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SCIENTIFIC PAPER

UDC 678.746.4:645.497

DOI 10.2298/CICEQ110911018J

EFFECTS OF ALUMINUM TRICHLORIDE AND MAGNESIUM CHLORIDE ON THE SYNTHESIS OF LADDER POLYPHENYLSILSESQUOXANE

Ladder polyphenylsilsesquioxane (Ph-LPSQ) has been synthesized at 80 °C through the hydrolysis and condensation of phenyltrichlorosilane (PhSiCl₃), with aluminum chloride (AlCl₃) or magnesium chloride (MgCl₂) as an assistant reactant. The Ph-LPSQ obtained has been characterized and analyzed by SEM, FTIR, TGA, ²⁹Si-NMR, and MALDI-TOF MS, and the effects of AlCl₃ and MgCl₂ on the structure regularity of Ph-LPSQ and the condensation polymerization have also been studied. The results showed that Ph-LPSQ could be obtained in the AlCl₃ and MgCl₂ systems, respectively, but the experimental phenomena and results showed significant differences between the two systems. SEM observation revealed spherical Ph-LPSQ particles from the PhSiCl₃/AlCl₃ system, but irregular and agglomerated Ph-LPSQ particles from the PhSiCl₃/1.5(MgCl₂) system. TGA, ²⁹Si-NMR, and MALDI-TOF MS indicated that the ladder structure of Ph-LPSQ from the PhSiCl₃/1.5(MgCl₂) system was more regular. In the PhSiCl₃/AlCl₃ system, Al could be incorporated into the ladder chain structure through competing reactions between Si-O-Al and Si-O-Si, which slightly decreased the regularity of the ladder chain structure of Ph-LPSQ. Mechanistic analysis suggests that the presence of AlCl₃ or MgCl₂ in the hydrolysis and condensation system favors the intermolecular condensation of intermediate products of polyhydroxyl silanol to form a regular ladder structure.

Keywords: polyphenylsilsesquioxane; ladder structure; aluminum chloride; magnesium chloride; synthesis.

Polyphenylsilsesquioxane (PPSQ) is a polysiloxane with the formula (C₆H₅SiO_{1.5})_n, which adopts a variety of structures such as random, cage, ladder, and bridge. Ladder polyphenylsilsesquioxane (Ph-LPSQ), which has a special rigid structure (Figure 1), offers a number of advantages, including good thermal stability, electrical insulation, selective permeability to gases, and good solubility in common organic solvents, and has thus attracted much research interest in recent years [1-4].

As early as 1960, Brown [5] first obtained Ph-LPSQ through thermal equilibrium condensation polymerization with KOH as catalyst, but a high boiling

point solvent such as biphenyl was needed in a later stage of the reaction; moreover, the regularity of the structure of the product was not very high. Since the 1980s, Zhang [6-8] has carried out a lot of work on the preparation and characterization of ladder-polysilsesquioxane, and presented a new synthetic method termed “stepwise coupling polymerization”, but the synthetic route was very complex.

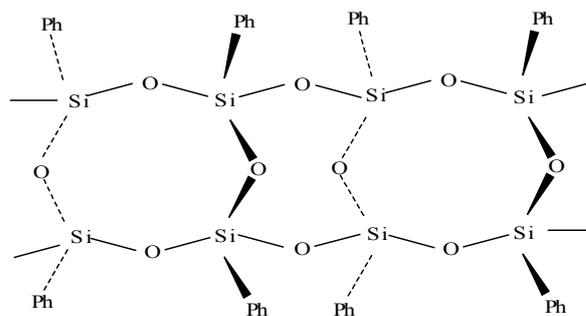


Figure 1. Typical chemical structure of Ph-LPSQ.

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Paper received: 11 September, 2011

Paper revised: 3 January, 2012

Paper accepted: 3 March, 2012

Many articles on the preparation of PPSQ have been published since. The structure and properties of PPSQ are influenced by the synthetic conditions, and the ladder structures of Ph-LPSQ are not identical under different synthetic conditions. For example, Takahashi [9] studied the effect of solvent on the thermoplasticity and thermosetting of PPSQ, and found that ethanol significantly affected the thermal softening of PPSQ, and that the regularity of the PPSQ was not very high. Li and Shi [10,11] studied the effect of polymerization conditions on the molar mass of PPSQ, and noted that the amount of catalyst and reaction temperature were important factors, and that different synthetic conditions could lead to differences in the solubility of the PPSQ. Moreover, Ph-LPSQ synthesized under different polymerization conditions with four kinds of catalyst (namely CaF_2 , LiF, KOH and dicyclohexylcarbodiimide) showed obvious differences in the regularity of the Ph-LPSQ chain structure. The authors identified KOH as a suitable catalyst for synthesizing ladder PPSQ of high regularity. Nishida and Yamane [12] discussed the effects of the catalyst, temperature, solvent, and other synthetic conditions on the structure of Ph-LPSQ. They concluded that using a low concentration of monomer and a hydrophilic solvent was optimal for obtaining an oligomer with low silanol content that could further polymerize to form regular Ph-LPSQ.

In our previous work [13], Ph-LPSQ was synthesized at 80 °C through the hydrolysis and condensation of phenyltrichlorosilane (PhSiCl_3), with aluminum chloride (AlCl_3) or magnesium chloride (MgCl_2) as assistant reactant. In this paper, we discuss the different effects of AlCl_3 and MgCl_2 on the regularity of the chain structure and the condensation polymerization of Ph-LPSQ.

EXPERIMENTAL

Materials

Phenyltrichlorosilane (PhSiCl_3) was purchased from Dalian Yuanyong Organosilicon Plant, China. Tetramethylammonium hydroxide solution ($\text{N}(\text{CH}_3)_4\text{OH}$) was purchased from Xingfu Fine Chemicals Research Institute, China. AlCl_3 , MgCl_2 , benzene, methanol, ethanol and hexane were purchased from Beijing Chemical Reagent Company and were used without further purification.

