

SYNTHESIS AND CHARACTERIZATION OF LADDER-LIKE POLYDECYLSILSESQUIOXANE*

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Abstract Ladder-like polydecylsilsesquioxane (LPDS) was synthesized by a preaminolysis reaction of decyltrichlorosilane with ethylene diamine, followed by hydrolysis and polycondensation reaction. LPDS is soluble in a nonpolar solvent such as heptane and insoluble in a high polar solvent such as methanol. It was characterized by IR, $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, GPC and X-ray diffraction.

Keywords Ladder-like polydecylsilsesquioxane, Preaminolysis reaction

INTRODUCTION

Since Brown first reported the synthesis and stereochemical configuration of a ladder-like polyphenylsilsesquioxane in 1960^[1], many chemists have been interested in its special structure and potential applications. In recent years, a series of highly regular ladder-like polysilsesquioxanes and their copolymers, including polymethylsilsesquioxane^[2], polyphenylsilsesquioxane, polyhydrosilsesquioxane^[3] and polyvinylsilsesquioxane^[4] have been successfully synthesized by our group via the preaminolysis method. They exhibit high regularity, good film-forming ability and excellent solubility in many organic solvents. To date, however, the ladder-like polysilsesquioxanes with long side-chain group have not been reported in the literature. In order to explore the new approach to the ladder-like polymer derived from trifunctional monomer with a bulky group by the preaminolysis method, the ladder-like polydecylsilsesquioxane, which has potential applications as lubricant, was first synthesized. Its structure was characterized by IR, $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, GPC and X-ray diffraction.

EXPERIMENTAL

Materials and Techniques

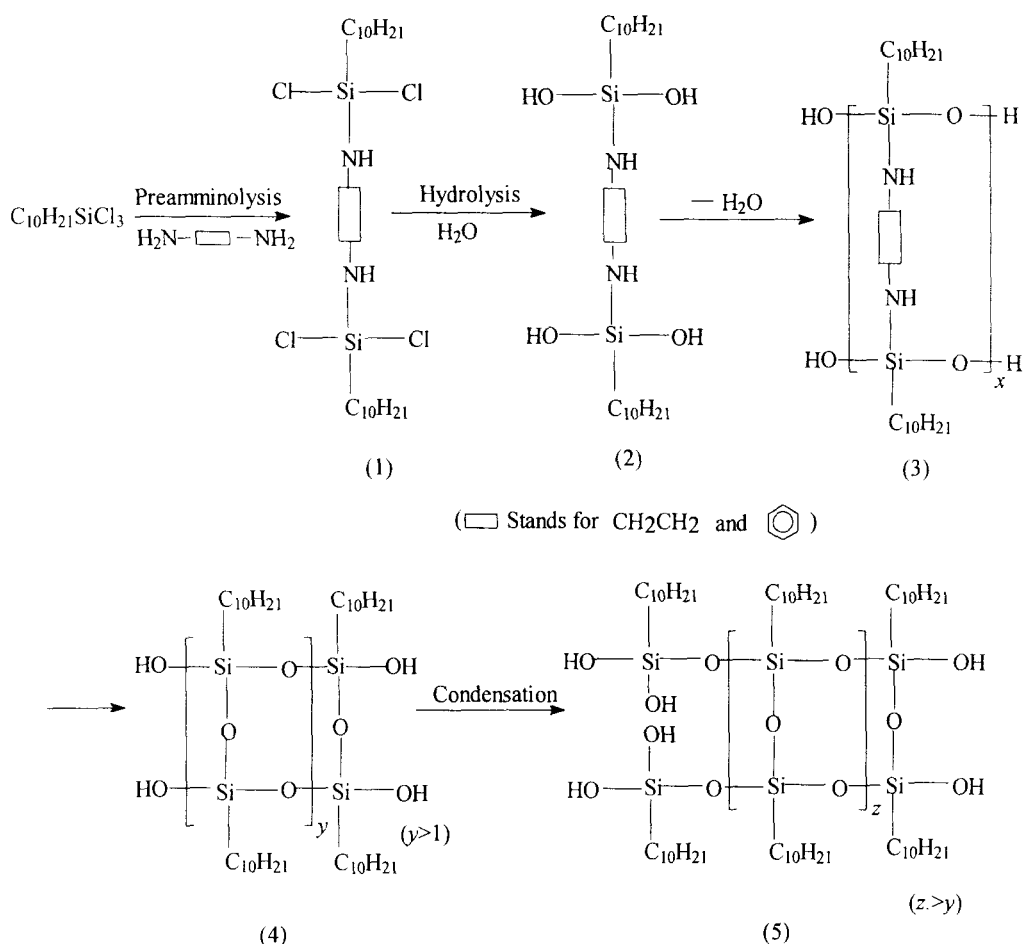
All reagents and solvents are commercially available and of analytical reagent grade. Toluene was purified by completely removing methylthiophene with concentrated sulphuric acid and distilled out on sodium sand. The IR spectrum was recorded on PE-80 IR spectrophotometer. The X-ray diffraction was carried out on Rigaku DMAX/38 diffractometer. $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$ measurements were performed on JNH-FX100 (JBOX). Molecular weight was determined with C-R2AX (Shimadzu) GPC.

