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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Gas Chromatography/Mass Spectrometry Study of the Low-Molecular-Weight Fraction of Plasma-Polymerized N,N'-Bis-(Dimethylsilyl)Tetramethylcyclodisilazane

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To cite this Article Wróbel, A. M.(1989) 'Gas Chromatography/Mass Spectrometry Study of the Low-Molecular-Weight Fraction of Plasma-Polymerized N,N'-Bis-(Dimethylsilyl)Tetramethylcyclodisilazane', *Journal of Macromolecular Science, Part A*, 26: 5, 743 — 759

To link to this Article: DOI: 10.1080/00222338908052008

URL: <http://dx.doi.org/10.1080/00222338908052008>

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GAS CHROMATOGRAPHY/MASS SPECTROMETRY STUDY OF THE LOW-MOLECULAR-WEIGHT FRACTION OF PLASMA-POLYMERIZED *N,N'*-BIS- (DIMETHYLSILYL)TETRAMETHYLCYCLODISILAZANE

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ABSTRACT

The composition of a low-molecular-weight fraction from plasma-polymerized *N,N'*-bis(dimethylsilyl)tetramethylcyclo-disilazane has been studied by gas chromatography/mass spectrometry. Identification of the separate components of this fraction based on the mass spectra revealed the presence of various monomer derivatives mostly having the general structure of a *N*-silyl-substituted cyclo-disilazane skeleton. This strongly suggested that this structural unit displays a high resistance to plasma fragmentation and that it was incorporated as such into the polymer film. Mechanisms have been proposed for the elementary plasma reactions involved in the formation of the identified compounds.

INTRODUCTION

We have found that plasma-polymerized organosilicon films, which are mostly composed of highly crosslinked material insoluble in organic solvents, contain a small amount of a soluble, volatile, low-molecular-weight fraction [1-3]. As the components of this fraction are the intermediates of plasma

polymerization, a knowledge of their structure may provide valuable information regarding the mechanism of elementary plasma reactions contributing to the overall polymerization process and the structure of the resulting plasma polymer. However, examination of this fraction requires complex analytical methods due to its extremely low concentration. Our previous studies [1-3] showed that gas chromatography/mass spectrometry (GC/MS) is very useful for this purpose. By this technique the low-molecular-weight fraction isolated from plasma polymer either by extraction [1] or evaporation by heating the polymer to a relatively mild temperature [2, 3] can first be separated by gas chromatography, and then the separated products can be identified by mass spectrometry.

The present paper deals with GC/MS examination of the low-molecular-weight fraction isolated from plasma-polymerized *N,N'*-bis(dimethylsilyl)-tetramethylcyclodisilazane (PP-NSCDSN) which was selected as a model monomer representing *N*-silyl-substituted cyclodisilazanes. In the light of our recent data [4], this group of monomers seems to be particularly attractive for production of high-temperature-tolerant plasma-polymerized coatings due to the presence of the *N*-silyl-substituted cyclodisilazane (Si_4N_2) skeleton in the molecules.

EXPERIMENTAL

Plasma polymerizations were carried out in a stationary-electrode glow-discharge system operated at 20 kHz, which has been described elsewhere [4, 5]. The discharge chamber consisted of a 20-L glass bell jar containing two parallel, rectangular (5×10 cm), stainless steel electrodes. The polymerizations were performed under the following constant conditions: Electrode gap, d , 3 cm; initial monomer pressure, p_0 , 0.3 torr; current density, j , 1 mA/cm²; and discharge duration, t , 30 s. Polymer films used for the study were deposited on stainless steel tape mounted on the electrode surface. In order to avoid the effects of aging, the films were subjected to examination immediately after polymerization.

GC/MS examination was carried out on polymer samples of about 0.2 mg isolated from the substrate and placed in a JEOL pyrolyzer unit, Model 727. The samples were heated in a helium atmosphere at 350°C for 30 s. The volatile products were fed directly to a JEOL gas chromatograph, Model JGC 1100, equipped with a flame ionization detector and a 2000 \times 3 mm stainless steel separation column filled with 10% OV 101 supported on 80/100 mesh Varaport. The column was heated from 30 to 270°C at 10°C/min.

The separated products were then analyzed with a LKB mass spectrometer, Model 2091, at a standard ionizing electron energy of 70 eV.

Infrared spectra of polymer films were recorded on a Perkin-Elmer, Model 457, spectrophotometer by using the ATR technique.