Synthesis of Ph-LPSQ

Ph-LPSQ was synthesized by the hydrolysis and condensation of PhSiCl_3 . PhSiCl_3 was hydrolyzed in benzene by the dropwise addition of water at 0 °C. AlCl_3 or MgCl_2 was dissolved in water to prepare an

aqueous solution. The organic phase of the hydrolysate was mixed with the aqueous solution of AlCl_3 or MgCl_2 by stirring, the mixture was heated to 80 °C, and then a methanolic solution of $\text{N}(\text{CH}_3)_4\text{OH}$ of a certain concentration was added to the mixture. The solution condensation reaction was allowed to proceed for 24 h under vigorous stirring. After the reaction was complete, the solid product from side reaction was filtered off, and the filtrate was collected. A white precipitate was obtained upon addition of ethanol to the filtrate. Finally, Ph-LPSQ was collected by filtration, washed with hexane, and dried in a vacuum oven at 100 °C.

At a $\text{PhSiCl}_3/\text{AlCl}_3$ or $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ mole ratio of 6, the Ph-LPSQ obtained is referred to as Ph-LPSQ-Al or Ph-LPSQ-Mg, respectively.

Measurements

Scanning electron microscopy (SEM) observation was performed with a Hitachi S650 instrument. Main accessory: energy dispersive x-ray spectroscopy (EDX), EDAX9100.

Thermal gravimetric analysis (TGA) was performed with a Netzsch 209 F1 thermal analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere over the range from room temperature to 800 °C.

Fourier-transform infrared spectroscopy (FTIR) analysis was performed on a Thermofisher 6700 spectrometer at a resolution of 4 cm^{-1} with a total of 32 scans. Raman analysis was performed on a RFS100 spectrometer at a resolution of 4 cm^{-1} with a total of 100 scans.

^{29}Si -nuclear magnetic resonance (^{29}Si -NMR) spectra and ^1H -nuclear magnetic resonance (^1H -NMR) spectra were recorded on a Bruker AV600 instrument with a pulse width of 5 μs and a pulse delay of 5 s. The solvent was C_6D_6 .

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis was performed on a Bruker BIFLEX III device. It was equipped with a pulsed nitrogen laser ($\lambda = 337$ nm, pulse width = 3 ns, average power = 5 MW at 20 Hz). The extraction voltage in the TOF analyzer was 20 kV, and ions were obtained by irradiation just above the threshold laser power (about 1/3 of the average laser power). Samples were measured in the positive-ion mode. Usually, 50 spectra were accumulated.

RESULTS AND DISCUSSION

Yield of Ph-LPSQ-Al: 7.64 g (59.1%). GPC: $M_n = 5183$, polydispersity = 1.10. FTIR: $\nu = 3050, 1594, 1434 \text{ cm}^{-1}$ (phenyl), $\nu = 1100$ and 1021 cm^{-1} (Si–O–Si),

$\nu = 580\text{--}780\text{ cm}^{-1}$ (C–C, C–Si). Raman: $\nu = 3053$ and 1000 cm^{-1} (Ar–H), $\nu = 1594\text{ cm}^{-1}$ (phenyl). $^1\text{H-NMR}$ (C_6D_6 , δ , ppm, TMS): 7.74, 7.15, 6.98 (H in phenyl). $^{29}\text{Si-NMR}$ (C_6D_6 , δ , ppm): -82 to -76 . XRD (2θ): 7.3 and 19.4° .

Yield of Ph-LPSQ-Mg: 5.14 g (39.7%). GPC: $M_n = 5780$, polydispersity = 1.12. FTIR: $\nu = 3050$, 1594 and 1434 cm^{-1} (phenyl), $\nu = 1100$ and 1021 cm^{-1} (Si–O–Si), $\nu = 580\text{--}780\text{ cm}^{-1}$ (C–C, C–Si). Raman: $\nu = 3053$ and 1000 cm^{-1} (Ar–H), $\nu = 1594\text{ cm}^{-1}$ (phenyl). $^1\text{H NMR}$ (C_6D_6 , δ , ppm, TMS): 7.74, 7.15, 6.98 (H in phenyl). $^{29}\text{Si-NMR}$ (C_6D_6 , δ , ppm): -82 to -76 . XRD (2θ): 7.3 and 19.4° .

These characterization results verify that the Ph-LPSQ synthesized from the two systems had a

structure of ladder chains free from remaining hydroxyl groups [13]. Their XRD spectra are almost the same, as Figure 2 shows.

Figure 3 shows the morphologies of the Ph-LPSQ-Al and Ph-LPSQ-Mg particles. Most of the Ph-LPSQ-Al particles were spherical and had diameters of $0.5\text{--}1.5\text{ }\mu\text{m}$, while the Ph-LPSQ-Mg particles were irregular and agglomerated with sizes of $1\text{--}3\text{ }\mu\text{m}$.

