

SYNTHESIS AND CHARACTERIZATION OF A NEW POLYSILOXANE CONTAINING *N,N'*-BIS(DIPHENYLSILYL)TETRAPHENYLCYCLODISILAZANE

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Abstract A new kind of polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was prepared by anionic non-equilibrium polymerization with a "seed solution" as initiator. The monomer, *N,N'*-bis(hydroxydiphenylsilyl)tetraphenyl-cyclodisilazane (BHPTPC), was synthesized via the hydrolysis of *N,N'*-bis(chlorodiphenylsilyl)tetraphenyl-cyclodisilazane (BCPTPC). A new method for the preparation of BCPTPC is also reported here with high yield and simpler manipulation. The synthesized polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was characterized by $^1\text{H-NMR}$, $^{29}\text{Si-NMR}$, gel permeation chromatography (GPC) and intrinsic viscosity.

Keywords Polysiloxane, *N,N'*-Bis(diphenylsilyl)tetraphenylcyclodisilazane, Synthesis

INTRODUCTION

It is known that polysiloxanes have many excellent properties such as good resistance to heat, to cold and to weathering, good hydrophobicity and good electroinsulating properties. They have been used in many devices to withstand very crucial conditions or environments^[1], for example, aviation, aerospace, automobile industry and medical apparatus. In many such applications polysiloxanes should be able to resist very high temperature. A special kind of polysiloxane containing cyclodisilazane in the main chain was reported to have good resistance to high temperature^[2-4]. But the application of this polysiloxane was limited by the complicated synthesis of the monomer, *N,N'*-bis(chlorodiphenylsilyl)tetramethylcyclodisilazane (BCPTMC)^[4], just like that for polycarboranylenesiloxanes^[5]. It was also reported in the literature that the greater the amount of phenyl groups in cyclodisilazane, the better the thermal stability of this polysiloxane will be^[4].

In this paper, a new kind of polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was prepared. The synthesis of monomers, BHPTPC and BCPTPC is also reported.

EXPERIMENTAL

Materials

The solvents, THF, hexane, toluene, octane and xylene were distilled from sodium. Butyllithium and octamethylcyclotetrasilazane were prepared according to the literature methods^[6, 7].

Measurements

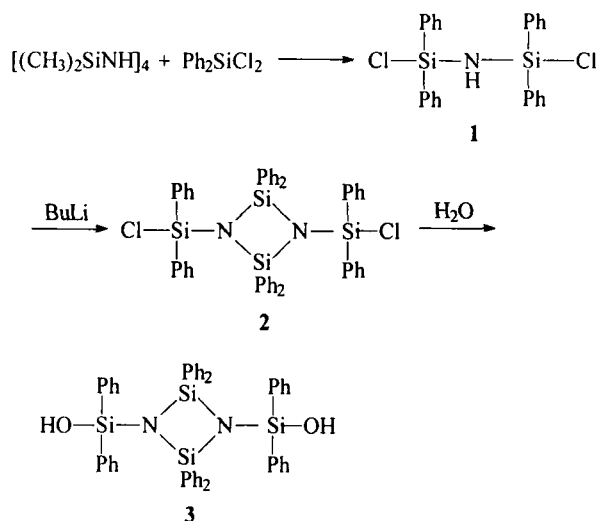
$^1\text{H-NMR}$ and $^{29}\text{Si-NMR}$ were performed on a Unity 200 MHz spectrometer ($\text{Me}_3\text{SiOSiMe}_3$ (MM) standard in $^{29}\text{Si-NMR}$). Mass spectrum (MS) was obtained from Biflex III MalDI-ToF. Elemental analysis was performed with a Carlo Erba 1106 Analyzer. Melting points were measured with a Mettler FP61 melting point apparatus. Molecular weight was measured using gel permeation chromatography (GPC) (Waters 515-2410, polystyrene standard). Intrinsic viscosity was determined in toluene at 30°C with an Ubbelohde viscometer.

