Oligomeric Products in Plasma=Polymerized Organosilicones

A. M. Wróbel[a]; M. Kryszewski[a]; M. Gazicki[a]

[a] Department of Polymer Physics Centre of Molecular and Macromolecular Studies Polish, Academy of Sciences, Boczna 5, Poland

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Oligomeric Products in Plasma-Polymerized Organosilicones

A. M. WRÓBEL, M. KRYSZEWSKI, and M. GAZICKI

Department of Polymer Physics
Centre of Molecular and Macromolecular Studies
Polish Academy of Sciences
Boczna 5, 90-362 Łódź, Poland

ABSTRACT

Plasma polymers were deposited from a number of methylsilazane and methylsiloxane monomers of linear and cyclic structure. The oligomeric phase evolved from the polymers by a mild thermal treatment was analyzed using gas chromatography/mass spectrometry combined techniques. The oligomeric phase was found to be composed of the low-molecular-weight products with the weight being mostly no higher than two monomer units. The results suggested that the oligomers might be formed in the gas phase and then they diffuse to the surface of the growing polymer film. The structure of the oligomeric products indicated that their formation must proceed via the Si–N and Si–O bonds fission in silazane and siloxane monomers, respectively. An ionic nature of the primary active species involved in this process was assumed owing to the high susceptibility of these bonds toward heterolytic fission. The postulated ionic mechanism, considered to account for the formation of the observed oligomers, seems to be more reasonable than the radical mechanism. Pyrolysis/gas chromatography and infrared investigations of plasma polymers revealed that methylsilyl groups in the monomers were highly susceptible to form disilymethylene and disilymethylene and disylyethylene cross-linkages. This pro-

cess was assumed to proceed via homolytic fission of the Si—C and C—H bonds in methylsilyl groups and subsequent recombination of formed radical species. Based on these results, the elementary reactions contributing to the overall plasma polymerization processes of both ionic and radical mechanisms were formulated.

INTRODUCTION

Knowledge of the structure of plasma-polymerized coatings is of interest both from practical and theoretical viewpoints. Our recent results have proven the close relation that exists between the structure of plasma polymers and their surface [1], electrical [2], and thermal [3] properties. On the other hand, structural studies may also provide valuable information on the mechanism of the plasma polymerization process. However, in view of the large number of elementary reactions taking place in plasma, the structure of the polymer is very complex indeed. In an earlier report [4] we showed that plasma polymers contain mostly insoluble (in organic solvents) highly cross-linked material and several percent of a soluble oligomeric fraction. Furthermore, our model of density distribution along the thickness of plasma polymer films has also revealed their composite structure [5]. The films were found to be composed of a dense cross-linked internal phase and a low-density thin oligomeric surface layer.

Composition of the oligomeric fraction in plasma polymers seems to be of particular importance since it contains intermediate polymerization products. However, the separation and identification of the oligomers requires a complex analytical method due to their extremely low content in polymeric material. Thermogravimetric data [6, 7] have indicated that the oligomeric products can easily be released from the polymer to the gaseous phase by using a mild thermal treatment. The products can then be resolved by gas chromatography and analyzed by mass spectrometry. Therefore, gas chromatography/mass spectrometry (GC/MS) combined techniques appeared to be very promising for this purpose.

The current paper deals with GC/MS and IR studies on plasma polymers formed from numerous methylsilazane and methylsiloxane monomers of linear and cyclic structure. Based on these results, an overall mechanism of plasma polymerization is discussed.

EXPERIMENTAL

Plasma polymerizations were carried out in the electrode stationary system whose main features have already been described [8]. The apparatus incorporated a vacuum bell jar of 20,000 cm^3 capacity containing two parallel stainless steel electrodes spaced 3 cm apart, each with a 50-cm^2 surface area. Polymer films were deposited on the surface of

electrodes in an audiofrequency glow discharge operated at 20 kHz. In all experiments a steady initial pressure of monomer of p = 0.3 torr, a current density of j = 1 mA/cm^2, and a discharge duration of t = 30 s were used. The thickness of polymer films deposited under these conditions was within the 0.1 to 1.5 μm range.

Gas chromatography/mass spectrometry examinations were carried out on polymer samples of about 0.2 mg removed from the electrodes. Samples placed in a Jeol pyrolyzer unit, Model 727, were heated in a helium atmosphere at 300°C for 30 s. The volatile products were fed directly to the injection part of a Jeol, Model JGC 1100, gas chromatograph equipped with a flame ionization detector and a 2 m × 3 mm stainless steel separation column filled with 10% OV101 supported on a 80/100 mesh Varaport. The column was heated from 30 to 270°C using a linear heating rate of 10 deg/min and a steady helium flow of 40 cm^3/min.

The volatile products separated by gas chromatography were then analyzed with a LKB, Model 2091, mass spectrometer equipped with a PDP11 computer. Mass spectra were recorded at an electron beam energy of 70 eV. Some of the products were also identified chromatographically by using retention time coincidence with pure standard compounds.

Polymer samples were also pyrolyzed at 550°C for 15 s. The gaseous pyrolysis products were separated in this case by means of a 1 m × 3 mm stainless steel column filled with a 5A 60/80 mesh molecular sieve. The same column was used to separate the gaseous products of a plasma reaction sampled from the reactor.

Infrared spectra of the polymer films were run on a Perkin-Elmer Model 457, spectrophotometer by using the attenuated total reflection (ATR) technique.

The organosilicon monomers, supplied by PCR Research Chemicals Inc., were purified prior to plasma polymerization by vacuum rectification and then their purity was tested by gas chromatography.

RESULTS AND DISCUSSION

Gas Chromatography/Mass Spectrometry Examination

In order to restrain undesirable effect of secondary thermal reactions which may decompose the oligomeric products evolved from plasma polymers, they were heated at a relatively low temperature (300°C) for a short time (30 s). Gas chromatograms of the volatile products released during heating are illustrated in Fig. 1. The products corresponding to the respective peaks in chromatograms of particular plasma polymers were identified by mass spectrometry and gas chromatography with the aid of certain standard compounds. Their individual structures are shown in Table 1. It should be noted that a strongly
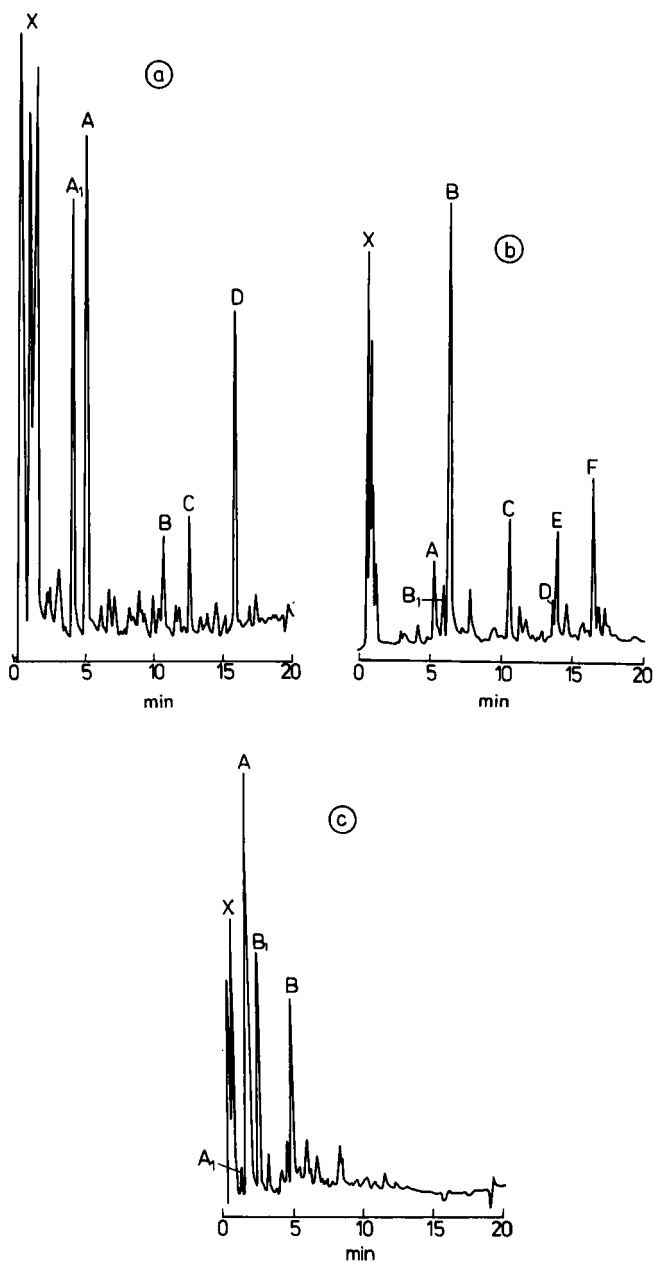
FIG. 1. Gas chromatograms of the oligomeric phase evolved from
(a) PP-HMDSN, (b) PP-HMCTSN, (c) PP-HMDSO, (d) PP-HMCTSO,
and (e) PP-OMCTSO.
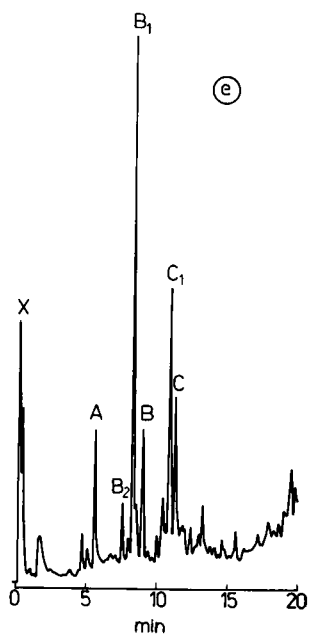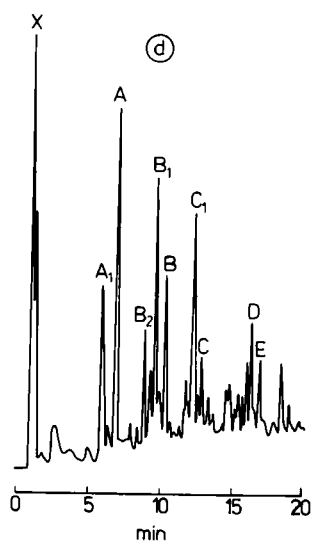
FIG. 1 (continued)