Phenomena descriptions in synthesizing Ph-LPSQ-Al and Ph-LPSQ-Mg

Ph-LPSQ-Al

As summarized in Table 1, hydrolysis of PhSiCl_3 in the $\text{PhSiCl}_3/\text{AlCl}_3$ system was accompanied by emulsification in the organic phase, as manifested in

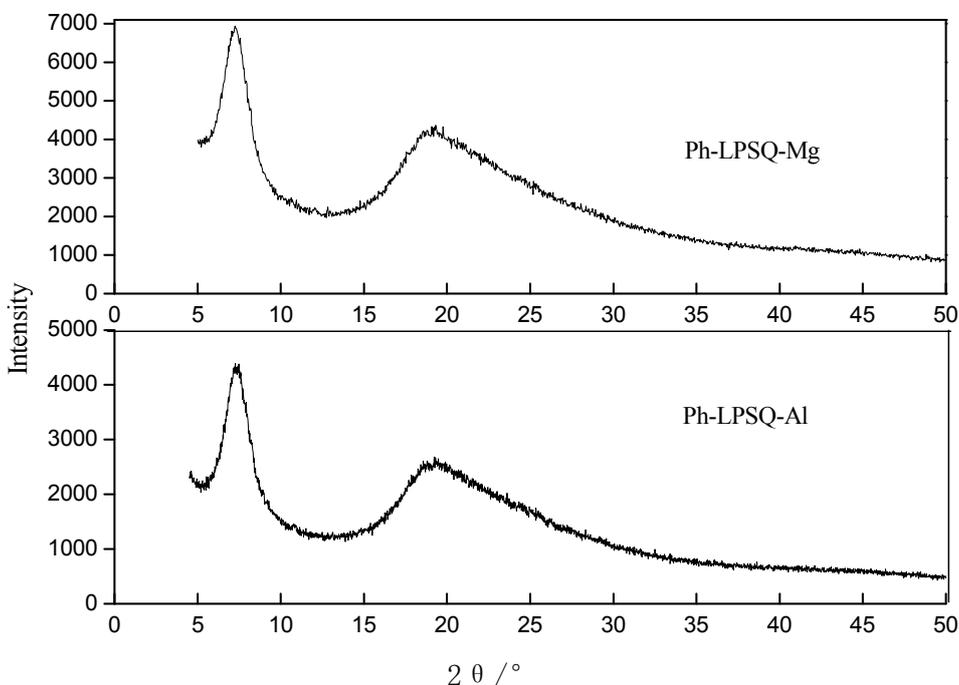


Figure 2. XRD Spectra of Ph-LPSQ.

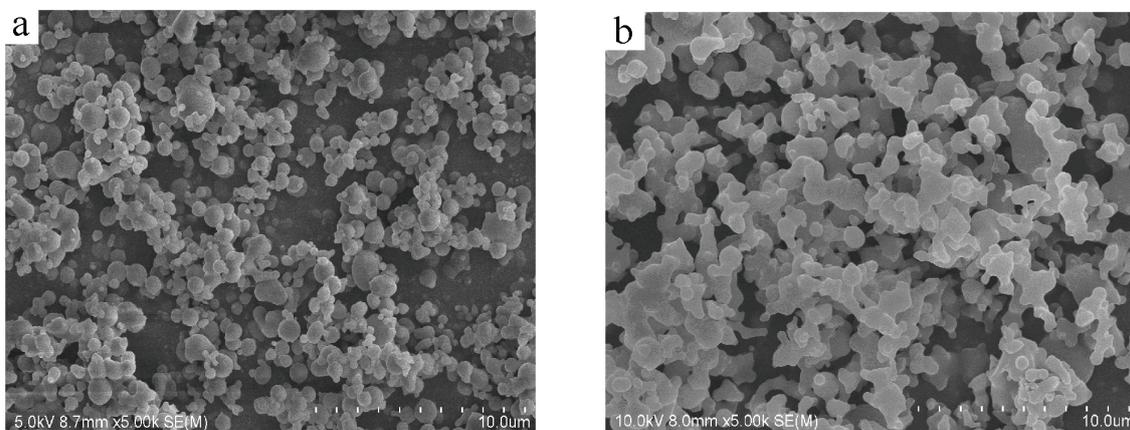


Figure 3. SEM Micrographs (5.0 k) of a) Ph-LPSQ-Al and b) Ph-LPSQ-Mg particles.

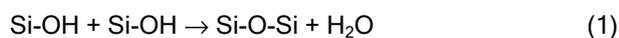
Table 1. Comparison of phenomena in synthesizing Ph-LPSQ-Al and Ph-LPSQ-Mg

Observations	Experimental phenomena	
	PhSiCl ₃ /AlCl ₃ system	PhSiCl ₃ /1.5(MgCl ₂) system
Change in appearance of the organic phase upon hydrolysis of PhSiCl ₃ at 0 °C	Clear → ivory-white	Clear → ivory-white
Change in appearance of the organic phase upon addition of aqueous solution of metal chloride	Ivory-white → clear	Ivory-white → slightly turbid
Color of product from side reaction after polycondensation	White	Light-yellow
Appearance of organic phase after polycondensation	Relatively clear	Slightly ivory-white
Yield of Ph-LPSQ	Relatively high	Relatively low

a change in appearance from clear to ivory-white. Upon addition of the aqueous solution of AlCl₃ and stirring for 5 min at room temperature, the organic phase reverted to clear, that is, the emulsification disappeared.

In order to further study the effect of the aqueous solution of AlCl₃, the reaction solution was analyzed by FTIR. The resulting spectra are shown in Figure 4.

Although the temperature was low (0 °C) when the PhSiCl₃ was hydrolyzed, from Figure 4A it is apparent that due to the energy imparted to the reaction solution by vigorously stirring, there was a low degree of self-condensation of silanol according to reaction (1) to form Si-O-Si with bands at 1000–1100 cm⁻¹. Of course, non-condensed Si-OH (3280 and 890 cm⁻¹) remained in the solution.



By addition of the aqueous solution of AlCl₃ and stirring for 5 min, the reaction (1) might be reversed

due to the presence of a little water. This was manifested in a reduction in intensity of the Si-O-Si peak at 1000–1100 cm⁻¹, as shown in Figure 4B. However, it is strange that the broad absorbance peak at 3280 cm⁻¹ also diminished. This may have been due to the influence of Al³⁺. There might be an interaction between Al³⁺ and Si-OH to form Si-O-Al, which would reduce the amount of Si-OH and promote the reverse of reaction (1).