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Scheme 1 The synthetic route of the ladder-like polydecylsilsesquioxane

Synthesis of the Ladder-Like Polydecylsilsesquioxane

A solution of 40 mL dried acetone containing 13.3 mL (0.2 mol) of ethylenediamine (EDA) was added dropwise into a solution of 100 mL of toluene dissolved with 55.1 g (0.2 mol) of decyltrichlorosilane upon vigorous stirring at 0°C for preamminolysis and the stirring was continued for 3 h; a light pink ammonium salt was then produced. Then, a mixture of 20 mL acetone, 25 mL water and 1.6 mL hydrochloric acid was added into the flask and stirred for 10 h at 0 ~ 8°C, and kept stirring for an additional 6 h at 90°C. A small amount of distilled water was poured into the flask to dissolve all the pink ammonium salt formed. The organic layer was washed with NaCl-saturated aqueous solution and distilled water until it reaches neutral pH, then acetone was removed by vacuum distillation and the solution was dried with anhydrous sodium sulphate for 10 h. After the anhydrous sodium sulphate was filtered out and toluene was removed under reduced pressure, 50 mL of xylene as condensation solvent was poured into the flask, the system was stirred in the presence of 2 drops of potassium hydroxide dissolved in methanol solution (6 mg/mL) as polycondensation catalyst and equilibrated at 125°C for 48 h. The reaction product was washed the same way as before. The final polymer product was dried at 50°C in a vacuum oven. An oil-like liquid was obtained at 90 % yield.

RESULTS AND DISCUSSION

Synthesis

In comparison with the hydrolysis for producing ladder-like polyhydrosilsesquioxane and polymethylsil-sesquioxane at the low temperature of $-10 \sim -15^{\circ}\text{C}$ [2, 3], the temperature of hydrolysis for preparing polydecylsil-sesquioxane was raised to 90°C , but hydrolysis was still incomplete. Hydrochloric acid must be added to the system, so that hydrolysis can be accelerated and accomplished completely. From Scheme 1, we can see that the steric hindrance around Si—N bond of (1) is large because decyl group is larger than H-atom and methyl group, therefore, the hydrolysis for producing polydecylsil-sesquioxane was difficult.

The ladder-like polymethylsil-sesquioxane could usually be condensed under basic conditions and the molecular weight easily reached 10^6 [2], but condensation of the polysilsesquioxane with a bulky group is far more difficult, and the molecular weight obtained was rather low [5-10]. During the condensation of LPDS, condensation catalysts such as *tri-i*-butylamine, *tri*-ethylamine, ethylenediamine, tetramethylammonium hydroxide and tetrabutylammonium hydroxide were used, but the molecular weight of products measured by GPC were less than 2000.

Potassium hydroxide was chosen as catalyst and higher-boiling xylene was used as the solvent for condensation and water was removed azeotropically along with xylene at 125°C . The condensation time was 48 h. From Fig.1, it can be seen that molecular weight of the product detected by GPC is 6000, and the molecular distribution is narrow. Similarly, the steric hindrance of long side-chain group affects the condensation of Si—OH, it is difficult to obtain high molecular weight product.

The long chain in the title polymer is nonpolar, while Si—O has polarity, therefore, LPDS is soluble in nonpolar solvent such as heptane and insoluble in strong polar solvent such as methanol.