TABLE 1. Oligomeric Products Isolated from Plasma Polymers of Methylsilazane and Methylsiloxane Monomers

MONOMER — OLIGOMERIC PRODUCTS

Monomers listed:

- $Me_3Si-NH-SiMe_3$ — HEXAMETHYLDISILAZANE (HMDSN)
- HEXAMETHYLCYCLOTRISILAZANE (HMCTSN)
- $Me_3Si-O-SiMe_3$ — HEXAMETHYLDISILOXANE (HMDSO)
- HEXAMETHYLCYCLOTRISILOXANE (HMCTSO)
- OCTAMETHYLCYCLOTETRASILOXANE (OMCTSO)

1) PRODUCTS OF HMCTSO, 2) PRODUCTS OF OMCTSO.

overlapped group of peaks marked by X, observed in all chromato-
grams at very short retention times (Fig. 1), corresponds to unsepa-
rated mixture of the light hydrocarbons and methylsilanes, and there-
fore their identification is difficult. In general, it is seen from Table
1 that the pyrolysis products consist of low-molecular-weight organo-
silicon compounds with linear and cyclic structures.

By comparing our previous gas chromatography and mass spec-
trometry data on the soluble fraction in plasma-polymerized hexamethyl-
cyclotrisilazane (PP-HMCTSN) [4] with the present results, we note
that the soluble fraction is composed of the same products as those found
in the present study.

Furthermore, similar examinations carried out for the polymers fol-
lowing their extraction in boiling carbon tetrachloride revealed the dis-
appearance of the peaks which are observed in chromatograms of non-
extracted polymers (Fig. 1). These results evidently show that the com-
pounds in Table 1 are not the pyrolysis products liberated by thermal
bond-breaking reactions but they appear to be evolved from the oligo-
meric phase of plasma polymers. It is very likely that these products
are formed in the gas phase by plasma conversion of the monomer
molecules and then they diffuse to the surface of the growing polymer
film.

Mass Spectra

On account of the large number of low-molecular-weight products
isolated from particular plasma polymers (Table 1), it is not possible
to discuss here all the mass spectra and therefore their discussion will
be confined to compounds of a more complex structure only.

Plasma-Polymerized Hexamethyldisilazane (PP-HMDSN)

It is seen from Table 1 that the oligomeric products of PP-HMDSN
corresponding to the respective chromatographic peaks in Fig. 1(a)
contain monomer (A), its monohydro-derivative (A_1), octamethyltri-
silazane (B), cyclic (C), and branched (D) dimeric structures. The
latter three structures are the most important to verify.

The mass spectrum of Product B (Fig. 2) exhibits the base peak at
m/e 219 which is assumed to arise from the $(M-CH_3)^+$ ion (where M
means the mass number of molecular ion), as the abstraction of methyl
group attached to silicon is the characteristic fragmentation pathway of
most methyl-substituted organosilicon compounds [9, 10]. The peak at
m/e 234 of low-intensity (0.8%) and the more intense peak at m/e 102
correspond to the molecular M^+ ion and the doubly charged $(M-2CH_3)^{2+}$
ion, respectively. The appearance of peaks at m/e 186, 202, and 203
is associated with the loss of methane and/or ammonia from the
$(M-CH_3)^+$ ion, and they are assigned to the $(M-CH_3-CH_4-NH_3)^+$,
$(M-CH_3-NH_3)^+$, and $(M-CH_3-CH_4)^+$ metastable ions, respectively.
Formation of the ions with the ammonia loss is typical of methylsila-
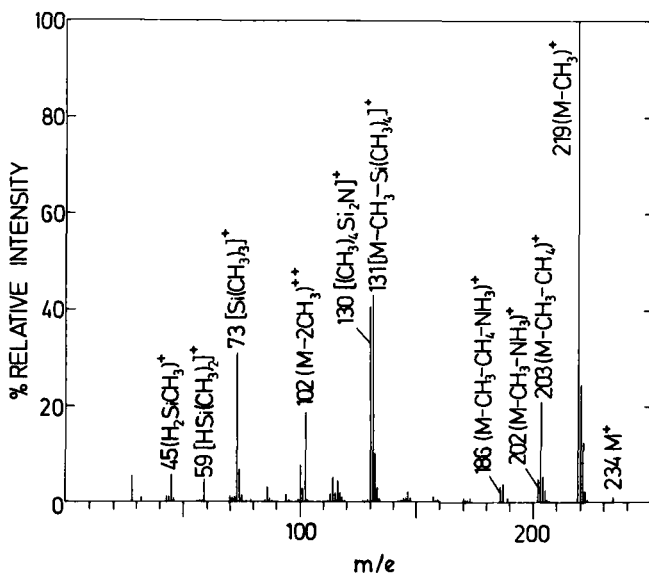
FIG. 2.   Mass spectrum of Product B isolated from PP-HMDSN.

zanes [11-13] and indicates the presence of −NH− units in Compound B. Based on these data, the molecular formula $Si_3 C_8 H_{26} N_2$ can be assigned to product B. The evidence for its octamethyltrisilazane structure is the intense peaks at m/e 73, 130, and 131 which correspond to the $[Si(CH_3)_3]^+$, $[(CH_3)_4Si_2N]^+$, and $[M-CH_3-Si(CH_3)_4]^+$ ions respectively. The presence of the $[(CH_3)_4Si_2N]^+$ ion at m/e 130 was found in the mass spectra of other linear methylsilazanes [10]. By considering the different steric rotamers of octamethyltrisilazane, these ions can be formed from the molecular ion according to the fragmentation patterns (1)-(4) proposed in Scheme 1.