However, the FTIR spectrum of the reaction solution reverted to the original spectrum shown in Figure 4A on leaving the mixture to stand for an extended period. It is believed that the Si-O-Al was unstable due to the presence of H₂O. Si-O-Al could be hydrolyzed to Si-OH in the absence of the stirring energy, maintaining the reaction solution in a low degree of condensation. These observations indicate that Si-O-Si was more stable than Si-O-Al. It seems that the self-condensation reaction of Si-OH was suppressed or slowed down by the aqueous solution of AlCl₃. Under heating in the presence of a catalyst, compe-

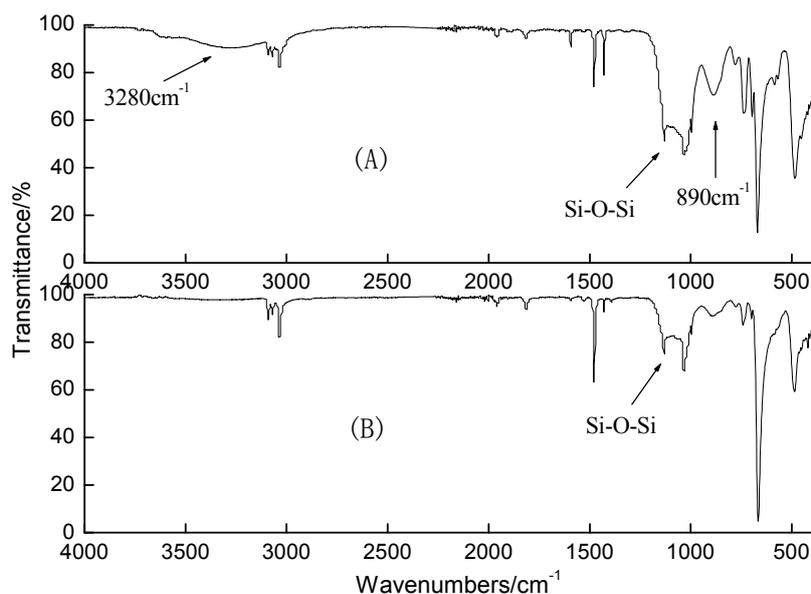


Figure 4. FTIR spectra of reaction solutions: A) organic phase of hydrolysis solution of PhSiCl₃; B) after adding an aqueous solution of AlCl₃ to the organic phase and stirring for 5 min.

ting reaction between Si-O-Si and Si-O-Al may have occurred.

If no aqueous solution of AlCl_3 was added to the organic phase of the hydrolysate of PhSiCl_3 , the condensation reaction could result in a high yield of polyhedral oligomeric octaphenyl silsesquioxane (OPS) [14] upon changing the concentration of catalyst. In addition, in synthesizing Ph-LPSQ-Al, a small amount of product from side reaction was obtained in the form of a white powder, which was considered to be OPS by comparison of its FTIR spectrum (Figure 5) with that of an authentic sample. Furthermore, it was found that the FTIR spectrum of the product from side reaction did not vary with the amount of AlCl_3 . EDX analysis of the TGA residue of the product from side reaction indicated that it contained Si, O and C, but that no Al was present.

Ph-LPSQ-Mg

As summarized in Table 1, initial emulsification in the organic phase was also seen in the hydrolysis of PhSiCl_3 in the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ system, but the emulsification phenomenon still persisted after adding the aqueous solution of MgCl_2 and stirring for 5 min at room temperature. This was characterized by a change in the appearance of the organic phase from ivory-white to slightly turbid. The organic phase was still ivory-white after the polycondensation.

The product from side reaction obtained from the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ system was a light-yellow powder that was easily agglutinated; it was different from that obtained for the $\text{PhSiCl}_3/\text{AlCl}_3$ system. In addition, the structure of the product from side re-

action varied with the amount of MgCl_2 , as shown in Figure 6.

The concentration of PhSiCl_3 was kept constant. When the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ mole ratio was 7, the FTIR spectrum of the product from side reaction featured a sharp absorption peak at 3701 cm^{-1} , which might be attributed to free hydroxyl, and absorption peaks at $1000\text{--}1100\text{ cm}^{-1}$, which indicated the presence of Si-O-Si. When the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ mole ratio was 6, the absorption peaks of Si-O-Si ($1000\text{--}1100\text{ cm}^{-1}$) and phenyl (1434 , 1594 and 3050 cm^{-1}) were clearly intensified, while the sharp absorption peak at 3701 cm^{-1} was clearly diminished. Moreover, this FTIR spectrum was similar to that of OPS. When the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ mole ratio was 5, a broad peak appeared in the region $3100\text{--}3560\text{ cm}^{-1}$, but the other absorbance peaks were similar to those in Figure 6A. These observations indicated that in the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ system, the structure of the product from side reaction was greatly influenced by the amount of MgCl_2 .

The TGA residue of the product from side reaction obtained from the synthesis of Ph-LPSQ-Mg was analyzed by EDX. It was found that the residue contained Si, O, C and Mg. In particular, the atomic percentage of Mg could reach 27%, thus constituting a large proportion of the product from side reaction.

