

Synthesis and Properties of Polysiloxane Containing *N,N'*-Bis(diphenylsilyl)tetraphenylcyclodisilazane

N. ZHOU, Z. J. ZHANG, C. H. XU, Z. M. XIE

Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

Received 22 September 2000; accepted 29 October 2000

ABSTRACT: A new kind of polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was prepared by the anionic polymerization with a “seed solution” as initiator. The synthesis of monomers *N,N'*-bis(hydroxydiphenylsilyl)tetraphenylcyclodisilazane (BHPTPC), *N,N'*-bis(chlorodiphenylsilyl)tetraphenylcyclodisilazane (BCPTPC), and 1,3-dichloro-1,1,3,3-tetraphenylcyclodisilazane (DCTPS) are all reported in this study. The synthesized polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane was characterized by ¹H-NMR, ²⁹Si-NMR, gel permeation chromatography (GPC), and intrinsic viscosity. The thermal stability of the polysiloxane was studied by isothermal gravimetric analysis (IGA). The results demonstrated that the synthesized polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane had excellent thermal stability. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 929–933, 2001

Key words: polysiloxane; synthesis; thermal stability; *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane

INTRODUCTION

It is well known that polysiloxanes have many excellent properties such as good resistance to heat and to cold, good hydrophobicity, and good electroinsulating properties. They have been used in many devices to withstand very crucial conditions or environments¹ such as aviation, aerospace, the automobile industry, and medical apparatus. The increasing need for thermally stable materials is constantly bringing demands for new polysiloxanes having resistance to even higher temperatures. A special kind of polysiloxanes containing cyclodisilazane in the main chain was reported by our laboratory to have good resistance to high temperatures.^{2–4} However, the application of this polysiloxane was limited by the complicated synthesis of the monomer, *N,N'*-bis(chlorodiphenylsilyl)tetra-

methylecyclodisilazane (BCPTMC),⁴ just like that for polycarboranylensiloxanes.⁵

In this study the synthesis and thermal stability of a new kind of polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane is reported.

EXPERIMENTAL

Materials

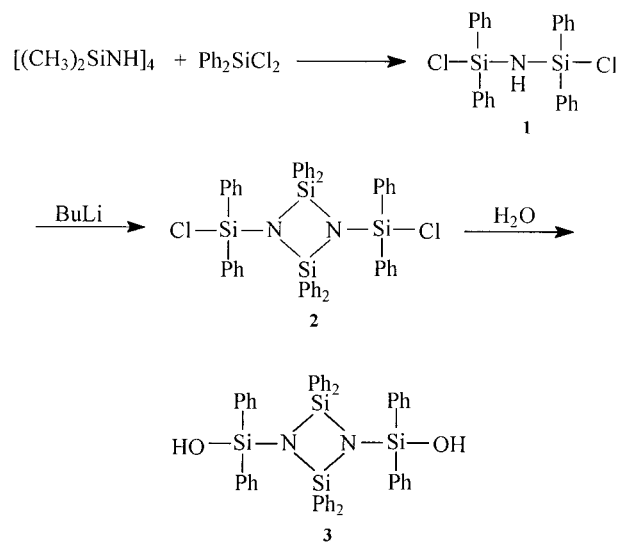
The solvents THF, hexane, toluene, octane, and xylene were purchased from Beijing Chemical Works and distilled from sodium. Octamethylcyclotetrasilazane and butyllithium were prepared according to methods reported in the literature.^{6,7}

Measurements

¹H-NMR and ²⁹Si-NMR were performed on a Unity 200-MHz spectrometer [Me₃SiOSiMe₃ (MM) standard in ²⁹Si-NMR]. MS spectrum was obtained

Correspondence to: Z. M. Xie (xiezm@infoc3.icas.ac.cn)

Journal of Applied Polymer Science, Vol. 82, 929–933 (2001)
© 2001 John Wiley & Sons, Inc.



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) (Walters 515-2410, polystyrene standard). Intrinsic viscosity ($[\eta]$) was determined in toluene at 30°C with a Ubbelohde viscometer. Isothermal gravimetric analysis (IGA) was measured by drying oven (DL102).

