

Synthesis of HMDS radical terminated perhydropolysilazane

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The chemical stability of perhydropolysilazane is improved by the introduction of HMDS (1, 1, 1, 3, 3, 3-hexamethyldisilazane) radical. The increase rate of the number average molecular weight of HMDS radical-introduced perhydropolysilazane was ten times slower than that of raw perhydropolysilazane. $^1\text{H-NMR}$ analysis revealed that HMDS molecules mainly reacted with terminal Si-H₃ groups of perhydropolysilazane. © 1998 Kluwer Academic Publishers

1. Introduction

Perhydropolysilazane is a valuable precursor polymer for silicon-based ceramics. One of these ceramics is silicon nitride; it has excellent properties, such as high strength, resistance to thermal shock, and corrosion. High-performance silicon nitride fiber can be obtained by the dry-spinning of perhydropolysilazane and pyrolysis in N₂ above 800 °C [1, 2].

Another is silicon dioxide. One of the advantages of using perhydropolysilazane is that pure and dense silicon dioxide coating can be obtained by pyrolysis in air up to 450 °C, which is a lower temperature than that of the sol-gel process [3]. Perhydropolysilazane has already been applied as the precursor of the interlayer dielectric films in ultra-large scale integrated circuits (ULSI).

Disadvantages of perhydropolysilazane include its low chemical stability, which results in an increase of molecular weight. Accordingly, its difficult handling property is induced from these factors. A change of molecular weight may also cause a lack of uniformity in the derived ceramics. HMDS (1, 1, 1, 3, 3, 3-hexamethyldisilazane) is well known as a versatile silylation reagent and is able to block or protect Si-H, N-H and O-H bonds [4, 5]. This paper describes the improvement of chemical stability in perhydropolysilazane by the reaction with HMDS, and the characterization of HMDS radical-terminated perhydropolysilazane.

2. Experimental procedure

2.1. Synthesis of HMDS radical terminated perhydropolysilazane

Perhydropolysilazane was synthesized by ammonolysis of dichlorosilanepyrindine adduct, followed by the filtration of ammonium chloride [6]. HMDS was mixed with 5 weight % of a pyridine solution of perhydropolysilazane. HMDS was 5.0, 10, 20 and 30 weight % of perhydropolysilazane. These solutions were fed into an autoclave, which had been substituted by dry N₂ gas, and heated at 80 °C for 3 h with

stirring. After being cooled to ambient temperature, dry m-xylene was added to the reaction mixture. The solvent and excess HMDS were removed by distillation at 50 °C under 5 mmHg to give a clear, viscous liquid. This liquid (HMDS radical-terminated perhydropolysilazane) was found to be soluble in chloroform, cyclohexane and dibutylether.

2.2. Characterization

Molecular weight distributions were measured with a gel permeation chromatography (GPC) system (Model 801-SC, 830-RI, JASCO, Tokyo, Japan) using chloroform as the solvent. Molecular weights quoted are based on polystyrene standards.

The stability of HMDS radical-terminated perhydropolysilazane was evaluated by the following method. 150 ml of a polymer solution, adjusted to 20 weight % in m-xylene, was charged into a 250 ml glass vessel. After purging the atmosphere with dry N₂ gas, the vessel was sealed with a plug. This vessel was heated at 40 °C in an oven. The GPC was measured after 10, 20, 30 and 40 days.

Fourier transform infrared spectra (FT-IR) were recorded on polymer coated KBr pellets (Model Paragon 1000, Perkin Elmer). ^1H nuclear magnetic resonance spectra ($^1\text{H-NMR}$) (Model EX-400, JEOL) were recorded of the polymer in CDCl₃ solutions at room temperature. Elemental analyses for silicon, oxygen, nitrogen, carbon and hydrogen were obtained for the polymer.

Reaction gas analyses were obtained with a gas chromatography-mass spectrometry system (Model HP-5890 II, HP-5921A(AED), Hewlett Packard)-(Model JMS-DX303, JOEL).