The NSCDSN monomer was synthesized in the Laboratory of Organosilicones of the Technical University of Łódź. Prior to plasma polymerization the monomer was purified by vacuum distillation on a Perkin-Elmer, Model 151, distillation column with a Teflon spinning band, following which its purity was tested by gas chromatography.

RESULTS AND DISCUSSION

GC/MS Examination

A gas chromatogram of the volatile fraction evolved from PP-NSCDSN on heating is shown in Fig. 1. The most prominent peaks were identified by mass spectrometry, and the individual molecular and structural formulas of the compounds corresponding to them are presented in Table 1. It should be noted that the group of peaks appearing at the shortest retention time, marked with the letter X, corresponds to an unresolved mixture of light hydrocarbons and monosilanes, and was, therefore, difficult to interpret.

It can be seen from Table 1 that the volatile fraction contains trimethylsilane (I), monomer (IV), its various derivatives with the Si_4N_2 skeleton (II, III, V, and VII), and a monomer derivative with an opened cyclodisilazane ring (VI). The confirmation of these structures based on mass spectrometry is discussed below.

Mass Spectra

The mass spectrum of Compound I was in good agreement with MS data in the literature [6] for trimethylsilane and showed the presence of the most abundant peak at m/e 59 (100%) due to the $(\text{M}-\text{Me})^+$ ion (where M means the mass number of the molecular ion) and the peaks at m/e 73 (18.7%), 58 (49.1%), 45 (51.9%), 43 (45.3%), 31 (19.7%), and 29 (12.6%) correspond to Me_3Si^+ , Me_2Si^+ , H_2MeSi^+ , MeSi^+ , H_3Si^+ , and HSi^+ fragment ions, respectively. Thus, the Me_3SiH structure can be assigned to Compound I.

The spectrum of Compound II was analogous to that of Compound III presented in Fig. 2, suggesting similar structures. As can be seen from Fig. 2, the spectrum exhibits the base peak at m/e 233, which is attributed to the

TABLE 1. Compounds Identified in the Volatile Fraction of PP-NSCDSN

Compound	Molecular weight	Molecular formula	Structural formula
I	74	$\text{Si}_1\text{C}_3\text{H}_{10}$	HSiMe_3
II	248	$\text{Si}_4\text{C}_7\text{H}_{24}\text{N}_2$	
III	248	$\text{Si}_4\text{C}_7\text{H}_{24}\text{N}_2$	
IV (monomer)	262	$\text{Si}_4\text{C}_8\text{H}_{26}\text{N}_2$	
V	276	$\text{Si}_4\text{C}_9\text{H}_{28}\text{N}_2$	
VI	278	$\text{Si}_4\text{C}_9\text{H}_{30}\text{N}_2$	
VII	320	$\text{Si}_5\text{C}_{10}\text{H}_{32}\text{N}_2$	

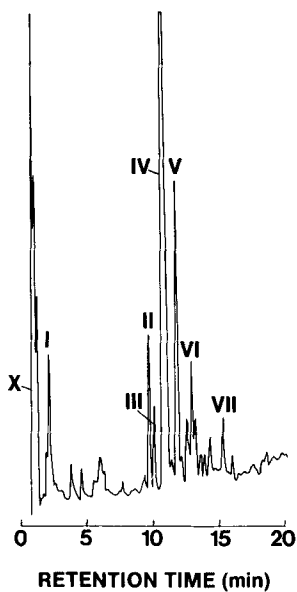


FIG. 1. Gas chromatogram of the volatile fraction evolved from PP-NSCDSN.