Synthesis

Monomer Synthesis (1–3)

The synthesis of monomers is shown in Scheme 1.

Preparation of Compound 1. A mixture of Ph_2SiCl_2 (207 mL) and octamethylcyclotetrasilazane (29.2 g) was stirred at 180°C for over 24 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 (ppm): 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 (ppm): –14.58 [s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{Cl}$]. ANAL. 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, after which 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 (ppm): 6.8–7.6 [m, $(\text{C}_6\text{H}_5)_8$]. $^{29}\text{Si-NMR}$ (CDCl_3), δ (ppm): –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 ($\text{M} + \text{Na}^+$). ANAL. 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), ammonia water (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.

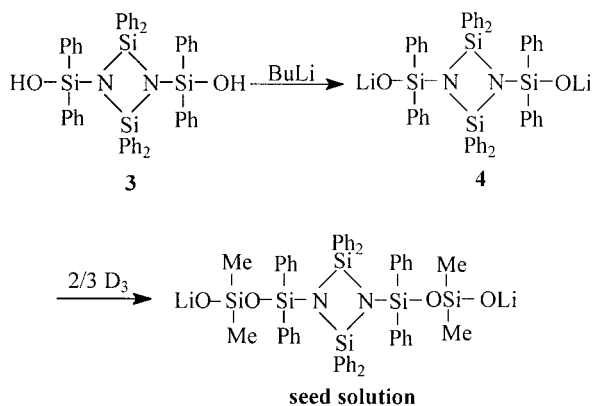
$^1\text{H-NMR}$ (CDCl_3), δ (ppm): 2.05 (s, 2H, OH), 6.8–7.5 [m, 40H, $(\text{C}_6\text{H}_5)_8$]. $^{29}\text{Si-NMR}$ (CDCl_3), δ (ppm): –20.39 [s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{N}$], –37.10 [s, $\text{NSi}(\text{C}_6\text{H}_5)_2\text{OH}$]. MS: m/z 791 ($\text{M} + \text{H}^+$); 813 ($\text{M} + \text{Na}^+$). ANAL. 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 synthesis of lithium salt and polysiloxane **5** is shown in Scheme 2.

Synthesis of Lithium Salt 4. To a solution of butyllithium (0.01 mol) in hexane (4.0 g) the hydrolysis product **3** in 50 mL THF was added dropwise. It was stirred at –10°C for 1 h. Stirring was continued for 2 h at room temperature. The residual butyllithium was removed by washing with hexane. The whole procedure was protected under nitrogen atmosphere. 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 polymerization of D_3 under stirring at 80°C for



24 h with "seed solution" as initiator and THF or DMSO as promoters. The M_n of the polymer measured by GPC was 32,000 and its M_v was 39,000 calculated from the equation $[\eta] = 0.03M^{0.63}$.

The obtained polymer was characterized by ^{29}Si -NMR (CDCl_3), δ (ppm): -25.5 (N_2SiPh_2), -28.3 (OSiMe_2O), -37.3 (NSiPh_2O); ^1H -NMR (CDCl_3), δ (ppm): -0.2 – 0.2 (CH_3), 7.0 – 7.6 (C_6H_5).

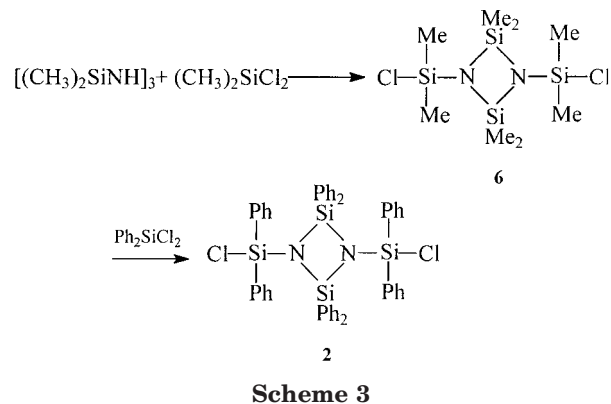
Thermal Analysis

The thermal stability of the polysiloxane **5** was studied by IGA. A 0.2- to 0.3-g sample in a nickel boat accurately weighed by analytical balance was put into a glass tube. After being heated at 120°C for 4 h, the air in the glass tube was replaced with nitrogen for 15 min and then sealed. The sealed glass tube was heated in a drying oven at different conditions with different temperatures and different times. After cooling, it was accurately measured by analytical balance again. The weight loss of the sample was obtained.

