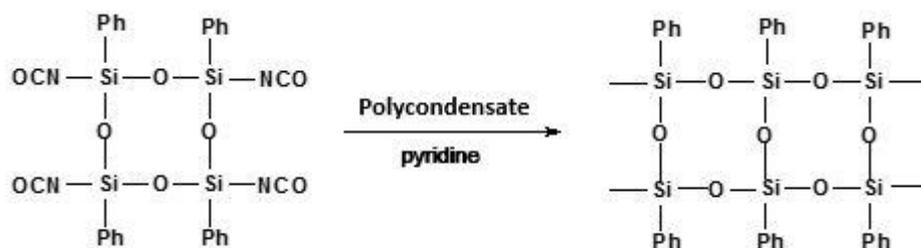


Figure 2.1.10 Synthesis scheme of isocyanate ladder SQ

Also, the synthesis of the ladder structure is also quite difficult in terms of structure control. Hence, a lower reaction rate alkoxy silane is preferred for the hydrolysis a monomer.

In addition, Uo synthesized ladder type SQ by hydrolysis of tetra cyclo disilane. It seems they have proposed a method for synthesizing a ladder type SQ than the precursors of -Si-Si- bonds⁸⁵. (Figure 2.1.11)

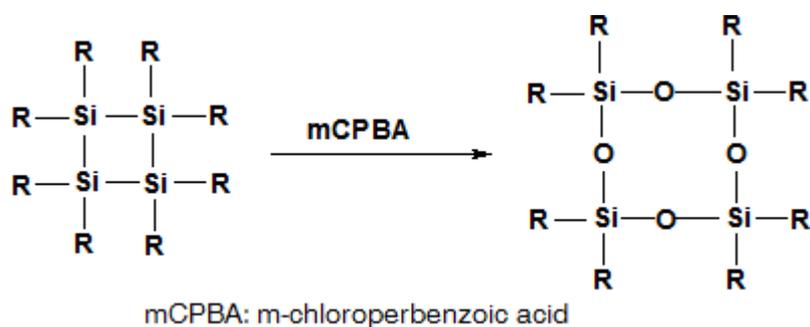


Figure 2.1.11 Basic synthesis of ladder SQ by oxidation of cyclic-silane

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The synthesis of the ladder structure SQ is still in progress, but still has not reached the maturity level that generally researchers handle POSS. Difficulties in the synthesis, viz. adjustment of precursor materials are still to be resolved. For the research based on the ladder structure to progress, further improvement of the synthesis scheme is desperately required.

2.2 Application of Silsesquioxanes

Silsesquioxane, due to its heat resistance, electrical properties, optical properties have been attracting attention in recent years in the field of electronic materials. In particular, photosensitive siloxane has been investigated as a candidate in the field of electronic materials as a heat-resistant resist. Also recently with the progress of oxide semiconductors (IGZO, IZO) and improvement in heat resistant organic insulating film is pursued. In the LCD field too, siloxane polymer is considered as a possible material to replace existing acrylic resin in the TFT forming process.

Uraoka et al. evaluated SQ in an oxide semiconductor (a-IGZO) as a passivation film of TFT and found that the characteristics are similar to CVD-SiO₂ films as shown in Figure 2.2.1⁹⁵.

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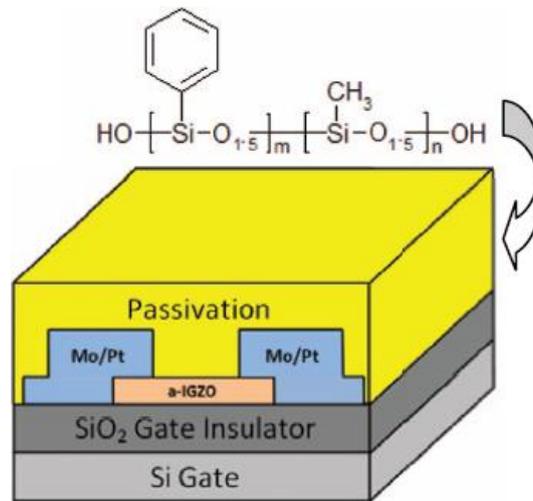


Figure 2.2.1 A-passivated a-IGZO TFT structure: passivation layer is silsesquioxane

Silsesquioxane was produced by Merck PM Manufacturing G.K.

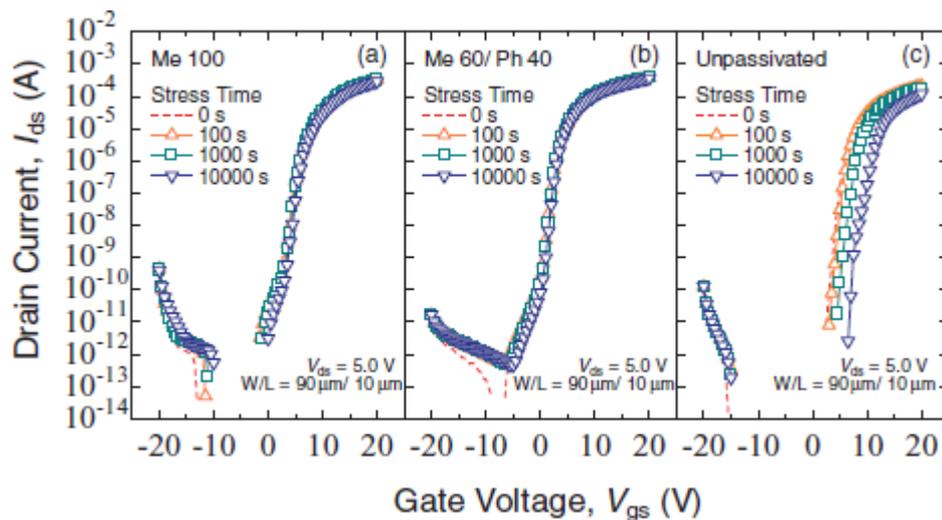


Figure 2.2.2 Transfer characteristic a)Methylsilsesquioxane, b) Methyl. Phenyl

silsesquioxane under PBS ($V_{gs}=20\text{V}$)

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2.2.1 Photosensitive formulation based on silsesquioxane polymer

In the field of electronic materials photosensitive silsesquioxane is under consideration mainly for applications with 2 layer resist, etc. Kawai and Ban et al. had prepared an alkali soluble silicon resin, acetylated polyphenylsilsesquioxane oligomer (APSQ) from phenylsilsesquioxane oligomer (Mw is 900) by Friedel Crafts acylation using $\text{AlCl}_3/\text{AcCl}$ as shown in Figure 2.2.3⁹⁶. And they also prepared various two-component resists (SPP/Novolac) using APSQ as a matrix resin in order to play a crucial role in defining pattern feature in LSI. APSQ-sensitizers resist called SPP (silicone-based positive photoresist) exhibits high resolution with ultraviolet (UV), deep UV, electron beam and X-ray exposure.(Figure 2.2.4)

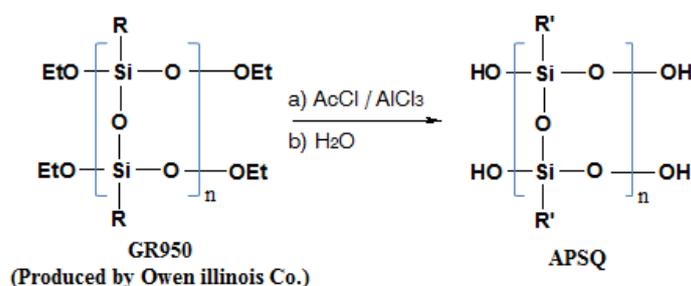


Figure 2.2.3 Synthesis scheme of APSQ

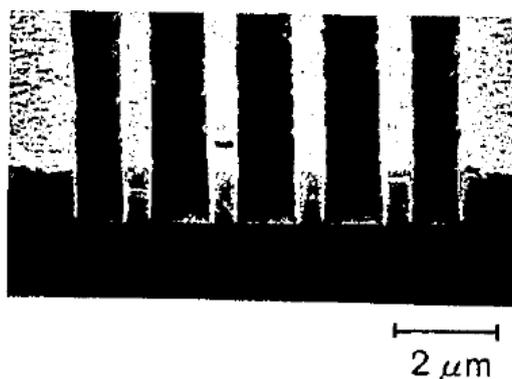


Figure 2.2.4 Photo Image of Line & Space Pattern

Hitachi had announced two-layer silicon photo-resist which is composed of benzoilphenylsilsesquioxane and PAC (photo-Active-Regent)⁹⁷.

Tashiro et al. had prepared an alkali soluble silicone resin, acetylated phenylsilsesquioxane oligomer from cage-like phenylsilsesquioxane oligomer (include T^{ph}_9 structure). The photosensitive phenylsilsesquioxane (called p-PPSQ) which was the component of alkali soluble PPSQ and diazonaphtoquinone, is used as a planarity layer of TFT in LCD. The p-PSQ is sensitive to *g, h, i* broad band ultraviolet (UV) and resolution was $2.0\mu\text{m}$ on Line and Space⁹⁸ (Figure 2.2.5)

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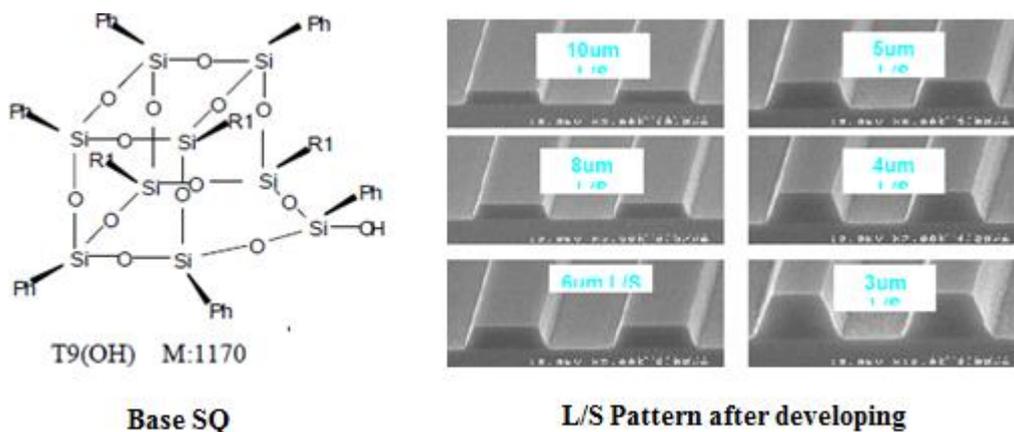


Figure 2.2.5 Base polymer and lithography of L/S by positive-tone

Ni and Zheng prepared photosensitive octacinnamanidophenyl polyhedral oligomeric silsesquioxane (OcapPOSS) by synthesis via the reaction between cinnamoyl chloride and octa-aminophenyl polyhedral oligomeric silsesquioxane(OapPOSS). This polymer is obtained by photo-crosslinking under UV exposure⁹⁹.

Sugiyama et al. prepared alkali-developable organosilicon positive photoresist for a bi-layer resist system. An alkali-soluble organosilicon polymers, polysilsesquioxane, polysiloxane, and polysilmethylene were prepared as the matrix polymers. Among these polymers, poly(p-hydroxybenzylsilsesquioxane)(I) exhibited the highest O₂ RIE resistance. A composite (OSPR-1334) formulated (I) and naphthoquinone diazide becomes an alkali-developable positive photoresist which is sensitive to *g*, *h*, *i* line light¹⁰⁰. (Figure 2.2.6)

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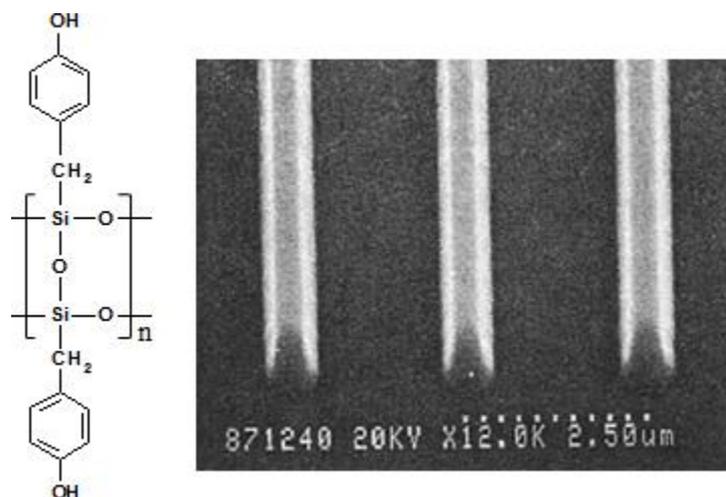


Figure 2.2.6 Photo-Image of line & Space (CD: 0.75 μ m) of OSPR-1334

(Ref. SPIE Vol. 920 Advanced in Resist Technology and Processing V 1988)

Sachadev and Whitaker prepared bi-layer resist from poly(p-hydroxybenzylsilsesquioxane-co-p-methoxybenzylsilsesquioxane) compositions with OCH_3/OH ratio varying between 50/50 to 20/80 were prepared from poly(p-methoxybenzyl silsesquioxane) by partial demethylation reaction¹⁰¹.

Initially the study was to develop bi-layer resist for the IC field, however, recently it is focused to obtain heat resistant materials required as photo-patternable SOG in the TFT forming process in the LCD field. Interestingly, photosensitive materials based on silicon-containing polymers are much desired by the industry.

3. Purpose of this research

The “new materials” which are currently attracting a large attention are inorganic-organic hybrids, which are created by using various combinations of organic functional groups and the physical properties ceramics materials. Currently, new polymers incorporating silicon, in particular the structure controlled polysilsesquioxane has been undergoing through investigation as an alternative to the standard inorganic-silicon compounds in the field of electronics, photonics and other hi-tech materials technology.

The studies on cage structured SQ (POSS[®]) are centered on the establishment of stable synthetic procedures for obtaining POSS[®]. Thus, various reactions studies based on POSS[®], hybridization of an organic resin and even as a novel functional polymer such as elemental block polymer are being actively conducted in this field.

On the other hand, studies on the ladder structure got accelerated primarily in the recent decades and that too only looking at precision synthesis processes. However, the different synthesis schemes through various functional groups of the precursor siloxane compound consider only the synthesis and subsequent condensation. This is because, such synthesis processes are multi-step operations, they are not so suitable for mass

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production. For this reason, the studies on properties of ladder structure SQ and their applied research have not progressed as compared to POSS[®].

Structurally controlled ladder type SQ polymers and POSS[®] are similarly interesting materials as they possess unique properties as organic-inorganic a hybrid resin (thermal properties including heat resistance, electrical properties, optical properties, etc.) with high expectation of applied research. Also, this work can be applied to the organic resin and block polymer complex, etc. For the characterization and application of the ladder structure type SQ, it is necessary to develop a simple synthesis scheme for their mass production.

For this purpose, trihalosilane is selected as the starting materials and mono-, bi, tri-dentate amine with lone electron-pair is used for the Lewis acid-base adducts formation through the aqueous phase - organic phase interface reaction, the possibility of ladder type SQ synthesis was investigated in this scheme.

In addition, from the point of view of applications, I investigated the resulting polymer ladder structure SQ polymers for its photosensitivity properties and lithographic properties. This study (my dissertation) is composed of introduction (Silicon containing polymer chemistry), synthesis experiments with amine and its characterization, photo-patternable oligo- ladder PPSQ and general conclusion and scope.

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Chapter 2

Synthesis of oligo-ladder polyphenylsilsesquioxane (PPSQ) via phenyltrichlorosilane-amine adducts at aqueous-organic liquid phase boundary

1. Introduction

The organic-inorganic hybrid materials have received considerable interest in past decades due to their prospects in developing materials with unique optical, thermal and electronic properties. Recently, silsesquioxanes (SQ) has been noticed as an organic-inorganic hybrid material in the field of Flat Panel Display. Especially, SQ with a high regularity structure like a ladder is expected to deliver superb properties such as high thermal resistance, high transparency, low dielectric constant and high cracking threshold as compared to a SQ with low regularity structure.

Many reports could be found addressing on the synthesis of ladder SQ, especially for the methods utilizing the alkali equilibrium reaction.¹⁻²¹ Almost all these ladder SQ polymers were synthesized by multi-step condensation approach as explain in Chapter 1; first condensation to form cis,cis,cis-1,3,5,7-tetrahydroxy-tetraphenylcyclotetrasiloxane (cyclic-^{ph}T₄) by hydrolysis

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of tri-halosilane or tri-alkoxysilane monomer, then the yielded cyclic SQ was further condensed to give target ladder SQ. Brown et.al were the first to describe this synthetic method for ladder PPSQ by equilibrium reaction of the cyclic oligo-(phenylsilsesquioxane) with potassium hydroxide¹. Seki et al. had synthesized ladder methylsilsesquioxane by condensation of intermediate compound such as silanol-functionalized tetramethylcyclotetrasiloxane using amine catalyst.¹⁸ The regularity in the ladder structure frame can be obtained by stereo-controlled approach.¹³ However, the synthesis of the intermediate compounds i.e. cyclic SQ, is difficult due to fast hydrolysis¹ of trichlorosilane. The above two step condensations for target ladder SQ will increase process complexity, manufacturing cost and lower final product. Thus, there are not suitable for an industry use.

