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A Facile Approach for Preparing Polymethylphenylsilsesquioxane with Well-defined Ladder Structure via Nonhydrolytic Condensation

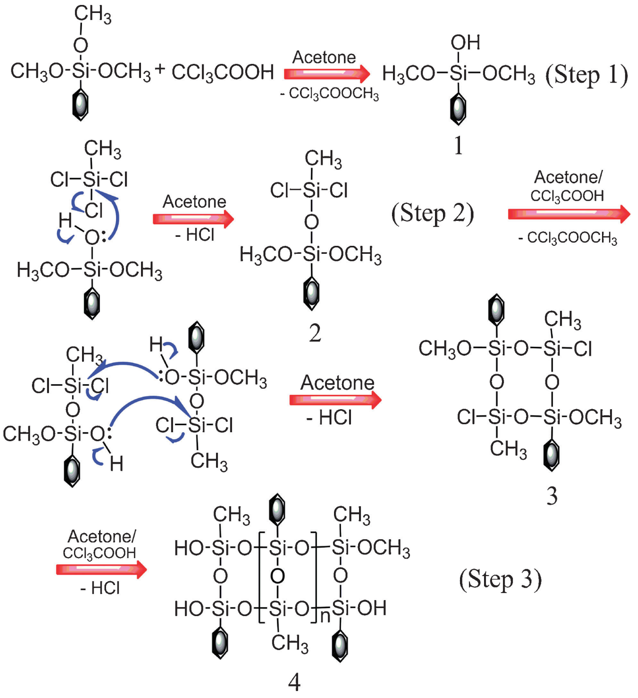
Xiu Wei Jia,[1] Min Zhi Rong,*[2] Ming Qiu Zhang,*[2] and Xiao Ji Ye[1]
[1]*Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, DSAPM Lab, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, P. R. China*
[2]*Materials Science Institute, Sun Yat-sen University, Guangzhou 510275, P. R. China*

(Received June 17, 2010; CL-100565; E-mail: cesrmz@mail.sysu.edu.cn, ceszmq@mail.sysu.edu.cn)

A novel nonhydrolytic condensation approach was proposed, which enabled successful synthesis of well-ordered ladder-like polymethylphenylsilsesquioxane for the first time. In comparison with aqueous hydrolysis, the present route is more promising, which is easily carried out with readily available starting materials, and is applicable to a wide range of organosilanes.

Due to the unique two-dimensionally ordered structures, ladder-like polysilsesquioxane (LPSQ) are anticipated to be superior to single-chain silicones in terms of chemical, physical, and electrical properties. The first ladder polyphenylsilsesquioxane (PPSQ) was obtained by Brown et al.,[1] however, their results were controverial.[2] So far, various methods have been developed for construction of polysilsesquioxane with real ladder chains.[3] It is worth noting that all the reported works utilized aqueous hydrolysis and polycondensation starting from $RSiX_3$ precursors ($X = Cl$ and OR). In general, hydrolysis of highly active $RSiX_3$ proceeds very quickly, and condensation occurs concurrently with hydrolysis, which inevitably results in structure defects and randomness along with ladder double-chains. To solve this problem, strict control of each step between hydrolysis and condensation has to be achieved.[4] The weak interaction arising from silanol groups and/or template molecules of precursors also helps to retain the pseudo-ladder model of hydrolysates before polycondensation.[5] Nevertheless, these approaches are designed for certain precursors carrying specific groups. A widely applicable, simple, and facile technique for synthesis of polysilsesquioxane with perfect ladder structure has yet to be developed.