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). This method is



more 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, thus the second step proceeds only at very high temperature ($\sim 400^\circ\text{C}$). 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 although the cyclodisilazane containing N,N' -bis(diphenylsilyl)tetraphenyl group was not previously reported.

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

Fink first gave a method to prepare the hydrolysis product **3** in a patent¹³; the molecular weight and element analysis of the hydrolysis product agreed with the calculation very well. Following his reported method, we also obtained the same result. However, in the ^{29}Si -NMR spectrum three peaks were shown: δ (ppm): -29.28 , -37.14 , and -50.32 , whereas the peak of the silicon in the ring (about -20) disappeared. These results indicate that it was not the target hydrolysis product **3** but an isomer instead.

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

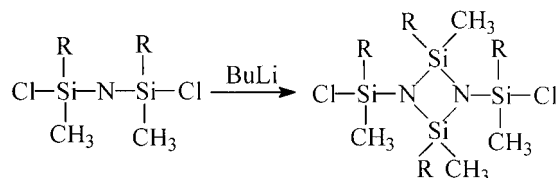


Table I The Weight Loss of Polysiloxane in Nitrogen

No.	Blending Ratio of Polysiloxane Containing <i>N,N'</i> -bis(diphenylsilyl)tetraphenylcyclodisilazane and Common Methyl Polysiloxane	Temperature (°C)	Time (h)	Weight Loss (%)
1	0 : 10	325	24	8.27
2	0 : 10	350	24	15.2
3	1 : 10	325	24	1.73
4	1 : 10	350	24	7.87
5	1 : 10	350	48	15.9

^1H -NMR, molecular weight, and element analysis.

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

Synthesis and Characterization of Polysiloxane 5

As previously reported in the literature,⁶ organic lithium could be used as the initiator in the polymerization of cyclodisiloxane. In our present work, the lithium salt **4** was first synthesized from the hydrolysis product **3**. To avoid the residual butyllithium to initiate the polymerization of hexamethylcyclotrisiloxane, it was washed with hexane completely. Because the lithium salt **4** was very sensitive to water and acid, all the operations were carried out under the protection of nitrogen atmosphere.

Given that the lithium salt **4** is not soluble in common organic solvents, it cannot be directly used as the initiator in this experiment. It was previously reported that the polymerization of cyclodisiloxane with "seed solution" as initiator was a useful method.¹⁴ In our work, polysiloxane **5** was easily prepared with the "seed solution" as initiator

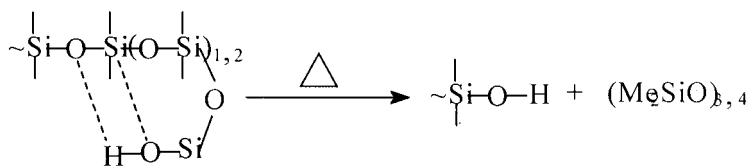
in the solution, and the molecular weights of the polysiloxane were easily controlled by using the technique of the "seed solution."