In this chapter, I developed new synthesis methods for the oligo-ladder PPSQ via silicon-amine adducts using mono-, di-, tri-dentate compounds. Trichlorophenylsilane (TCP) is used as a monomer in the one-pot synthesis at the aqueous-organic boundary (*n*-propylacetate (nPA) /water). The silicon-amine adducts can control hydrolysis of TCP and the liquid boundary reaction which has a slow kinetic rate of homo-condensation by limiting the reaction area at nPA-water liquid boundary; can thus lead to a thermodynamically stable ladder structure.²⁸ This direct synthesis of

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oligo-ladder SQ using amine-adduct at water-nPA liquid boundary has not yet been reported. The developed methods are based on simple one-step reaction, which will open possibilities for low cost ladder SQ production for industrial applications. Oligo-ladder has some silanols and their reactivity is higher than the high molecular ladder. We can apply this process for hybrid polymers, photo-sensitive using silanol chemistry, etc.

2. Experimental Section

2.1 Materials

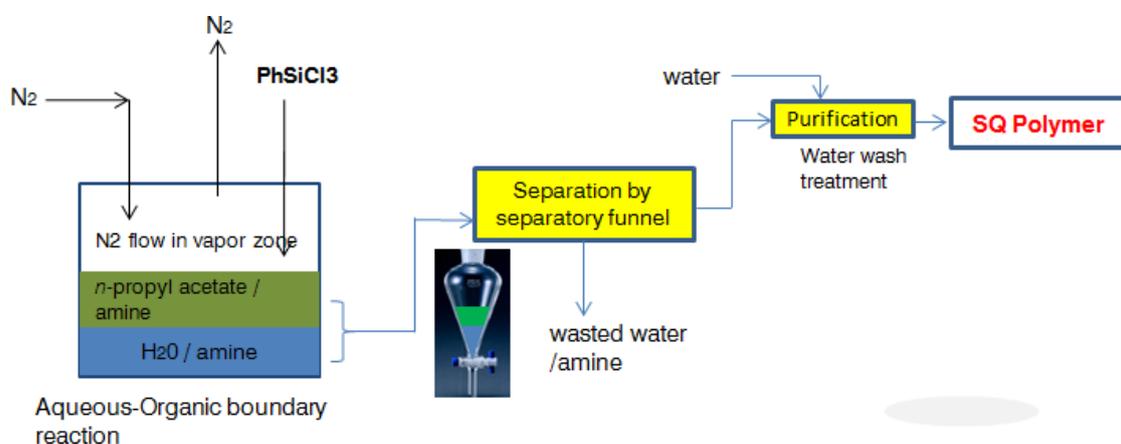
TCP (Trichlorophenylsilane) was purchased from Shin-Etsu Chemical. The purity was EL Grade. Pyridine, Tetramethylethylenediamine (TMEDA), Pentamethyldiethylenetriamine (PMDETA), Normal-propylacetate (nPA), and *n*-hexane were purchased from Tokyo Kasei. Crude pyridine was dehydrated by using molecular sieves (4A) to remove H₂O to less than 10 ppm. The other reagents were used without further purification. All the water used in the experiment was treated by ion exchange resin until its conductivity reaches below 0.1s.

2.2 Synthesis of oligo-ladder PPSQ

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2.2.1 Synthesis scheme

I obtained SQ polymers using different types of amine with a lone electron-pair and with their different amount of additions to the reaction mixture as shown in Table 3 (see section 2.5, page 65). The synthesis schematic is shown as follows; in this work for simplicity I call it as Scheme 2.2.1.1.



Scheme 2.2.1.1 Synthesis scheme of oligo-ladder PPSQ

In pyridine 0.2 mol case (SQ-1) as the reference, three-neck-flask was charged with 100 gr H₂O, 65 gr nPA and 15.8 gr pyridine (0.2 mol.). The flask was held until the water layer and nPA layer separated completely. The flask was cooled in ice bath until the temperature of the internal reaction mixture dropped down between 0°C to 5°C. Then TCP (0.1 mol) was added into nPA layer at very slow speed (around 0.005 mol/min: 1.06 ml/min) without disturbing the nPA/water phase boundary. In nPA layer,

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white compound immediately appeared upon TCP addition due to the formation of pyridine–silicon adducts.

At liquid nPA/water phase boundary, the TCP/pyridine adduct will slowly react with water. This reaction was maintained for about one hour after TCP (0.1 mol.) was completely added to the reaction mixture. Finally, nPA layer became clear solution. (a white solid is generated in the water layer.) Subsequently, separation of the nPA layer was carried out using funnel and further purification is performed by ion-exchanged water. After this process, the SQ with nPA layer was recovered. Other amine case was carried out same as SQ-1 case. Only SQ-2 (pyridine: 1.0 mol) case, white solid generated into water layer and liquid boundary after the reaction. It was recovered using funnel and 4A paper filter and it was treated vacuum dried at 40°C. This solid showed poor solubility, it could not dissolve in nPA. However it could little dissolve in Pyridine, DMSO. Therefore I carried out further analysis with DMSO and pyridine solution. In other types of amines ligands, all samples did dissolve into nPA.

2.3 Measurement Techniques

Fourier Transfer Infrared Spectroscopy (FTIR): The FT-IR measurement were conducted using a JASCO-FTIR4500 at room temperature. Resolution was 2 nm/s.

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MALDI-TOF/TOFMS Spectrometer: The SQ samples were dissolved in a certain amount of DMSO-D₆ to obtain a homogeneous solution. The MALDI-TOF/TOFMS spectrum was recorded using the Bruker Daltonics Ultraflexreme.

DHB (2, 5-Dihydroxybenzoic acid) was used as matrix and thus the detected mass number include (M + Na)⁺.

Nuclear Magnetic Resonance Spectroscopy (NMR): The ²⁹Si NMR measurements were carried out using a JEOL JNM ECS-400 spectrometer at 25°C. The sample was dissolved with DMSO-D₆ and the solution was measured with tetramethylsilane (TMS) as an internal reference. The 90° pulse width of 11.25 μs was employed with FID signal accumulation, and the observed frequency was 79.42 MHz.

Thermo-Gravimetric Analysis (TGA): The RIGAKU thermo-gravimetric analyzer (Thermo-Plus) was used to investigate the thermal stability of PPSQ. The sample (about 10 mg in weight) was heated under nitrogen atmosphere from ambient temperature to 400°C and at a heating rate of 10°C /min for all cases.

2.4 Kinetic study of condensation (polymerization) process

At first, as a pre-study was performed, the polymerization process was kinetically studied for the various interaction catalysts such as pyridine, 1-phenyl-butandion

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(beta-diketone) and malonic acid in order to clarify the influence on polymerization at the aqueous-organic boundary system as shown in Scheme 2.2.1.1 and the change in molecular weight was analyzed during titration of TCP as shown in Figure 2.4.1.

Pyridine is well known to generate adduct with halo-silanes such as H_2SiCl_2 , MeHCl_2 ²⁵. The beta-diketone was generated by chelate compound with keto-enole transport under the partial electron-charge reaction theory of Si-atom. Malonic acid was used as a diester-type acid. In this study, all synthesis conditions were similar as shown in Table 2.4.1.

Table 2.4.1 Experimental conditions for the kinetic study in each interaction catalyst

Exp. No	Interaction Catalyst (mol)	PhSiCl ₃ (mol)	Reaction Temp. (°C)	Titration Time (min)	Reaction Layer	
					H ₂ O (gm)	nPA (gm)
Control	Non	0.1	0 – 5	20	100	65
Ex.1	Beta-diketone	0.1	0 – 5	20	100	65
Ex.2	Malonic acid	0.1	0 – 5	20	100	65
Ex.3	Pyridine	0.1	0 – 5	20	100	65

Polymerization of TPC was estimated using unit structure (-PhSiO_{1.5}-) under the following reaction scheme. Figure 2.4.1 shows the change of polymerization number

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base on $\text{PhSiO}_{1.5}$ unit during titration of TCP for the various catalyst used. Pyridine showed a different polymerization behavior as compared to the other catalysts. This behavior of pyridine seems to suggest that the reaction is in equilibrium similar to Brown's reaction. In the hydrolysis and condensation reaction, equilibrium reaction can take enough long time to obtain a thermo-dynamically stable structure such as all-cis cyclic- PhT_2SQ .⁵⁻⁶ Pyridine this proves its effectiveness in obtaining oligo-ladder PPSQ.

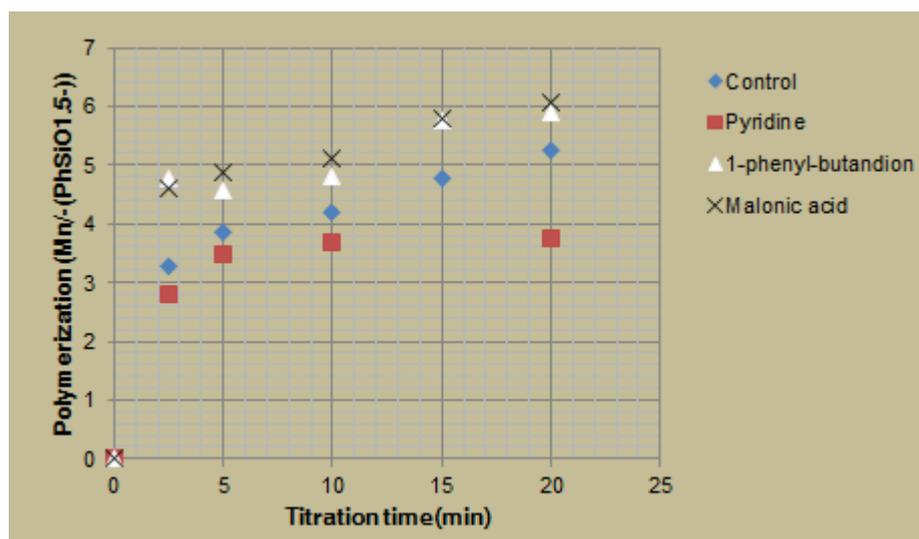


Figure 2.4.1 Change of polymerization rate with various catalysts.

Furthermore, Table 2.4.2 shows the calculated polymerization ratio by using linear regression for the change in molecular weight.

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Table 2.4.2 Total condensation rate of each interaction catalyst used.

Interaction Catalyst	Total Condensation Rate (unit ratio/mol/s)
Control(No catalyst)	0.1058
Malonic acid	0.0857
1-phenyl-1,3-butandion	0.0792
Pyridine	0.0075

In case of pyridine, the condensation ratio is lowest as compared to the other acid-like catalysts. This suggests that the alkaline condition is more effectiveness in controlling of the hydrolysis reaction and homo-condensation based on the Lewis-base adduct formation by $d\pi - p\pi$ overlaps.

This behavior seems to suggest that the reaction is in equilibrium similar to Brown's reaction. In the hydrolysis and condensation reaction, the equilibrium reaction can take enough long time to obtain a thermo-dynamically stable structure such as all-cis cyclic- PhT_4SQ which is a building block or raw material structure for ladder.⁵ The alkaline interaction compounds such as pyridine-like compounds exhibit their effectiveness in obtaining the oligo-ladder PPSQ.

Then I choose the mono-, bi-, tri- dentate compounds with interaction catalyst such as pyridine for the synthesis of oligo-ladder PPSQ at the aqueous-organic liquid boundary

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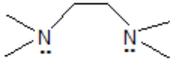
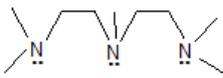
reaction.

2.5 Synthesis of oligo-ladder PPSQ using pyridine and bi-, tri- dentate compounds

As shown in the kinetic study, the base-Lewis acid adduct type compounds could probably be the most useful to generate the ladder structure. Thus, I choose the pyridine and bi-, tri- dentate compounds as these interaction catalyst have lone electron-pare for synthesis of oligo-ladder PPSQ at aqueous-organic liquid boundary reaction.

Tables 2.5.1 and 2.5.2 are shown for each compounds structure and pK_b , with the experimental conditions, respectively.

Table 2.5.1 Structure and pK_b of catalysts used.

Interaction Catalyst	Structure	Number of ligands	Boiling Point (° C)	pK_b
Pyridine (Py)		1	115	8.5
Tetramethylethylenediamine (TMEDA)		2	120-122	5.85
Pentamethyldiethylenetriamine (PMDETA)		3	198	5.07

Each catalyst is well known to easily form chelate compounds or adduct with metal.

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Table 2.5.2 Synthesis conditions and obtained polymer structures.

Samples	Kind of Ligands	Amount of ligands (mol)	TCP (mol)	Estimated structure	Polymer Yield (%/Si base)
SQ-1	Pyridine	0.2	0.1	Main: Cy-T4	92
SQ-2		1.0	0.1	Oligo-ladder	65
SQ-3	TMEDA	0.1	0.1	Oligo-ladder	94
SQ-4		1.0	0.1	Oligo-ladder	89
SQ-5	PMDETA	0.1	0.1	Oligo-ladder	60
SQ-6		1.0	0.1	Oligo-ladder	58

3. Characterization of each polymers

3.1 GPC Analysis

Table 3.1.1 shows GPC data of each polymer. The significant difference in molecular weight (M_w) indicates that the amount and the type of catalyst used in the polymer synthesis have a large impact on the polymerization process. In the case of pyridine, excess pyridine may have probably accelerated the homo-condensation of silanols as compared to the other types of catalyst because the pK_b of pyridine is higher than that of the others as shown in Table 2.5.1. The bi- and tri-dentate compounds formed the

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chelate compounds and their methyl unit forms a steric hindrance. For this reason, the polymerization behavior was different for each catalyst. A SQ-2 (Py: 1.0 mol) could only form a white solid in the aqueous phase. This solid has a poor solubility in nPA and CHCl₃, but it could be dissolved in DMSO and Pyridine.

Table 3.1.1 Change in Molecular weight for each polymer using GPC.

Exp.No.	Interaction Catalyst	Amount of Catalyst (mol)	GPC		Catalyst/Si molar Ratio
			Mn	Mw	
SQ-1	Pyridine	0.2	704	810	2
SQ-2		1.0	1900	2950	10
SQ-3	TMEDA	0.1	1074	1528	1
SQ-4		1.0	1226	1689	10
SQ-5	PMDETA	0.1	778	1032	1
SQ-6		1.0	952	1131	10

(Comment: GPC measurement were carried out using polystyrene standard)

The behavior of molecular weight differed in each amine (pyridine, TMEDA, PMDETA). The reaction depends on pK_b which has different values, number of dentate and steric hindrance characteristics. Especially, TMEDA and PMDETA are well known as strong steric hindrance, thus these amines are expected to affect the reactivity of structure control on the reaction process.

3.2 FT-IR Analysis

FT-IR spectroscopy has been an effective technique used to analyze the ladder structure of siloxane materials.²²⁻²⁴ Unno et al. reported that Si-O-Si asymmetric vibration mode depend on the ladder chain size¹⁷. Besides, Brown et al. had previously reported that the inter-conversion between cage and ladder structures in PPSQ could be monitored using FT-IR spectroscopy since, the cage structure shows one strong broad absorption band at 1120 – 1130 cm^{-1} , while two absorption peaks can be observed at 1150 – 1130 cm^{-1} and 1045 cm^{-1} for ladder structures.³

Figures 3.2.1-3.2.3 show FT-IR spectra of each SQ polymer obtained by using various interaction catalysts. The characteristic asymmetric vibration mode of Si-O-Si bond at 1030 – 1150 cm^{-1} region was estimated to shift from 1050 cm^{-1} to around 1040 cm^{-1} , which indicates repeating length of cyclic SQ unit⁹. In case of 0.1 mol catalyst, all SQ samples show strong absorption bands attributed to asymmetric stretching at 1140 cm^{-1} and weaker absorption at 1045 cm^{-1} compared to that of 1140 cm^{-1} , was observed. The case is opposite, for 1.0 mol interaction catalyst (Catalyst/Si molar ratio is 10) the asymmetric vibration Si-O-Si peak at 1040 cm^{-1} relatively increased as compared to the 1140 cm^{-1} peak. From this result, the structure of obtained PPSQ in the 1.0 mol catalyst case (Catalyst/Si molar ratio is 10) were expected to have mainly the oligo-ladder

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structure. On the other hand, in the 0.1 mol catalyst case (catalyst/Si molar ratio is 1.0) no clear absorption at around 1040 cm^{-1} is observed, this suggests that the main structure is not probably a ladder structure.