3. Results

3.1. GPC and evaluation of stability

Fig. 1 shows the GPC of HMDS-introduced perhydropolysilazane(a) (30 weight % of HMDS) and perhydropolysilazane (b). No marked difference was

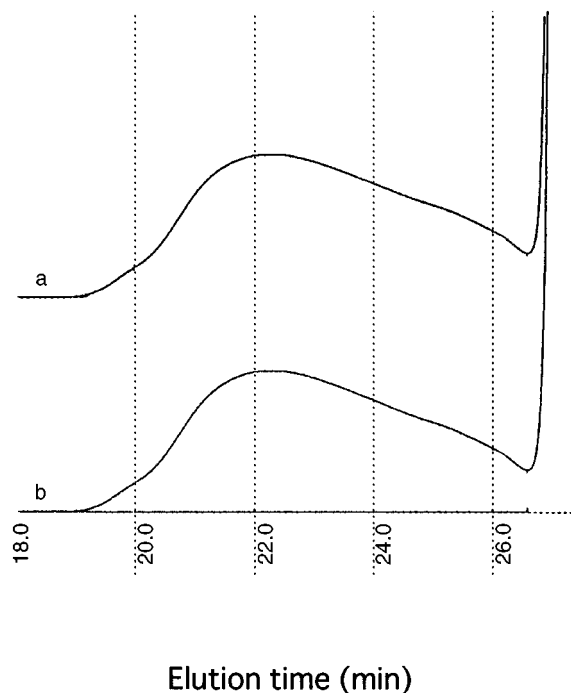


Figure 1 GPC of (a) HMDS-introduced perhydropolysilazane and (b) raw perhydropolysilazane.

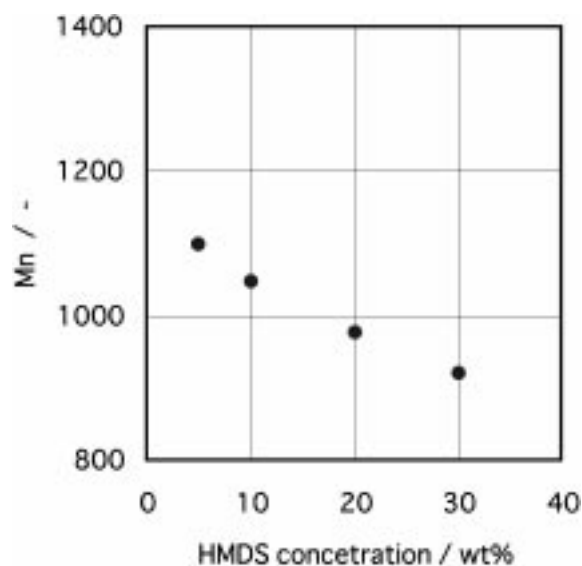


Figure 2 Relation between Mn of HMDS-introduced perhydropolysilazane just after the reaction and HMDS concentration before reaction.

observed between the before-and-after reaction with HMDS. Fig. 2 shows the relation between number average molecular weight, Mn, of HMDS-introduced perhydropolysilazane just after the reaction, and the amount of HMDS fed into the autoclave. A slight decrease of Mn was observed with the increase of the amount of HMDS.

Fig. 3 shows the changes of Mn of the HMDS-introduced perhydropolysilazane holding at 40 °C. The rate of increase of Mn became slower with the increase of the amount of HMDS.

3.2. FT-IR

Fig. 4 shows the FT-IR spectra of HMDS-introduced perhydropolysilazane (30 weight % of HMDS) (a) and