Regularity of the Ph-LPSQ-Al and Ph-LPSQ-Mg ladder chain structures

There was little difference between Ph-LPSQ-Al and Ph-LPSQ-Mg in terms of their FTIR, Raman and $^1\text{H-NMR}$ spectra or XRD analyses. The $^{29}\text{Si-NMR}$

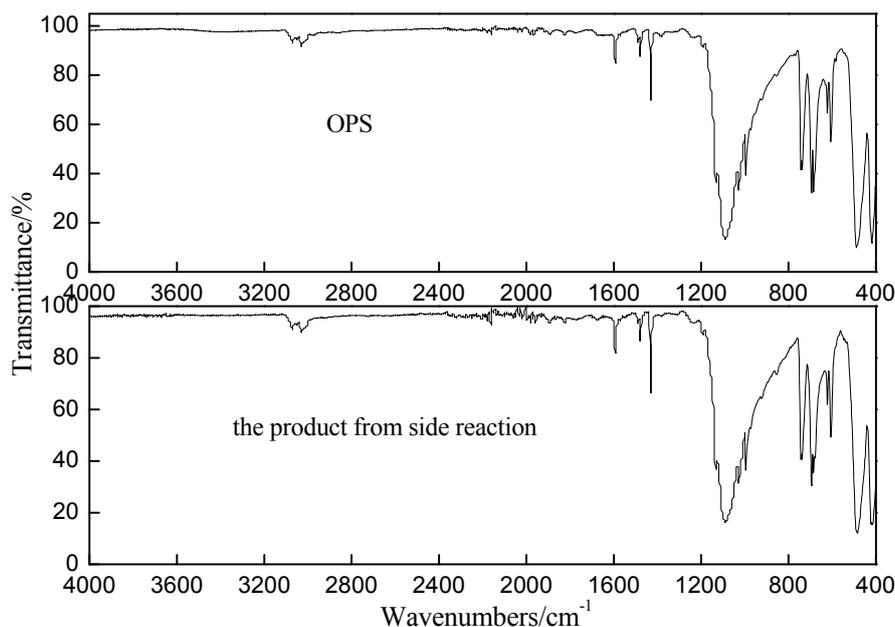


Figure 5. FTIR Spectra of the OPS and the product from side reaction in synthesizing Ph-LPSQ-Al.

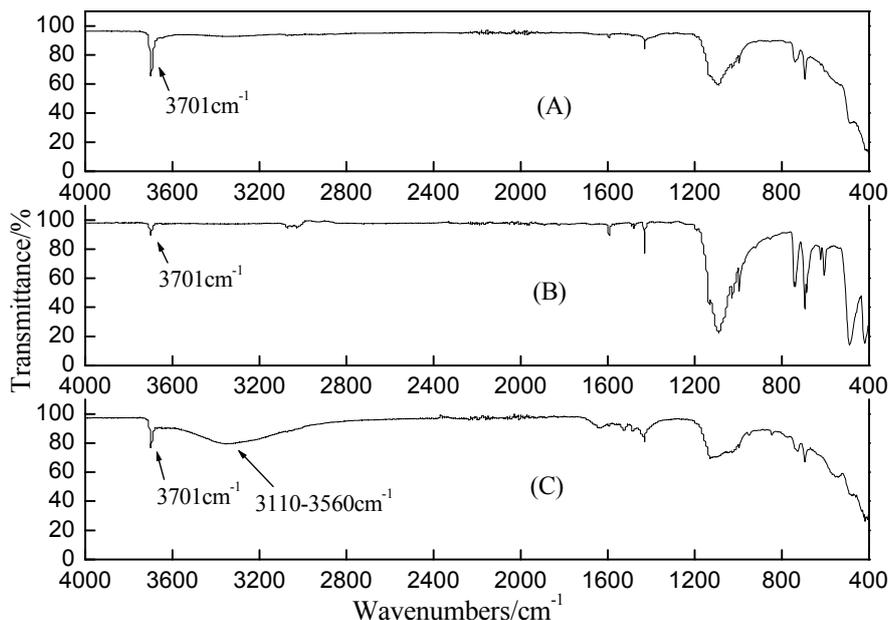


Figure 6. FTIR Spectra of products from side reaction from $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ systems: A) $\text{PhSiCl}_3/1.5(\text{MgCl}_2) = 7$; B) $\text{PhSiCl}_3/1.5(\text{MgCl}_2) = 6$; C) $\text{PhSiCl}_3/1.5(\text{MgCl}_2) = 5$.

spectra of Ph-LPSQ-Al and Ph-LPSQ-Mg were shown in Figure 7. Prado [15] presented that, a very narrower resonance peak width at half-height ($w_{1/2}$) means a highly ordered ladder structure, and the smaller the $w_{1/2}$, the more regular the structure. The $w_{1/2}$ of the sample from Prado was 6.7 ppm, and it could be seen from Figure 7 that the $w_{1/2}$ was 2.5 ppm. Besides, Figure 7 showed that both samples are seen to show the same resonance peak position, but there are some differences in the peak shapes. The ^{29}Si -NMR spectrum of Ph-LPSQ-Mg is smoother than that of Ph-LPSQ-Al, indicating simpler Si atom environments. In other words, the ladder structure of Ph-LPSQ-Mg was more regular.

The thermal stability of Ph-LPSQ is closely related to the regularity of its ladder chain structure.

TGA data for Ph-LPSQ are presented in Table 2, including the T_{onset} , defined as the temperature at 5% weight loss, and the T_{max} , defined as the temperature at maximum weight loss rate, along with the char residues at 800 °C. It can be seen that the thermal stability of Ph-LPSQ-Mg ($\text{PhSiCl}_3/1.5(\text{MgCl}_2) = 6$) was better than that of Ph-LPSQ-Al ($\text{PhSiCl}_3/\text{AlCl}_3 = 6$), and that the T_{onset} of Ph-LPSQ-Mg was about 40 °C higher than that of Ph-LPSQ-Al. This provided indirect evidence that the ladder chain structure of Ph-LPSQ-Mg was more regular.