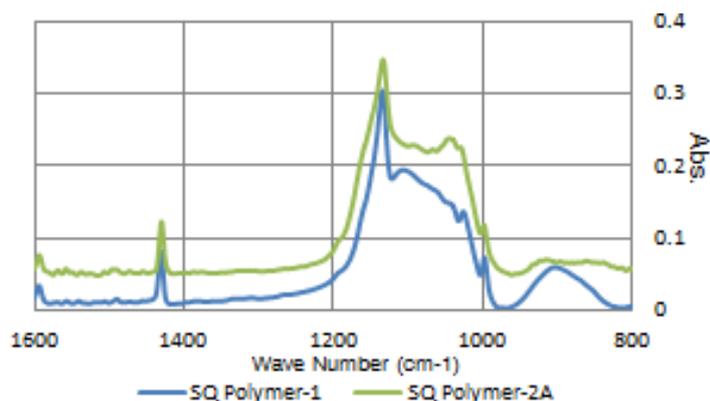


Figure 3.2.1 FT-IR Spectra of SQ-1,-2 using Pyridine

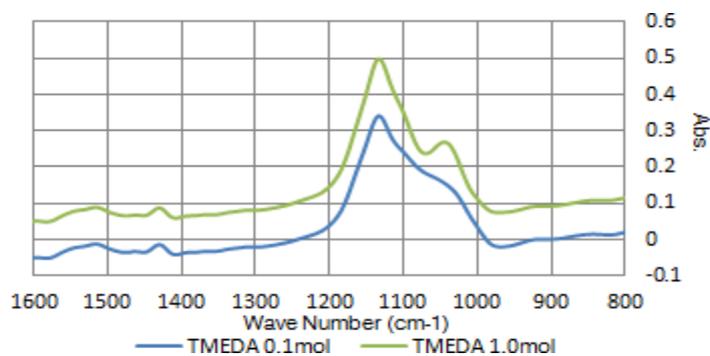


Figure 3.2.2 FT-IR spectra of SQ-3,-4 using TMEDA

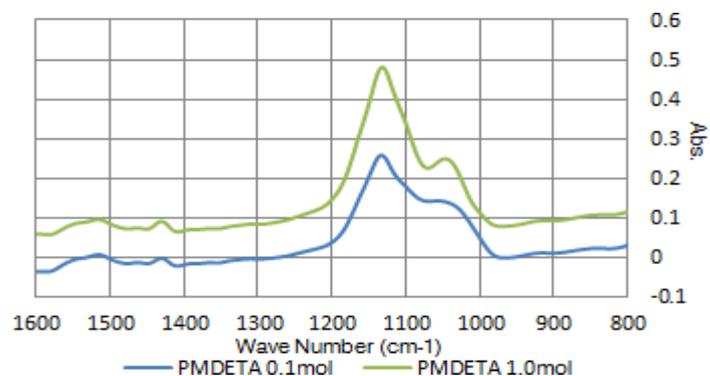


Figure 3.2.3 FT-IR spectra of SQ-5,-6 using PMDETA

3.3 MALDI –TOF/TOF MS Analysis

Figures 3.3.1-3.3.6 show MALDI-TOF/TOF MS spectra of PPSQs and Appendix 1 and 2 explain in details the reinforcement data showing the assigned structures corresponding to the m/z of each polymer.

In case of SQ-1 (Py: 0.2mol), it is estimated that the cyclic- PhT_4 SQ and oligo-ladder is the main structures as shown in Figure 3.3.1. However complete and other incomplete ladder structures are also included. In the case of other SQ, it is composed of ladder structures from mass number and the regularity in peaks path distance of m/z (129) is that for $\text{PhSiO}_{1.5}$. This result clearly shows that oligo-ladder PPSQ was produced by one-step condensation in aqueous-organic boundary reaction with an excess pyridine, TMEDA and PMDETA. Especially, TMEDA and PMDETA is effectiveness for the ladder structure formation without relying on the amount added. MS data suggests that the basic structure is a mixture of completely ladder and incompletely ladder.

Furthermore, from the Appendix 1 and 2, change of ladder structure formation route of for the case of 0.1mol TMDEA ligand as shown in Figure 3.3.7. It is intrinsically interesting and suggests that the ladder formation reaction is conceivable sequentially by addition reaction of $\text{PhSi}(\text{OH})_3$. And in the 1.0ml case, change of estimated structure was similar to the 0.1mol catalyst case except for the condensation of a single

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end-point.

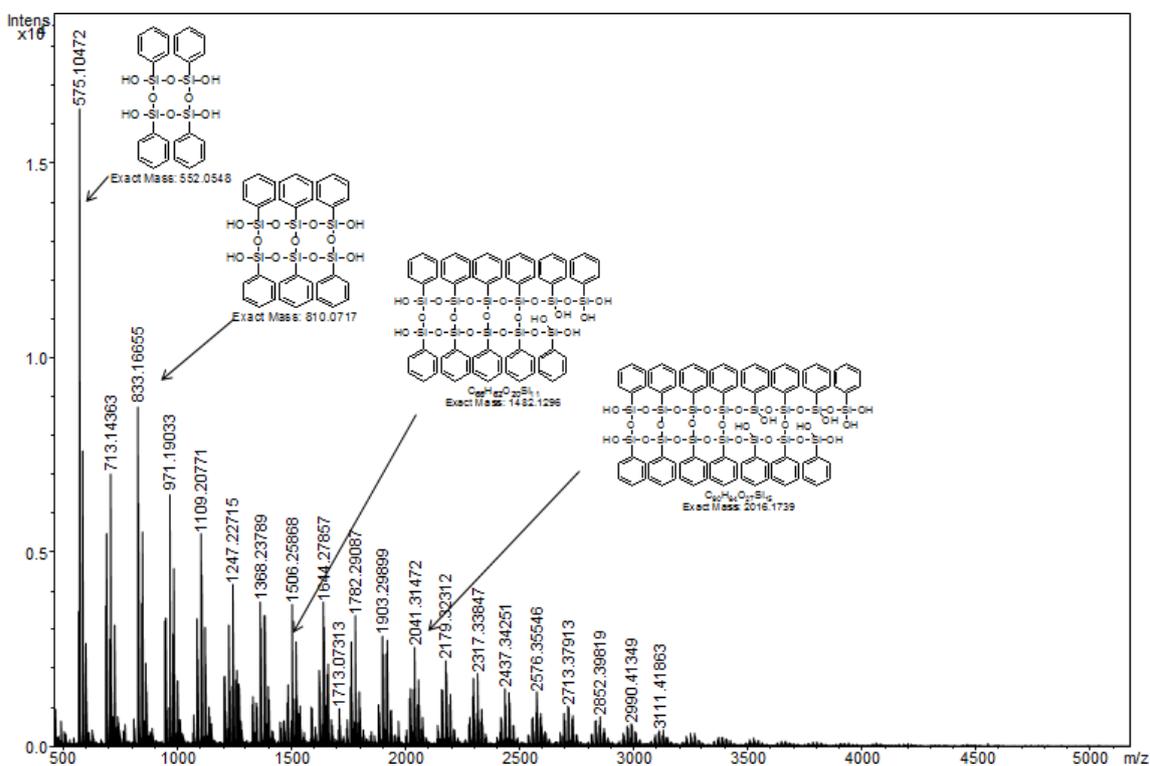


Figure 3.3.1 MALDI-TOF/TOF MS Spectrometer of SQ-1(Py: 0.2mol)

The structure shown in above graph is a representative structure. As aforesaid, the peak distance between m/z is 129 (PhSiO_{1.5}). This structure is analyzed using FT-IR data shows a ladder structure. Support of the NMR measurements is effective to make clear the argument about the ladder structure.

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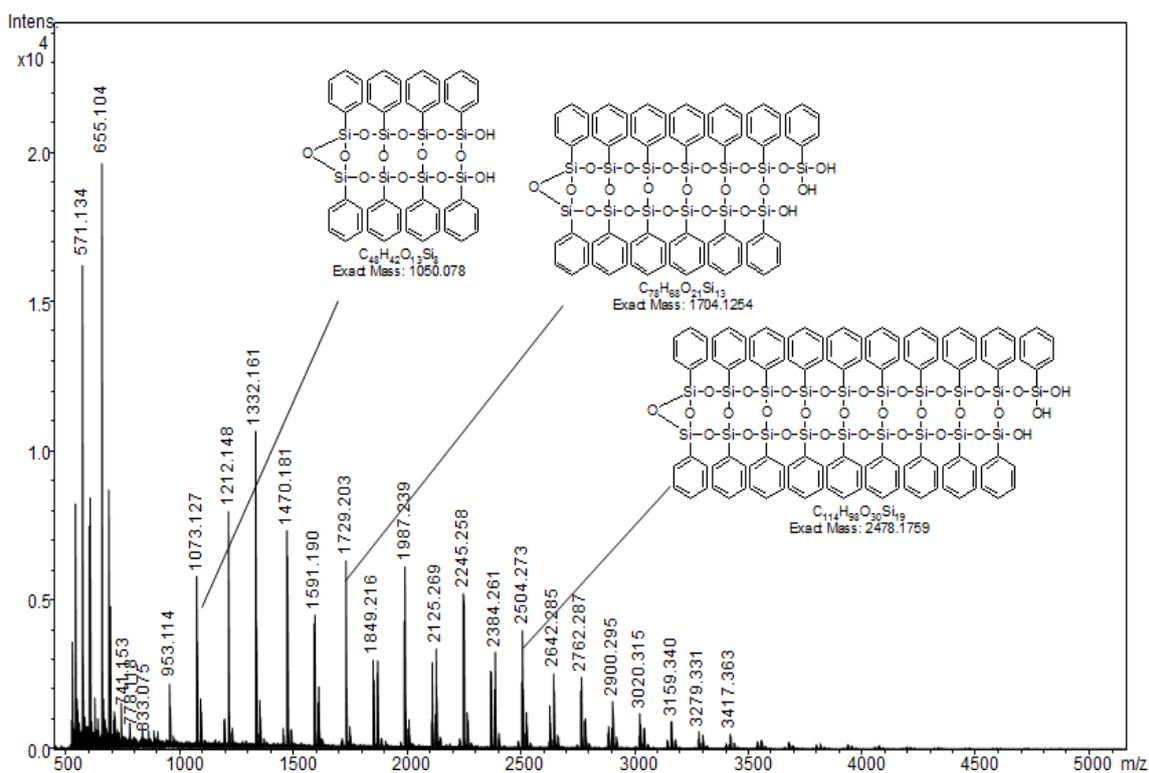


Figure 3.3.2 MALDI-TOF/TOF MS Spectrometer of SQ-2(Py: 1.0mol)

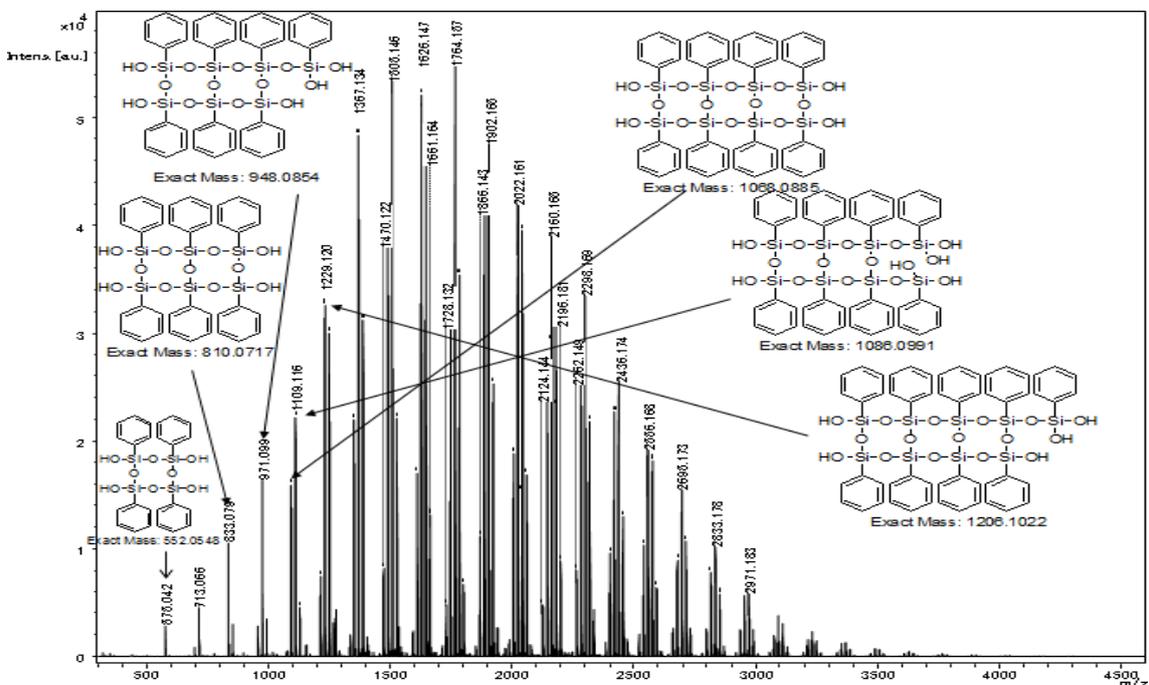


Figure 3.3.3 MALDI-TOF/TOF MS of SQ-3 (TMEDA: 0.1mol)

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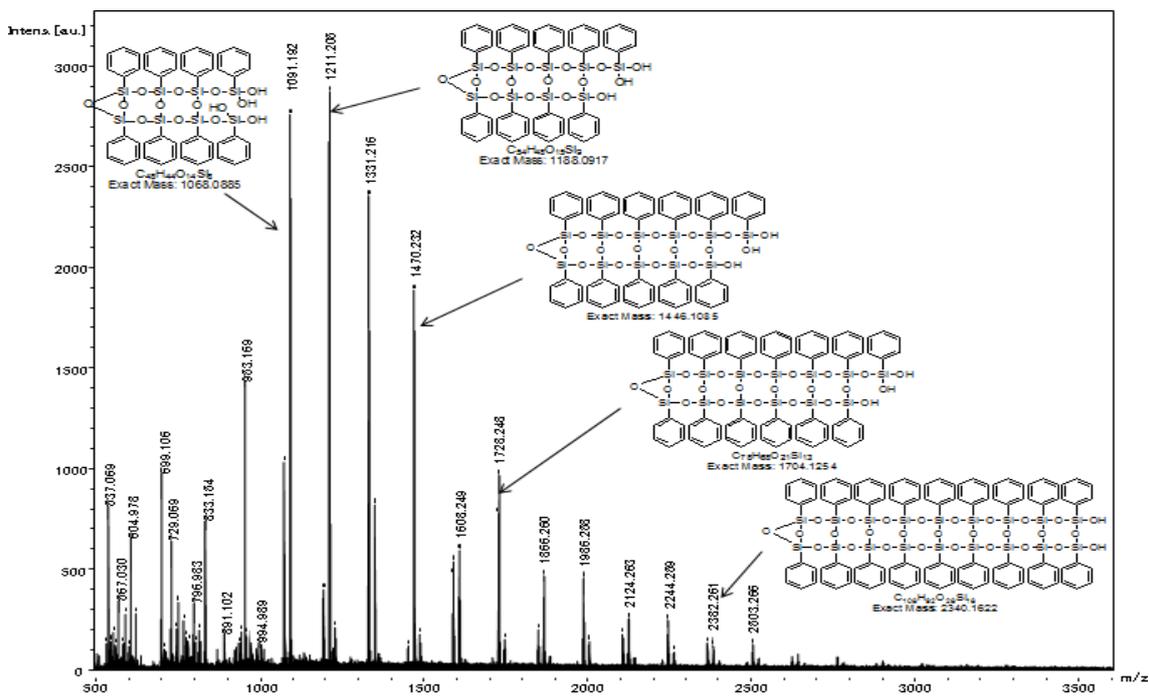


Figure 3.3.4 MALDI-TOF/TOF MS Spectrometer of SQ-4(TMEDA: 1.0mol)

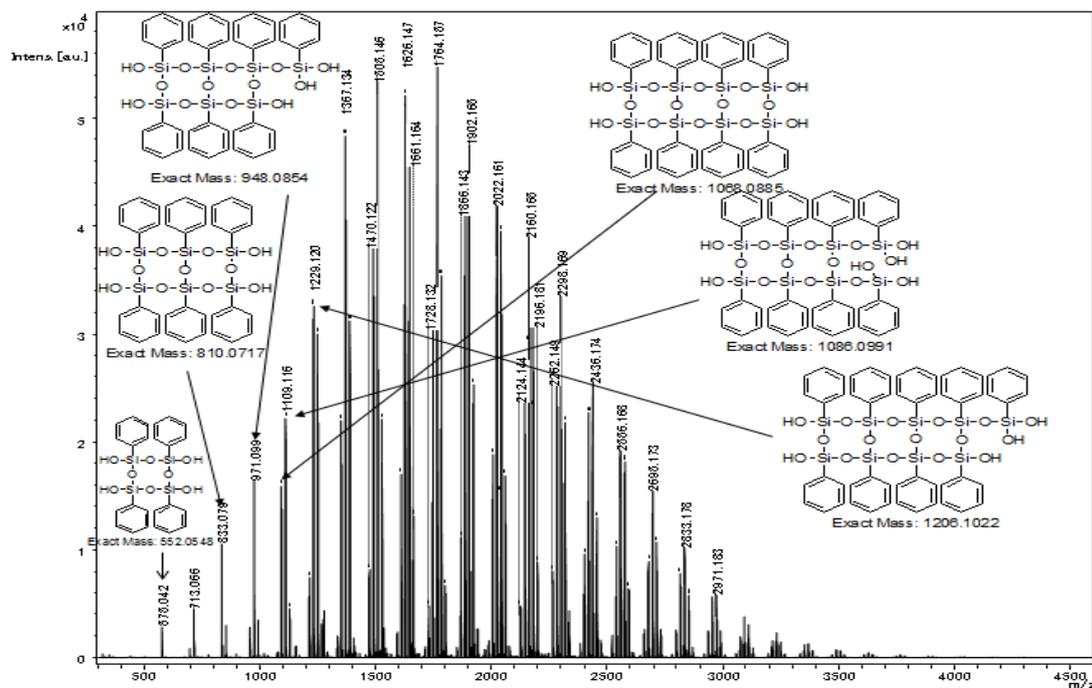


Figure 3.3.5 MALDI-TOF/TOF MS Spectrometer of SQ-5(PMDETA: 0.1mol)