The spectrum of Product C (Fig. 3) displays a low-intensity peak at m/e 290 (1.1%), the base peak at m/e 275, and the second most intense peak at m/e 130. These peaks may be assigned to the M^+, $(M-CH_3)^+$, and $(M-2CH)^{2+}$ ions, respectively. By assuming the methylsilazane structure, the molecular formula $Si_4C_{10} H_{30} N_2$ may be ascribed to Product C which corresponds to 1,3-bis(trimethylsilyl) tetramethylcyclodisilazane. This structure was confirmed by gas chromatography and mass spectrometry using the mentioned compound as a standard. It is also important to note that no significant CH_4 and NH_3 eliminations were detected in this case, since the ion peaks at m/e 259 $(M-CH_3-CH_4)^+$ (3.7%), 258 $(M-CH_3-NH_3)^+$ (0.1%), and 242 $(M-CH_3-CH_4-NH_3)^+$ (0.9%) are of minor intensity. This can be explained by the absence of hydrogen atoms at nitrogen atoms in Compound C which reduces these eliminations markedly [12].
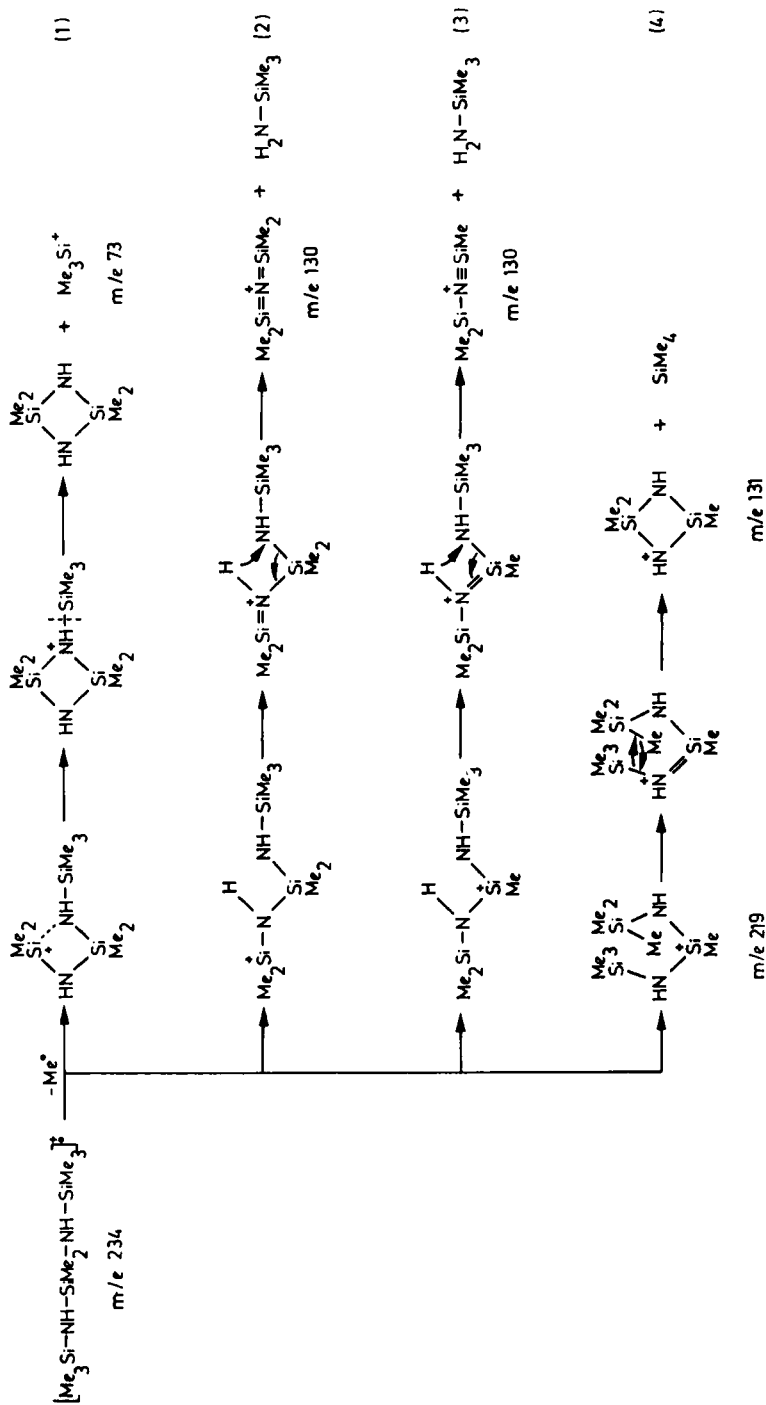
SCHEME 1.
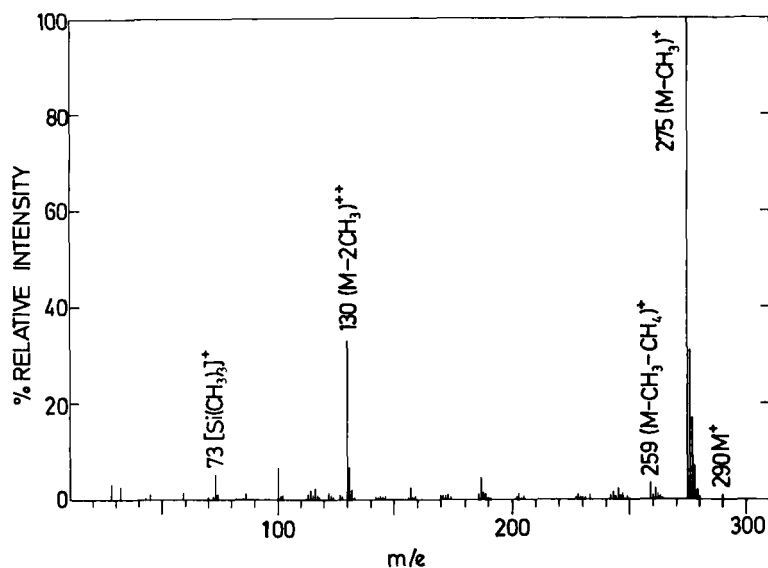
FIG. 3. Mass spectrum of Product C isolated from PP-HMDSN.

The M^+, $(M-CH_3)^+$, and $(M-2CH_3)^{2+}$ ions in the spectrum of Product D (Fig. 4) are revealed by a low-intensity peak at m/e 306 (0.9%), the base peak at m/e 291, and a medium-intensity peak at m/e 138, respectively. One can also distinguish the peaks at m/e 258 and 275 as being due to the $(M-CH_3-CH_4-NH_3)^+$, and $(M-CH_3-CH_4)^+$ ions, respectively, characteristic of the methylsilazane structure. From these data, Product D may be represented by the formula $Si_4C_{11}H_{34}N_2$ which corresponds to octamethyl-2-(trimethylsilyl) trisilazane. This structure explains the presence of intense peaks at m/e 73, 130, and 203 which may arise from the $[Si(CH_3)_3]^+$, $[(CH_3)_4Si_2N]^+$, and $[M-CH_3-Si(CH_3)_4]^+$ ions, respectively. Assigning the octamethyl-2-(trimethyl silyl)trisilazane structure to Product D formation of these ions involves different steric conformations and can occur according to the fragmentation patterns (5)-(8) proposed in Scheme 2. Thus, the mass spectrometric data interpreted in terms of those fragmentation mechanisms strongly suggest the mentioned structure for Product D.

Plasma-Polymerized Hexamethylcyclotrisilazane (PP-HMCTSN)

Table 1 shows the oligomeric products of PP-HMCTSN referred to the respective gas chromatographic peaks in Fig. 1b. They consist of monomer (B), its monooxy- (A) and monohydro- (B₁) derivatives, octamethylcyclotetrasilazane (C), bicyclic (D), and tricyclic (E) structures, and dimer (F). The mass spectra of Products D and E are the
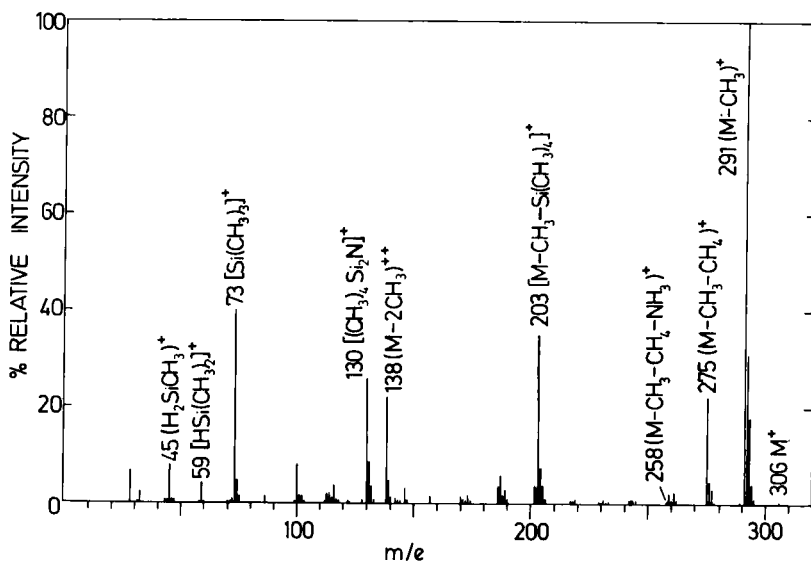
FIG. 4. Mass spectrum of Product D isolated from PP-HMDSN.

most important to discuss since the structures of the other products have been verified previously [4].