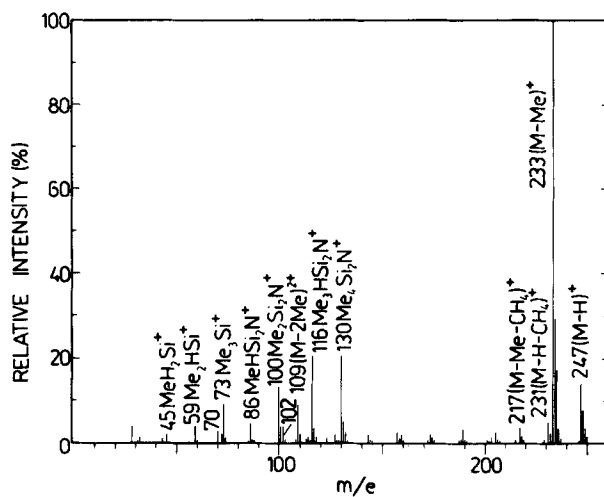


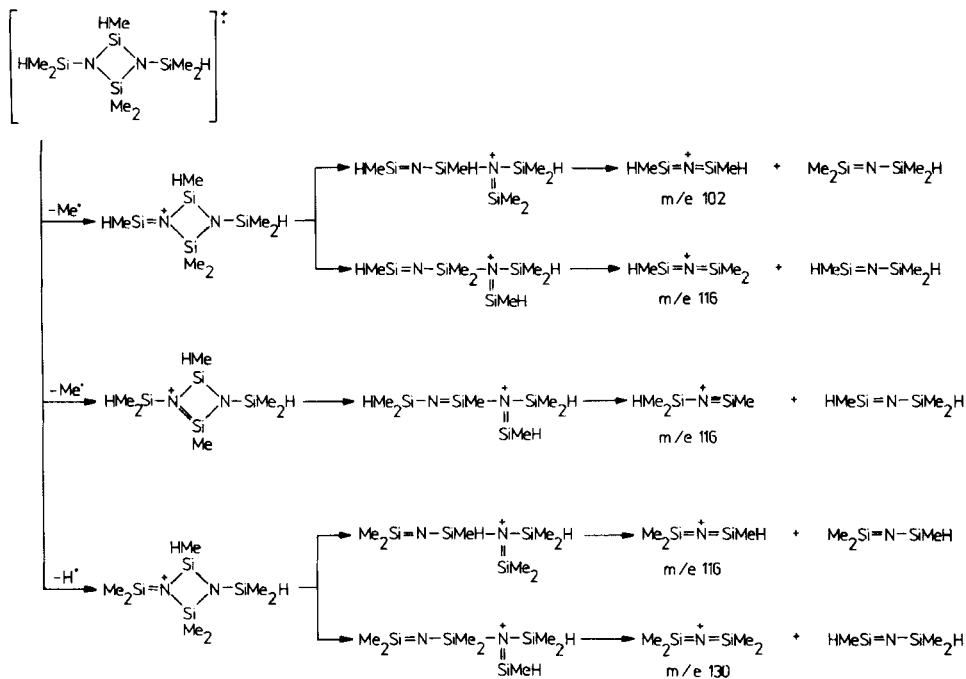
FIG. 2. Mass spectrum of Compound II.

(M–Me)⁺ ion and a peak at *m/e* 109 corresponding to the doubly charged (M–2Me)²⁺ ion. The ion peak at *m/e* 247 arises from the loss of hydrogen from the molecular ion, and the ion peaks at *m/e* 231 and 217 are due to the elimination of methane from the (M–H)⁺ and (M–Me)⁺ ions, respectively. The peaks at *m/e* 130, 116, and 102 are assigned to the Me₄Si₂N⁺, HMe₃Si₂N⁺, and H₂Me₂Si₂N⁺ ions, respectively, resulting from transannular fragmentation of the Si₄N₂ skeleton. Based on these data, the same molecular formula Si₂C₇H₂₄N₂ and the *N*-silyl-substituted cyclodisilazane structure can be assigned to Compounds II and III, which are formed from the monomer by substitution of one methyl group with hydrogen either in the *N*-silyl substituent (Compound II) or in the cyclodisilazane ring (Compound III). This structural difference determines the different volatility of these compounds as revealed by the gas chromatograph (Fig. 1).

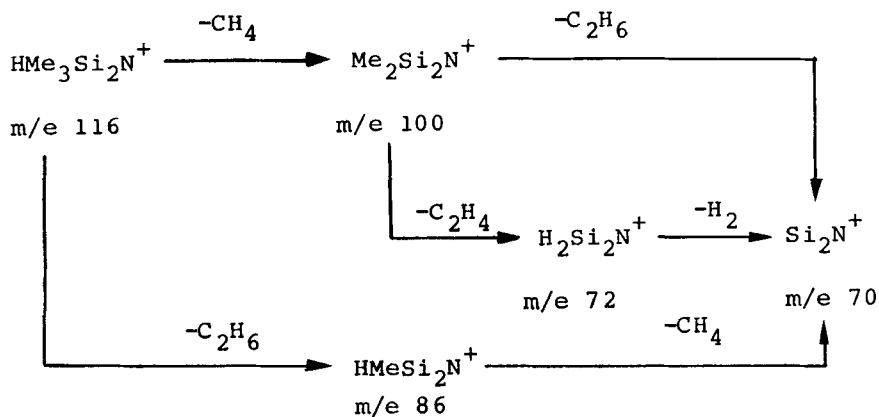
The postulated structures for Compounds II and III can be verified by the fragmentation patterns involved in the formation of the above-mentioned Me₄Si₂N⁺, HMe₃Si₂N⁺, and H₂Me₂Si₂N⁺ ions. For example, by assuming the *N,N'*-bis(dimethylsilyl)trimethylcyclodisilazane structure for Compound III, these ions can be produced from the molecular ion according to the fragmentation patterns in Scheme 1. Ions thus formed may subsequently undergo further fragmentation to the Me₂Si₂N⁺, HMeSi₂N⁺, H₂Si₂N⁺, and Si₂N⁺ ions, which are revealed by the presence of the lower intensity peaks at *m/e* 100, 86, 72, and 70, respectively (Fig. 2). The formation of these ions is represented by the fragmentation patterns of the HMe₃Si₂N⁺ ion *m/e* 116 in Scheme 2.