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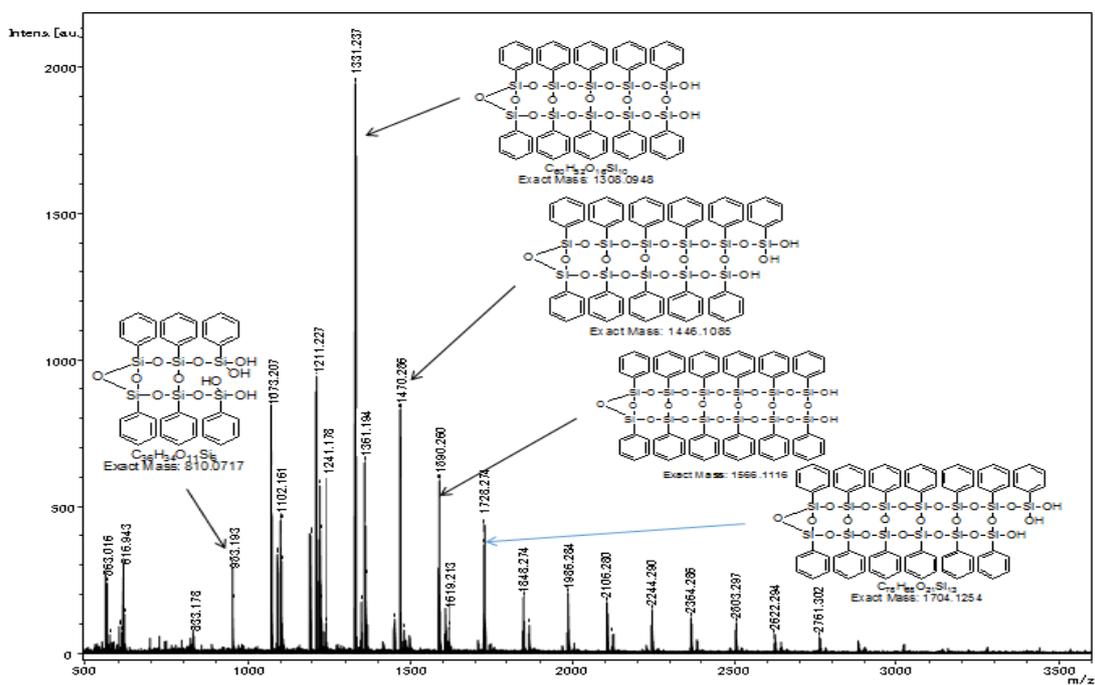


Figure 3.3.6 MALDI-TOF/TOF MS Spectrometer of SQ-6 (PMDETA: 1.0mol)

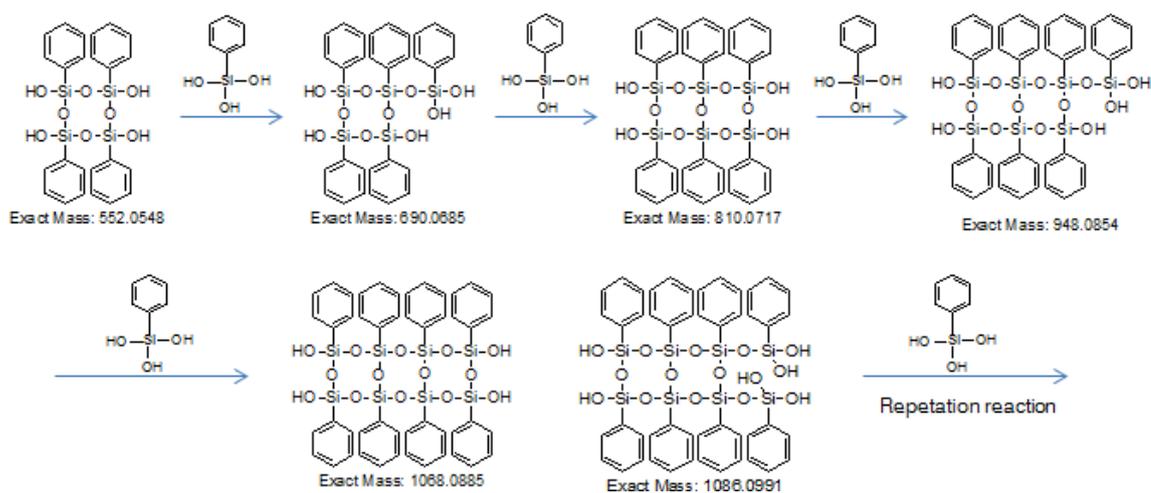


Figure 3.3.7 Observed ladder structure in MALDI-TOF/TOF MS and formation scheme of ladder

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3.4 ^{29}Si NMR spectra

The regularity of structure in ladder PPSQ can also be characterized by ^{29}Si NMR spectrum. A literature survey suggests that the signals at -68 ppm and around -80 ppm can be assigned to end Si atom and center Si atom respectively in the ladder structure of PPSQ^{9, 25}.

The ^{29}Si NMR spectrum of SQ's signal peak at -77.5 ppm ($^{\text{phT}^3}$: PhSiO_3) and -68.5 ppm ($^{\text{phT}^2}$: $\text{PhSiO}_2(\text{OH})$) are shown in Figures 3.4.2-3.4.4 and Table 3.4.1. The integration ratio of SQ signal was almost about the value as the $^{\text{phT}^3}$ peak. This suggests a ladder-structure.²⁵

Moreover, the split peaks of $^{\text{phT}^2}$ structure ($\text{PhSiO}_2(\text{OH})$) unit were observed in all samples. This suggests that there are two different mode of -Si-OH unit such as end-silanol, incomplete internal silanol were estimates to exist from MALDI-TOF/TOF MS data as shown in Figure 3.4.1.



Figure 3.4.1 One of assigned structure by MALDI-TOF/TOF MS Spectrometer

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Table 3.4.1 Results of ^{29}Si NMR Spectra in each Samples

Samples	Ligands	Amount of ligands ration by Si atom (mol/ Si-mol)	Observed Peaks (δppm / TMS)			Integration ratio of p^{hT^2} / p^{hT^3}
			p^{hT^1} structure	p^{hT^2} structure	p^{hT^3} structure	
SQ-1	Pyridine	2	-61.5, -62.1, -62.4	-69.7, -70.3, -71.4,	-78.9	3.07
SQ-2		10	Not observed	-68.3, -70.0	-75.3, -76.3, -78.1, -79.4	0.200
SQ-3	TMEDA	1	Not observed	-68.1, -69.6	-76.8, -78.0, -79.3	0.154
SQ-4		10	Not observed	-68.3, -69.9	-76.9, -78.2, -79.4	0.129
SQ-5	PMDETA	1	-62.5, -62.9	-68.0, -70.0, -70.6, -71.5	-76.5, -77.2, -78.2, -79.6	0.433
SQ-6		10	Not observed	-68.3, -69.8	-76.9, -78.5, -79.5	0.194

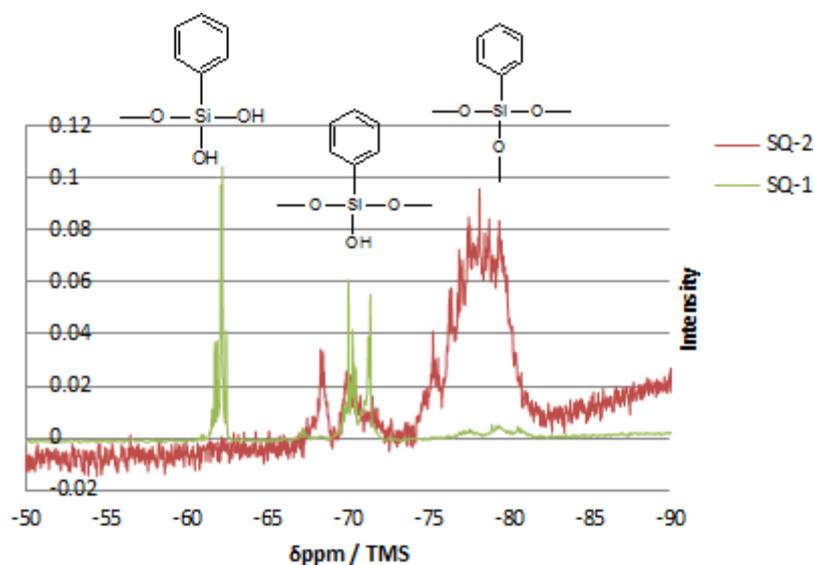


Figure 3.4.2 ^{29}Si NMR Spectra of SQ-1 and SQ-2 using Pyridine

In the pyridine case, the around -62 ppm is assigned p^{hT^1} structure, it suggest that condensation reaction was in completely, then main structure of SQ-1 is estimated

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cyclic- PhT_4 SQ, incompletely ladder and tetrasilanoldisiloxane derived to $\text{PhSi}(\text{OH})_3$.

On the other hand, in case of pyridine 1.0 mol, the condensation reaction extremely advanced. In case of TMEDA (SQ-4, 5), ^{29}Si NMR spectra differed compared to other ligands case. Ladder structure formation was stable generated in low amount of ligand as shown in Figure 17. Polymer yield is higher than other ligand case as shown in Table 5, Consequently, TMEDA is best ligand for obtain ladder-structure.

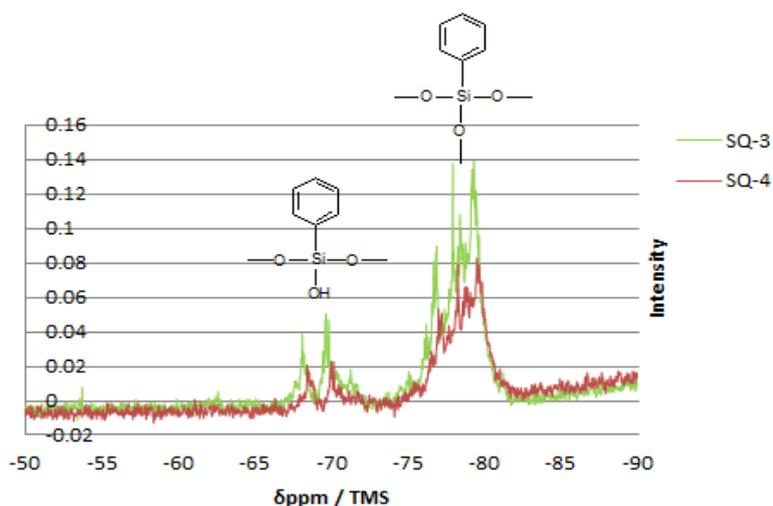


Figure 3.4.3 ^{29}Si NMR Spectra of SQ-4 using TMEDA

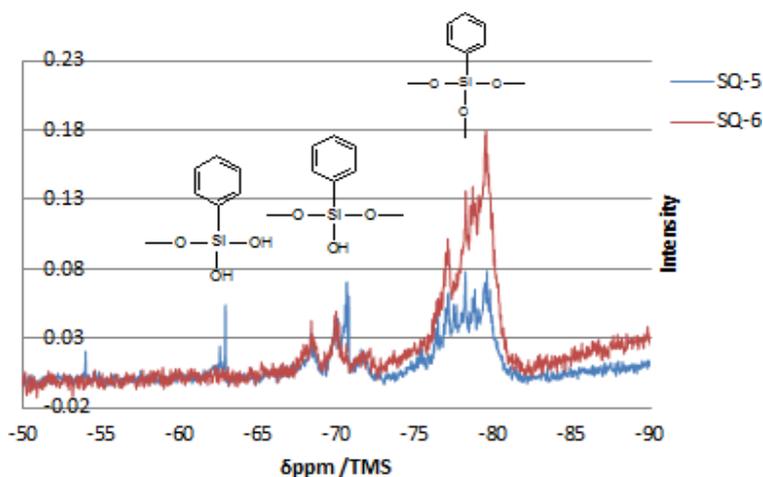


Figure 3.4.4 ^{29}Si NMR Spectra of SQ-5 and SQ-6 using PEDETA

3.5 Recrystallization of SQ-1(Py: 0.2 mol)

3.5.1 Procedure of Recrystallization

SQ-1(Py: 0.2 mol) was only synthesized using same recipe as of other SQs. After TCP titration, white solid (pyridine-silicon adduct) was immediately generated in nPA layer. This white solid disappeared through hydrolysis reaction in the water-nPA liquid boundary. Finally, both the water layer and nPA layer became transparent. Subsequently, separation process was carried out using the separable funnel. The nPA and water layer was introduced into 300 ml separation funnel. Finally, nPA layer with SQ polymer-1 was recovered after pH of washed water became 4 to 5. Next, the recovered nPA layer which includes SQ polymer-1 was titrated using 400ml *n*-hexane, with volume ratio (*n*-hexane/nPA) around 20:1 and stirred for 1hr. The precipitated white powder from the mixture was collected for filtration using funnel with 5A paper filter and dried in oven at 40 °C in order to remove the remaining solvent. Thus, obtained white solid (SQ-1R) could easily dissolve into nPA and the polymer yield was about 85%.

3.5.2 GPC Analysis

Table 3.5.2.1 shows change of molecular weight in recrystallization of SQ-1 together with those of SQ-1. The increase of molecular weight suggests progress of further homo-condensation in the cyclic-like SQ. (Recrystallization polymer is called SQ-1R.)

Table 3.5.2.1 Change of Molecular weight by Recrystallization

Sample	Mn	Mw	Polymer state	Yield (%)
SQ-1	704	810	viscosity	92
SQ-1R (Recrystallization)	1100	1600	Whitesolid	85

3.5.3 FT-IR Analysis

Figure 3.5.3.1 shows change of FT-IR spectra of SQ-1R as compared with SQ-1. As already discussed above, the increase of signal at 1030–1040 cm^{-1} and Si-O-Si signal separation reveal suggests ladder structure formation in SQ-1R.

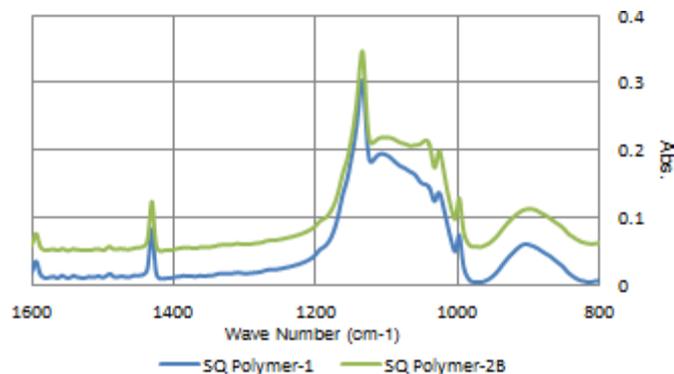


Figure 3.5.3.1 Change of FT-IR Spectra in recrystallization process

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3.5.4 MALDI-TOF/TOF MS Spectrometer

Figure 3.5.4.1 shows the MALDI-TOF/TOF MS spectra and Appendix 1 - 2 shows m/z assigned structure for SQ -1R. From above results, it can be concluded that the simple recrystallization process can also render oligo-ladder PPSQ from SQ-1 which is composed of Cyclic- $\text{PhT}_2\text{Si}_4\text{O}_4$ (main structure) and oligo-ladder.

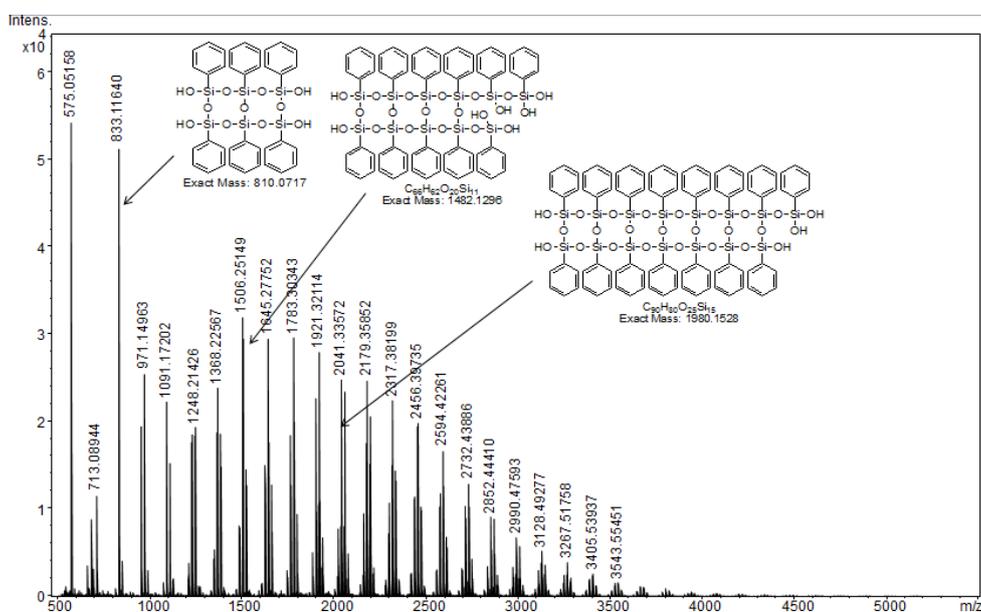


Figure 3.5.4.1 MALDI-TOF/TOF MS Spectrometer of SQ-1R

3.5.5 ^{29}Si NMR Analysis

Figure 3.5.5.1 shows ^{29}Si NMR of SQ-1 and SQ-1R (after recrystallized SQ-1). As discussed in section 3.4, the main structure of SQ-1 is cyclic- $^{\text{ph}}\text{T}_4^2$ SQ and disiloxane derived $\text{PhSi}(\text{OH})_3$. Even though, the cyclic SQ structure is composed to $^{\text{ph}}\text{T}^2$ units the obtained ^{29}Si NMR spectra showed a weak $^{\text{ph}}\text{T}^1$ and $^{\text{ph}}\text{T}^2$ signal at around -60.5 ppm and -70.0 ppm, respectively. Consequently, the structure of SQ-1 is assumed to be other cyclic SQ, incompletely condensation compound and oligo-ladder compounds, as suggested by MALDI-TOF/TOF MS data. It seems that, recrystallization in hexane solution accelerates the homo-condensation of end silanols. In SQ-1R the observed $^{\text{ph}}\text{T}^2$ and $^{\text{ph}}\text{T}^3$ structure signal are similar as that of SQ-2, thus the structure is estimated to be oligo- ladder. Even though the main structure of SQ-1 was estimated to be a cyclic- $^{\text{ph}}\text{T}_4^2$ structure, cyclic- $^{\text{ph}}\text{T}_4^2$ SQ has four structural isomers, all cis type, cis-trans-cis type, cis-cis-trans type and all-trans type. When we thought about the generation of ladder structure, the selective generation of the all-cis type which has all same binding angle of silanol is necessary. However, we cannot mention the selectivity of the structural isomer from this analysis and have to have further examination from the point of view of the effect of amine complex on the selectivity of all-cis cyclic- $^{\text{ph}}\text{T}_4^2$ structure.

