

Note

SYNTHESIS AND CHARACTERIZATION OF SILAZANE OLIGOMER
CONTAINING 1,1,3,3,5,5-HEXAMETHYLCYCLOTRISILAZANE

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Abstract A new silazane oligomer containing cyclotrisilazane was synthesized by KH-catalyzed dehydro-coupling reactions between diphenylsilane and 1,1,3,3,5,5-hexamethylcyclotrisilazane (D_3^N).

Keywords Silazane oligomer, Diphenylsilane, Cyclotrisilazane, Dehydro-coupling reaction

INTRODUCTION

There is considerable interest in synthesizing new type polysilazanes and in searching for new routes to synthesize polysilazanes, since silicon-based ceramics were prepared from the pyrolysis of polymers containing silicon^[1]. Seyferth and co-workers have performed extensive work on the polymerization of cyclo- $[CH_3Si(H)NH]_n$ and/or mixture by potassium hydride (KH) -catalyzed dehydro-coupling reaction^[2-5]. However, in their work, all the silazanes (or oligosilazanes) used as reactants contain at least two units of adjacent Si—H and N—H bonds, $=SiH-NH-$, in the same molecules. For the reactions in which N—H, Si—H bonds belong to different molecules, no report has been available. In an attempt to find a new way to prepare polysilazane precursors, we studied the reaction of Si—H and N—H bonds that belong to different molecules, respectively, and obtained novel silazane oligomers. In this paper, dehydro-coupling reaction between diphenylsilane ($(C_6H_5)_2SiH_2$) and two different cyclotrisilazanes (1,1,3,3,5,5-hexamethyl-cyclotrisilazane (D_3^N), 1,1,3,3,5,5-hexaphenylcyclo-trisilazane (P_3^N)) will be described.

EXPERIMENTAL

Materials and Instrument

$(C_6H_5)_2SiH_2$, D_3^N and P_3^N were prepared according to the literature^[6-8], respectively. KH was purchased from Acros as 25% slurry in mineral oil. This was washed with hexane under nitrogen to remove the oil before use. CH_3I was distilled under nitrogen over P_2O_5 . Tetrahydrofuran (THF) and hexane were distilled from sodium benzophenone ketyl.

The ^1H -NMR spectra were recorded on a Bruker WM 300 spectrometer, and ^{29}Si -NMR spectra on a Unity 200 spectrometer using chloroform- d as solvent, and $Me_3SiOSiMe_3$ (MM) was used as an external standard for ^{29}Si -NMR. IR spectra were measured on a VR-10 infrared spectrometer. The molecular weights of oligomers were estimated using a Knauer vapor pressure osmometer. C, H and N contents were determined using a ST-02 elemental analyzer.

Synthesis

In a typical run, 0.05 g (1.24 mmol) KH and 20 mL THF were placed in a 50 mL three-necked flask under nitrogen. The mixture was stirred for 10 min and 2.49 g (13.52 mmol) $(C_6H_5)_2SiH_2$, 2.12 g (9.66 mmol) D_3^N were

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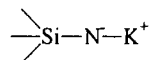
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injected into the flask under the protection of nitrogen. After constant stirring under reflux for 4 h, the reaction mixture was cooled to room temperature and quenched with 0.5 mL CH_3I (8.04 mmol). THF was removed under reduced pressure; a white slurry was obtained and then 20 mL dried *n*-hexane was added. The mixture was filtered to remove white solid. After removal of the solvent and residual reactants by distillation under vacuum (1.7 kPa/170°C), a colorless transparent oil was obtained in 60% yield.

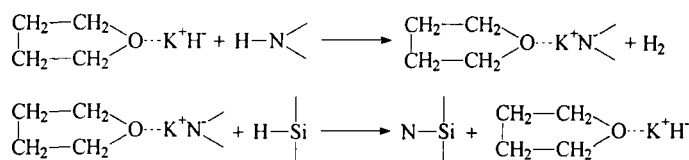
RESULT AND DISCUSSION

The reactions between $(\text{C}_6\text{H}_5)_2\text{SiH}_2$ and different cyclotrisilazanes (D_3^{N} , P_3^{N}) under the same condition were compared. D_3^{N} and $(\text{C}_6\text{H}_5)_2\text{SiH}_2$ reacted rapidly in THF solution and reaction was complete in 4 h; however, P_3^{N} did not react with $(\text{C}_6\text{H}_5)_2\text{SiH}_2$ even when refluxed for 30 h. This can be attributed to different substitutions on Si atoms in the two cyclotrisilazanes. Phenyl group is bulkier than methyl group, and the steric effects of four phenyl groups in $-\text{NH}-\text{Si}(\text{C}_6\text{H}_5)_2$ and $(\text{C}_6\text{H}_5)_2\text{SiH}_2$ hinder the approach between N—H and Si—H bonds. The unfavourable electron-effect of phenyl groups may be the another reason. Hence, the reaction takes place with great difficulty.

Solvent also has some effect on the reaction. For the reaction of D_3^{N} with $(\text{C}_6\text{H}_5)_2\text{SiH}_2$, three different conditions, using THF or *n*-hexane as solvents and bulk reaction were studied, respectively. The results show that the effect of solvents is very important. Without solvent, the reaction did not occur after heating for 16 h at 70°C; using THF as solvent, the reaction takes place rapidly and completely in 4 h. However, in *n*-hexane, the reaction did not occur even when the mixture was heated for 23 h under reflux temperature. The reason may be that in polar THF, KH can form loose ion pairs because solvation favors the formation of transition state



which makes its reaction with Si—H easier (see Scheme 1). But after two N—H bonds in cyclotrisilazane have reacted with $(\text{C}_6\text{H}_5)_2\text{SiH}_2$, the steric effects and electronic effects of the substituents prevent the third N—H bond in cyclotrisilazane from reacting further with $(\text{C}_6\text{H}_5)_2\text{SiH}_2$, so three-dimensional polymers are not obtained.