The spectrum of Product D (Fig. 5) exhibits a low-intensity molecular ion peak M^+ at m/e 349 (0.8%) and the base peak at m/e 334 which is again due to the $(M-CH_3)^+$ ion. The doubly charged ion $(M-2CH_3)^{2+}$ is revealed by the peak at m/e 159.5. The peaks at m/e 301, 317, and 318 are associated with the loss of CH_4 and/or NH_3 from the $(M-CH_3)^+$ ion and they correspond to the $(M-CH_3-CH_4-NH_3)^+$, $(M-CH_3-NH_3)^+$, and $(M-CH_3-CH_4)^+$ metastable ions, respectively. These data evidently indicate the methylsilazane structure of Product D and determine the molecular formula $Si_5C_9H_{31}N_5$ which corresponds to nanomethylbicyclopentasilazane (see Table 1). No other alternative structure whose formation would be more probable can fit these data. It is important to note that a compound of similar structure containing a six-membered methylsilazane ring has also been obtained from HMCTSN by a conventional reaction [14].

Analyzing the spectrum of the Product E (Fig. 6), similar ion peaks can be found as in the case of the Product D (Fig. 5) except that here they are shifted toward higher m/e values. The shift for the singly charged ion peaks at m/e 357 $(M-CH_3-CH_4-NH_3)^+$, 373 $(M-CH_3-NH_3)^+$, 374 $(M-CH_3-CH_4)^+$, 390 $(M-CH_3)^+$, and 405 M^+ corresponds to 56 mass units and for the doubly charged ion peak at m/e 187.5, $(M-2CH_3)^{2+}$ is half of this number, i.e., 28 mass units. These data suggest that Product
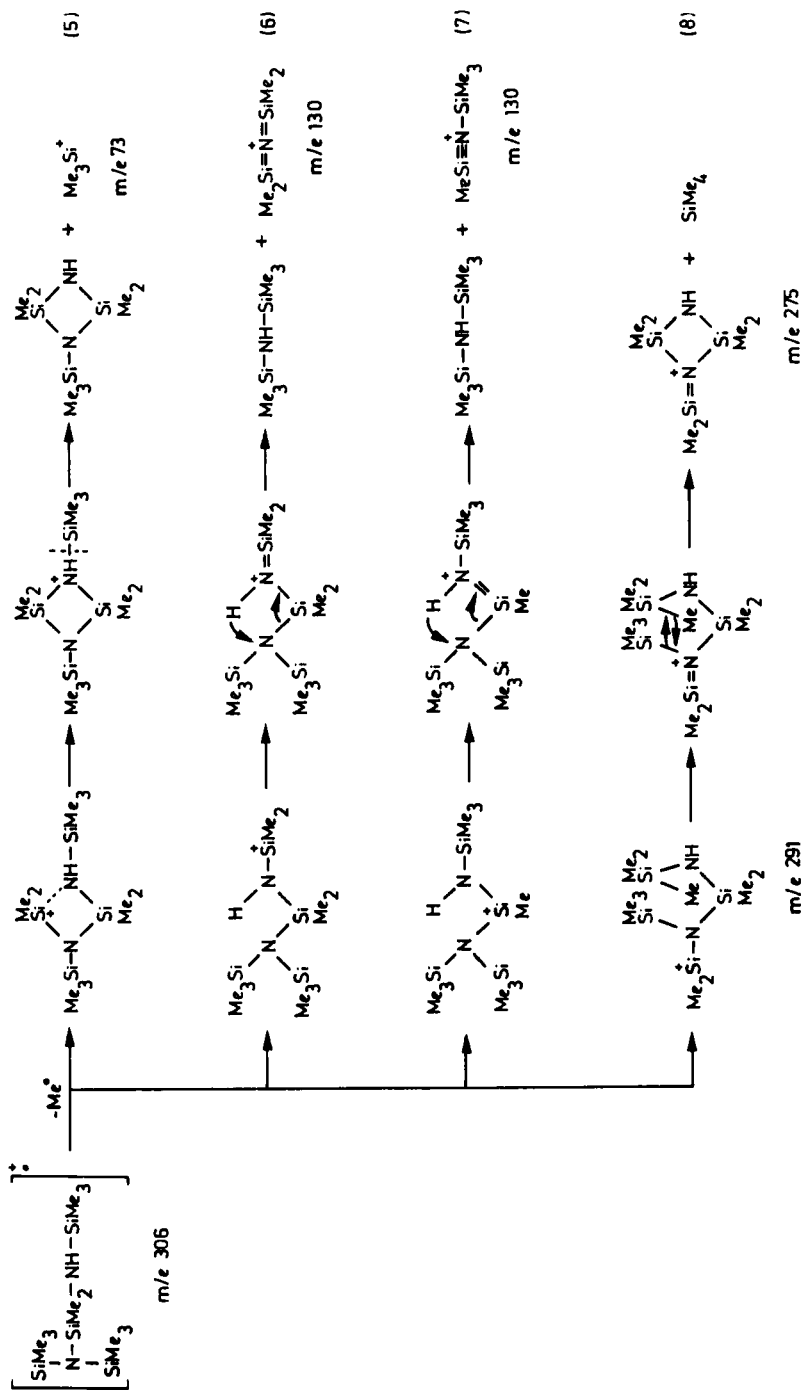
SCHEME 2.
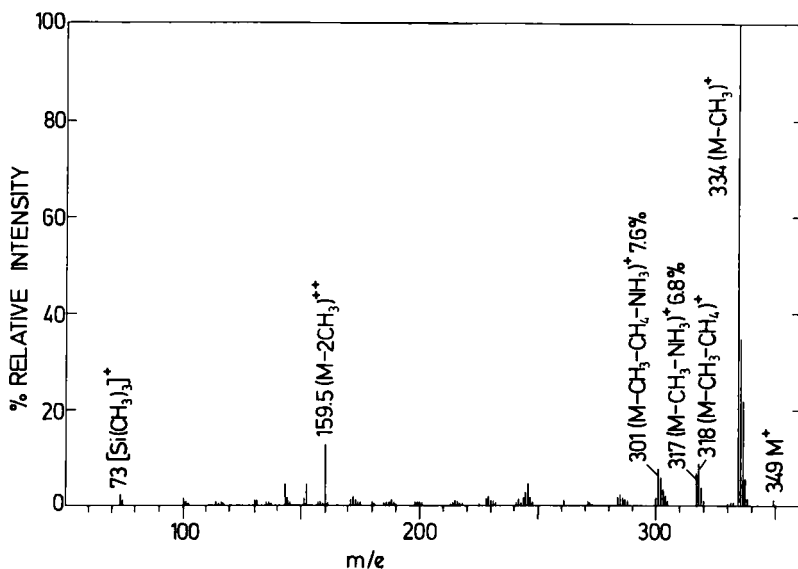
FIG. 5. Mass spectrum of Product D isolated from PP-HMCTSN.

E is a derivative from Product D with a mass enlarged by 56 units. Its structure can be derived by the substitution of hydrogen atoms at two nitrogens bonded to the bridged silicon atom in nanomethylbicyclopenta-silazane with the dimethylsilyl, $-Si(CH_3)_2-$, group (see Table 1). Thus, a tricyclic methylsilazane structure containing two six-membered rings and one four-membered ring corresponding to the formula $Si_6C_{11}H_{35}N_5$ may be ascribed to Product E. Further proof for this structure is a decrease in the intensities of the $(M-CH_3-NH_3)^+$ and $(M-CH_3-CH_4-NH_3)^+$ ion peaks (Fig. 6) compared to those in the spectrum of Product D (Fig. 5), which is due to a decreased number of hydrogen atoms at the nitrogen atoms in Structure E and the result-ing reduced NH_3 elimination. It should be noted that an analogous tri-cyclic silazane structure with ethyl substituents has also been report-ed by Andrianov et al. [15]. Finally, the very close location of the gas chromatographic peaks corresponding to Products D and E (Fig. 6) in-dicates the similarity of their structures.