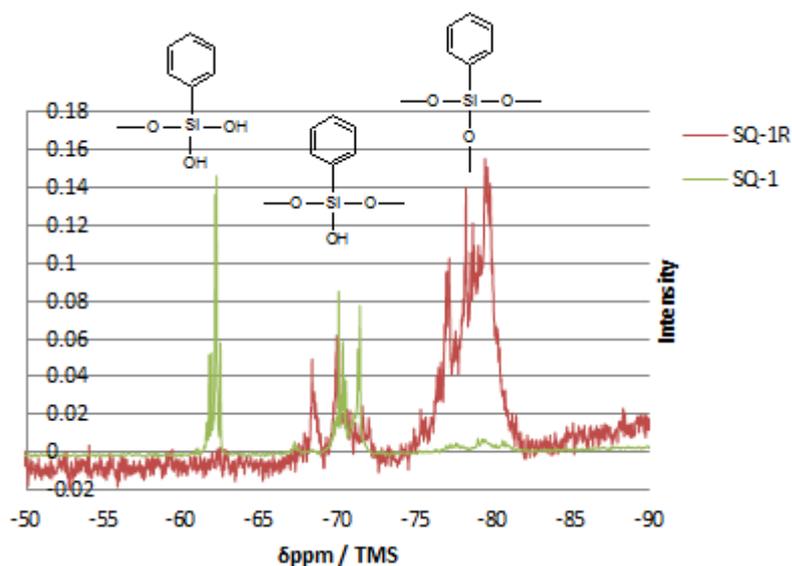


Figure 3.5.5.1 ^{29}Si NMR Spectra of SQ -1 and SQ-1R by Recrystallization

The NMR Spectra of SQ-1R was same as SQ-2, poly-condensation was advanced by recrystallization process. And $^{\text{ph}}\text{T}^2$ peak was separated due to incomplete homo-condensation of ladder structure.

3.6 Thermal Stability of Oligo-ladder PPSQ by TGA

Highly regular ladder structure is expected to show specific material properties. Figure 3.6.1 clearly indicates a oligo-ladder structured SQ-2 possesses quite superior heat resistance, about 5% weight loss temperature is 525°C and weight loss at 800°C was 23%. Moreover, in the TMEDA and PMDETA case, ceramic yield at 800°C showed about 80% similar to SQ-2.

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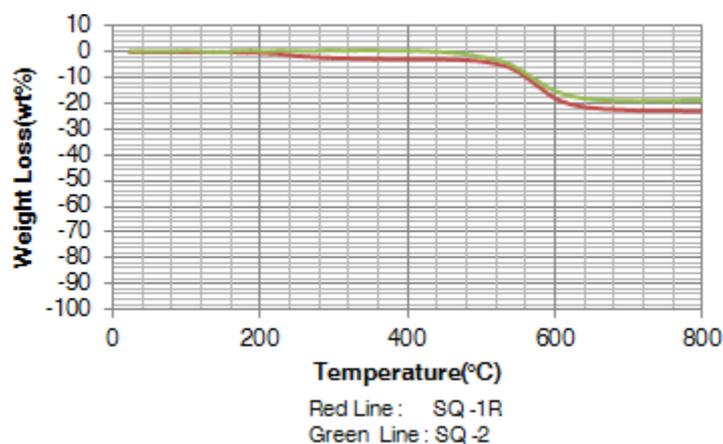


Figure 3.6.1 TGA charts of SQ-2, SQ-1R

Weight loss was observed at 200°C ~ 300°C and 500°C ~ 800°C in the SQ-1R.

The weight loss at 0°C ~ 300°C was associated to the formation of H₂O due to homo-condensation of silanol as shown in Figures 3.6.2 and 3.6.3.

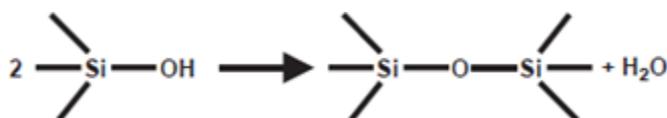


Figure 3.6.2 Reaction scheme of homo-condensation

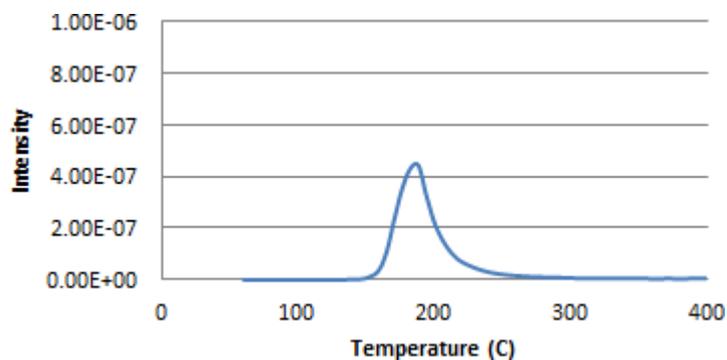


Figure 3.6.3 m/z=18(H₂O) peak by TDS analysis

TDS: thermal desorption spectroscopy

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Thermal desorption spectroscopy is composed of a Q-mass analyzer in a high vacuum chamber, wherein the sample can be heated by infrared mechanism. This system thus measures all kinds of outgassing using the Q-mass and the total vapor volume can be estimated by the total gas pressure wherein range is also $1\text{E-}9$ torr \sim $1\text{E-}7$ torr for this system.

On the other hand, the weight loss at $500^\circ\text{C} \sim 600^\circ\text{C}$ was observed all samples. It is associated to the thermal degradation of phenyl ligand as shown in Figure 3.6.4.

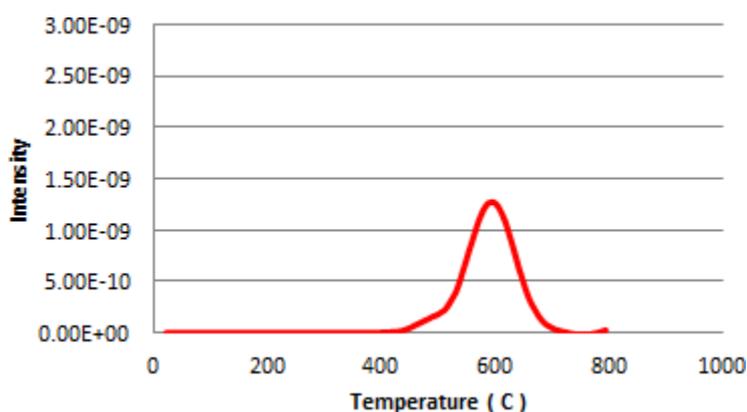


Fig. 3.6.4 $m/z = 77$ (phenyl) peak by TDS analysis

These peaks of TDS nearly correspond to that obtained from the TGA data.

4. Adduct formation and reaction pathway in pyridine

4.1 Hydrolysis reaction of pyridine–silicon adduct

In the hydrolysis and condensation reaction of TCP, pyridine is well known as good

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catalyst to produce cyclic SQ³. Generally, catalytic amount of pyridine has been used with water/organic-solvent mixture for the hydrolysis reaction. We here propose that the oligo-ladder PPSQ can be synthesized by hydrolysis reaction through octahedral pyridine-silicon adduct formation as shown in Figure 4.1.1.

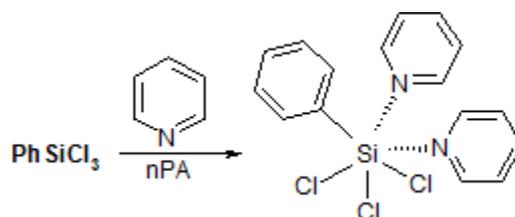


Figure 4.1.1 Octahedrally-coordinated pyridine-silicon adduct formation

An optimum structure of pyridine-silicon adduct was simulated to understand the reaction behavior of TCP with pyridine using the molecular orbital method of MP6 as shown in Figure 4.1.2. The octahedrally-coordinated pyridine-silicon adduct, (PhSiCl₃(Py)₂) are created and pyridine adducts using vacantly d-orbit of Si are similar to MeHSiCl₂ and HSiCl₃²⁵.

On the other hand, single chlorine increases the electron charge density. This shows that the bonding of single chlorine is easy release.

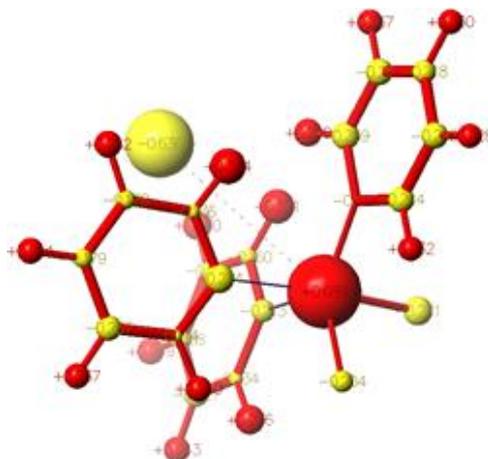


Figure 4.1.2 Optimized structure of $\text{PhSiCl}_3(\text{Py})_2$ complex formation by MO (MP6)

Consequently, one chlorine molecular orbital becomes unstable by the alkalinity of pyridine. Moreover, we further simulated change of adduct formation in case of weak single chlorine change to silanol (OH) for consideration of reaction pathway for hydrolysis with TCP as shown in Figure 4.1.3. As a result, we can consider that pyridine to TCP coordination changes to penta-coordinate, due to decrease of Lewis acidity by generation of silanol. This suggests that pyridine adduct controls the hydrolysis reaction in a stepwise manner.

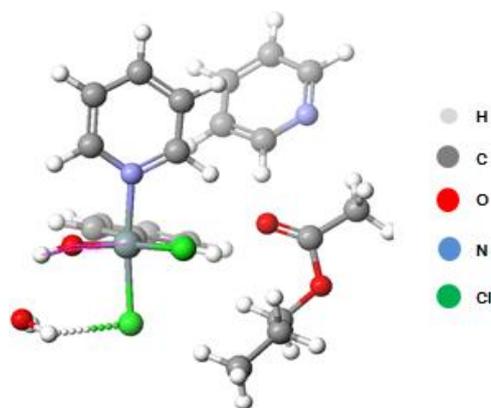


Figure 4.1.3 Simulation of reaction intermediate on PhSiCl₂(OH) /Pyridine / H₂O /nPA system

Thus, it is assumed that a stepwise hydrolysis procedure probably can yield syndiotactic configured cyclic- ${}^{\text{ph}}\text{T}_4$ SQ intermediate, since step-wise process gives enough time for the system to reach the most thermodynamic stable status. Syndiotactically configured cyclic- ${}^{\text{ph}}\text{T}_4$ SQ favors ladder structure formation according to the reported mechanism by Kimura et. al.⁵ Further, Yamamoto et. al also reported the reaction mechanism of hydrolysis by monitoring ${}^{29}\text{Si}$ NMR in the different catalysts⁷. They proposed the generation of PhSi(OH)₃ is important in order to obtain cyclic- ${}^{\text{ph}}\text{T}_4$ structure as a pre-compound for ladder SQ's.

4.2 Homo-condensation of PhSi(OH)₃ under pyridine

This chapter elucidates that pyridine amount strongly affects the degree of polymerization for SQ polymers and favors the ladder structure generation. These results

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give an insight in consideration of pathway mechanism of silanol homo-condensation reaction. As shown by Gun'ko, pyridine can interact with hydrogen of silanol in organo-siloxane.²⁶ Therefore, pyridine probably promotes hydration due to the strong acidity of silanol on intermediate siloxane in homo-condensation of $\text{PhSi}(\text{OH})_3$. In addition, pH of water layer is weak alkali (pH=8) for generation of pyridine-hydrochloride salt (Py:HCl) as shown in Table 4.2.1.

Table 4.2.1 Change of pH in water layer after condensation

Polymer	Pyridine amount for TCP 0.1 mol	pH in water layer after hydrolysis
SQ-1	0.2 mol	2
SQ-2	1.0 mol	8

Consequently, I propose a possible reaction pathway for the hydrolysis reaction of TCP and homo-condensation reaction of intermediate compounds by following considerations as shown in Figure 4.2.1. Pakjamsai et al proposed loop formation mechanism by inter- and intra- condensation of silanol⁶. However, in this study, MALDI-TOF/TOF MS spectrometer supports sequential formation base on cyclic- PhT_4 structure.

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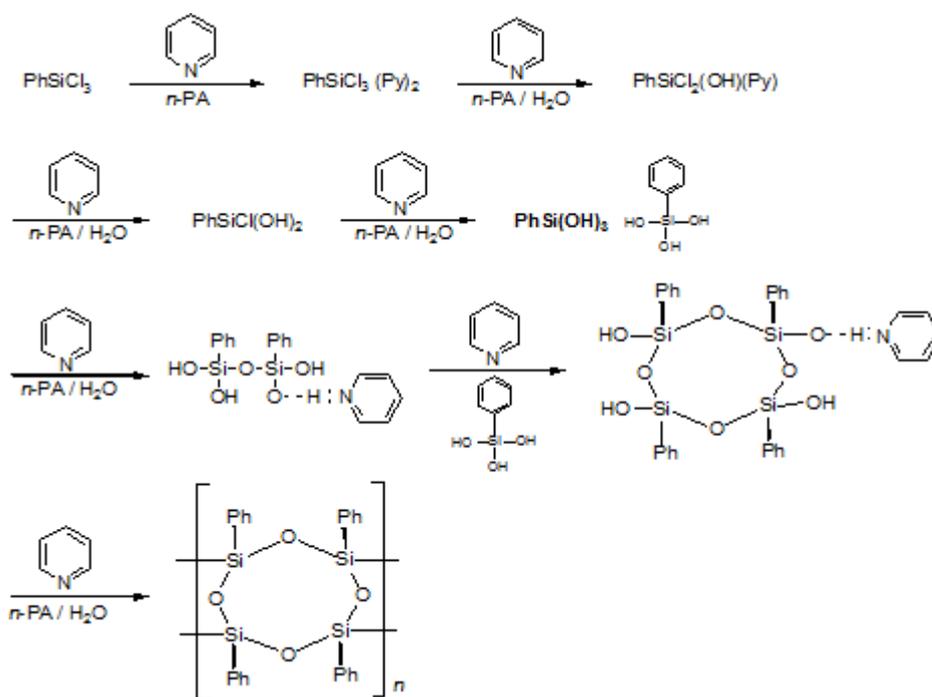


Figure 4.2.1 Proposed homo-condensation pathway of PhSi(OH)_3 in the presence pyridine

That proposal pathway for ladder SQ supports the following chemistry for generation of ladder SQ forms. Lewis-base silicon adduct ($\text{PhSiCl}_3(\text{Py})_2$) is a precursor of phenylsilanetriol (PhSi(OH)_3) which is good raw material for ladder-SQ. A pyridine hydrochloride salt is generated after hydrolysis reaction it changes the pH in water layer, then the homo-condensation reaction is controlled to obtain the ladder structure. Generally, if the alkaline component is absent, homo-condensation reaction is $\text{S}_{\text{N}}2$ (nucleophilic deprotonated reaction) type²⁷. Many papers have reported that ladder SQ can be synthesized in homo-condensation using alkali catalyst by equilibrium reaction.

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Consequently, pyridine amount was shown to be effective for SQ structure control. However, pyridine is weak base, with a pK_b of 8.5. Thus, the homo-condensation was not accelerated and as the results, final products become oligomer-like. On the other hand, TMEDA and PMDETA are intrinsically similar in theory to that of pyridine case too.