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Monomer Synthesis

The reaction sequence for the synthesis of BHPTPC **3** is shown in Scheme 1.



Scheme 1

Preparation of compound 1

A mixture of Ph_2SiCl_2 (207 mL, 1.0 mol) and octamethylcyclotetrasilazane (29.2 g, 0.1 mol) was stirred at 180°C for 50 h. Then the precipitated crystals were filtered out at room temperature and washed with hexane. The crude product was recrystallized from the mixed solvent of hexane and toluene to give 140.4 g, (78%) of pure **1** as white crystals. Melting point: 117.1°C . $^1\text{H-NMR}$ (CDCl_3), δ : 2.5 (s, 1H, NH), 7.2–7.6 (m, 20H, $(\text{C}_6\text{H}_5)_4$). $^{29}\text{Si-NMR}$ (CDCl_3), δ : -14.58 (s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{Cl}$). Elemental analysis: Calcd. for $\text{C}_{24}\text{H}_{21}\text{Si}_2\text{NCl}_2$ (%): C 64.00, H 4.67, N 3.11, Cl 15.78. Found (%): C 63.70, H 4.56, N 2.91, Cl 15.49.

Preparation of cyclodisilazane 2

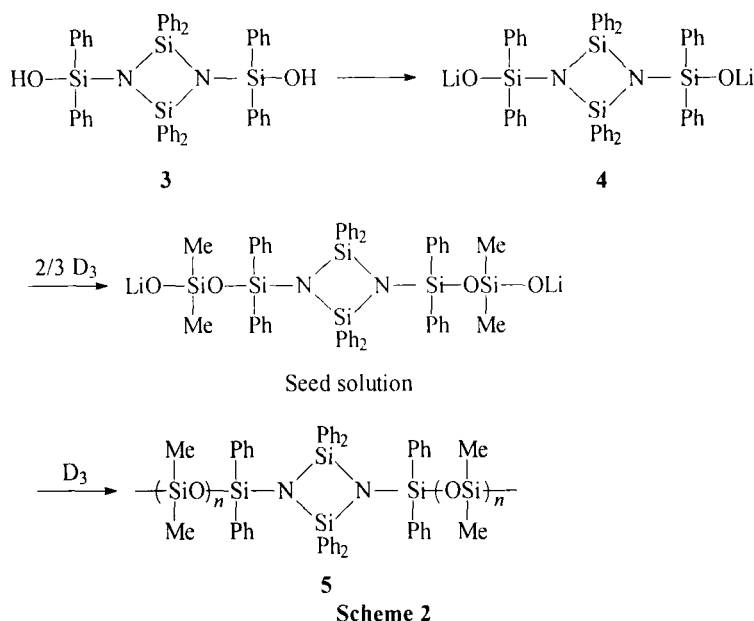
Compound **1** (15.9 g, 0.035 mol) was dissolved in 150 mL xylene and to this solution was added the butyllithium (0.035 mol). The solution was stirred at room temperature for 4 h. Then hexane was removed. Stirring was continued at 140°C for 2 h. The reaction mixture was filtered quickly and xylene was removed under reduced pressure to give the crude product. It was recrystallized from the mixed solvent of toluene and octane to give 10.7 g (73%) pure cyclodisilazane **2** as white crystals. Melting point: 256.7°C . $^1\text{H-NMR}$ (CDCl_3), δ : 6.8–7.6 (m, $(\text{C}_6\text{H}_5)_8$). $^{29}\text{Si-NMR}$ (CDCl_3): 19.89 (s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{N}$), -18.47 (s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{Cl}$). MS: m/z 828 ($\text{M} + \text{H}^+$); 850 ($\text{M} + \text{Na}^+$). Elemental analysis: Calcd. for $\text{C}_{48}\text{H}_{40}\text{Si}_4\text{N}_2\text{Cl}_2$ (%): C 69.65, H 4.84, N 3.39, Cl 8.59. Found(%): C 69.72, H 4.78, N 3.21, Cl 8.36.