In addition, it was found that the thermal stability of Ph-LPSQ varied little with the amount of MgCl_2 (such as $\text{PhSiCl}_3/1.5(\text{MgCl}_2) = 5$ or 6), but more obviously with the amount of AlCl_3 (such as $\text{PhSiCl}_3/\text{AlCl}_3 = 5$ or 6), as shown in Table 2. This may be

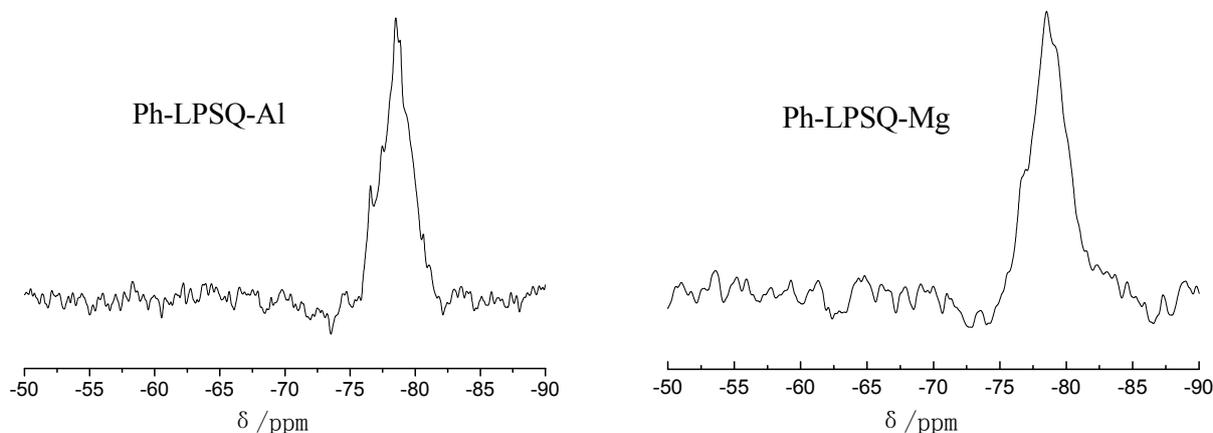


Figure 7. ^{29}Si -NMR spectra of Ph-LPSQ.

correlated with the fact that Al could be incorporated into the ladder chains.

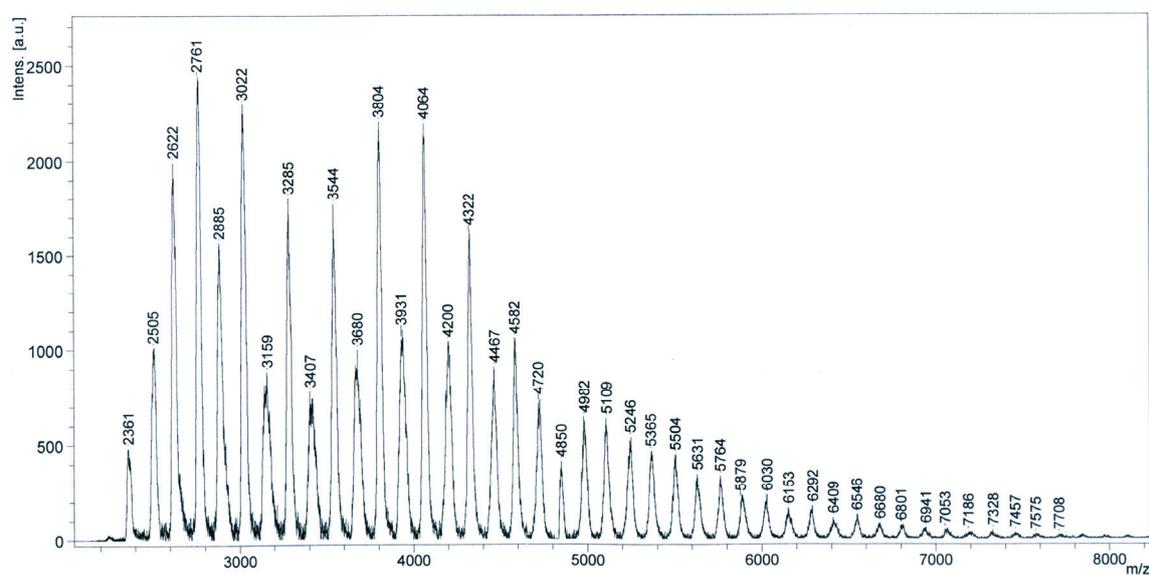
Table 2. TGA data for Ph-LPSQ

Mole ratio		T_{onset} °C	T_{max} °C	Residue at 800 °C, %
PhSiCl ₃ /AlCl ₃	6	521	572	75.7
	5	413	523	56.5
PhSiCl ₃ /1.5(MgCl ₂)	6	560	581	75.4
	5	542	566	75.2

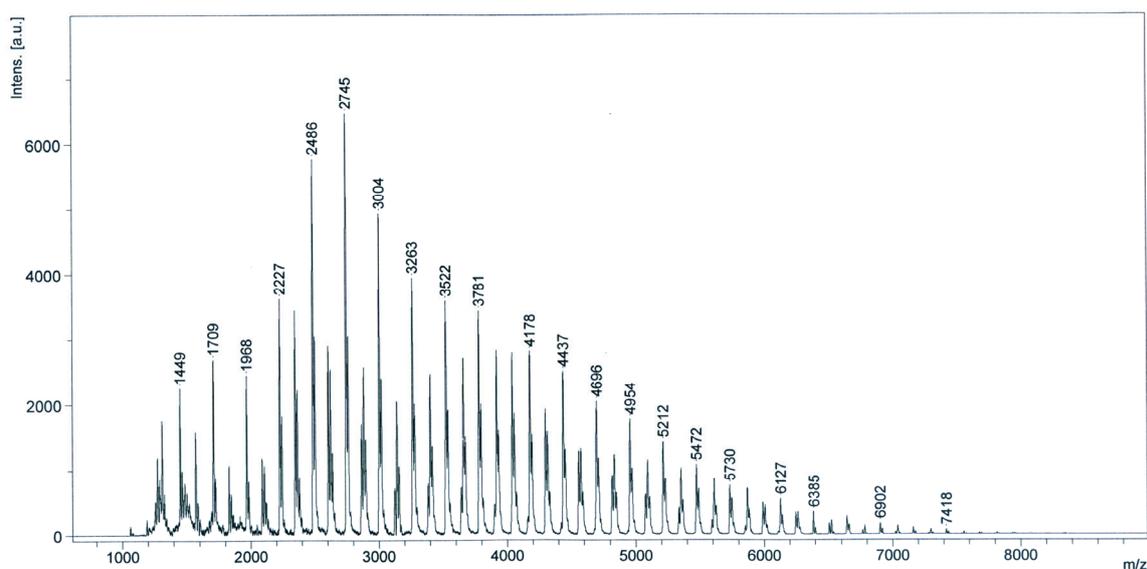
For the synthesized Ph-LPSQ, the ladder chain should have different lengths, that is to say, different