Scheme 1

The silazane oligomers were characterized by IR, ^1H -NMR, ^{29}Si -NMR and VPO techniques. The IR spectrum shows that the characteristic stretching vibration and bending vibration of $-\text{NH}$ appear at 3380 cm^{-1} and 1160 cm^{-1} , respectively. The stretching vibrations of $-\text{SiH}$ and $\text{Si}-\text{N}-\text{Si}$ are observed at 2100 cm^{-1} , 910 cm^{-1} and 960 cm^{-1} , respectively. The ^1H -NMR and ^{29}Si -NMR spectra are shown in Figs 1 and 2. The ^1H -NMR spectrum shows SiCH_3 signals at $\delta = 0\sim 0.25$, $\text{N}-\text{H}$ at $\delta = 0.83$, $\text{Si}-\text{H}$ at $\delta = 5.4$ and a broad signal at $\delta = 7.3\sim 7.6$ which is assigned to $-\text{SiC}_6\text{H}_5$. Additional information about the structure of the silazane oligomer was obtained from ^{29}Si -NMR. Figure 2 shows the ^{29}Si -NMR spectrum of the silazane oligomer. In comparison with the spectra of D_3^{N} ($\delta = -11.6$) and $(\text{C}_6\text{H}_5)_2\text{SiH}_2$ ($\delta = -39.3$), it is clear that peaks at $\delta = -31.9$, -32.9 correspond to $-\text{Si}(\text{C}_6\text{H}_5)_2-$ and the peaks at $\delta = -8.1$, -9.6 , -10.6 belong to $-\text{Si}(\text{CH}_3)_2$.

Elemental analysis and molecular weight determination provide considerable information giving further insight into the structure of the silazane oligomer. Elemental analysis gave C = 56.71%, N = 9.12%, H = 7.17% and Si = 26.36%, indicating the oligomer has a composition of $\text{Si}_{1.4}\text{NC}_7\text{H}_{11}$. According to VPO measurement, the number molecular weight of the silazane oligomer is 1344.

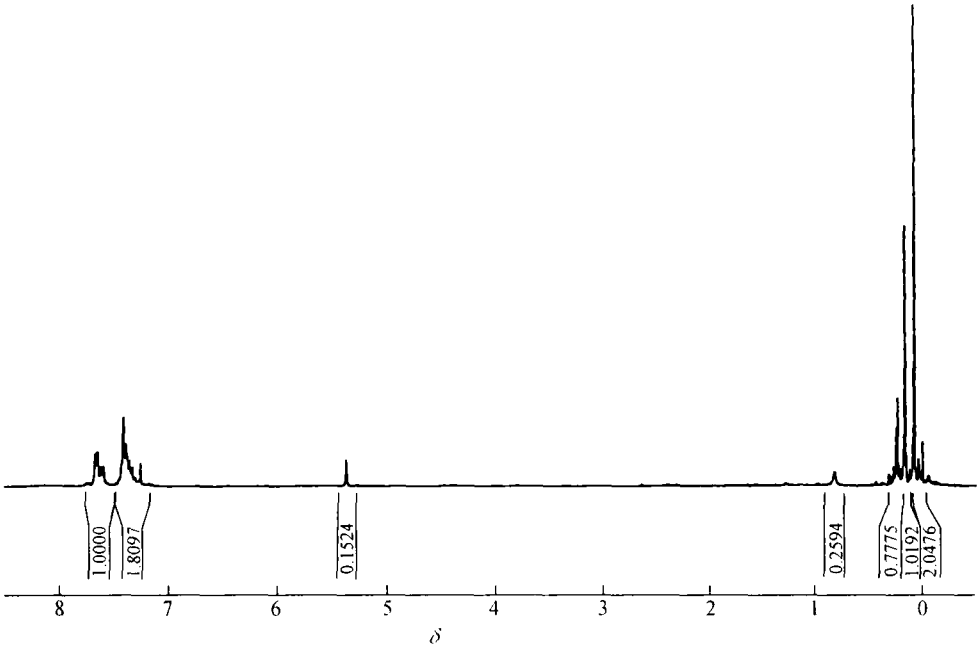


Fig. 1 ¹H-NMR spectrum of polysilazane

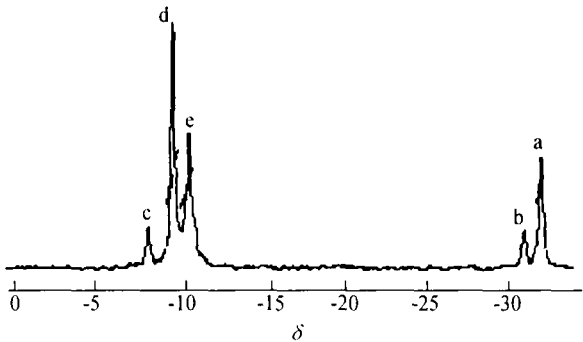
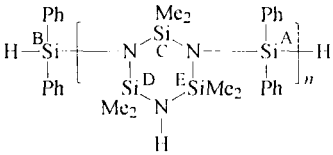


Fig. 2 ²⁹Si-NMR spectrum of polysilazane



Scheme 2

All the above analyses suggests that the silazane oligomer has the structure as shown in Scheme 2.

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