Preparation of hydrolysis product 3

A suspension of cyclodisilazane **2** (2.5 g, 0.003 mol) in 20 mL ethyl ether was added dropwise to a mixture of ethyl ether (20 mL), aqueous ammonia solution (5 mL) and distilled water (5 mL). It was stirred at room temperature for 1 h. The precipitated crystals were filtered out and washed with hexane. The crude product was recrystallized from the mixed solvent of THF and hexane to give 1.7 g, (71%) of pure **3** as white crystals. Melting point: 218.5°C . $^1\text{H-NMR}$ (CDCl_3), δ : 2.05 (s, 2H, OH), 6.8–7.5 (m, 40H, $(\text{C}_6\text{H}_5)_8$). $^{29}\text{Si-NMR}$ (CDCl_3), δ : -20.39 (s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{N}$), -37.10 (s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{OH}$). MS: m/z 791 ($\text{M} + \text{H}^+$); 813 ($\text{M} + \text{Na}^+$). Elemental analysis: Calcd. for $\text{C}_{48}\text{H}_{42}\text{Si}_4\text{N}_2\text{O}_2$ (%): C 72.91, H 5.32, N 3.54. Found (%): C 72.89, H 5.44, N 3.29.

Polymer Synthesis

The reaction sequence for the synthesis of polysiloxane **5** is shown in Scheme 2.



Synthesis of the lithium salt 4

To a solution of butyllithium (0.01 mol) in hexane, the hydrolysis product **3** (4.0 g, 0.005 mol) in 50 mL THF was added dropwise. It was stirred at -10°C for 1 h. Then stirring was continued for 2 h at room temperature. The residual butyllithium was removed by washing with hexane. All the operations were carried out under the protection of nitrogen. The yield of the product was 70%.

Synthesis of the "seed solution" and polymer 5

Hexamethylcyclotrisiloxane (D_3) (0.5 g, 0.002 mol) dissolved in 30 mL toluene was added to the lithium salt **4** (2.48 g, 0.003 mol) and was stirred at 110°C for 10 h to obtain a transparent "seed solution". The polysiloxane **5** was prepared by the reaction of the "seed solution" with D_3 under stirring at 80°C for 24 h using THF or DMSO as promoters. The polymer obtained was determined by ^{29}Si -NMR (CDCl_3), δ : -25.5 (N_2SiPh_2), -28.3 (OSiMe_2O), -37.3 (NSiPh_2O); ^1H -NMR (CDCl_3), δ : -0.2 – 0.2 (CH_3), 7.0 – 7.6 (C_6H_5). The M_n of the polymer measured by GPC was 32000 and its M_v was 39000 calculated from equation: $[\eta] = 0.03M^{0.63}$. $[\eta]$ was measured in toluene at 30°C .

RESULTS AND DISCUSSION

Synthesis and Characterization of the Monomers

Compound **1** was synthesized by the reaction of octamethylcyclotetrasilazane (D_4^{N}) with excess diphenyldichlorosilane (Ph_2SiCl_2). The method is simple and has higher yield than reported^[8, 9].

The reported method for the preparation of cyclodisilazane **2** is shown in Scheme 3^[10, 11].

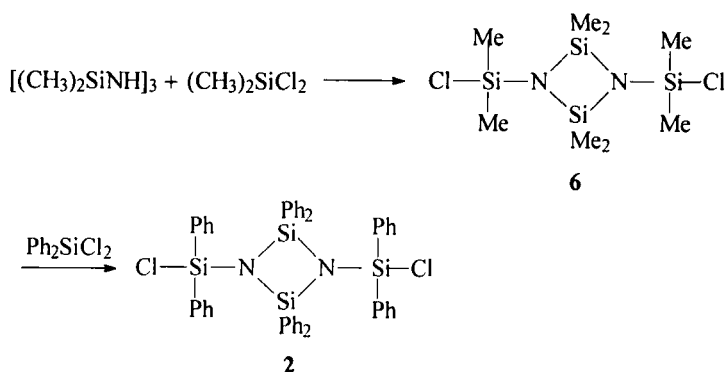
Compound **6** was very sensitive to water and acid and the second step will proceed only at very high temperature ca. 400°C . The purification of the product was also very complicated.