It is interesting to note that this group of ions was also detected in the mass spectra of the remaining components of the volatile fraction. The relative intensities of particular ions for each investigated component (except for Compound I) are depicted in Table 2. These ions seem to be characteristic of methylsilicon compounds containing disilazane units.

The spectra of Compounds IV and V, shown in Figs. 3 and 4, closely resemble that of Compound III (see Fig. 2), revealing the presence of similar groups of ion peaks. The main difference in these spectra is that the ion peaks for (M–Me)⁺ and the accompanying ones for (M–H)⁺, (M–H–CH₄)⁺, and (M–Me–CH₄)⁺ are shifted to higher *m/e* values by 14 units for Compound IV (Fig. 3) and by 28 units for Compound V (Fig. 4) with respect to Compound III (Fig. 2). The shift values observed for these peaks correspond to an increase of one or two methyl groups in Compounds IV and V with respect to Structure III. This agrees well with the decreasing intensity of the (M–H)⁺ ion peak, as noted in Figs. 2–4. By taking other spectral features into account, such as the positions of doubly charged (M–2Me)²⁺



SCHEME 1.



SCHEME 2.

TABLE 2. Relative Intensities of the Fragment Ions Characteristic of the Mass Spectra of the Most Abundant Components of the Volatile Fraction of PP-NSCDSN

<i>m/e</i>	Ion	Relative intensity, %, of Compound					
		II	III	IV	V	VI	VII
130	Me ₄ Si ₂ N ⁺	33.4	20.7	30.5	27.9	21.9	32.9
116	HMe ₃ Si ₂ N ⁺	33.2	20.8	19.5	8.3	16.1	10.7
102	H ₂ Me ₂ Si ₂ N ⁺	5.7	4.1	3.7	2.6	3.3	2.6
100	Me ₂ Si ₂ N ⁺	22.1	13.6	21.2	12.4	12.5	16.0
86	HMeSi ₂ N ⁺	6.6	4.6	6.2	2.9	3.3	2.8
72	H ₂ Si ₂ N ⁺	2.8	2.1	2.8	1.4	1.5	1.2
70	Si ₂ N ⁺	4.3	2.8	4.0	1.5	1.5	1.7

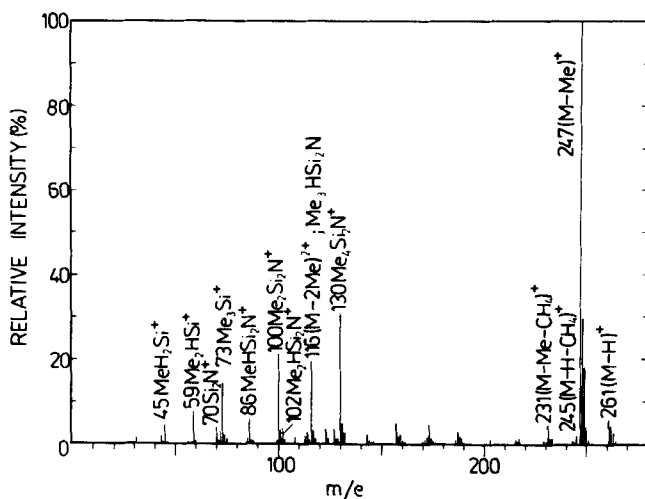


FIG. 3. Mass spectrum of Compound IV.