molecular weights. According to the chemical structure (Figure 1), the difference in molecular weight between different Ph-LPSQ chains should be 258, or multiples of 258, corresponding to $(\text{Si}_2\text{Ph}_2\text{O}_3)_n$ ($n \geq 1$).

Figure 8 shows the MALDI-TOF mass spectra of Ph-LPSQ-Al and Ph-LPSQ-Mg synthesized from the two systems. It can be seen that for Ph-LPSQ-Mg the difference in molecular weights between two neighboring molecular ion peaks was 258 or 259, while the peak interval for Ph-LPSQ-Al was 251, 258, 261 or 266. These observations indicated that the ladder structure of Ph-LPSQ-Mg was indeed more regular than that of Ph-LPSQ-Al, which is in agreement with the results of the ²⁹Si-NMR analysis.



(a)



(b)

Figure 8. MALDI-TOF Mass spectra for Ph-LPSQ.

The TGA residues obtained from Ph-LPSQ-Al and Ph-LPSQ-Mg at 800 °C were analyzed by EDX. It was found that the residue from Ph-LPSQ-Mg contained only Si, O and C, and was free from Mg, whereas the residue from Ph-LPSQ-Al contained Si, O, C and Al, and the atomic percentage of Al was about 0.78%. From this, we surmise that Mg did not participate in the condensation polymerization of the hydrolysate, and thus was not incorporated into the ladder chains, but that Al might have participated in this way and so might have been incorporated into the ladder chains through competing reactions to form Si-O-Si and Si-O-Al bonds, respectively. The presence of a small amount of Al-O in the structure could slightly affect the regularity of the Ph-LPSQ-Al chain (Figure 9).

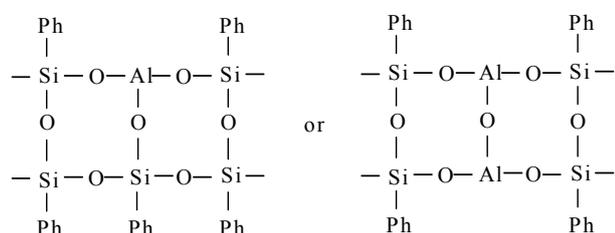


Figure 9. Suggested structures for Ph-LPSQ-Al ladder chain incorporating Al atoms.

Mechanistic analysis

Differences in the structures and morphologies of the Ph-LPSQ and products from side reaction derived from the two systems can be attributed to the effects of the respective metal ions, which have different physical and chemical properties. Mg is an alkaline earth metal and Mg^{2+} is alkaline, whereas Al is a main group element and the alkalinity of Al^{3+} is weak. It is known that the hydrolysate of PhSiCl_3 is weakly acidic due to the presence of a small amount of HCl, while the catalyst $(\text{N}(\text{CH}_3)_4\text{OH})$ is weakly alkaline. Hence, the pH and the emulsification state will be changed to a certain extent by the addition of AlCl_3 or MgCl_2 . These changes may not only affect the target product Ph-LPSQ [16,17], but also the products from the side reaction.

In particular, Mg is present only in the form of Mg^{2+} in the reaction system, whereas Al may not only be present in the form of Al^{3+} , but probably also in covalent bonds (Si-O-Al). The presence of Si-O-Al will certainly affect the condensation of Si-OH in the reaction system and the regularity of the final Ph-LPSQ ladder chain structure.

In the hydrolysis and condensation of RSiX_3 (where X = OH, Cl, OCH_3 , OCH_2CH_3 , and so on), many intermediate structures can be formed depend-

ing on the reaction conditions and the nature of the monomers. These intermediates include linear, cyclic, and polycyclic silanols [18]. Sprung and Guenther [19] assumed that a cage-structured siloxane, like OPS, could ultimately be formed by the frequent formation of these intermediates. Under other conditions, irregular or ladder polymeric silsesquioxanes can be produced.

Brown and Vogt [20] postulated that cage polyhedral oligomeric silsesquioxanes were formed because large cyclic intermediates underwent intramolecular condensation to form polycyclic siloxanes rather than intermolecular condensation. Nishida [12] suggested that soluble ladder polysilsesquioxane could only be obtained by reducing the functionality of the hydrolysate (that is, the amount of OH groups), which would favor intermolecular condensation of the intermediates.

It is known [14] that the hydrolysis and condensation of PhSiCl_3 can result in cage-structured OPS in high yield in the absence of an aqueous solution of AlCl_3 or MgCl_2 . That is to say, the reaction tends towards the intramolecular condensation in this case. The fact that the presence of Al^{3+} or Mg^{2+} results in ladder polyphenylsilsesquioxane implies that these metal ions disfavor the cage and random structures, but favor the formation of the ladder polysilsesquioxane structure by the intermolecular condensation of intermediates such as polyhydroxylated cyclic siloxane molecules, as shown in Figure 10.