Plasma-Polymerized Hexamethyldisiloxane (PP-HMDSO)

As shown in Table 1, the oligomeric products of PP-HMDSO corre-sponding to the respective gas chromatographic peaks in Fig. 1(c) con-sist of monomer (A), its monohydro-derivative (A_1), heptamethyltri-siloxane (B_1), and octamethyltrisiloxane (B). Since the structures of the former two products were verified with the aid of standard com-pounds, only the mass spectra of Products B and B_1 will be discussed.
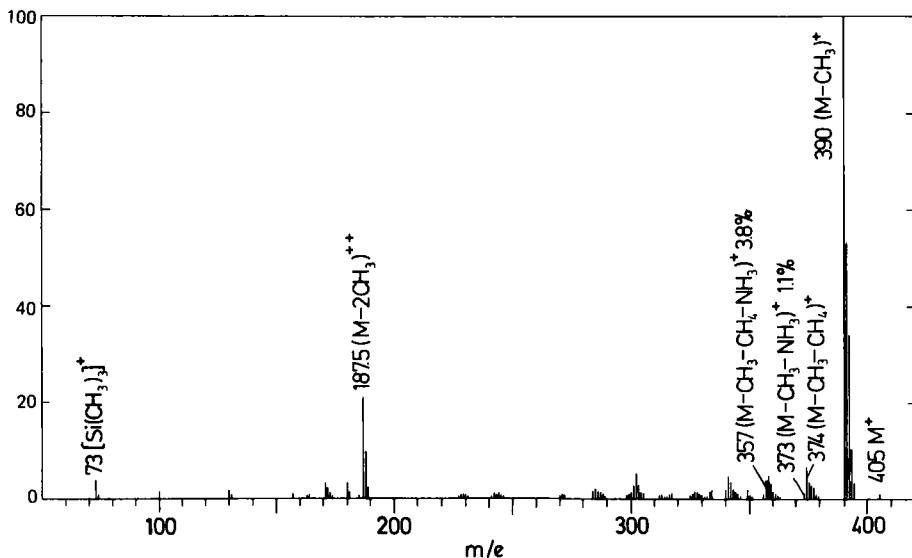
FIG. 6. Mass spectrum of Product E isolated from PP-HMCTSN.

The spectrum of Product B (Fig. 7) shows the base peak at m/e 221, and the second most intense peak at m/e 73 arising from the $(M-CH_3)^+$, and $[Si(CH_3)_3]^+$ ions, respectively. The peaks at m/e 103, 191, and 205 correspond to the doubly charged $(M-2CH_3)^{2+}$, and the singly charged $(M-CH_3-C_2H_6)^+$ and $(M-CH_3-CH_4)^+$ ions, respectively. The molecular ion peak M^+ which should appear at m/e 236 was not detected in this case. This is characteristic of methylsiloxanes where the molecular ion peaks were found to be of extremely low intensities, mostly below 0.05% [13, 16, 17]. The peaks at m/e 133 and 147 are due to the loss of CH_2 and/or $(CH_3)_2SiO$ units from the $(M-CH_3)^+$ ion, respectively, and indicate the methylsiloxane structure [17]. According to these data, Product B may be identified as octamethyltrisiloxane. This was also confirmed by the close resemblance of this spectrum to those reported for the mentioned compound [16- 18]. The evidence for octamethyltrisiloxane structure in Product B is the appearance of a very intense ion peak $[Si(CH_3)_3]^+$ at m/e 73 and also the $[M-CH_3-(CH_3)_2SiO]^+$ ion peak at m/e 147. By assuming different rotamers of octamethyltrisiloxane, these ions may be formed from the $(M-CH_3)^+$ ion as follows from the fragmentation patterns (9) and (10) in Scheme 3. The loss of the neutral molecule as tetramethylcyclodisiloxane (Reaction 9) from the $(M-CH_3)^+$ ion has been postulated by Tanny et al. [19].

The spectrum of Product B_1 (Fig. 8) is very similar to that of Product B (Fig. 7) except that here most of the peaks are shifted by 14 mass units toward lower m/e values. This is due to the presence
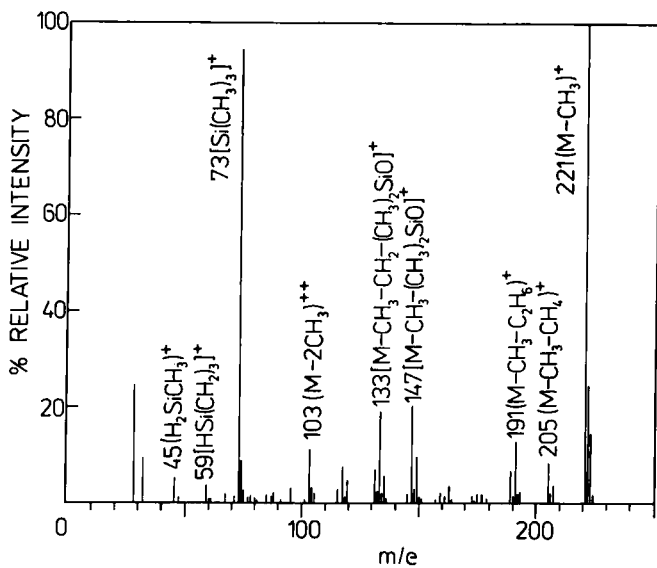
FIG. 7. Mass spectrum of Product B isolated from PP-HMDSO.
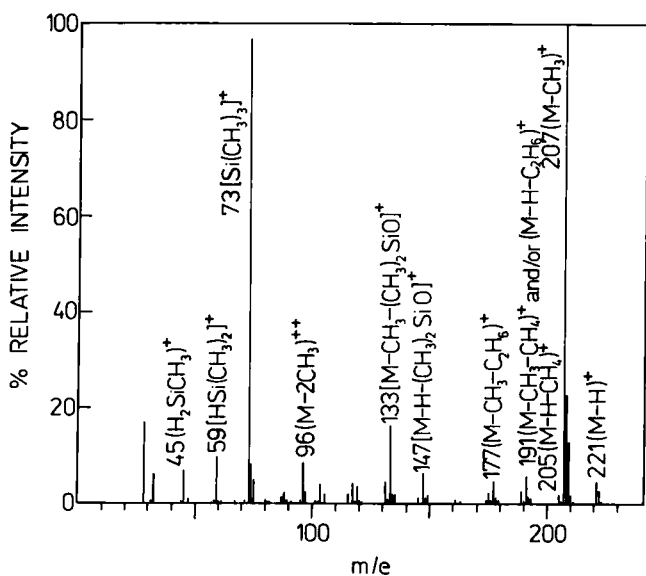
FIG. 8. Mass spectrum of Product B₁ isolated from PP-HMDSO.

$$[\text{SiMe}_3-\text{O}-\text{SiMe}_2-\text{O}-\text{SiMe}_3]^{+\cdot}$$

m/e 236

$-\text{Me}^{\cdot}$

m/e 221

(9)

$+ \ \text{Me}_3\text{Si}^+$

m/e 73

$\text{Me}_2\text{Si}=\text{O} \ + \ \text{Me}_2\overset{+}{\text{Si}}-\text{O}-\text{SiMe}_3$

(10)

m/e 147

SCHEME 3.

of the SiH group in Product B_1 and suggests its heptamethyltrisilox-
ane structure. The most pronounced proof for this structure is the
peaks resulting from the proton elimination appearing at m/e 221, 205,
191, and 147 which correspond to the $(M-H)^+$, $(M-H-CH_4)^+$, $(M-H-$
$C_2H_6)^+$, and $[M-H-(CH_3)_2SiO]^+$ ions, respectively, and also the doubly
charged $(M-2CH_3)^{2+}$ ion peak at m/e 96. These data do not give the
precise location of the SiH group in heptamethyltrisiloxane; however,
its formation in plasma at a terminal position (see Table 1) is con-
sidered to be most favorable.

Plasma-Polymerized Hexamethylcyclotrisiloxane (PP-HMCTSO) and Octamethylcyclotetrasiloxane (PP-OMCTSO)

As can be seen in Table 1, the oligomeric products isolated from
PP-HMCTSO and PP-OMCTSO (marked by 1 and 2, respectively) and
assigned to the respective gas chromatographic peaks in Figs. 1(d) and
(e) contain cyclic methylsiloxanes of various ring sizes. Six to four-
teen membered rings for PP-HMCTSO, and six to ten membered rings
for PP-OMCTSO are noted. Some of the products have one hydrogen
(A_1, B_1, C_1, and E) or two hydrogen (B_2) substituents. The structure
of most of them was verified gas chromatographically and mass spec-
trometrically by using suitable standard compounds.