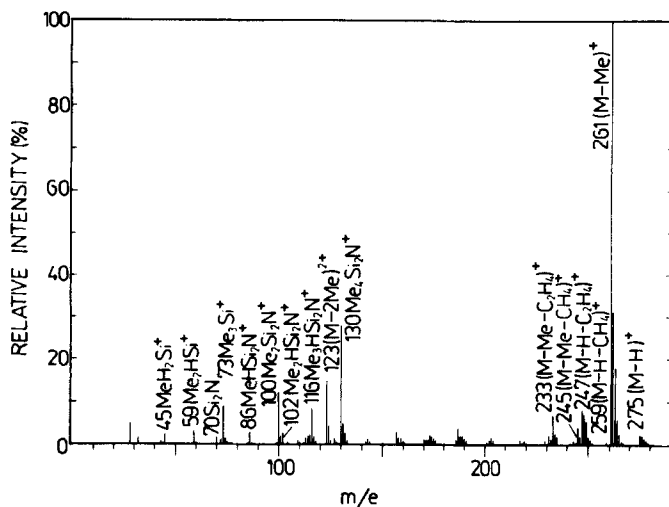
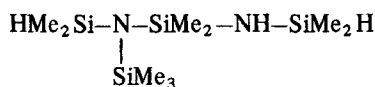


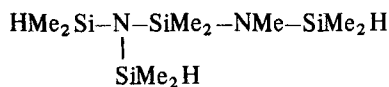
FIG. 4. Mass spectrum of Compound V.

ion peaks and the presence of disilazane fragment ions from Table 2, Compound IV is recognized as NSCDSN monomer, and the *N*-dimethylsilyl-*N'*-trimethylsilyltetramethylcyclodisilazane structure is proposed for Compound V. The structure of Compound IV was additionally verified by using NSCDSN monomer as a standard for GC/MS. In this case the GC retention time and the mass spectrum of NSCDSN were almost identical to those found for Compound IV.

The mass spectrum of Compound VI in Fig. 5 shows the presence of the base peak at m/e 263, again due to the $(M-Me)^+$ ion, the medium intensity peak at m/e 277 from the $(M-H)^+$ ion, and derivative peaks at m/e 247 and 261 associated with loss of methane, which are ascribed to the $(M-Me-CH_4)^+$ and $(M-H-CH_4)^+$ ions, respectively. Furthermore, the appearance of a weak-intensity doubly charged $(M-2Me)^{2+}$ ion at m/e 124 and a group of the above-mentioned disilazane ion peaks in the range of m/e 70-130 is also noted. From these data the following two alternative structures with opened cyclodisilazane rings can be postulated for Compound VI:



A



B

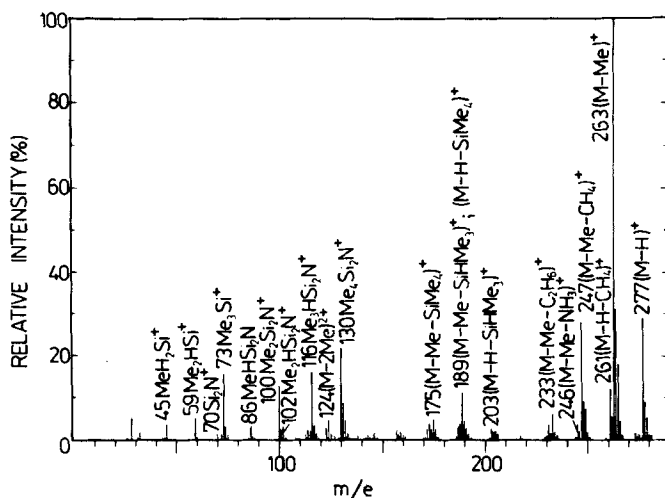
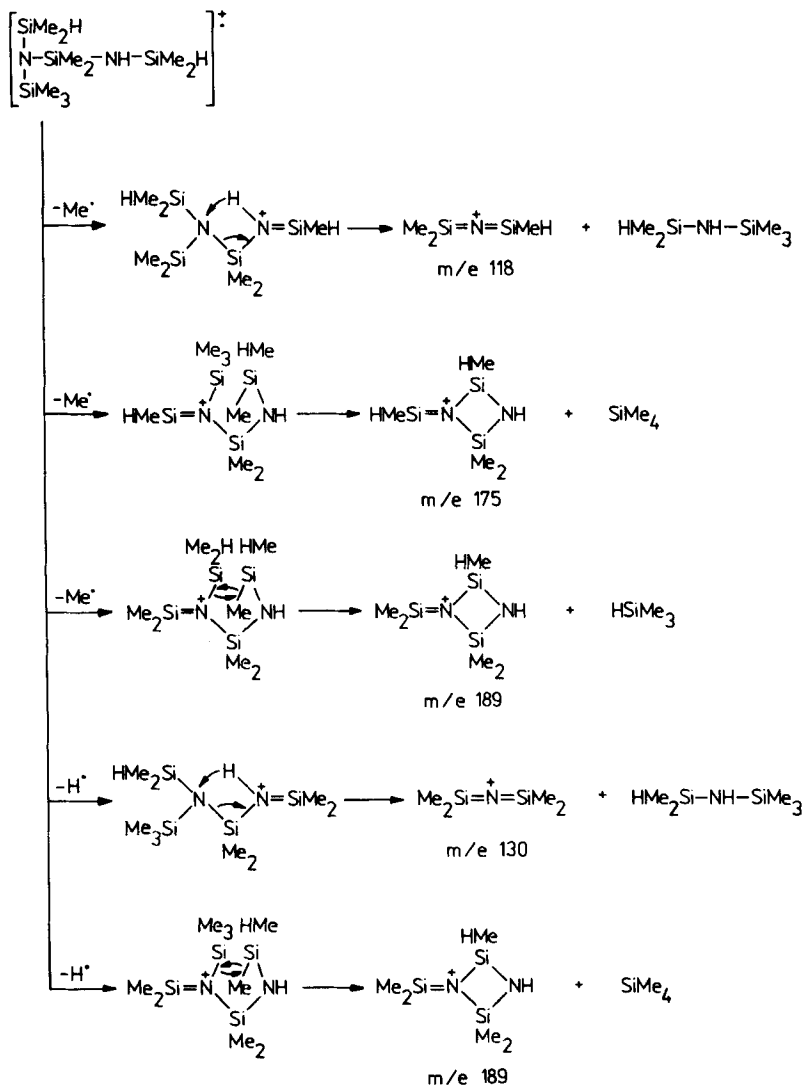