In contrast to the rapid process associated with aqueous hydrolytic polycondensation, "nonaqueous" hydrolysis condensation is characterized by slow reaction and straightforward control. These might somehow endow the latter condensation with high selectivity.[6,7] Hereinafter we show the feasibility of this idea (Scheme 1). CCl_3COOH was used as a catalyst because it can be removed from the ultimate product. Synthesis of **4** begins with acidolysis of 0.085 mol $PhSi(OCH_3)_3$ in the presence of 0.014 mol CCl_3COOH for 3–6 h in 110-mL methyl isobutyl ketone (Step 1) under dry argon atmosphere at 20 °C, which leads to dimethoxyhydroxyphenylsilane (**1**) and by-product methyl trichloroacetate. Then, an important intermediate, **2**, 1,1-dichloro-1-methyl-3,3-dimethoxy-3-phenyldisiloxane ($MeCl_2Si–O–SiPh(OCH_3)_2$) forms via single selective dehydrochlorination between **1** and $MeSiCl_3$ (0.120 mol, Step 2. Here, an excess amount of $MeSiCl_3$ has to be used regarding its mild escape from the system during the reaction). After that, one methoxy group of the resultant disiloxane **2** is transformed into hydroxy by acidolysis again. Meanwhile, selective condensation between two-single-acidolyzed disiloxane molecules **2** gives a cyclotetrasiloxane structure **3**, and the latter gradually grows to ordered ladder-like polymethylphenylsilsesquioxane (PMPSQ) in a similar way (**4**, Step 3. More details of the synthesis procedures are available in the Electronic Supporting Information quoted as ref. 8). That is, cyclotetrasiloxane **3** is acidolyzed to form cyclotetrasiloxanediols, which react with two acidolyzed disiloxane **2** to give a three-ring system. This process repeats via hetero-functional condensation based on "nonaqueous" hydrolysis condensation, and at last **4** is obtained. The strong organic acid catalyst, CCl_3COOH, favors acidolysis of $PhSi(OCH_3)_3$ by forming CCl_3COOCH_3 rather than chlorination of $PhSi(OCH_3)_3$, and then recovers by reacting with HCl to give out a by-product of CH_3Cl. Other acids, like acetic acid, HCl and H_2SO_4, fail to catalyze the reaction, because they cannot take the role of CCl_3COOH in the above reaction mechanism.



Scheme 1. Non-hydrolytic condensation for construction of ladder-like polymethylphenylsilsesquioxane.

After the reaction, the white powder product was collected by distillation in vacuo, dissolved in toluene and precipitated in methanol, filtrated, and dried in vacuum, giving a yield of 31.2%, number average molecular weight (M_n) and distribution

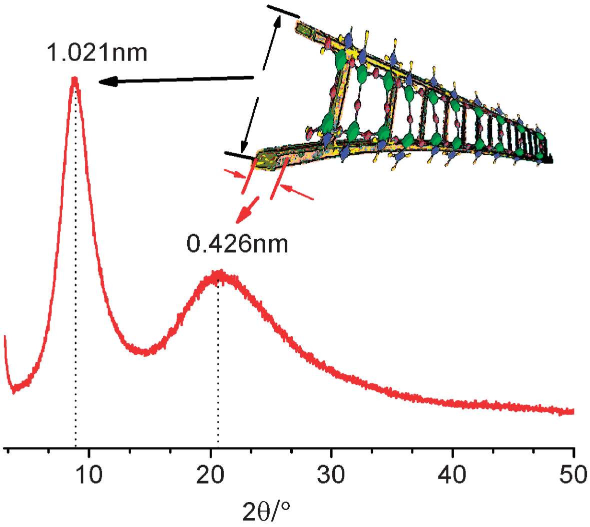


Figure 1. XRD spectrum of **4** with simulative charts showing spacing width and thickness of the ladder-like structure.

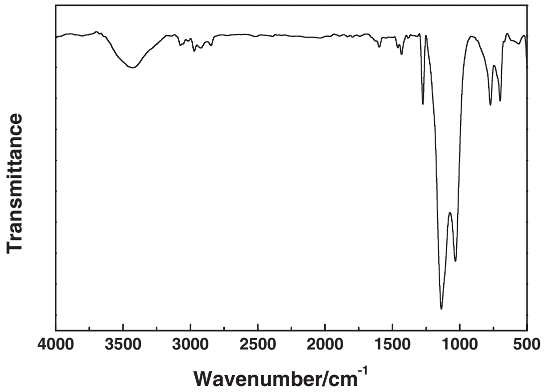


Figure 2. FTIR spectrum of ladder PMPSQ prepared by non-hydrolytic condensation using trichloroacetic acid as catalyst and methyl isobutyl ketone as solvent. The peaks coincide with the molecular structure of the product: –Si–O–Si– (1132 and 1033 cm^{-1}), $–C_6H_5$ (3100, 1430, and 701 cm^{-1}), $–CH_3$ (2900, 1461, and 779 cm^{-1}), $Si–C_6H_5$ (1602 cm^{-1}), $Si–CH_3$ (1272 cm^{-1}), end Si–OH (3350, 1450, and 732 cm^{-1}), and end $Si–OCH_3$ (2847 cm^{-1}).