In general, the mass spectra of Products A_1, A, B_2, B_1, and B ex-
hibited the most intense peak due to the $(M-CH_3)^+$ ion and the second
most intense peak due to the doubly charged $(M-2CH_3)^{2+}$ ion. This
is in accordance with the data reported for HMCTSO and OMCTSO
[10, 17, 20]. Detailed analysis revealed a cyclotrisiloxane structure
in Products A_1 and A and a cyclotetrasiloxane structure in Products
B_2, B_1, and B. The spectra of Products C_1, C, D, and E were charac-
terized by the base peak at m/e 73 due to the $[Si(CH_3)_3]^+$ ion and the
intense peak arising from the $[M-CH_3-Si(CH_3)_4]^+$ ion. The presence
of both these ions is characteristic of cyclic methylsiloxanes with a
ring size of from ten to fourteen membered [10, 17, 21]. A transannu-
lar mechanism has been proposed to account for their formation [22].
The MS data indicated the cyclic structures pentasiloxane for C_1 and C,
hexasiloxane for D, and heptasiloxane for E. The $(M-H)^+$ ion peaks
appearing in the spectra of Products A_1, B_2, B_1, and C_1 were evidence
for the SiH groups in their structures.

The shift by 14 mass units toward lower m/e values noted for some
of the ion peaks in the spectra of A_1, B_1, and C_1, as compared with
those of A, B, and C, respectively, indicated the presence of one hydro-
gen substituent. A similar shift by 28 mass units noted in the spectrum
of B_2, as compared to that of B, proved the presence of two hydrogen
substituents.

It should be mentioned that the chemical formulas derived from the
MS data for particular oligomeric products were verified by compari-
son of the observed and calculated relative intensity values of the first
and second isotope peaks of the $(M-CH_3)^+$ ion peaks. The differences
between the observed intensity values and those calculated on the basis

of the accepted chemical formulas were within the limits of repro-
ducibility in each case.

Infrared Spectra

The GC/MS data were correlated with the infrared study of the sur-
face of plasma polymer films. The ATR-IR spectra of plasma poly-
mers are shown in Fig. 9. Omitted from this figure is the spectrum
of PP-OMCTSO which is identical to that of PP-HMCTSO. Assignment
of the IR absorption bands was based in data reported by Anderson [23].
Referring to Fig. 9, one may note numerous spectral features which
the plasma polymers have in common with their monomers. These in-
clude the absorption band appearing in each spectrum at 1400 and 1250
cm^{-1}, which correspond to the $-CH_3$ asymmetric and symmetric de-
formation vibrations, respectively, in methylsilyl groups, and in the
800-780 cm^{-1} region, attributed to the $-CH_3$ rocking and the Si–C
stretching vibrations. The band at 840 cm^{-1} in the spectra of PP-
HMDSO and PP-HMDSN (Figs. 9A and 9C) is assigned to the $Si(CH_3)_3$
endgroups. Plasma polymers from siloxane monomers are character-
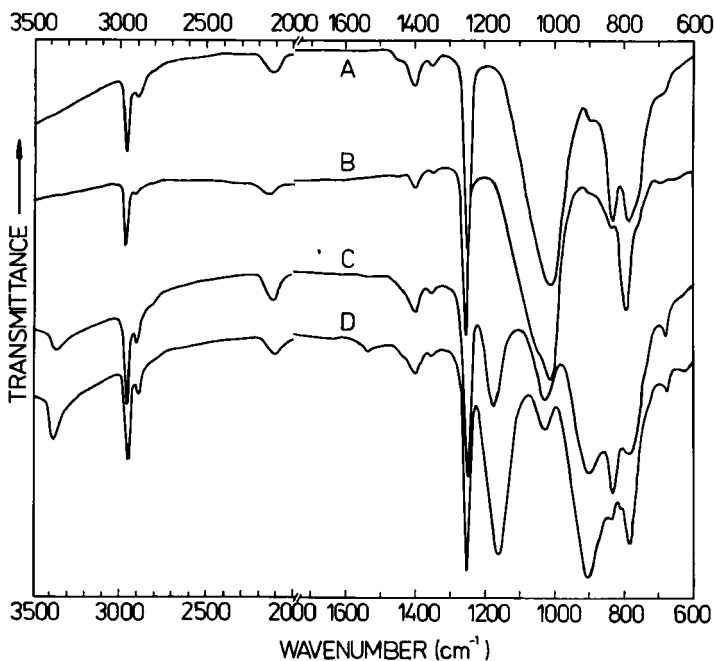
FIG. 9. ATR-IR spectra of plasma polymers from: (A) HMDSO,
(B) HMCTSO, (C) HMDSN, and (D) HMCTSN.

ized by a strong absorption within the 1100-1000 cm^{-1} region (Figs. 9A and 9B), corresponding to the asymmetric Si–O–Si stretching vibration. The spectra of silazane plasma polymers (Figs. 9C and 9D) exhibit absorption bands at 3390, 1175-1160, and 900 cm^{-1} which originate from the N–H stretching, N–H bending, and the asymmetric Si–N–Si stretching vibrations, respectively, of the Si–NH–Si system. These data show that the original structural units in the monomers are incorporated into plasma polymers, apparently indicating their methylsiloxane or methylsilazane character as revealed by the GC/MS study.

The polymers spectra also exhibit bands which are absent from the monomers spectra. These are demonstrated by a broad band with a maximum in the 2140-2100 cm^{-1} region attributed to the Si–H stretching vibration, and distinct bands at 1350 and 1030 cm^{-1} corresponding to the –CH$_2$– scissoring and wagging vibrations, respectively, in disilymethylene (Si–CH$_2$–Si) and disilyethylene (Si–CH$_2$–CH$_2$–Si) bonds. The appearance of the first band agrees well with GC/MS data which proved the presence of the SiH groups in the digomers. The band at 1030 cm^{-1} is only seen in the spectra of PP-HMDSN and PP-HMCTSN (Figs. 9C and 9D) and cannot be detected in the spectra of siloxane plasma polymers (Figs. 9A and 9B) due to overlap with the Si–O–Si absorption also appearing in this region. The marked broadening of this band indicates that both disilymethylene and disilyethylene bonds are present in the polymers. Moreover, the low-intensity band at 840 cm^{-1} in the spectra of PP-HMCTSO and PP-HMCTSN (Figs. 9B and 9D) and the band at 1540 cm^{-1} appearing in the spectrum of the latter polymer (Fig. 9D), which originate from the Si(CH$_3$)$_3$ and SiNH$_2$ groups, respectively, account for the ring-breaking reactions.

Formation of Oligomers

To elucidate the formation of the oligomeric products, the nature of the primary reactive species taking part in this process has to be considered. The high concentration of radicals trapped in plasma polymers [24, 25] accounts for the predominance of their free-radical character. On the other hand, a grid experiment by Westwood [26] and an ion-deflection experiment by Thompson and Mayhan [27] revealed that positively charged organic ions also contribute to the plasma polymerization process. This seems to be strongly supported by the results of Smolinsky and Vasile [28], and most recently by Hays [29, 30] who detected the presence of carbon and silicon cationic species in methane [28], methyltrimethoxysilane [29], and hexamethyldisiloxane [30] plasmas, respectively, by using direct mass spectrometric sampling from the discharge zone. Moreover, our grid experiment [31] carried out for methylsilazane and methylsiloxane monomers in a manner similar to that of Westwood [26] also showed a marked increase in the polymer deposition rate with increasing dc negative potential of the polymer-collecting electrode, thus giving evidence of cationic species in the plasmas of these monomers.

Inspection of the oligomeric structures in Table 1 shows that the formation of most of them must be associated with Si–N and Si–O bond rupture in the monomer molecules. Due to their relatively high percentage of ionic character (30% for Si–N and 50% for Si–O) [32], these bonds are known to be highly resistive to homolytic fission and, on the other hand, they display a strong tendency to undergo heterolytic cleavage [33, 34]. In the light of these data it is reasonable to assume an ionic nature of the primary reactive species involved in the formation of the observed oligomeric products. These species can be produced in the gas phase by inelastic collisions of highly energetic plasma electrons with the monomer molecules. As a result of this process, active cationic sites are formed on the silicon atoms by analogy to the ionization of methylsilicon compounds that occurs in a mass spectrometer [9, 10]. In the next step the primary cationic species are considered to react with strongly nucleophilic nitrogen and oxygen atoms in the monomers to produce intermediate dimeric cations which then can undergo various intermolecular rearrangements toward formation of the oligomers.