FIG. 5. Mass spectrum of Compound VI.

Structure A, however, seems to be more likely since it explains the appearance (Fig. 5) of the ion peaks at m/e 116, 130, 175, and 189. By assuming Structure A for Compound VI, the formation of these ions can be described by the fragmentation patterns of the molecular ion presented in Scheme 3.

Structure A also agrees reasonably with a trend observed in the IR spectra of NSCDSN monomer and its plasma polymer (Fig. 6). The polymer spectrum (Fig. 6B) exhibits absorption bands at 3360 and 1175 cm^{-1} which are absent from the monomer spectrum (Fig. 6A). These bands are characteristic of the Si-NH-Si units and correspond to N-H stretch and N-H bend vibrations, respectively [7]. Detailed discussion of the IR spectra has been reported elsewhere [4].

The mass spectrum of Compound VII (Fig. 7) markedly differs from those of the former compounds. The base peak seen at m/e 261 appears to be due to loss of a dimethylsilyl (HMe₂Si) group from the molecular ion, whereas the (M-Me)⁺ ion peak of m/e 305 reveals only 42.5% relative intensity. This is consistent with MS data reported for hexamethyldisilane [8, 9], where the most prominent peak observed for the M₃Si⁺ ion and the Me₅Si₂⁺ ion showed 47.5% relative intensity, thus indicating that fragmentation via Si-Si bond rupture dominates over that involving the loss of a methyl group. These results evidently prove the presence of a disilane Si-Si bond



SCHEME 3.

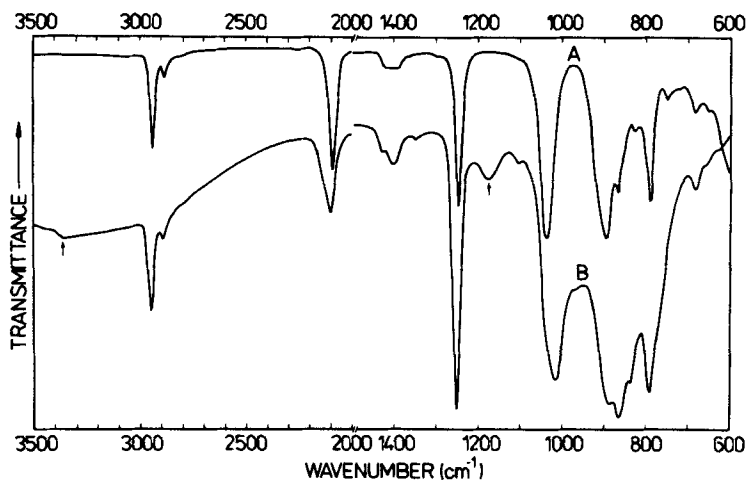


FIG. 6. Infrared spectrum of NSCDSN monomer (A) and its plasma polymer (B).

