

Studies on Soluble Fraction of Glow-Discharge Polysilazane Formed from Hexamethylcyclotrisilazane

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Synopsis

The soluble part of glow discharge polysilazane prepared from hexamethylcyclotrisilazane was studied. The composition of the soluble fraction was examined by gas chromatography and mass spectrometry. It was found that the fraction contained five main components, and two of them, identified by mass spectrometry, were octamethylcyclotetrasilazane and bicyclic silazane dimer. A reaction mechanism leading to dimer formation from hexamethylcyclotrisilazane in glow discharge was proposed.

INTRODUCTION

Polysilazane thin films prepared by glow discharge polymerization of hexamethylcyclotrisilazane exhibit many interesting features such as very high thermal stability¹ and good electric properties.² Our recent research^{3,4} indicates that both the structure and the properties of glow discharge polysilazanes are strongly dependent on the glow discharge conditions. It was observed that polysilazanes formed with low discharge current densities contained a small fraction soluble in nonpolar solvents such as benzene or carbon tetrachloride. The content of the soluble fraction decreases with increasing current density and the polymers obtained over 4 mA/cm² are completely insoluble.

The low solubility of glow discharge polysilazane is due to crosslinking occurring during glow discharge polymerization. The degree of crosslinking increases with the current density which is manifested by the loss of a soluble fraction of the polymer products obtained at higher current densities.³ The amount of soluble fraction is relatively small. The composition and the structure of its components may give some information about the reactions of hexamethylcyclotrisilazane exposed to the glow discharge. Investigations of this fraction may, therefore, throw more light on the polymerization of hexamethylcyclotrisilazane in plasma conditions as well as the polymer structure.

The present paper deals with the soluble fraction of glow discharge polysilazane and the structure of some of the components involved.

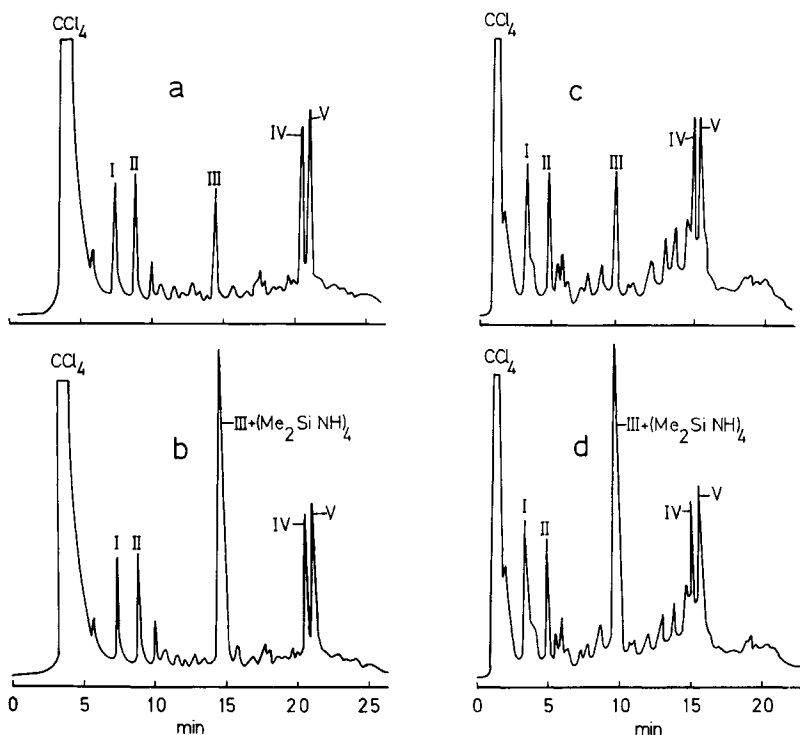


Fig. 1. Chromatograms of soluble part of glow discharge polysilazane: (a) extract sample on column OV 101 (nonpolar); (b) extract + standard $(\text{Me}_2\text{SiNH})_4$ sample on column OV 101; (c) extract sample on column OV 225 (polar); (d) extract + standard sample on column OV 225.

EXPERIMENTAL

Hexamethylcyclotrisilazane was polymerized in the electrode glow discharge system described previously.³ The polymerizations were carried out at constant discharge parameters, such as a discharge frequency of 20 kHz, current density of 1 mA/cm², monomer vapor pressure of 0.3 torr, and discharge time of 30 sec.