5. Conclusion

I found new methods for synthesis of oligo-ladder PPSQ via halosilane-amine adduct under pyridine, TMEDA and PMDETA with *n*-propyl acetate at liquid boundary by one-step reaction.

In this study, I found out that TMEDA are good amine ligand to obtain oligo-ladder PPSQ with a high yield through adducts (chelate compounds) with TCP at aqueous-organic liquid boundary reaction scheme. This is first report for a new route of oligo-ladder synthesis via adducts (chelate) compounds.

PPSQ structure is controlled by interaction of the alkaline catalyst which has lone electron-pair of nitrogen such as pyridine, TMEDA and PMDETA.

Several characterizations performed are well consistent to indicate the ladder structures of SQ polymers. It is proposed that alkaline compounds/TCP adduct and intermediate

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siloxane compound/alkali interaction impacts both TCP hydrolysis and homo-condensation processes. Furthermore, the mechanism of ladder formation is estimated to generate cyclic- phT_4^2 SQ and sequential additional reaction of phenylsilanetriol (PhSi(OH)_3) with cyclic- phT_4^2 SQ.⁵

TMEDA and PMDETA are intrinsically similar in theory to that of pyridine case. However, a point unlike of pyridine is the alkaline strength (pK_b) and a coordination number and steric hindrance characteristics. Therefore, in this study, change of molecular weight, effectiveness of catalyst amount for ladder structure is different. TMEDA is suitable in control characteristics of the ladder structure and also in point of view of increase in molecular weight and high polymer yield.

My methods of synthesis in this work also open new possibilities for oligo-ladder SQ mass production for industrial use as they have less complexity and better controllability of process for SQ Polymers.

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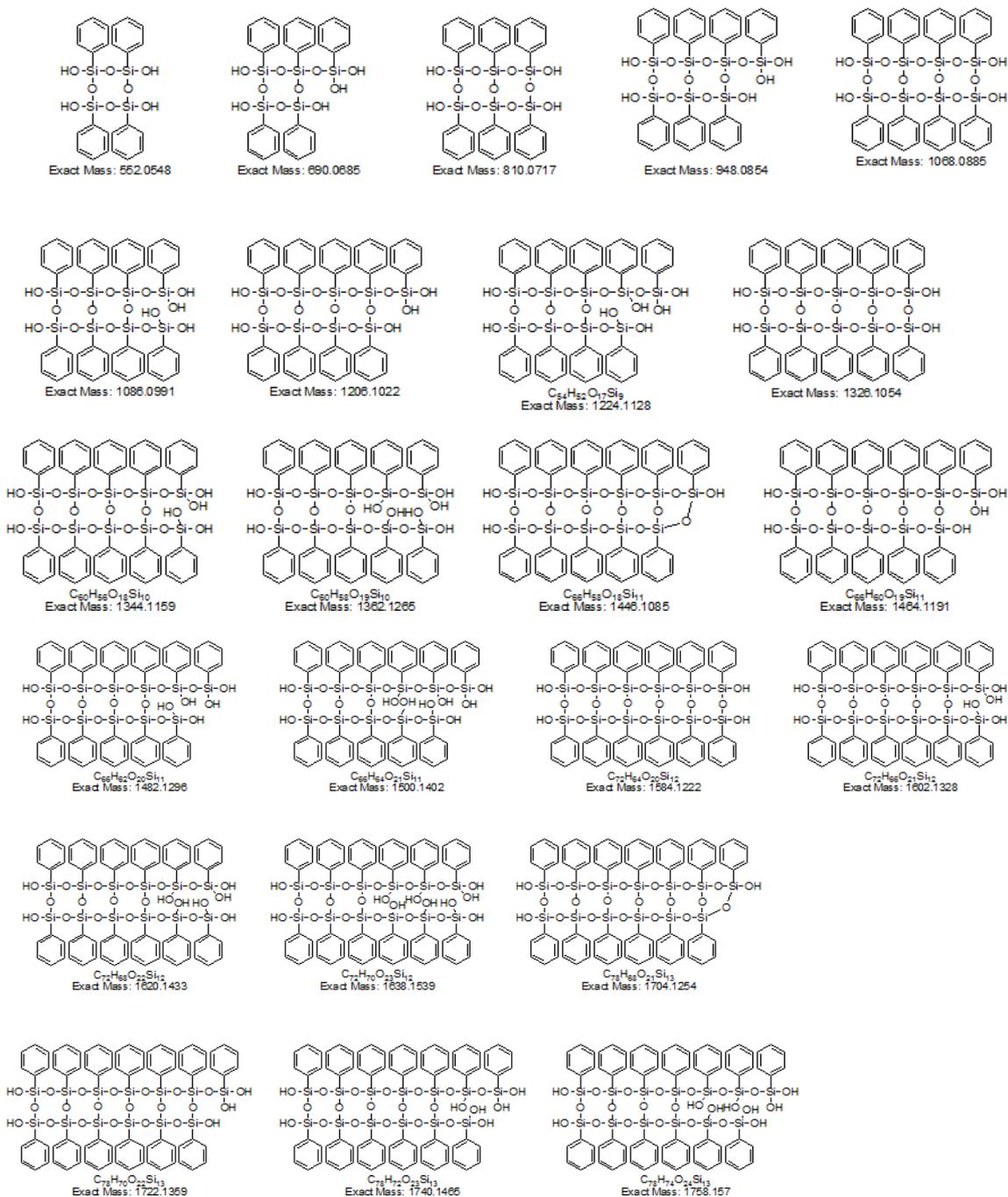
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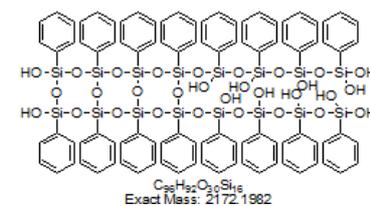
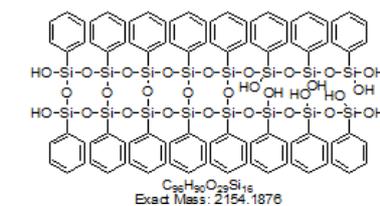
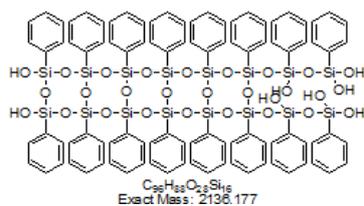
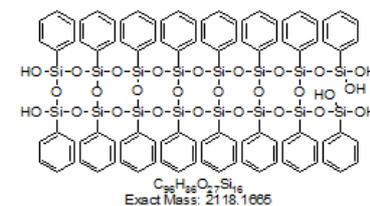
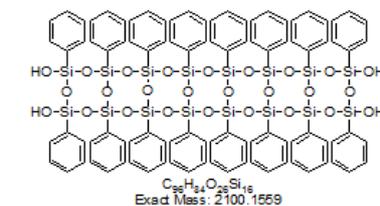
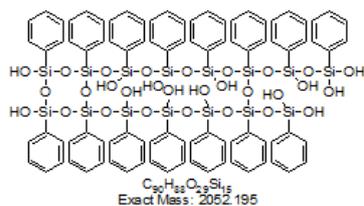
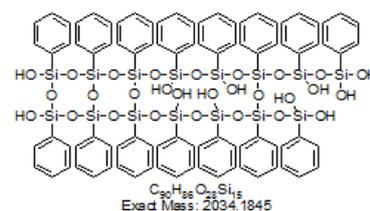
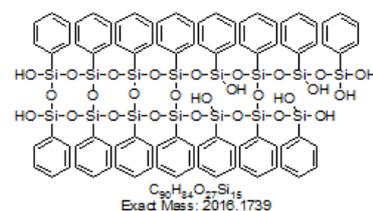
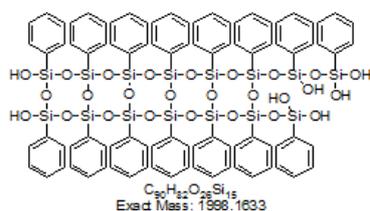
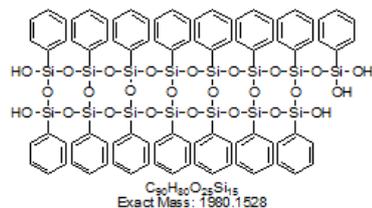
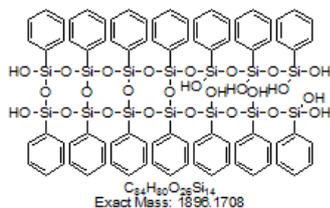
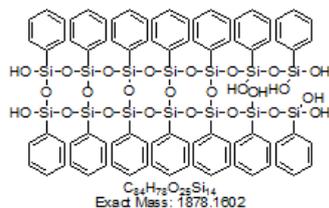
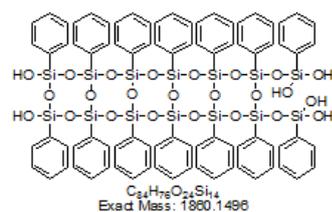
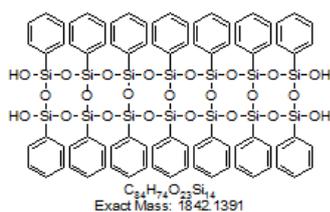
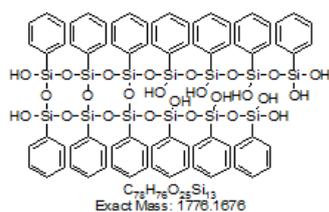
A study on synthesis of oligo-ladder phenylsilsesquioxane via halosilane-amine adducts and their photosensitive characters

Appendix 1 Assignment of structure in MALDI-TOF/TOF-MS spectrometer

(SQ-1, SQ-1R, SQ3 and SQ-5)



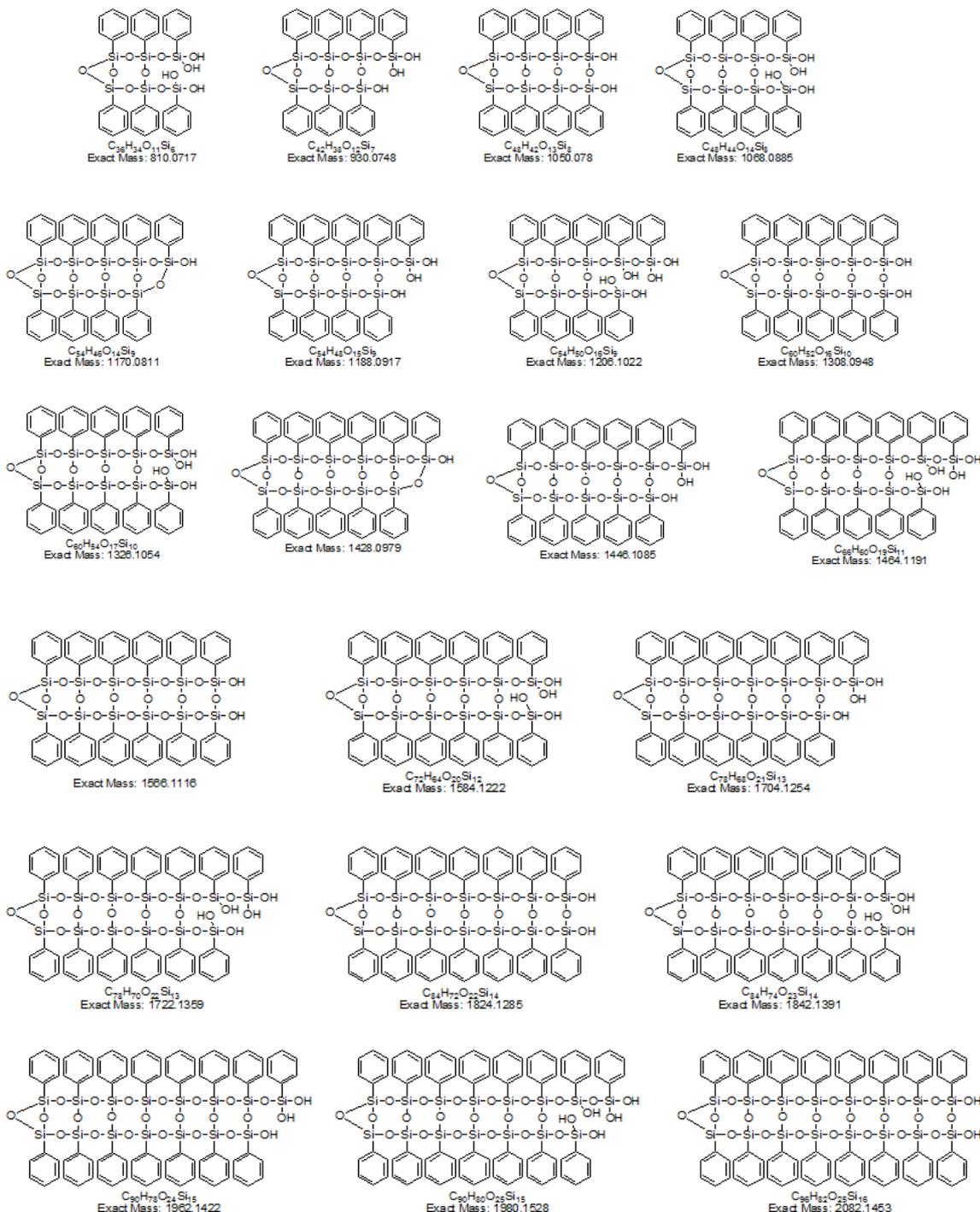
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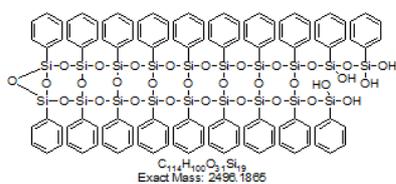
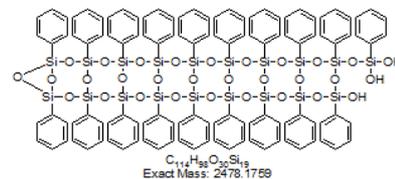
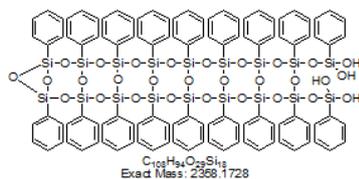
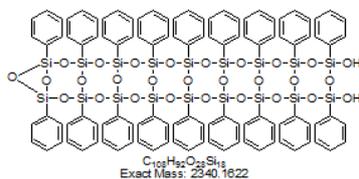
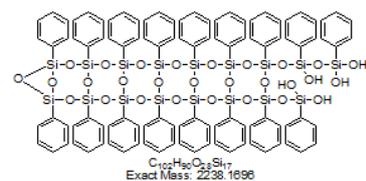
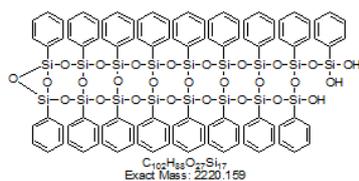
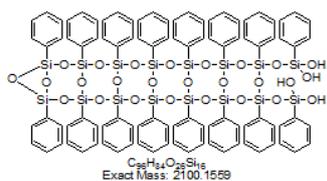
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Appendix 2 Assignment of structure in MALDI-TOF/TOF MS Spectrometer

(SQ-2, SQ-4 and SQ-6)



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Chapter 3

Photosensitive oligo-ladder PPSQ

1. Introduction

At first, the ladder-structure phenyl silsesquioxanes (LPSQ) were studied by Brown *et.al.* And many reports on the synthesis of ladder SQ can be found¹⁻⁶. The ladder type SQ is expected to exhibit some unique properties which are high thermal resistance, high optical transparency and low dielectric constant similar as compared to the cage structures.

Recently, the cage type and ladder type structure has been investigated as an intermediate for the inorganic-organic hybrid material. I also found out new synthesis method for oligo-ladder phenyl silsesquioxane (LPSQ) which is primarily comprised of ladder-1-4 structures. This synthesis scheme is characterized by a liquid-liquid boundary reaction with pyridine as the interaction compound. Even though the synthesis scheme is almost a two-step reaction, first reaction is synthesis of all-cis cyclic- PhT_4 SQ under catalyst and the second reaction is the silanol homo-condensation of first reaction product under alkali catalyst. It is indeed a difficult reaction with a low reaction yield. However, our synthesis method is a single-reaction thus the simplicity of chemistry

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involved and a high reaction yield³⁻⁶.

The films derived from SQ have been under investigation for a while, most importantly these materials have maintained our interest due to the high expectation of their unique characteristics. In recent years, their practical applications for semiconductor interlayer dielectrics, photo-resist material and flat panel display industry have been proposed.

SiNx and SiO₂ deposited by plasma enhanced chemical vapor deposition (PECVD) are well established dielectrics layers for TFT-LCD display. With increasing display sizes the CVD equipment and its processes become very costly and difficult. Thus Spin-on Glass (SOG) materials have been an attractive replacement for a long time about their possibility for vacuum CVD process by liquid coating process, as well as their superior properties such as high optical transparency, thermal and chemical durability⁷. Alkali metal alkoxide are well known coating material as Sol-Gel technique, but they require high temperature to convert the alkoxides into metal-oxide and the film thickness is normally very limited. Silsesquioxanes (SQ) are comprised of (-Si-O-) bonds, which show properties similar to inorganic materials, such as high thermal resistance, high transparency and good chemical durability.