of 10827 and 1.83, respectively. The lower yield should be ascribed to the slow reaction rate. The product can be dissolved in benzene, toluene, acetone, tetrahydrofuran, and chloroform, but cannot be dissolved in methanol, acetonitrile, and ethanol. The material possesses very high thermal stability, as characterized by the initial pyrolytic temperature of 532 °C.[8]

X-ray diffraction (XRD) reveals that the obtained PMPSQ exhibits characteristic peaks corresponding to typical ladder-like polysilsesquioxane (Figure 1). The sharp peak at $2\theta = 10^\circ$ corresponds to a spacing width of 1 nm between the double chains, while the other at $2\theta = 20^\circ$ represents a thickness of 0.40 nm of the ladder-like structure.[1,5,9] These values are in reasonable agreement with the results of molecular simulation.[8] The attributes of these XRD diffraction patterns have been widely accepted and were further ascertained by Harkness et al.,[10,11] who demonstrated a narrow and sharp small-angle diffraction peak at $2\theta = 8^\circ$ ascribed to the intramolecular gap between the chains during the transformation of crystalline phase to mesomorphic states of poly(diphenylsiloxane). Moreover, Fourier transform infrared (FTIR) spectrum of PMPSQ shows that the peak of Si–O–Si bond splits into two at 1132 and 1033 cm^{-1} (Figure 2), and the former is stronger than the latter, meaning PMPSQ falls into the category of well-ordered ladder polysilsesquioxane.[8,12] Other peaks assigned to $Si–C_6H_5$ and $Si–CH_3$ are also identified from the spectrum, while the appearance of Si–OH and $Si–OCH_3$ is derived from the end groups of PMPSQ. The ^{29}Si nuclear magnetic resonance (NMR) spectrum of PMPSQ exhibits only two signals attributed to $Ph–Si(OSi)_3$ and $Me–Si(OSi)_3$ at −64 and −78.6 ppm (Figure 3). ^1H NMR and ^{13}C NMR spectra show that the integral ratios of hydrogen or carbon peaks distributed to phenyl/methyl groups are 1.7:1 and 5.5:1, respectively. These results coincide with the strict composition correlated to regular PMPSQ.

We found that different solvents, incl. acetone, methyl isobutyl ketone, toluene, and chloroform, have no evident influence on the structure of PMPSQ except a slight change in M_n. In addition, varying reaction time of Step 1 results in a similar structure of PMPSQ as demonstrated by XRD and FTIR spectra, but dissimilar M_n and yields.[8] On the other hand, the resuming time of Step 3 obviously affects M_n and yield rather than regularity of the products. In general, longer Step 3 favors higher yield. Naturally, a question is raised: why the non-hydrolytic condensation is bound to produce ordered PMPSQ.

By carrying out in situ ^1H NMR and ^{13}C NMR, the formation of PMPSQ in a sealed cell was monitored.[8] Figure 4 shows that the content of Si–OH increases at a very slow rate during acidolysis until the start of Step 2 at 26 h, implying that $PhSi(OCH_3)_3$ is steadily acidolyzed with CCl_3COOH to give **1** that cannot be further acidolyzed or condensed to form disiloxane. This behavior can be ascribed to deactivation of one silanol group attached to organosilane.[12] Afterwards, the amount of Si–OH drastically decreases (by 11-fold) when $MeSiCl_3$ is added into the system (corresponding to Step 2). Clearly, formation of **2** due to dehydrochlorination proceeds very fast. The significant distinction between rates of acidolysis and condensation, the inertness of condensation among Si–OH groups, and the extremely high reactivity of Si–OH with Si–Cl ensure a superior selectivity for the condensation. In other words, the preferred dehydrochlorination of silanol groups with chlorosilanes rather than condensation among Si–OH themselves is facilitated. This mechanism provides the necessary basis for constructing real ladder structure. Then, Step 2 along with Step 3 proceeds steadily in the following two hours, leading to relatively tempered decrease of Si–OH content until the minimum. Subsequently, Step 3 plays the main role as reflected by the slow increase of the amount of end Si–OH of **4** in the next 147 h. Owing to the above-mentioned deactivation mechanism, i.e., single acidolyzed disiloxane ($MeCl_2Si–O–SiPh(OCH_3)OH$) is hard to be further acidolyzed, construction of **4** from the condensation of single acidolyzed **2** should be selectable and controllable in Step 3. Eventually, the reaction approaches equilibrium with constant content of Si–OH within a time span of 327 h. The diminishing trend of $Si–OCH_3$ basically coincides with that of Si–OH, but less evident because of the presence of CCl_3COOCH_3. The appearance of CCl_3COOCH_3