IR Spectrum

In the IR absorption spectrum (Fig.2), the absorption bands at 2960 cm^{-1} and 1375 cm^{-1} can be assigned to the asymmetrical stretching vibration of C—H and symmetrical deformation vibration of $-\text{CH}_3$. The bands appearing at 2925 cm^{-1} , 2850 cm^{-1} , 1460 cm^{-1} and 720 cm^{-1} are attributed to the C—H asymmetrical stretching, symmetrical stretching, asymmetrical deformation and rocking vibration of $-\text{CH}_2$, respectively. Meanwhile, the polymer shows broad absorption bands of Si—O

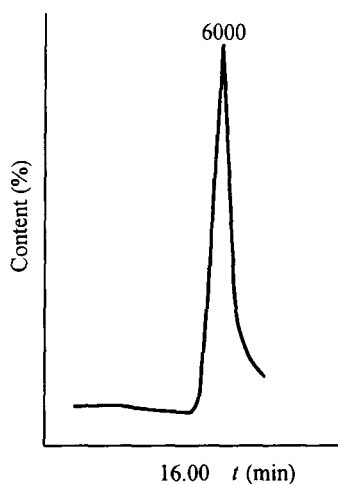


Fig.1 GPC curve

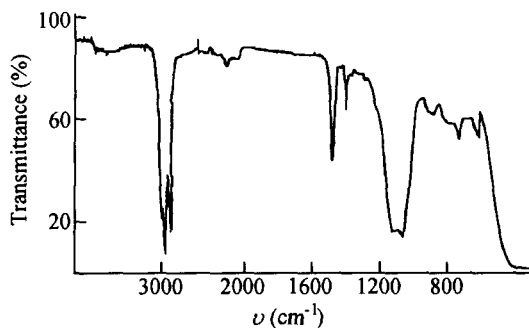


Fig.2 IR spectrum

at 1050 cm^{-1} and 1130 cm^{-1} . Therefore, the ladder-like polydecylsilsesquioxane has been successfully synthesized.

¹H-NMR Spectrum

Two peaks are seen in Fig.3. Because the H-atom absorption of —CH_3 and —CH_2 associated with Si-atom appears at nearly same position, two peaks overlap at $\delta = 0.8$. The other peak at $\delta = 1.22$ is due to the H-atom absorption of —CH_2 connecting with —CH_3 .

²⁹Si-NMR Spectrum

There are two main peaks in the ²⁹Si-NMR spectrum. The peak at $\delta = -70.42$ belongs to the absorption of the perfect Si-atom connecting to the $\text{—CH}_2\text{—SiO}_{3/2}$ group, while the peak at $\delta = -60.00$ belongs to the defective Si-atom connecting to the Si—OH. Therefore, There are some defective structures in the polymer.

X-ray Diffractogram

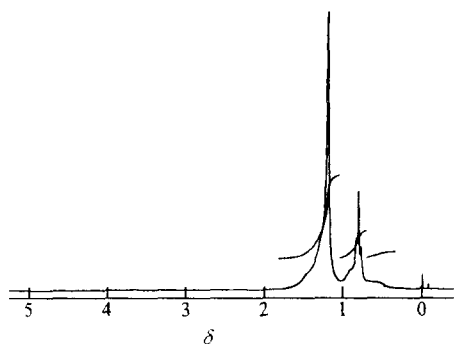


Fig.3 ¹H-NMR spectrum

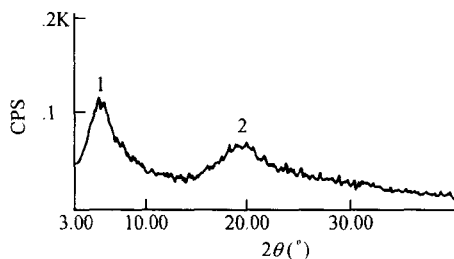


Fig.4 X-ray diffractogram

From Fig.4, we can see that there are two peaks in X-ray diffractogram. Peak 1 represents the plane to plane distance $d_1(\text{nm})$ which corresponds to the chain to chain distance based on the calculations of band angles and lengths. Peak 2 represents the thickness $d_2(\text{nm})$ of the molecular chains. The more regular the molecule is the larger the d_1 will be. The first peak is at $2\theta = 5.5^\circ$ ($d_1 = 1.605\text{nm}$). Based on the larger value of d_1 , the molecular chain of polydecylsilsesquioxane seems to be comparatively regular.

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