Thus, the oligomerization reactions leading to the respective products shown in Table 1 were formulated in terms of the ionic mechanism. Discussions for particular monomers are given below.

HMDSN

The possible series of steps that can occur in plasma of this monomer is shown in Scheme 4. The first step, exemplified by Reaction (11), is monomer activation under electron impact. This process is involved in electron ejection from the molecule, and subsequent detachment of the methyl radical results in the formation of the primary cation I with a charge on the silicon atom. Reaction (11) appears to be typical of the methylsilicon compounds that is observed in a mass spectrometer as mentioned earlier.

In the next step, cation I undergoes reaction with the monomer molecule to produce the intermediate dimeric cation II by Si–N coupling. Then intermediate II may fragment either by cleavage of the N–Si bond with detachment of the Me_3Si^+ cation (Reaction 12) or the N–H bond with detachment of proton (Reaction 13) to yield different products, B and D, respectively. The possibility of these competitive pathways of fragmentation seems to arise from the different amount of energy of cation I that is transferred to the monomer molecule during the reaction. However, the higher intensity of the gas chromatographic peak noted for product D as compared with that of B (Fig. 1a) implies that Reaction (13) is more favorable.

In a further step (Reaction 14), Product D is reactivated to the secondary cation III which then rearranges with proton detachment to the cyclic structure C.

HMCTSN

As follows from Scheme 5, the reaction of the primary cation IV (generated via Reaction 15) with monomer leads to formation of the

Me$_3$Si—NH—SiMe$_3$ $\xrightarrow{\textit{e, -e}}$ [Me$_3$Si—NH—SiMe$_3$]$^{+\bullet}$ $\xrightarrow{-\text{Me}^\bullet}$ Me$_2$Ṡi—NH—SiMe$_3$ (11)

I

Me$_3$Si—NH—Ṡi Me$_2$ + $\begin{array}{c}\text{SiMe}_3\\|\\ \text{NH}\\|\\ \text{SiMe}_3\end{array}$ $\longrightarrow$ Me$_3$Si—NH—SiMe$_2$—$\overset{+}{\text{N}}$Me$_2$—H $\begin{array}{c}\text{SiMe}_3\\|\\ \\|\\ \text{SiMe}_3\end{array}$ (12)

II

$\xrightarrow{-\text{Me}_3\text{Si}^+}$ Me$_3$Si—NH—SiMe$_2$—NH—SiMe$_3$ (13)

B

$\xrightarrow{-\text{H}^+}$ Me$_3$Si—NH—SiMe$_2$—N$\begin{array}{c}\text{SiMe}_3\\ |\\ \\ |\\ \text{SiMe}_3\end{array}$

D

D $\xrightarrow{\textit{e, -e}}$ $\left[\begin{array}{c}\text{SiMe}_3\\ |\\ \text{N—SiMe}_2\text{—NH—SiMe}_3\\ |\\ \text{SiMe}_3\end{array}\right]^{+\bullet}$ $\xrightarrow{-\text{Me}^\bullet}$ Me$_3$Si—N$\underset{\underset{\text{III}}{\displaystyle\underset{\text{Me}_2}{\overset{+}{\text{Si}}}}}{\overset{\overset{\text{Me}_2}{\text{Si}}}{\diagup\hspace{-0.3em}\diagdown}}$NH—SiMe$_3$ $\longrightarrow$ Me$_3$Si—N$\underset{\underset{\text{Me}_2}{\text{Si}}}{\overset{\overset{\text{Me}_2}{\text{Si}}}{\diagup\hspace{-0.3em}\diagdown}}\overset{+}{\text{N}}$H—SiMe$_3$ $\xrightarrow{-\text{H}^+}$ Me$_3$Si—N$\underset{\underset{\text{Me}_2}{\text{Si}}}{\overset{\overset{\text{Me}_2}{\text{Si}}}{\diagup\hspace{-0.3em}\diagdown}}$N—SiMe$_3$ (14)

C
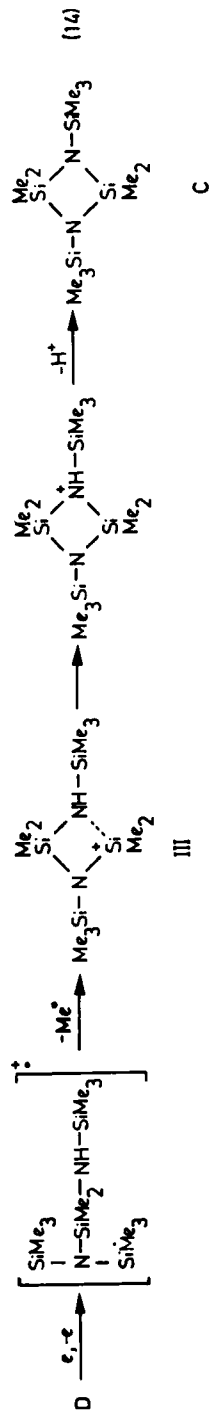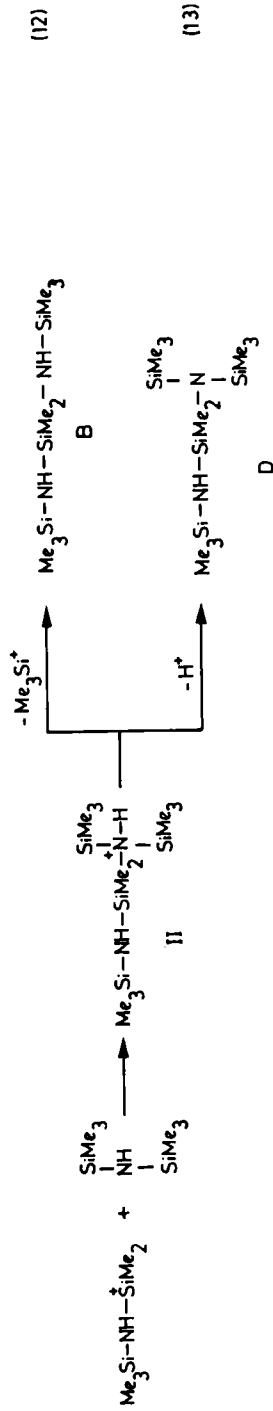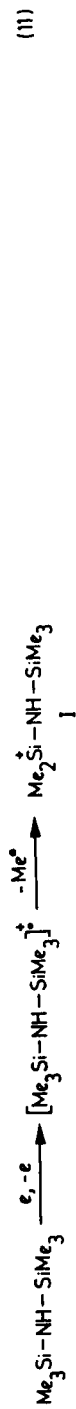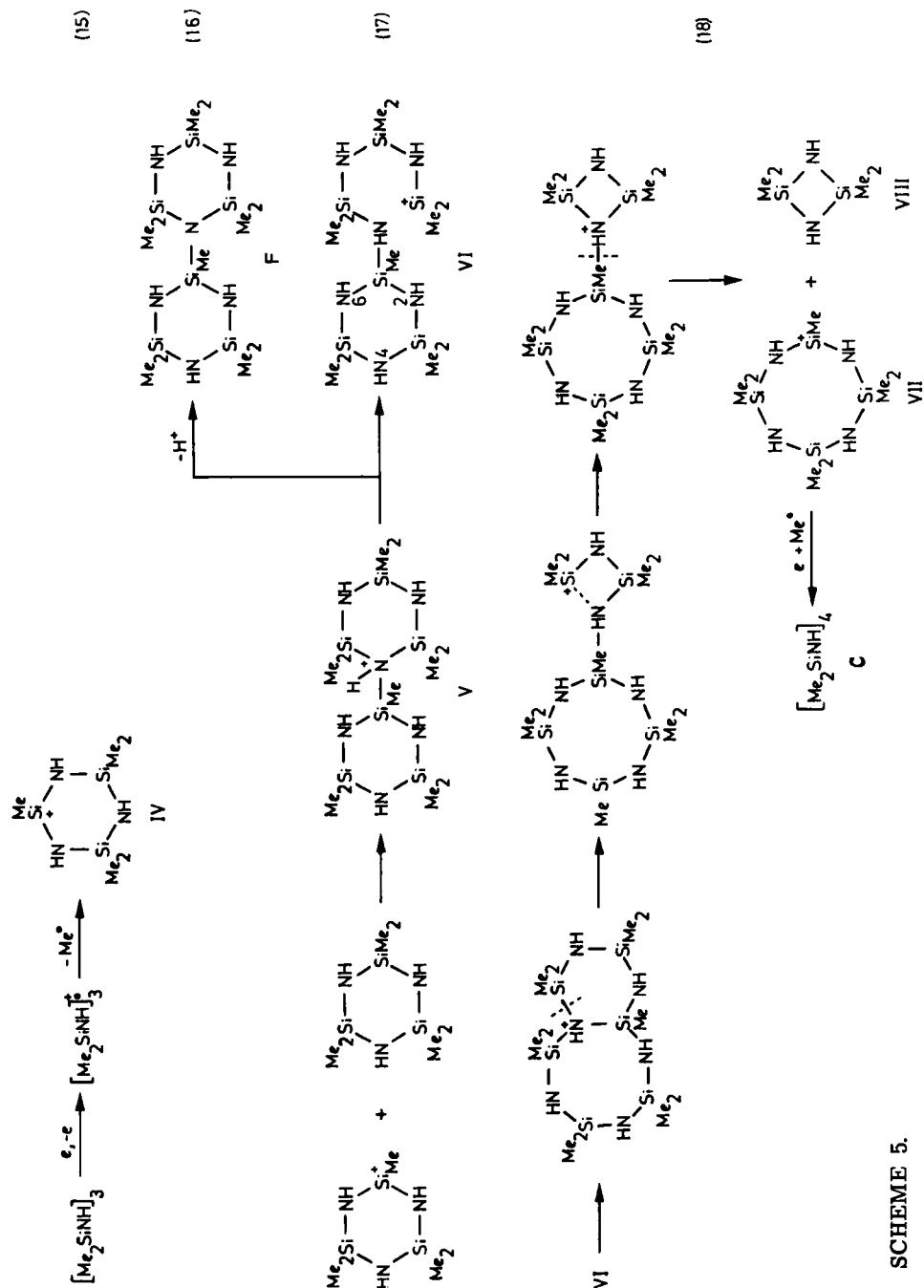
SCHEME 4.