By introducing organic groups, inorganic SQ can also possess organic features, like

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solubility in organic solvent, alkali solubility, UV cross-linking, flexibility and so on. There are many synthesis routes for SQ but roughly three types of structures could be generated in practice, such as amorphous (random), ladder and cage. Out of which, Ladder-type SQ and cage-type SQ shows promising characteristics in higher film thickness cracking threshold and thermal stability. Otherwise, more organic moiety will be necessary to achieve high film thickness cracking threshold. However, this will usually lead to a loss in high thermal and chemical durability.

Another attempt with organic SQ is in terms of their applications for planarization and passivation in TFT⁸. Organic planarization materials have been commonly used on TFT but their performance as passivation layer is far below the level expected in practical applications. For this the planarization layer in TFT's, should also possess photosensitivity property.

There are several reports about photosensitive SQ as multi layers resist application⁷⁻⁹. Sachdev¹⁰ reported a two layer resist by reacting terminal silanol and DNQ (Diazanaphthoquinone). These base polymers are random-structure SQ and include phenol-type ligand. Moreover, acrylic phenyl-SQ and Methyl-methacrylate modified SQ are also reported as base polymer of photosensitive SQ¹¹⁻¹².

In this chapter, I describe synthesis method for alkali soluble oligo-LPSQ and the first

report on photo-lithography system of ladder- type SQ.

2. Synthesis of oligo-ladder phenylsilsesquioxane (Oligo-LPSQ)

Oligo-LPSQ is synthesized with our original method that is characterized by a liquid-liquid boundary reaction with pyridine as interaction compound with *n*-propylacetate (nPA). Synthesis scheme is shown in Figure 2.1 and procedure is as follows, a 3-neck-flask was charged with 100ml H₂O, 65ml nPA and 0.2mol pyridine. It was then hold until water layer and nPA layer were completely separated. The flask was cooled in an ice bath until the temperature of the internal mixture went down to between 0°C - 2°C. Then trichlorophenylsilane (TCP) was added into nPA layer at very slow rate (around 0.005mol /min) without disturbing the nPA/water phase boundary. In nPA layer, a white compound immediately appeared upon TCP addition due to the interaction yielding TCP/pyridine complex.

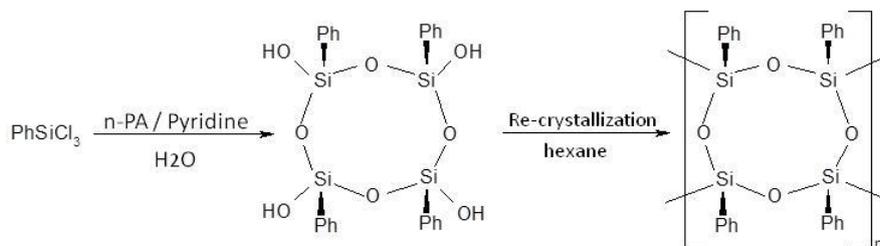


Figure 2.1 Schematic diagram of synthesis scheme

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In liquid nPA/water phase boundary, TCP/pyridine complex will react with restricted water. The reaction was allowed for one hour after 0.1mol TCP was totally titrated. Then the product was recovered by separation water layer and nPA layer. Moreover, the recovered product was purified using pure water until to get a pH of 4~5 by washing in clean water.

The nPA solution made the above synthesis procedure was titrated into n-hexane, with a volume ratio (n-hexane/nPA) of around 20:1. The precipitated white powder from the mixture was collected and dried in oven at 40°C in vacuum condition to eliminate the residual solvent.

Molecular weight of the obtained polymer was about 1600 from GPC analysis. The main structure of the polymer is estimated to be a cyclicsiloxane- phT_4 (ladder-1), completely ladder and incompletely condensation ladder structure as shown in Figure 2.2.

A study on synthesis of oligo-ladder phenylsilsesquioxane via halosilane-amine adducts and their photosensitive characters

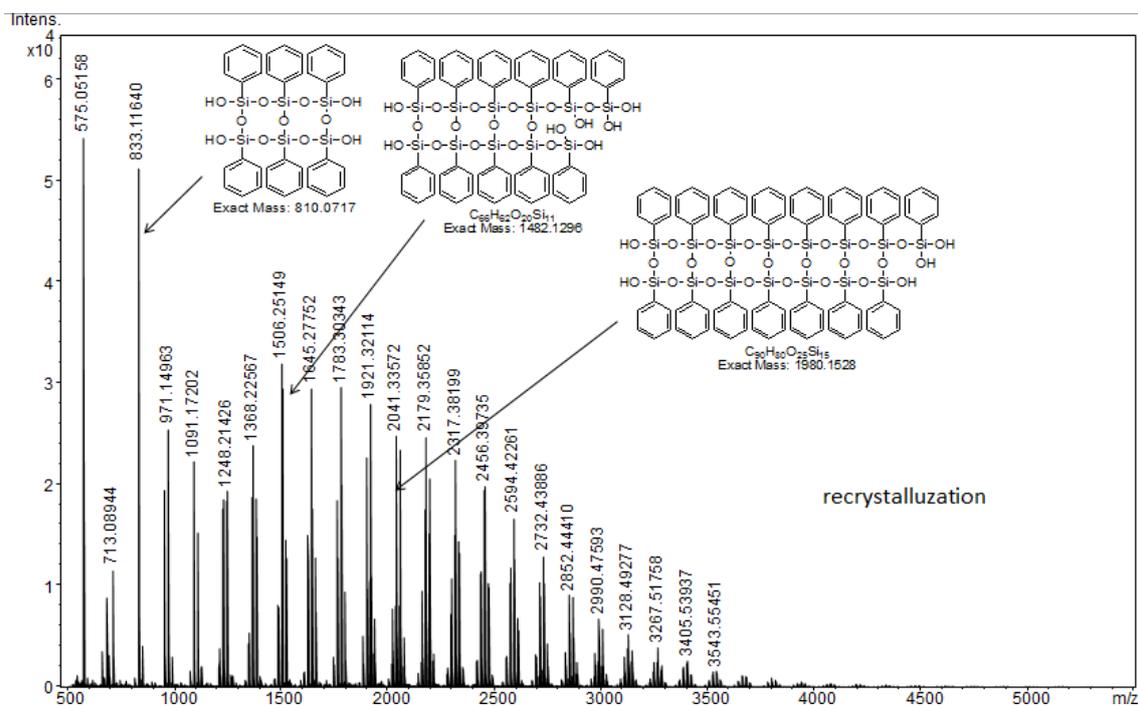


Figure 2.2 MALDI-TOF-MS Spectra of Obtained Polymer

Moreover, Figure 2.3 shows the ^{29}Si NMR spectra of the obtained polymer. The $^{\text{phT}^2}$ and $^{\text{phT}^3}$ structure at -69.5ppm and -79.5ppm can be observed. Each peaks is assigned to $^{\text{phT}^2}$ ($\text{Ph-Si}(\text{OSi})_2\text{OH}$) and $^{\text{phT}^3}$ ($\text{Ph-Si}(\text{OSi})_3$) respectively. This further is confirmed from the ladder structure formation in the recrystallized polymer. The ladder structure is composed of $^{\text{phT}^2}$ and $^{\text{phT}^3}$, cage structure is only $^{\text{phT}^3}$ structure.

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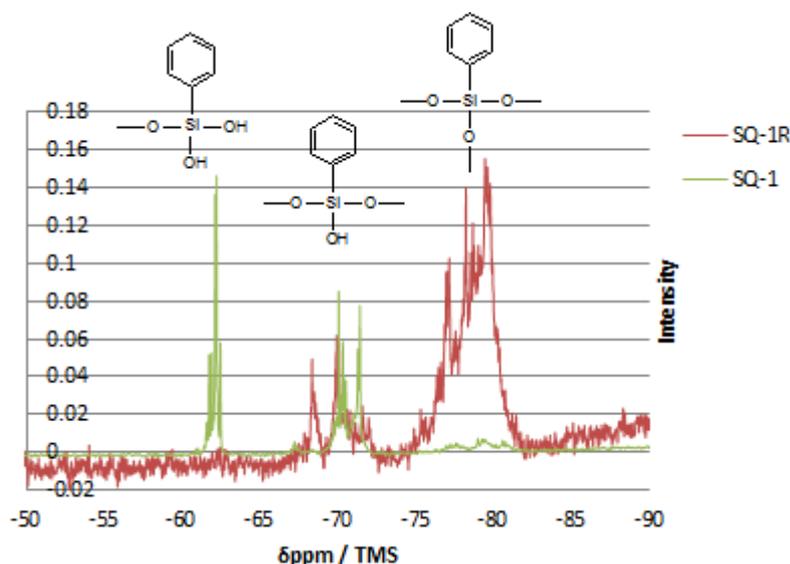


Figure 2.3 ^{29}Si NMR spectra of obtained polymer

As shown ^{29}Si NMR, main structure of SQ-1 is almost phT^3 and phT^2 structure suggested that presence of end-silanol or internal silanol as shown in chapter 2. The oligo-ladder's amount of silanol is much higher than complete condensation structure.

For example, the ladder-3 structure which was simulated by MP6 is shown in Figure 2.4. It takes the all-cis type structure, which forms as a 2D (2 dimensional) structure by silanol homo-condensation process in presence pyridine. The end point of the polymers is formed by silanol (-Si-OH), the silanol to total Si molar ratio is about 50mol% of ladder-3. The alkali solubility ratio also depends on the silanol ratio, so that the oligo-ladder can be soluble in 2.38%TMAH solution. Consequently, the alkaline solubility ratio of the obtained polymer is 2000 Å/s. This value is a sufficient number for alkaline solubility required in a photosensitive formulation.

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(Alkali solubility ratio: film's dissolve speed into 2.38%TMAH sol.)

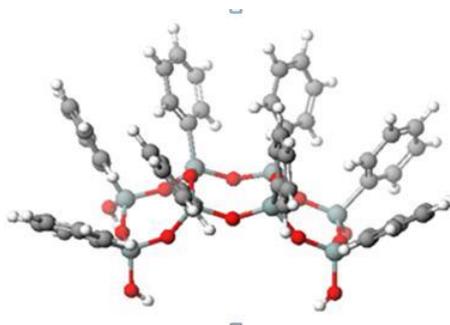


Figure 2.4 Optimized structure of Ladder-3 phenyl silsesquioxane by MP6

3. Result and Discussion

3.1 Positive-tone Photosensitive formulation (p-LPSQ)

I formulated photosensitive LPSQ materials using the oligo-LPSQ. Firstly, I will describe about the positive tone derived SQs in this section.

Positive-tone LPSQ (p-LPSQ) is formulated using diazonaphthoquinone (DNQ), which is photo-active-compound (PAC) and is sensitive to *g*(436nm), *h*(405nm), *i*(365nm) line UV as shown Figure 3.1.1¹³⁻¹⁴

As the LPSQ is an alkali soluble polymer, p-LPSQ can be simply formulated from DNQ with the addition of just oligo-LPSQ similar to the DNQ/Novolak system in an aqueous - alkaline developer (2.38% TMAH). The advantage of this system is that this photolithography process has been commonly used to produce TFTs. I applied 2000Å/s as ADR (Alkali Dissoluble Ratio into 2.38% TMAH sol.: Å /s) for standard

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positive tone formulation. 5 μ m L/S (Line and Space) and 0.5 μ m C/H (Contact Hole)

was processed according to the procedure shown in Table 3.1.1.

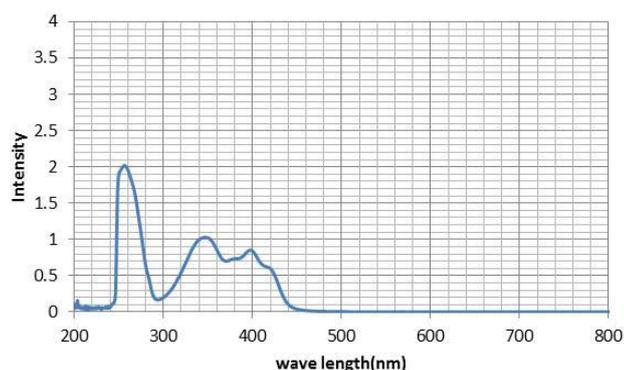


Figure 3.1.1 UV-Vis spectra of PAC

Table 3.1.1 Typical lithography procedure

	Procedure	Positive-tone
1	Pre-bake	100° C/90s
2	Exposure (Nikon FX-604F: g, h-line)	190mJ/cm ²
3	Development (2.38% TMAH)	120s
4	Rinse (Ion changed water)	60s
5	Bleaching (g,h,i-line)	900mJ/cm ²

The lithography system of p-LPSQ is estimated from the existing DNQ/Novolak resist system. However, the interaction site of Novolak and LPSQ is different (phenol and silanol). Since, the acidity of phenol is greater than that of silanol; the interaction with DNQ is weaker than that of the phenol-site. Thus, the lithographic characteristics

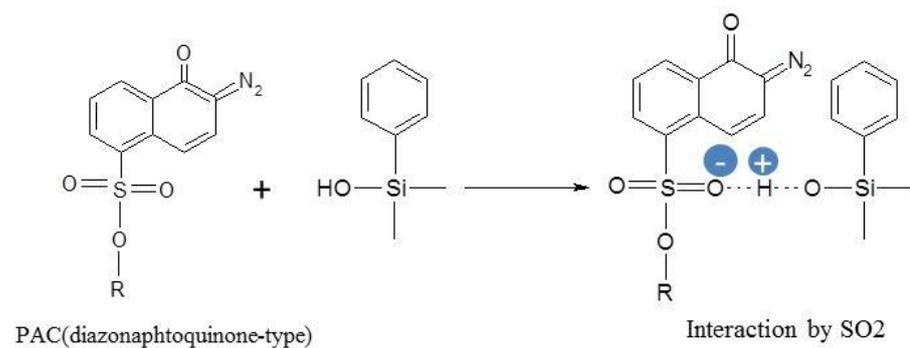
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are intrinsically different as compared to Novolak. However, as shown Figures 3.1.3 and 3.1.4, the lithography characteristics are sufficiently for TFT applications. The pattern resolution is 5 μ m and the film thickness remaining after developing is 95%.

The basic mechanism of positive-tone is composed of 2 reactions as explained in the following paragraph. In the unexposed area, the silanol interaction with PAC and the alkali soluble ratio thus decreases. The interaction site of PAC is estimated to be $-\text{SO}_3^-$, which is a strong acceptor of hydrogen as shown Figure 3.1.2¹⁴. On the other hand, indene-carbonic acid is generated by the degradation of DNQ in the exposed area. Indene-carbonic acid increases the alkaline solubility ratio. Consequently, a large difference in the alkali soluble ratio of each area (exposed and unexposed) region is generated. This is the principle driving force for photo-patterning.

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Interaction with silanole /PAC in the unexposed area



Degradation of diazonaphthoquinone in the exposed area

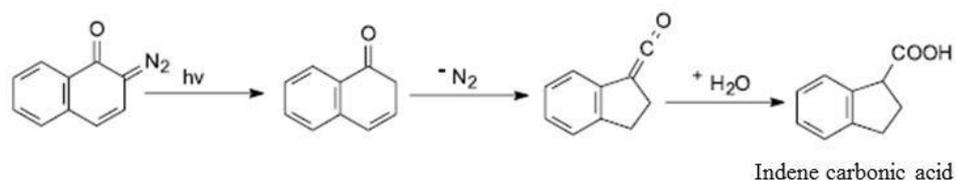


Figure 3.1.2 Basic reactions for lithography system of p-LPSQ

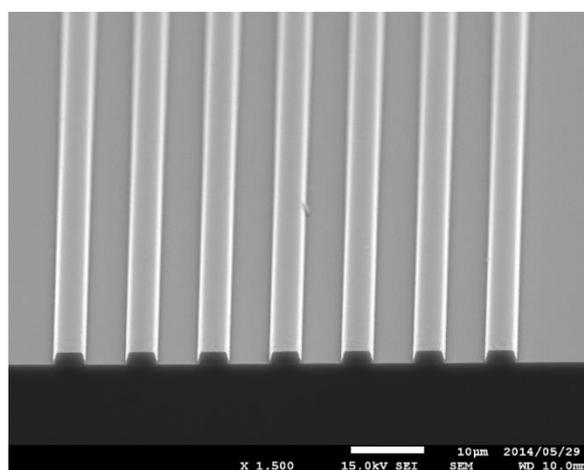


Figure 3.1.3 SEM picture (L/S: 5 μ m) of p-LPSQ
L/S: Line & Space Film thickness: 2 μ m

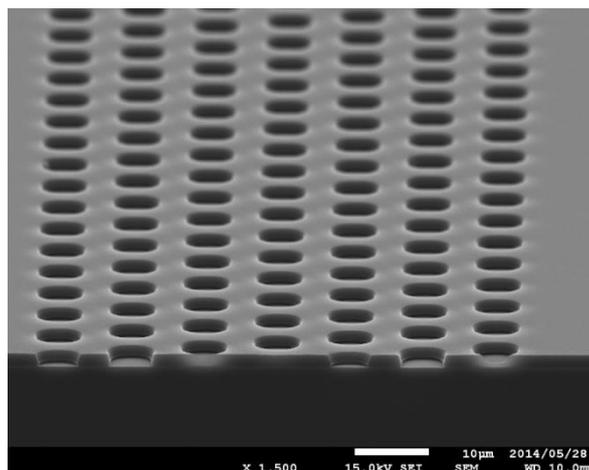


Figure 3.1.4 SEM picture (C/H: 5µm) of p-LPSQ
C/H: Contact hole. Film thickness: 2µm

3.2 Negative-tone photosensitive formulation (n-LPSQ)

On the other hand, n-LPSQ is simply formulated using PAG (photo-acid-generator) such as tri-sulfonium salt type as shown in Figure 3.2.1, which is sensitive to *i*-line (365 nm) UV. The lithography system of n-LPSQ is shown Figure 3.2.3 and the hardening of the polymer is based on the principle of homo-condensation of silanol. In other words, a reaction of silanol is promoted by the acid generated by the incident light from PAG as shown in Figure 3.2.2. As a result, the alkali dissolution speed decreases in the irradiant (exposed) area. A difference in the solubility thus occurs in the exposed area and unexposed area. In this way a pattern formation takes place.