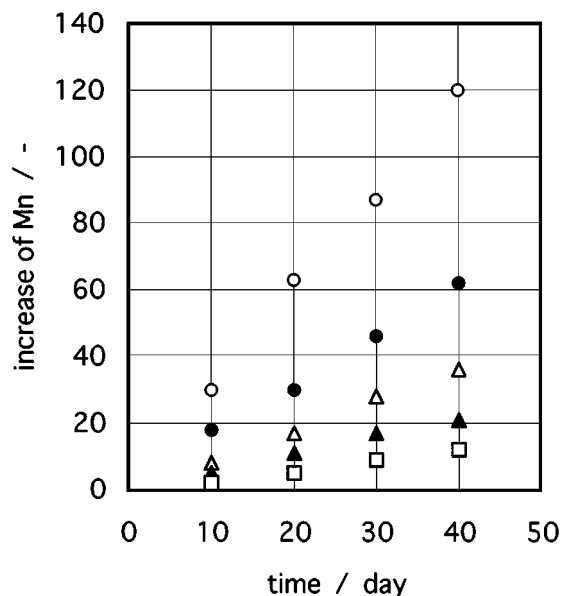


Figure 3 Mn increase/time curves of HMDS-introduced perhydropolysilazane and raw perhydropolysilazane. HMDS concentration before reaction: 5 wt % (●), 10 wt % (△), 20 wt % (▲), 30 wt % (□), raw perhydropolysilazane (○).

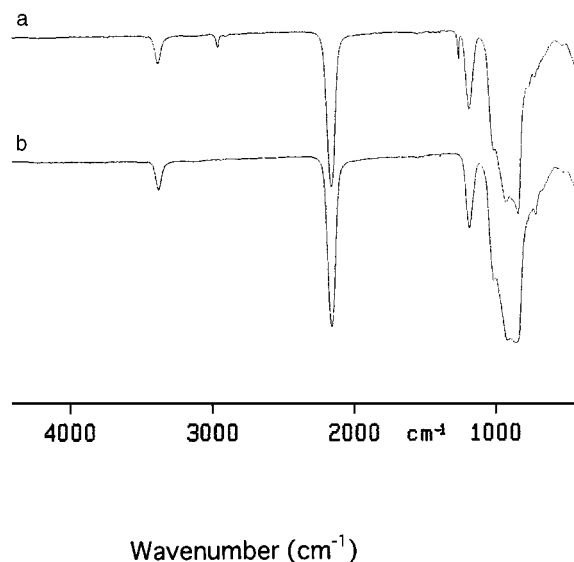


Figure 4 FT-IR spectra of (a) HMDS introduced perhydropolysilazane and (b) raw perhydropolysilazane.

raw perhydropolysilazane (b). A spectrum of HMDS-introduced perhydropolysilazane shows absorptions at 1260 cm⁻¹ (δ Si-CH₃ (3)), 2970 cm⁻¹ (ν C-H (1)) and 2850 cm⁻¹ (ν C-H (2)), indicating the presence of -Si-CH₃ groups. Absorptions of both spectra at 3400 cm⁻¹ (ν N-H (4)) and 1200 cm⁻¹ (ν N-H (6)) indicate the presence of -N-H (not N-H₂) groups and at 2150 cm⁻¹ (ν Si-H (5)), the presence of -Si-H_n (n = 1~3) groups.

3.3. ¹H-NMR

Fig. 5 shows the ¹H-NMR spectra of HMDS-introduced perhydropolysilazane (a) (30 weight % of HMDS) and perhydropolysilazane. (b) A spectrum of HMDS-introduced perhydropolysilazane shows peaks centered at 0.2 and 0.1 p.p.m corresponding to SiCH₃.

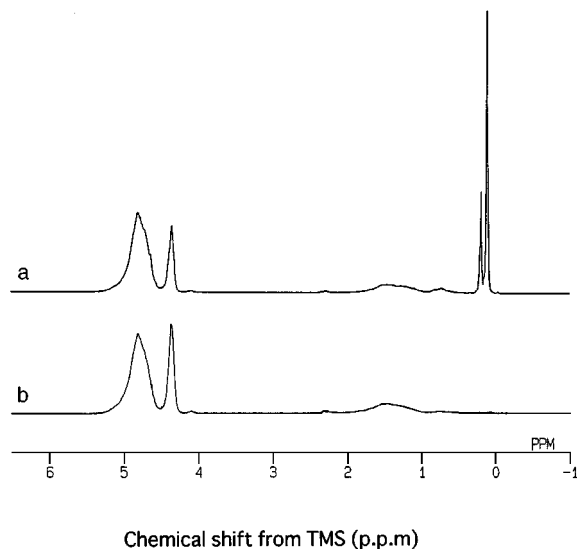


Figure 5 ^1H -NMR spectra of (a) HMDS-introduced perhydropolysilazane and (b) raw perhydropolysilazane.