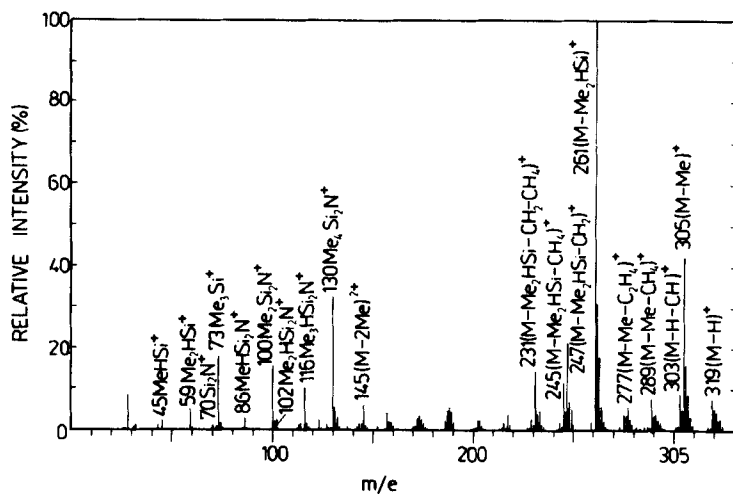


FIG. 7. Mass spectrum of Compound VII.

in Compound VII. The spectrum in Fig. 7 also exhibits the $(M-H)^+$ ion peak at m/e 319, a weak-intensity $(M-2Me)^{2+}$ ion peak at m/e 145, and a group of disilazane fragment ions, as listed in Table 2. In the light of these data, Compound VII is identified as *N*-dimethylsilyl-*N'*-dimethyl(dimethylsilyl)silyl-tetramethylcyclosilazane (see Table 1).

It should be noted that the fragmentation patterns observed in the mass spectra of the compounds containing the Si_4N_2 skeleton are in general consistent with those published for *N*-silyl-substituted cyclodisilazanes [10-12].

Finally, the molecular structures derived from the MS data for particular compounds were verified by comparison of the observed and calculated relative intensity values for the first and second isotope peaks of the most abundant ion peaks. The results in Table 3 show that the differences between the observed intensity values and those calculated on the basis of the accepted molecular structures are within the limits of reproducibility.

Formation of Low-Molecular-Weight Compounds

The structures identified in the low-molecular-weight fraction of the polymer (Table 1) imply that a variety of elementary plasma reactions lead to their formation. For example, Compounds II, III, and V, differing from the monomer by the numbers of hydrogen and methyl substituents, account for the fragmentation of monomer molecules involved in Si-C and Si-H bond breakage. These bonds may undergo an intense homolytic scission under the electron impact or by absorption of highly energetic UV photons emitted from the plasma according to



Reaction (1) is confirmed by the high concentration of ethane found in glow discharge products of NSCDSN [4].

Silyl radicals produced via Reaction (1) may then be involved in a secondary reaction with silylmethyl groups in the monomer molecule:

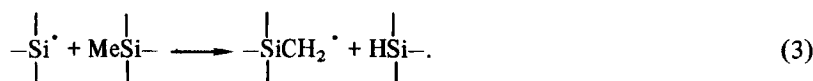


TABLE 3. Observed and Calculated Relative Intensities of the Peaks for the Most Prominent Ion Peaks in the Mass Spectra of Particular Compounds^a

Compound	Ion	<i>m/e</i>	Relative intensity, %	
			Observed	Calculated
I	(M–Me) ⁺	59	100	100
		60	9.3	7.9
		61	3.4	3.7
II	(M–Me) ⁺	233	100	100
		234	29.2	29.9
		235	17.5	17.0
III	(M–Me) ⁺	233	100	100
		234	29.3	29.9
		235	17.3	17.0
IV	(M–Me) ⁺	247	100	100
		248	29.5	31.0
		249	18.1	17.1
V	(M–Me) ⁺	261	100	100
		262	31.4	32.1
		263	17.9	17.2
VI	(M–Me) ⁺	263	100	100
		264	31.4	32.1
		265	18.1	17.2
VII	(M–HMe ₂ Si) ⁺	261	100	100
		262	31.3	32.1
		263	18.2	17.2