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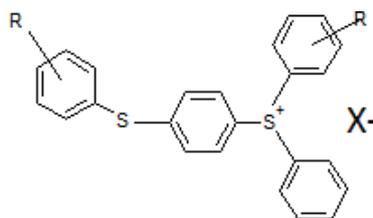


Figure 3.2.1 Sulfonium salt (PAG: SW-L1B produced by SANAPRO Co. Ltd.)

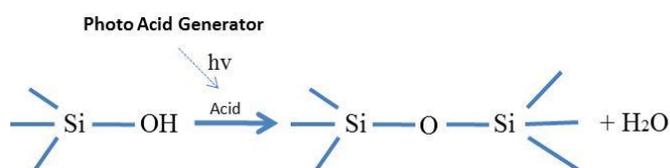


Figure 3.2.2 Basic reaction of negative-tone system

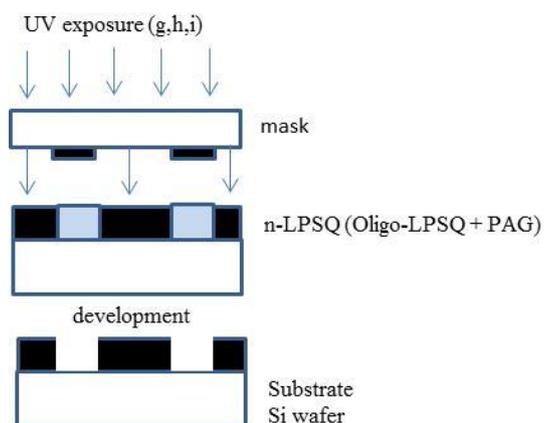


Figure 3.2.3 Schematic of Negative-tone system

The advantage of this system is that this type of photolithography process has been very commonly applied to produce TFTs similar to p-LPSQ. It is applied for 2000Å/s as ADR for standard negative-tone formulation. 3 μm L/S and 3 μm C/H was processed according to the procedure shown in Table 3.2.1.

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Table 3.2.1 Typical lithography procedure for n-LPSQ

	Procedure	Negative-tone
1	Pre-bake	100° C/90s
2	Exposure (Canon FX-604F: g, h, i-line)	20mJ/cm ²
3	PEB @ 100° C	90s
4	Development (2.38% TMAH)	120s
5	Rinse (Ion changed water)	60s
6	Flood exposure (g, h, i-line)	900mJ/cm ²

Lithographic character is sufficiently for TFTs in LCD (liquid crystal display) applications. The pattern resolution is about 3 μ m and the film thickness remaining after developing is about 96%. This performance is similar to the existing photosensitive material such as acrylic polymer which is the most commonly available and used photo-patternable organic polymer.

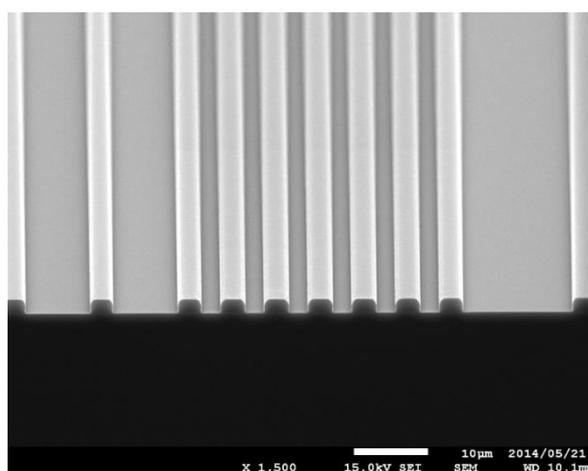


Figure 3.2.4 SEM picture (L/S: 3 μ m) of n-LPSQ (L/S: Line & Space. Film thickness: 2 μ m)

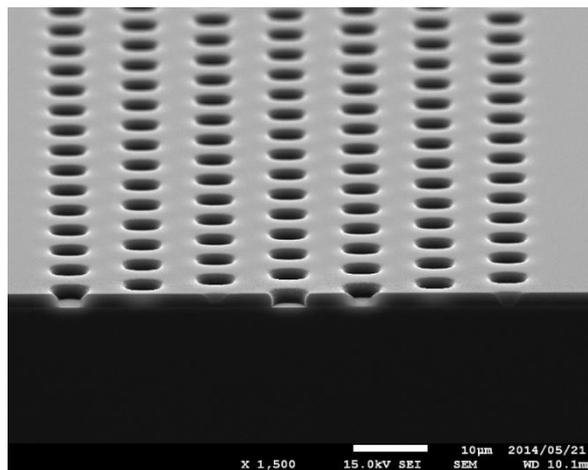


Figure 3.2.5 SEM picture (C/H: 3µm) of n-LPSQ (C/H: Contact hole. Film thickness: 2µm)

3.3 Transparency and thermal stability of oligo-LPSQ

3.3.1 Transparency

Optical transmittance of the oligo-LPSQ is very high (>98% @ 400nm with 2 µ m film thickness) as compared to other silicone materials and is stable exhibiting independence from post-bake temperature. Even after high thermal anneal at 400°C for 60mins. The oligo-LPSQ film maintain the same optical transparency as shown Figure 3.3.1.1.

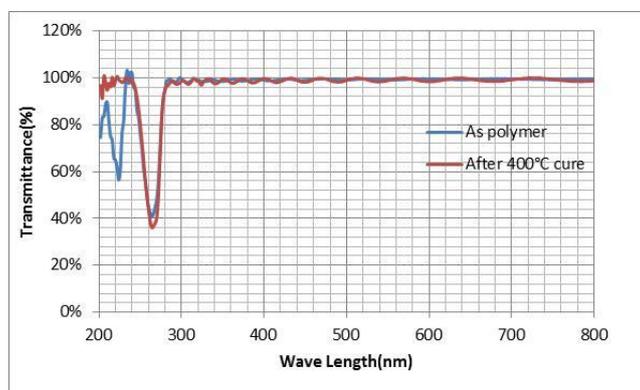


Figure 3.3.1.1 Optical transmittance of Oligo-LPSQ

3.3.2 TGA analysis

Figure 3.3.2.1 is shown thermal stability of raw polymer (SQ-1R) using TGA analysis.

SQ-1R showed high thermal stability and 5% degradation temperature was 525 °C.

This value is enough for application of TFT in LCD.

As the mention in Section 2, weight loss at 200°C was explain that it is caused by homo-condensation of silanol. It will be acceleration by photo-formulation.

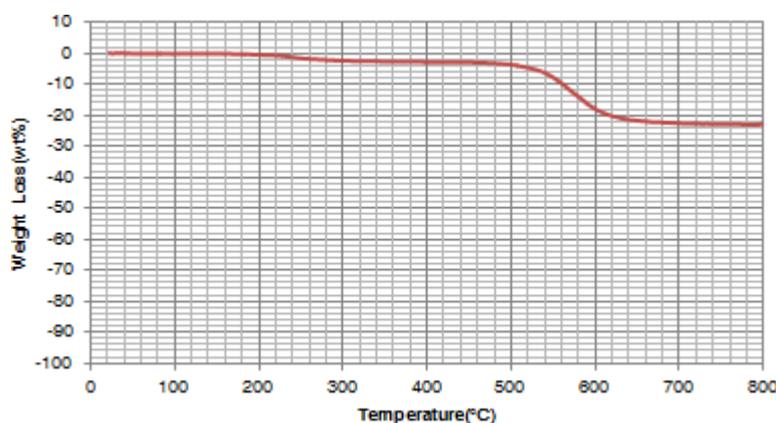


Figure 3.3.2.1 TGA analysis of SQ-1R

3.3.3 Dielectric Constant

Measurements of dielectric constant was carried out by casting MOS (metal-oxide-semiconductor) capacitor, wherein the polymer is considered as the oxide layer on an n-type Silicon substrate. The dielectric constant was calculated by using the set of following equations. A typical dielectric constant is under 3.2 at 1MHz as shown in Figure 3.3.3.1. This value is acceptable for applications related to dielectric layers in FPD and IC fields.

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$$1/C = 1/C_m - 1/C_{ox} \text{ -----1)}$$

At the storage layer of capacitance

$$1/C = 1/C_{ox}$$

C: Capacitance(F)

C_m: Measured Capacitance(F)

C_{ox}: Oxide (SQ) capacitance(F)

Here, dielectric constant is calculated using eq.2

$$C = \epsilon d/S \text{ -----2)}$$

$$\epsilon_r = \epsilon / \epsilon_0$$

ϵ_r : relative dielectric constant

ϵ : dielectric constant

ϵ_0 : dielectric constant in vacuum

d: thickness of film

S: area of electrode

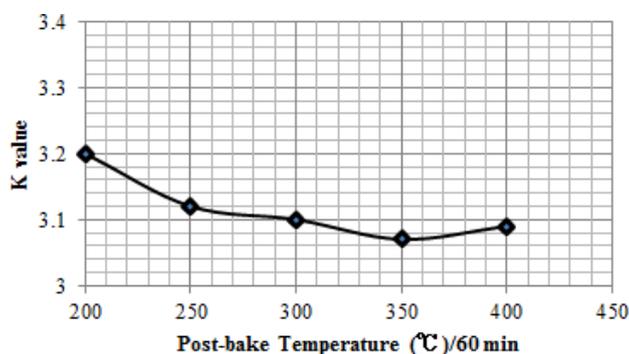


Figure 3.3.3.1 Variation in the dielectric Constant of SQ-Polymer with cure temp.

4. Conclusion

I have developed oligo-ladder phenylsilsesquioxane (oligo-LPSQ) and their derivatives. The scheme to synthesize oligo-LPSQ is easily and simple, the polymer yield is over 70% as the Si-base and has an alkaline solubility (2.38% TMAH solution).

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Here we presented features for the photo-pattern-able oligo-ladder SQ (p-type, n-type LPSQ) based on oligo-LPSQ. The process of p-LPSQ is basically compatible to conventional DNQ/Novolak system except for the different interaction strength of silanols as compared with phenols. And the patterning properties were good with a resolution of about 3 μ m at L/S pattern. On the other hand, n-LPSQ is easy to formulate with a PAG only. It is also good for pattern generation and the film shows high transparency even at 400°C. This result has enough properties as compared to existing organic based photo-patternable polymer such as acryl in the FPD technology field. And this is first report featuring LPSQ.

Moreover, further study is also necessary to maximize usage of the oligo-LPSQ performance, especially in the new positive tone system for silanol and negative tone system too.

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Chapter 4

General Conclusions and Scope in Future

SQ (silsesquioxane) is a resin consisting of three functional groups of $(\text{RSiO}_{1.5})$. By appropriately selecting a synthesis method, it is possible to obtain a cage structure or a ladder structure. These highly controlled structures are expected to result in extraordinary characteristics, which are generally not found with conventional silicones. The T^3_8 type of cage structures can be easily synthesized, thus by making a hybrid structure with existing resin or selecting a side chain structure with ligands it is possible to open various applications of these materials in terms of their photosensitive properties, etc. These achievements are mainly due to the rapid progress in synthesis techniques. However, the industrialization of these materials and their applications is still a distant dream.

On the other hand, after Brown et al. successfully explained these structures in the form of ladder structures, researchers had been working hard in this field since 1960s till date. However, as compared to POSS[®], due to the lack of specific details and difficulty in the synthesis of these structures much of the research work lacked to find any concrete applications. This suggests that the development of general synthetic methods for these structures could not proceed efficiently as expected till now.

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This time in this thesis, for the purpose of eliminating these difficulties in the synthesis process, I have investigated halosilane (trichlorosilane) and the alkal ligand having a lone pair of electrons for the synthesis of ladder structure. As a result, control of the monomer reactivity by complex formation between silicon and the ligand, which is similar to the ligand steric hindrance are assumed to take place. This structural control effect facilitates the possibility of easy formation of ladder type structures. The outstanding feature of this process is that, in order to reliably control the reactivity of the reaction through the use of solute is to control the reactivity at the liquid-liquid phase interface.

Moreover, several different ligands had been considered by me, but the bi-dentate ligand TMEDA was most superior in terms of its yield and reaction controllability. However, due to a few limitations I could not give sufficient considerations to the reaction mechanism. It still remains a challenge for us to work out in future. And as for the silicon ligand I examined only phenyl groups. In future, it is also necessary to consider methyl groups too.

In addition, if I undertake study on the variety of process factors involved, it is expected that the ladder structure could be obtained with a stable and high yield using the one-pot synthesis method demonstrated in this thesis. Even going further I strongly

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think that, similar to POSS[®], these ladder type structures can form hybrids with organic resins, could be easily constructed for studies in perspective of their applied research on photosensitivity, etc.

The structure control by ligands is a very interesting theme as such “chemistry” had not been deeply considered up till now.

As one of the important applied research, I have carried out work on a photosensitive ladder SQ, wherein the Novolak resin has been widely used as a base to assemble a photosensitive formulation for which, I investigated the lithographic characteristic. As a result, it could be shown that even lithography is highly possible using an oligo ladder SQ.

I think that there are the vast possibilities of an oligo-ladder SQ to various applications, which makes this work more meaningful.

I think the importance of silicon-based resins, especially in terms of SQ for electronic devices, heat resistance and transparency for FPD field have been wisely pointed out and I hope this study will help in further advancement of research and development in these fields. And in future, SQ materials will be use into FPD device as planarity layer, dielectric layer and new memories which is next generation architecture as shown in Figures 4.1 and 4.2.

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Figure 4.1 SQ Materials Insides in Future

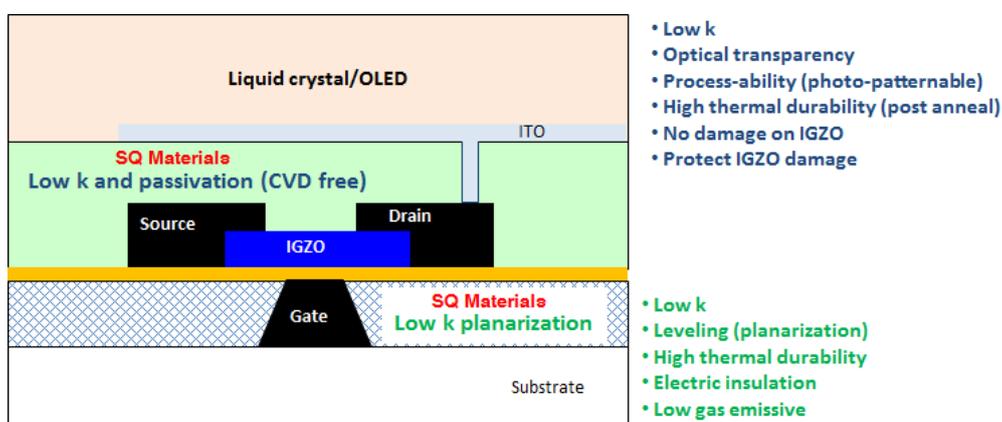


Figure 4.2 New Backplane Architecture for NXG (next generation) LCD and OLED-TV

Achievements

Presentation

1. **Y. Tashiro**, D. Yokoyama, T. Sekito, T. Nonaka.
“Characterization of New Silsesquioxane and Silsesquiazane Polymers”, **2010**, IDW
2. **Y. Tashiro**, D. Yokoyama, T. Nonaka.
“Development of New Silsesquioxanes” **2011**, 第 30 回 無機高分子研究討論会
3. **Y. Tashiro**, A. Miyazato and K. Ebitani
“Characterization of Photosensitive Composition based on oligo-ladder Phenylsilsesquioxane” ICPST-32, June 24-26, **2015**, B4-01.

Publication

1. **Y. Tashiro**, A. Miyazato and K. Ebitani
“One-Pot synthesis of Oligo-ladder Phenylsilsesquioxane (PPSQ) via Silicon-Amine Adducts at Aqueous-Organic Liquid Boundary”, *J. Inorg. Organomet. Polym.*, **2015**, DOI: 10.1007/s10904-015-0247-9
2. **Y. Tashiro**, A. Miyazato and K. Ebitani
“Characterization of Photosensitive Compositions based on Oligo-ladder Phenylsilsesquioxane”, *J. Photopolym. Sci. Technol.*, **2015**, 28(2) 239-245
3. **Y. Tashiro**, A. Miyazato and K. Ebitani
“One-Pot Synthesis of Oligo-ladder Phenylsilsesquioxanes via Silicon-Amine ligand adducts at aqueous-organic liquid boundary” *Dalton Transaction (RSC)* to be submitted.