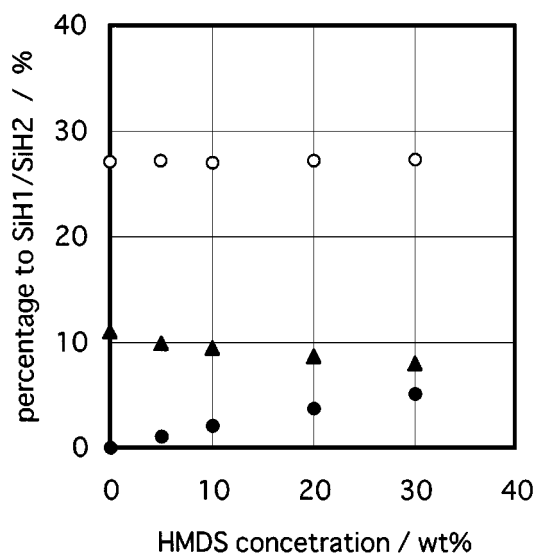


Figure 6 Relation between SiH_3 (\blacktriangle), SiCH_3 (\bullet), NH (\circ) of HMDS-introduced perhydropolysilazane and HMDS concentration before reaction.

Both spectra show peaks centered at 4.8, 4.3 and 1.4 (broad) p.p.m, corresponding to SiH/SiH_2 [1], SiH_3 [1] and NH [1] respectively.

Fig. 6 shows the relation between the ratios of SiH_3 , NH , SiCH_3 to SiH/SiH_2 and the amount of HMDS. The ratio was calculated from the area of each peak and the number of protons in each group. The percentage of SiCH_3 increases and SiH_3 decreases with the increase in the amount of HMDS. The percentage of NH does not change.

3.4. Elemental composition

The results of the elemental analyses of HMDS-introduced perhydropolysilazane and perhydropolysilazane are shown in Table I. Carbon content increases with the increase of HMDS. Silicon and nitrogen slightly decrease, and oxygen and hydrogen do not change.

TABLE I Elemental analysis of HMDS-introduced perhydropolysilazane

HMDS concentration wt %	Composition (wt %)				
	Si	N	O	C	H
5	62.3	24.9	1.7	1.0	8.8
10	60.0	24.6	2.0	1.8	8.8
20	59.1	24.3	2.0	3.1	9.0
30	58.7	24.0	1.4	4.2	9.2
perhydropolysilazane	62.5	24.9	1.0	0.1	8.8

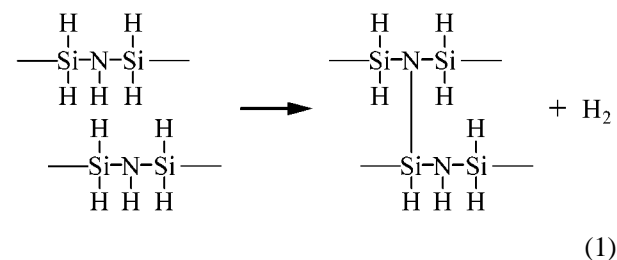
3.5. GC

Evolution of hydrogen was qualitatively detected in the gas phase of the autoclave during the reaction between perhydropolysilazane and HMDS. Other compounds such as trimethylsilane were not observed.

4. Discussion

4.1. Polymerization of perhydropolysilazane

Fig. 3 shows the molecular weight (M_n) of perhydropolysilazane easily increases. The increase rate of M_n is about 3 per day. This may be caused by the polymerization of perhydropolysilazane as follows:



Polymerization of perhydropolysilazane is promoted by basic solvents such as pyridine and amines. The base of these solvents, the lone pair of electrons of Nitrogen, catalyze the dissociation of N-H bonds of perhydropolysilazane. Fig. 3 shows that the polymerization of perhydropolysilazane proceeded even in an inert solvent. Nitrogen in perhydropolysilazane works as an autocatalyst.