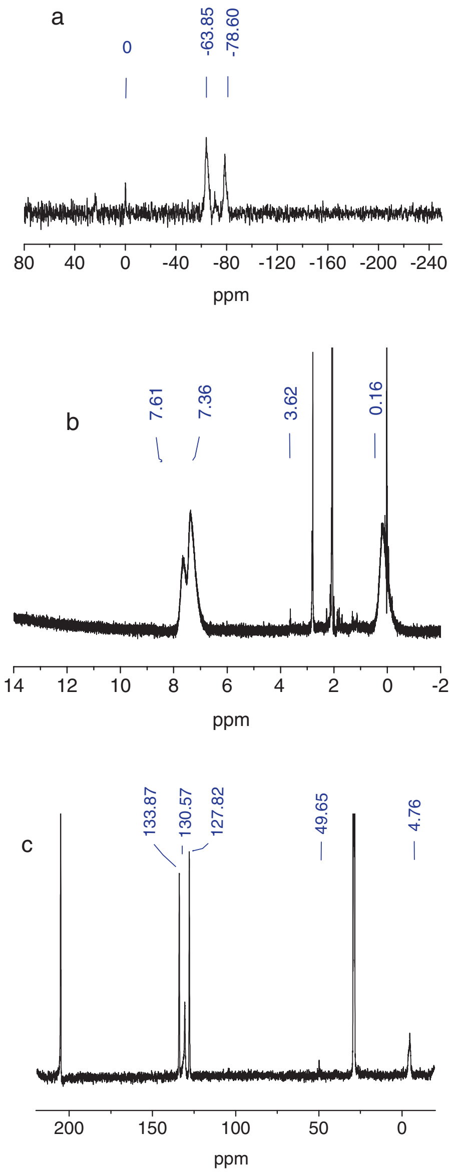


Figure 3. ^{29}Si NMR spectrum (a), ^{1}H NMR (b), and ^{13}C NMR (c) spectra of ladder PMPSQ prepared by nonhydrolytic condensation using trichloroacetic acid as catalyst and methyl isobutyl ketone as solvent. The characteristic peaks in the spectra are listed below. ^{29}Si NMR: Si–CH$_3$ (T^3, -64 ppm), Si–C$_6$H$_5$ (T^3, -78.6 ppm). ^{1}H NMR: Si–CH$_3$ (0.16 ppm), Si–C$_6$H$_5$ (7.61 and 7.36 ppm). ^{13}C NMR: Si–CH$_3$ (4.76 ppm), Si–C$_6$H$_5$ (127.8, 130.6, and 133.9 ppm).

and ClCH$_3$ accompanyed by the reaction, as revealed by the in situ ^{13}C NMR spectra, also evidences the mechanism.[8]

In this context, it is understood that the key steps of the nonhydrolytic route lie in the tardy acidolysis, the reaction inertness among Si–OH groups, and very fast condensation between Si–OH and Si–Cl groups, which permit selective condensation of the acidolyzed disiloxane and generate well-ordered ladder structure.

In conclusion, we have developed a novel nonhydrolytic condensation approach, enabling synthesis of well-ordered ladder-like polymethylphenylsilsesquioxane. Compared with aqueous hydrolysis, the present route is more promising, easy to conduct with readily available starting materials, and applicable to a wide range of organosilanes.

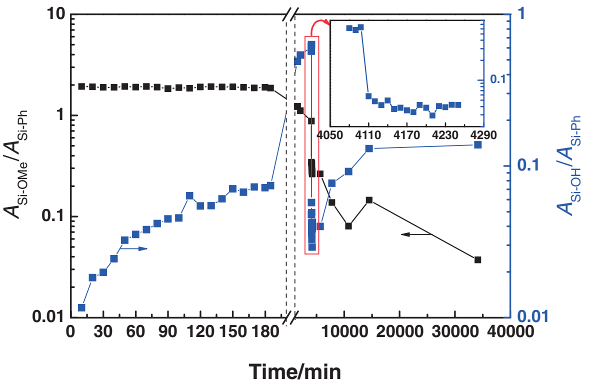


Figure 4. Dependences of Si–OH and Si–OCH$_3$ contents on reaction time measured by in situ ^{1}H NMR.

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