Breed reported the synthesis of several cyclodisilazanes containing methyl and other groups as shown in Scheme 4^[12]. While the cyclodisilazane containing the *N,N'*-bis(diphenylsilyl)tetraphenyl group has not been reported before.

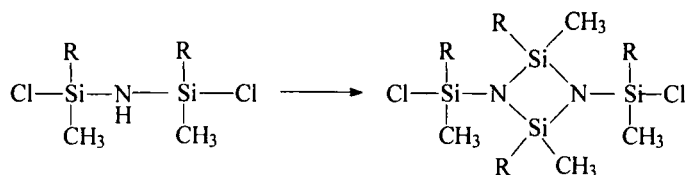
In the present work, cyclodisilazane **2** was prepared by the route illustrated in Scheme 1 with high yield and the reaction conditions were quite mild.

Fink^[13] found that the molecular weight and elemental analysis of the hydrolysis product agreed well with calculation. Followed his reported method, the molecular weight and elemental analysis of the product obtained were also in agreement with calculation. But the ^{29}Si -NMR spectrum showed three peaks: δ : -29.28 , -37.14 ,

-50.32, and the peak of the silicon in the ring (about -20) did not appear. These results indicate that it was not the hydrolysis product **3** but an isomer instead.



Scheme 3



Scheme 4

By using a suspension of cyclodisilazane **2** in ethyl ether, compound **3** was synthesized successfully. Its structure was identified by ^{29}Si -NMR, ^1H -NMR, molecular weight and elemental analysis.

A possible explanation is that in the literature method cyclodisilazane **2** can easily undergo the ring-opening (no peak $\delta = -20$ in ^{29}Si -NMR) and condensation reaction (the peak $\delta = -50.32$ in ^{29}Si -NMR) in a homogeneous phase system. In this paper, the hydrolysis reaction was carried out in a heterogeneous phase system. This reaction condition may be more favorable for preparing the hydrolysis product **3**.

Synthesis and Characterization of Polysiloxane **5**

As previously reported in the literature^[6], organic lithium can be used as the initiator in the polymerization of cyclosiloxane. In our present work, the lithium salt **4** was synthesized from the hydrolysis product **3** first. In order to avoid the polymerization of hexamethylcyclotrisiloxane initiated by the residual butyllithium it was washed with hexane because the lithium salt **4** was very sensitive to water and acid. All these operations were carried out under the protection of nitrogen.

The lithium salt **4** can not be used as the initiator directly in this experiment, since it is not soluble in common organic solvents. It was reported that the polymerization of cyclosiloxane by "seed solution" as initiator is a useful method^[14]. In our work, polysiloxane **5** was prepared easily with the "seed solution" as initiator in the solution, and the molecular weights of the polysiloxane were controlled easily by using the technique of the "seed solution".

The structure of the polymer was identified by ^{29}Si -NMR. The peak at $\delta = -25.5$ is assigned to the silicon in the ring ($-\text{NSi}(\text{C}_6\text{H}_5)_2\text{N}$) and the peak at $\delta = -37.3$ is assigned to the silicon of NSiPh_2O . The peak at $\delta = -28.3$ is assigned to the silicon of OSiMe_2O . In the ^1H -NMR spectrum, the peaks at $\delta = 7.0\sim 7.6$ are assigned to C_6H_5 and $\delta = -0.2\sim 0.2$ peaks are assigned to CH_3 . Both the ^{29}Si -NMR and ^1H -NMR spectroscopic results prove the polysiloxane **5** containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane.

CONCLUSIONS

A new kind of polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was synthesized successfully.

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