4.2. Introduction of HMDS

The FT-IR spectrum (Fig. 4) and the ^1H -NMR spectrum (Fig. 5) of HMDS-introduced perhydropolysilazane indicates that HMDS bonds to perhydropolysilazane. The curves in Fig. 6 suggest that HMDS reacts with Si-H groups, not N-H groups, of perhydropolysilazane. Si-H groups easily react with nucleophilic groups such as N-H . The bonds were formed between Si-H groups of perhydropolysilazane and N-H groups of HMDS. Si-H_3 groups which exist in the end of polymer chains are supposed to be most easily attacked. Elimination of hydrogen gases are thought to be accompanied with the formation of these Si-N bondings. The reaction between HMDS and

perhydropolysilazane proceeds as shown in the following equation:

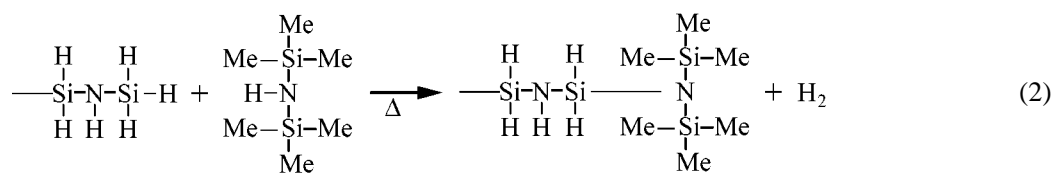


Fig. 6 shows the increase of Si-CH₃ groups is not consistent with the decrease of Si-H₃ groups (the increase of Si-CH₃ is about 50% larger). HMDS seems to react also with Si-H₁ or Si-H₂ groups of perhydropolysilazane.

The results of the carbon analyses in Table I and an Si-CH₃ curve in Fig. 6 reveal that the amount of HMDS radical introduced to perhydropolysilazane proportionally depends on the amount of HMDS fed into the autoclave. The ratio of moles of HMDS bonded to perhydropolysilazane compared to that of HMDS fed into an autoclave is approximately 30 percent. In the case of 30 weight % of HMDS fed, the amount of HMDS radical introduced to perhydropolysilazane is calculated at about 5 atomic % on the basis of silicon. The amount of HMDS radical can be controlled by the amount of HMDS.

4.3. Stabilization of perhydropolysilazane

The curves in Fig. 3 indicate that HMDS radical prevents the polymerization of perhydropolysilazane. The increase rate of Mn of 5 atomic % of HMDS radical-introduced perhydropolysilazane was about 0.3 per day, which was ten times slower than that of perhydropolysilazane. A slight increase of Mn was observed after the reaction with a decrease of the amount of HMDS (Fig. 2). This suggests that a polymerization reaction (1) also proceeded in the autoclave.

There are two effects of HMDS radical. One is the decrease of Si-H₃ bonds. Fig. 6 indicates that the amount of Si-H₃ bonds of 5 atomic % of HMDS radical-introduced perhydropolysilazane decreased about 20 percent compared to that of perhydropolysilazane. Si-H₃ bonds exist on the ends of perhydropolysilazane, and there are supposed to easily polymerize, compared to Si-H₁ and Si-H₂ bonds. We assume the steric hindrance as another effect of HMDS radicals. Bulky HMDS radicals are thought to prevent the polymer molecules from approaching each other. Si-H bonds adjacent to the

terminal HMDS radicals appear to react with the most difficulty to N-H bonds.

5. Conclusions

HMDS can be introduced to perhydropolysilazane by heating these mixtures with pyridine. N-H groups of HMDS mainly react with Si-H₃ groups of perhydropolysilazane, the terminal of the polymer chain, to form Si-N bonds. These additional reactions were accompanied by the elimination of hydrogen gases. The amount of HMDS radical introduced to perhydropolysilazane can be controlled by changing the concentration of HMDS before heating. HMDS radical-terminated perhydropolysilazane (5 atomic % of HMDS radical introduced) was 10 times as stable as perhydropolysilazane. The decrease of the amount of reactive Si-H bonds and the steric hindrance are the main effects of HMDS radicals introduced to perhydropolysilazane.

Recently, perhydropolysilazane comes to be remarked as the precursor polymer to silica coating, especially for the dielectric films in electrical devices. Improvement of the chemical stability by HMDS radical facilitates the mass production of perhydropolysilazane, and we expect it to be more widely used in the near future.

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Received 19 May 1997

and accepted 14 July 1998