(continued)

TABLE 3 (continued)

Compound	Ion	<i>m/e</i>	Relative intensity, %	
			Observed	Calculated
VII	(M-Me) ⁺	305	100 ^a	100
		306	38.1 ^a	38.8
		307	22.8 ^a	22.3

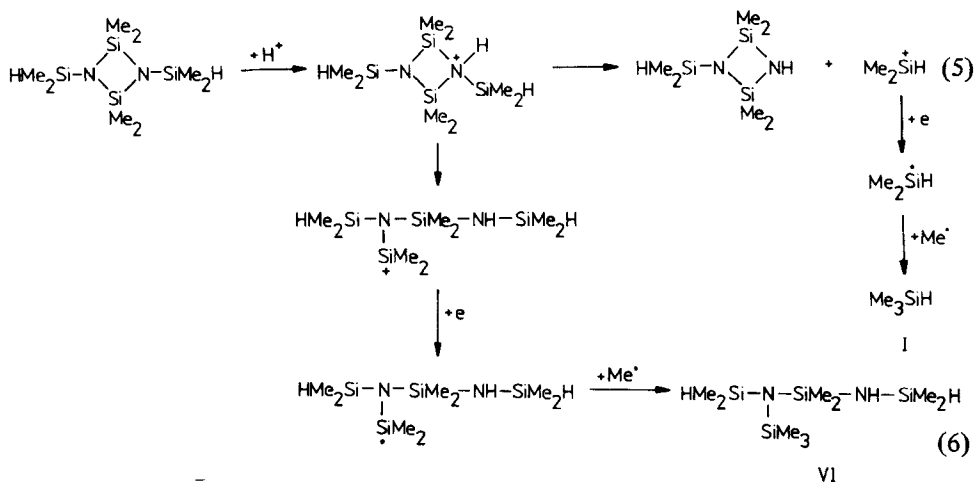
^aIntensities normalized to 100%.

Reaction (3) explains the formation of Compounds II and III. The combination of silyl radicals produced via Reaction (2) with methyl radicals,



leads to the formation of Compound V.

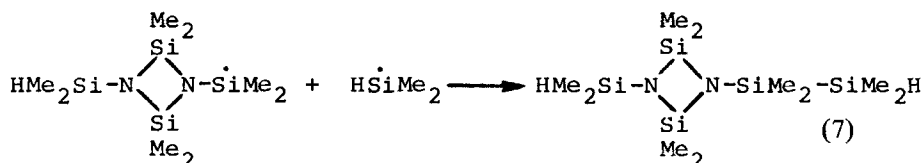
The formation of Compounds I and II is associated with Si-N bond rupture in the monomer molecule and accounts for the ionic reactions involved in their formation. This results from the nature of the Si-N bond which is known to be strongly resistant to homolytic fission and, on the other hand, is highly susceptible toward heterolytic cleavage [13]. The compounds mentioned may be produced via nucleophilic attack of the proton on the nitrogen atom in the monomer molecule according to Reactions (5) and (6), respectively.



VI

N-Dimethylsilyltetramethylcyclodisilazane produced in Reaction (5) was, however, not detected by GC/MS, presumably due to its low stability toward hydrolysis that would occur in contact with the atmosphere.

Compound VII may result from combination of the monomer fragmentation product, produced in Reaction (2), and dimethylsilyl radical, produced in Reaction (5):



The relatively high content of compounds with the Si_4N_2 skeleton in the volatile fraction, as revealed by the gas chromatogram in Fig. 1, accounts for the high stability of this unit toward plasma fragmentation processes. This would lead to a large contribution of the original Si_4N_2 unit to the structure of plasma polymer. This suggestion is reflected in the outstanding thermal stability found for PP-NSCDSN [4].

CONCLUSIONS

The results of this paper have shown that NSCDSN undergoes conversion into products containing mostly the original Si_4N_2 units during plasma polymerization. This accounts for the high resistance of the *N*-silyl-substituted cyclodisilazane skeleton toward plasma fragmentation and suggests its large contribution to the structure of the resulting plasma polymer.

The ion peaks observed in the mass spectra of silazane products at m/e 130, 116, 102, 100, 86, 72, and 70 are considered to be characteristic of methyl-silicon compounds containing disilazane units.

ACKNOWLEDGMENTS

The author is indebted to Professor Z. Lasocki and his coworkers from Laboratory of Organosilicones of the Technical University of Łódź for synthesis of the monomer for this study.

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Received March 31, 1988