CONCLUSIONS

Ph-LPSQ has been synthesized at 80 °C through the hydrolysis and condensation of PhSiCl_3 , with AlCl_3 or MgCl_2 as assistant reactant. Even though both the $\text{PhSiCl}_3/\text{AlCl}_3$ and $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ systems furnished the target product, ladder polyphenylsilsesquioxane, the difference between them was very evident. SEM revealed contrasting morphologies of spherical Ph-LPSQ-Al particles (0.5–1.5 μm) and irregular and agglomerated Ph-LPSQ-Mg particles (1–3 μm). The product from side reaction from $\text{PhSiCl}_3/\text{AlCl}_3$ was cage-structured octaphenylsilsesquioxane (OPS), while that from $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ was variable. ^{29}Si -NMR, TGA, and MALDI-TOF MS analyses have indicated the ladder structure of Ph-LPSQ-Mg to be more regular than that of Ph-LPSQ-Al.

In the $\text{PhSiCl}_3/\text{AlCl}_3$ system, some Al atoms could be incorporated into the ladder chain structure of polyphenylsilsesquioxane, which slightly affected its regularity. In the $\text{PhSiCl}_3/1.5(\text{MgCl}_2)$ system, however, Mg atoms could not be incorporated in this way. This is because Al atoms can form Si-O-Al bonds and

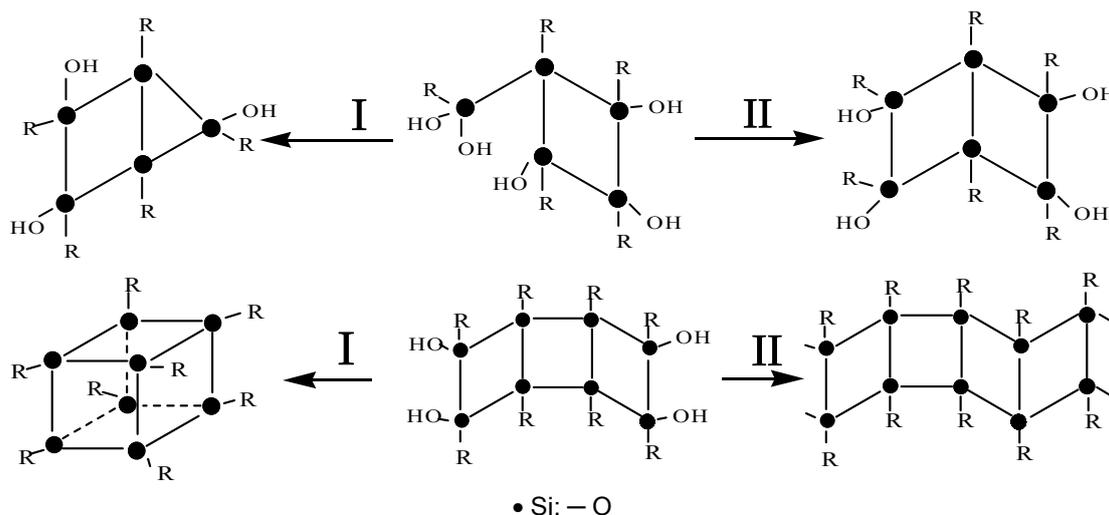


Figure 10. Scheme of intramolecular condensation (I) and intermolecular condensation (II) for cyclic polyhydroxyl siloxanes.

cause competition between Si-O-Si and Si-O-Al. Another important factor is that the different alkalinities of Mg^{2+} and Al^{3+} could influence the pH and emulsification state of the reaction solutions. The presence of Al^{3+} or Mg^{2+} favors the intermolecular condensation of polyhydroxyl intermediates to form a ladder chain, as opposed to intramolecular condensation to form cage structures or random chains.

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NAUČNI RAD

UTICAJ ALUMINIJUM-HLORIDA I MAGNEZIJUM-HLORIDA NA SINTEZU LESTVIČASTOG POLIFENILSILSESKVIOKSANA

Lestvičast polifenilsilsekskvioksan (Ph-LPSQ) je sintetisan na 80 °C procesima hidrolize i kondenzacije feniltrihlorsilana (PhSiCl₃) sa aluminijum-hloridom (AlCl₃) ili magnezijum-hloridom (MgCl₂) kao pomoćnim reaktantom. Dobijeni Ph-LPSQ je okarakterisan i analiziran SEM, FTIR, TGA, ²⁹Si NMR i MALDI-TOF MS metodama. Takođe, proučavani su uticaji AlCl₃ i MgCl₂ na regularnost strukture Ph-LPSQ i kondenzacionu polimerizaciju. Rezultati su pokazali da je Ph-LPSQ moguće dobiti u sistemima sa AlCl₃ i MgCl₂, ali su eksperimentalni fenomen i rezultati pokazali značajne razlike između ova dva sistema. SEM analizom su otkrivene sferne Ph-LPSQ čestice iz sistema PhSiCl₃/AlCl₃, ali i neregularne i aglomerisane Ph-LPSQ čestice iz sistema PhSiCl₃/1.5 (MgCl₂). TGA, ²⁹Si-NMR i MALDI-TOF MS su pokazale da je lestvičasta struktura Ph-LPSQ iz sistema PhSiCl₃/1,5 (MgCl₂) mnogo regularnija. U sistemu PhSiCl₃/AlCl₃, Al se može inkorporirati u lestvičastu strukturu lanca kroz konkurentske reakcije između Si-O-Al i Si-O-Si, koja znatno manja regularnosti strukture lestvičastog lanca Ph-LPSQ. Mehanicistička analiza ukazuje da prisustvo AlCl₃ ili MgCl₂ kod hidrolize i kondenzacije favorizuje međumolekularnu kondenzaciju intermedijarnih proizvoda polihidroksilsilanola radi formiranja regularne lestvičaste strukture.

Ključne reči: polifenilsilsekskvioksan; lestvičasta struktura; aluminijum-hlorid; magnezijum-hlorid; sinteza.