Polymer samples obtained under these conditions were extracted in boiling carbon tetrachloride for 5 hr using a Soxhlet apparatus.

The content of the soluble fraction separated in this way from the polymer was determined by means of gas chromatography using a Jeol gas chromatograph Model JGC 1100, equipped with a flame ionization detector. Two columns with different polarities were used: one was 5 feet \times $\frac{1}{8}$ in. with 3% OV-225 supported on Chromosorb WAW, 80–100 mesh, and the second was 2 m \times $\frac{1}{8}$ in. with 10% OV-101 on Varaport 30, 80–100 mesh. Nitrogen was the carrier gas in both cases.

The structure of soluble components was examined by means of a gas chromatograph coupled with a mass spectrometer LKB Corp. Model GCMS 9000 S, using a 1.5 m \times 15 mm column filled with 1% OV-1 on Chromosorb WAS 60/80 mesh. The mass spectra were obtained with an electron beam energy of 70 eV.

RESULTS AND DISCUSSION

Solubility investigations showed that glow discharge polysilazane formed at 1 mA/cm² contained 16–17% by weight fraction soluble in carbon tetrachloride. The results of gas chromatography revealed that the fraction consisted of numerous components, five of which accounted for 65% of the whole fraction [Figs. 1(a) and 1(c)].

The mass spectra of these five compounds are characterized by the following most abundant peaks: I, 206; II, 205; III, 277; IV, 408; and V, 407. Three of them (I, II, and IV) are cyclosiloxazanes in which one or two imine groups (mass = 15) are substituted by oxygen (mass = 16). The character of their mass spectra is almost the same as that of cyclosilazanes (e.g., hexamethylcyclotrisilazane with the most abundant peak 204), but all the peaks are shifted toward higher mass values by a unit or two. The presence of oxygen in glow discharge polysilazanes was proven in our previous studies.⁴

In the present work, we focused our attention on the remaining two compounds (III and V). The mass spectrum of compound III is presented in Figure 2(a). This spectrum is almost identical to that of octamethylcyclotetrasilazane reported by Silbiger et al.⁵ Relative abundance of isotopic ions, listed in Table I, confirms this compound as octamethylcyclotetrasilazane.

An additional experiment was performed to confirm the identification of compound III. Retention times in the standard sample of octamethylcyclotetrasilazane (PCR product, mp 97°C, bp 225°C; dissolved in CCl₄) chromatograms were measured using both columns described in the experimental part, which agreed well with the respective times of compound III in the extract sample chromatograms. Moreover, in both cases, when the gas chromatography experiments of the mixture of extracted sample + standard sample were performed, an increase in the peak corresponding to compound III was observed. The mixture chromatograms are shown in Figures 1(b) and 1(d).

This correspondence of retention times of compound III and standard octamethylcyclotetrasilazane, independent of the column polarity, as well as the mass spectrum provide the evidence for identification of this compound as octamethylcyclotetrasilazane.

The identification of compound V is much more complicated. The most abundant peak in its mass spectrum [Fig. 2(b)] corresponds to a mass of 407. It is generally known^{5–8} that the predominant fragmentation of organosilicon compounds in a mass spectrometer proceeds through splitting off of the methyl group from the parent ion resulting in the appearance of a peak M-15 in the mass spectrum. Therefore, we expect the molecular weight of compound V to be 422, which corresponds to the general formula Si₆C₁₁H₃₈N₆. A comparison of calculated relative intensities of isotopic peaks for the peak 407 with the observed ones (Table I) confirms this general formula. The metastable transitions observed in the mass spectrum of compound V (Table II) as well as the occurrence of doubly charged ions [(M - 2CH₃)⁺⁺, 196; (M - 2CH₃ - CH₄)⁺⁺, 188; and (M - 2CH₃ - NH₃)⁺⁺, 187.5] also confirm our assumption. This formula corresponds to the bicyclic silazane dimer, which may be expressed by one of the two competitive structures A or B:

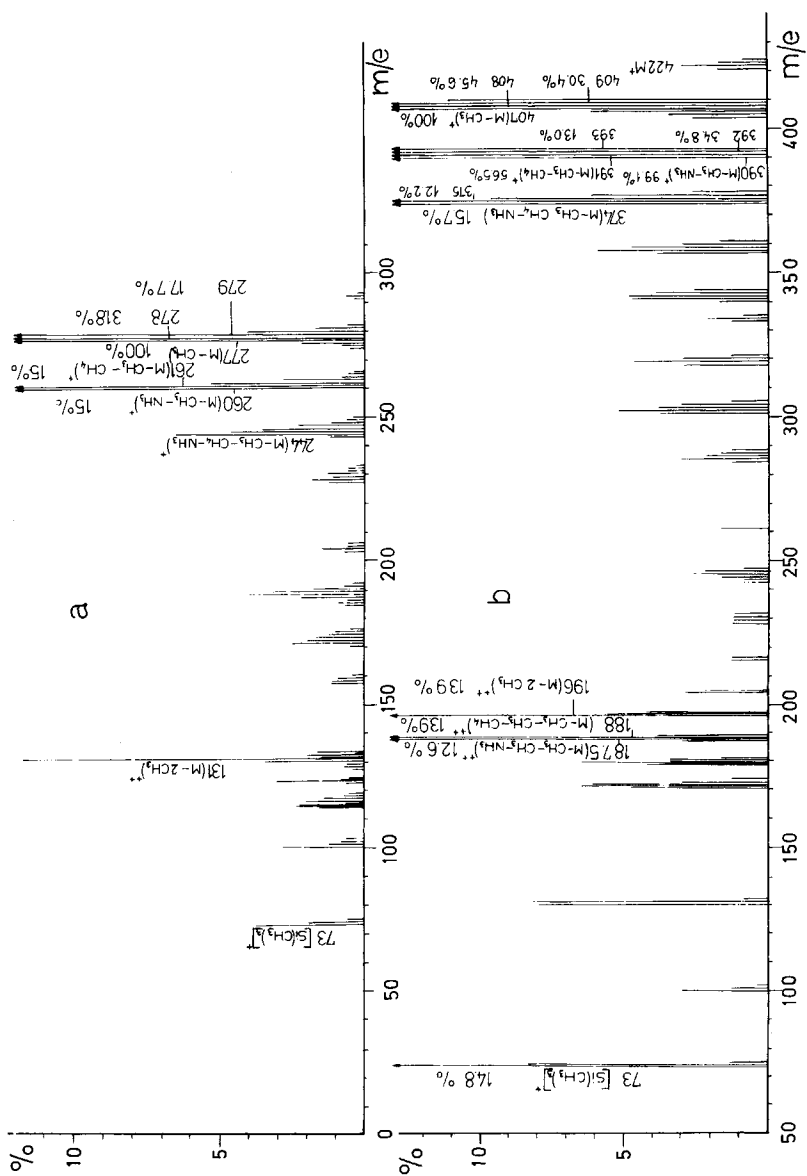
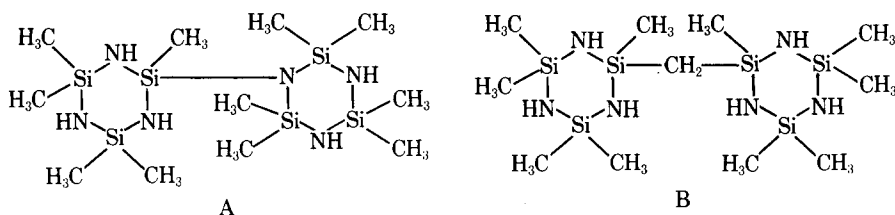
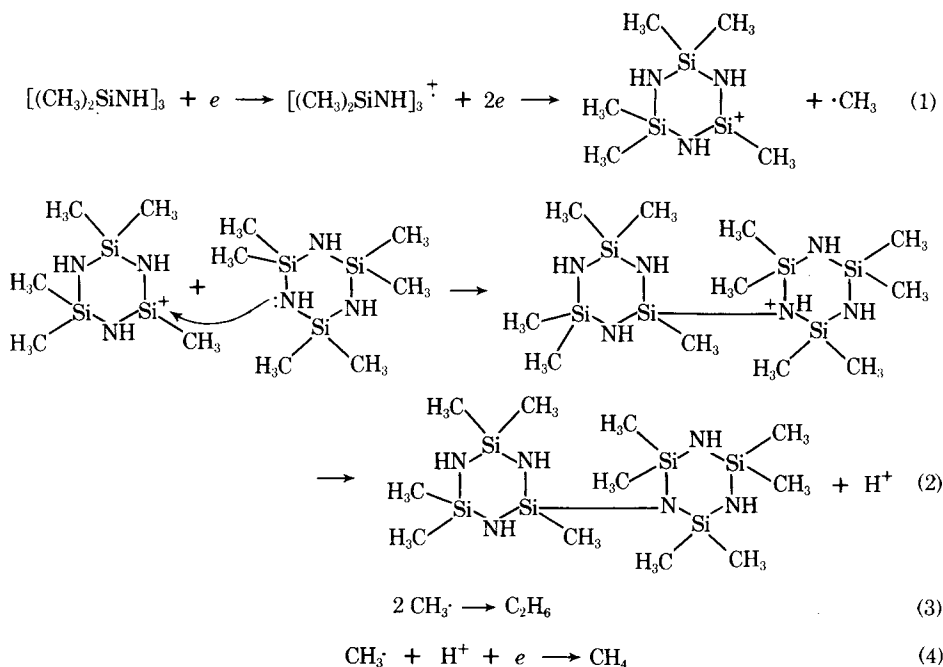