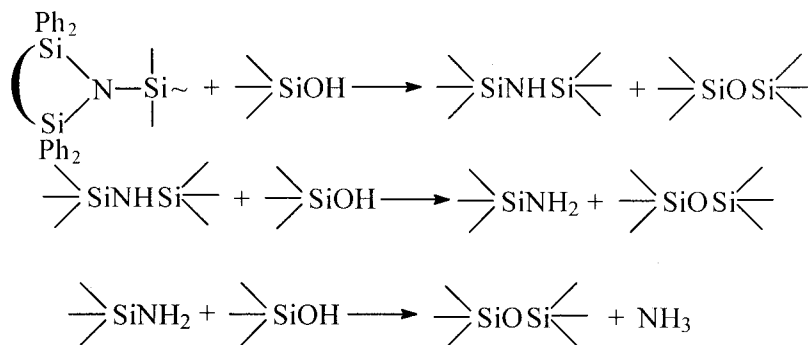
The structure of the polymer was identified by ^{29}Si -NMR. The peak at -25.5 ppm was assigned to the silicon in the ring $[-\text{NSi}(\text{C}_6\text{H}_5)_2\text{N}]$ and the peak at -37.3 ppm was assigned to the silicon of NSiPh_2O . The peak at -28.3 ppm was assigned to the silicon of OSiMe_2O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

Thermal Analysis

IGA is an important method to characterize thermal stability of polysiloxane. At a given temperature, the lesser the weight loss, the better the thermal stability of the polysiloxane. As shown in Table I, the weight loss of the polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane and common methyl polysiloxane were compared.

The data in Table I show that the polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane can improve the thermal stability of common polysiloxane. For the same temperature and same time, the weight loss of polysiloxane blended with polysiloxane containing *N,N'*-bis(diphenylsilyl)tetraphenylcyclodisilazane is two- to fourfold less than that of common polysi-

**Scheme 5**



Scheme 6

loxane (No. 1 versus No. 3; No. 2 versus No. 4); for the same temperature and same weight loss, the time is 24 h longer than that of common polysiloxane (No. 2 versus No. 5); for the same time and same weight loss, the temperature is 25°C higher than that of common polysiloxane (No. 1 versus No. 4).

It is well known that the residue SiOH or water in polysiloxane can result in main-chain degradation by forming small cyclosiloxanes¹⁵ (see Scheme 5). It is the most important reason for weight loss of polysiloxane at high temperatures.

Si—N bonds in the polymers react easily with SiOH and water (see Scheme 6). Through eliminating the SiOH and water in polysiloxane, the main-chain degradation, characterized by formation of small cyclosiloxanes at high temperatures, was eliminated and then the thermal stability of the polysiloxane was improved.

CONCLUSIONS

A new kind of polysiloxane containing *N,N'*-bis-(diphenylsilyl)tetraphenylcyclodisilazane was successfully synthesized. The thermal stability of the polysiloxane was studied by IGA. The results demonstrated that the synthesized Si—N polymer had excellent thermal stability.

We gratefully acknowledge the National Science Foundation of China (No. 20074040) for financial support.

REFERENCES

1. Belot, V.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Vioux, A. *J Polym Sci Part A Polym Chem* 1992, 30, 613.
2. Fink, W. *J Paint Technol* 1970, 42, 220.
3. Fink, W. *Helv Chem Acta* 1969, 52, 1841.
4. Xie, Z. M.; Li, Q. S.; Wang, J. T. *Acta Polym Sinica* 1979, 4, 215.
5. Karl, O. K.; Robert, N. S.; Herbert, K.; John, F. S. *J Polym Sci Part A Polym Chem* 1971, 9, 1071.
6. Li, L. Z.; Song, Y. L. *Principles and Technologies of Organic Chemistry* (in Chinese); Higher Education Press: Beijing, 1992.
7. Li, G. L. *Organosilicon Chemistry* (in Chinese); Science Press: Beijing, 1998.
8. Wannagat, U.; Bogusch, E. *Monatsh Chem* 1971, 102, 1806.
9. Gurkoba, S. N.; Gusev, N. B. *Zh Strukt Khim* 1984, 25, 153.
10. Fink, W. *Helv Chem Acta* 1968, 51, 1011.
11. Fink, W. *Helv Chem Acta* 1968, 51, 1743.
12. Breed, L. W.; Wiley, J. C. *Inorg Chem* 1972, 11, 1634.
13. Fink, W. (to Monsanto Co.) *Brit. Pat.* 1,252,147, 1968.
14. Enrique, M. V. *J Macromol Sci* 1992, A29, 391.
15. Li, Q. S.; Xie, Z. M. *Polym Commun* 1986, 3, 208.