Fig. 2. Mass spectra of silazane components: (a) compound III; (b) compound V.



The reactions leading to the dimer formation are regarded to be the first step in the formation of the crosslinked polymer structure. And although the nature of the linkage between the two cycles of the dimer cannot be immediately proven by means of mass spectrometry, our experiments concerning the quantitative analysis of IR spectra of the polymer samples obtained in the different energetic conditions show that the ratio of Si—N to N—H bonds increases with the discharge current density which proves that the crosslinking of the polymer takes place through the creation of new Si—N bonds.⁴ These results permit speculation that structure A of dimer is the most likely. The identification of the dimer structure by NMR spectroscopy is extremely difficult due to the fact that the amount of soluble fraction is too small to be separated by preparative gas chromatography. The NMR spectra of the crude extract did not give any conclusive result which could be used to distinguish the structure A or B of compound V.

Considering the mechanism which may lead to the formation of dimer (structure A), we took into account the fact that in the conditions of a mass spectrometer, the basic fragmentation of the monomer is the splitting off of the methyl group with the formation of the ion $[(\text{CH}_3)_2\text{SiNH}_3 - \text{CH}_3]^+$, independently of the electron beam energy used (in the range of 10–70 eV). It is then expected that this type of hexamethylcyclotrisilazane fragmentation may be the first step of a reaction scheme leading to the formation of a bicyclic structure in the glow discharge conditions:



This scheme involves the appearance of hydrocarbons like ethane [due to reaction (3)] and methane [due to reaction (4)] in the gaseous residue after glow discharge polymerization. Gas-chromatographic analysis of the residue formed under the same conditions as the extracted polymer has shown that it consists mainly of three hydrocarbons: methane, ethane, and ethylene in the proportion 5:33:4.

The results presented above show that at least two competitive reactions take place during the glow discharge in the hexamethylcyclotrisilazane vapor: one is the ring enlargement from six-membered to eight-membered, the other is the reaction leading to dimer and in consequence to polymer formation. An analogous phenomenon was described by Andrianov⁹ who investigated conventional reactions of hexamethylcyclotrisilazane in nucleophilic and electrophilic environments.

CONCLUSIONS

The results presented are significant if considered from the point of view of the polymerization mechanism and polymer structure:

1. The presence of octamethylcyclotetrasilazane in the soluble part of the polymer proves that one of the most important reactions of hexamethylcyclotrisilazane during glow discharge is ring enlargement. The eight-membered cycle created in this reaction may then act as a comonomer in the structure of the polymer.

2. The presence of the bicyclic dimer is even more important. Although its

TABLE I
Calculated and Observed Relative Abundances of Isotopic Ions of Composition M minus CH₃

<i>m/e</i>	Relative abundance	
	Calculated	Observed
	Compound III	
277	100	100
278	29.7	31.8
279	17.1	17.7
	Compound V	
407	100	100
408	45.2	45.6
409	29.1	30.4

TABLE II
Metastable Transitions Observed in the Mass Spectrum of Compound V

Transition	Calculated apparent mass $m^* = m_2^2 - m_1$	Approximate observed mass
407 ⁺ → 390 ⁺ + 17	373.8	374.1
390 ⁺ → 374 ⁺ + 16	358.6	358.5
374 ⁺ → 358 ⁺ + 16	342.7	342.6

structure is not fully confirmed, it is certain that it must be the result of at least a bimolecular reaction, which leads to the retention of the six-membered silazane rings in the product. Such a reaction is regarded as the first step in polymer formation, and it allows us to assume that trisilazane rings are also retained in the structure of the polymer.

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