SCHEME 5.

SCHEME 5a.
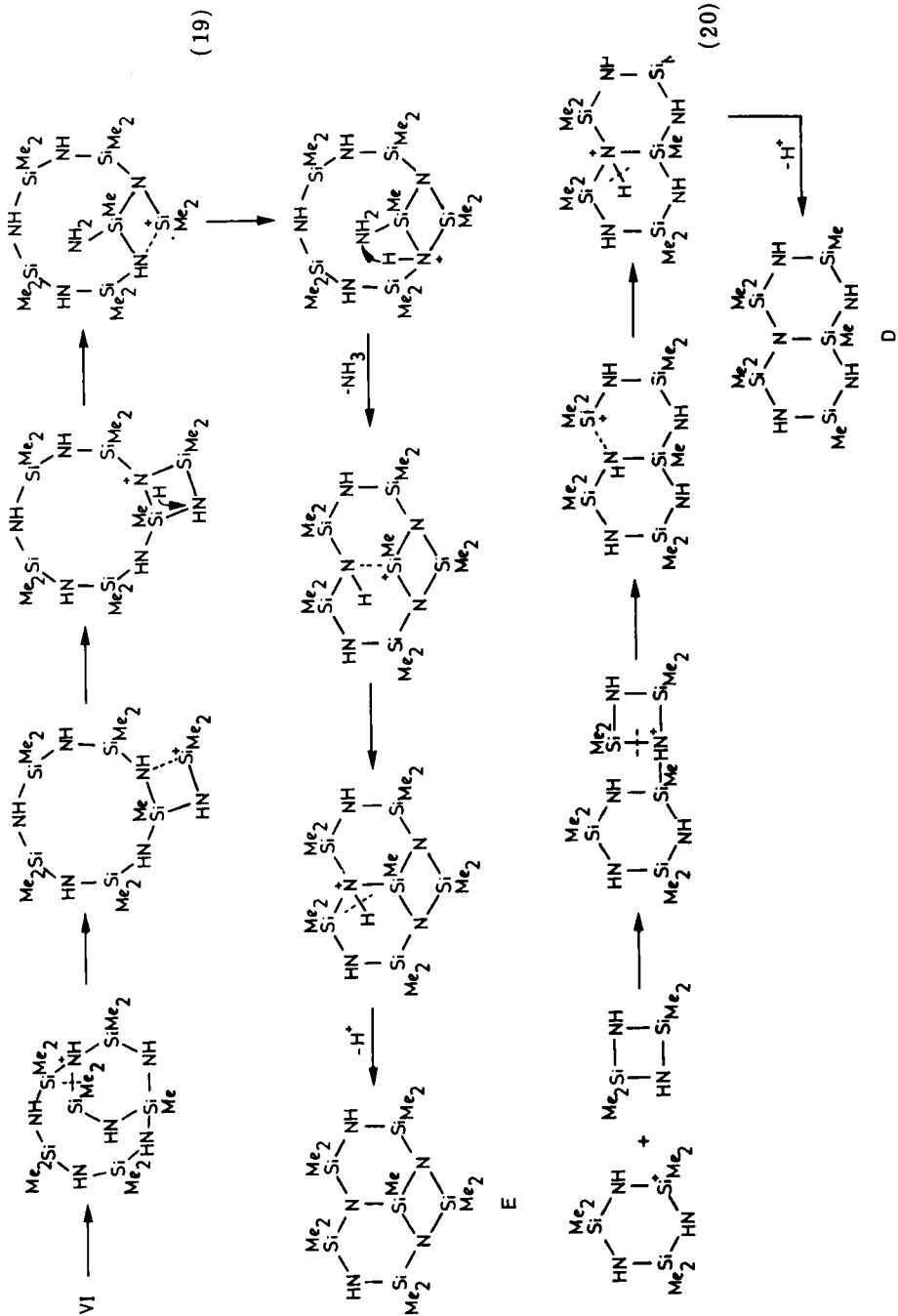
intermediate dimeric cation V which then may fragment according to the pathways described previously. The N–H bond cleavage (Reaction 16) produces bicyclic dimer F whereas the N–Si bond cleavage (Reaction 17) results in the formation of the intermediate cation VI of a cyclic-linear structure with a cationic site on the end of its linear fragment. The intermediate VI may undergo various intermolecular rearrangements depending on the attachment reaction of the active linear fragment with the different nitrogen atoms from a cyclic part of the molecule.

Reaction (18) illustrates the first case where the active linear fragment is assumed to attach to one of the two equivalent nitrogen atoms 2 or 6. The proposed rearrangement mechanism involves formation of the cyclic products, cation VII and neutral molecule VIII, with the rings being expanded and contracted by one dimethylsilaza unit, respectively, in comparison to the monomer. Cation VII is subsequently deactivated to the neutral Product C by recombination with an electron and a methyl radical. Reaction (18) shows the possibility of the ring expansion and the ring contraction processes taking place in one stage. The intermediate VIII, however, has not been detected by GC/MS analysis due to its extremely low resistance toward hydrolysis than can occur in contact with the atmosphere.

In the second case presented by Reaction (19) in Scheme 5a, an attachment of the active linear fragment to nitrogen 4 in VI was assumed to take place. A transannular mechanism has been proposed for the rearrangements involved in this reaction. The proposed mechanism accounts for the formation of the tricyclic structure E.

The primary cation IV may also undergo reaction with the secondary neutral product VIII (Reaction 20, Scheme 5a) to form a bicyclic Product D. However, the low intensity of the gas chromatographic peak corresponding to this product (Fig. 1b) proves the low probability of Reaction (20) occurring.

HMDSO

The most important reactions of this monomer are shown in Scheme 6. The primary cation IX obtained from the initiation step (Reaction 21) reacts in the next step with the monomer molecule to produce intermediate cation X (Reaction 22) by Si–O coupling. Fragmentation of the intermediate X by detachment of the Me_3Si^+ cation yields the observed Product B.

HMCTSO and OMCTSO

Owing to the large number of the oligomeric products observed for these monomers (see Table 1), it is not possible to present all the reactions accounting for their formation. Therefore, our discussion will be confined to only some of the typical reactions that can occur in plasma of these monomers.

Scheme 7 exemplifies the reaction steps of HMCTSO contributing to the ring expansion process. These include the initiation step (Reaction

$$Me_3Si-O-SiMe_3 \xrightarrow{e, -e} [Me_3Si-O-SiMe_3]^{+\cdot} \xrightarrow{-Me^{\cdot}} Me_2\overset{+}{Si}-O-SiMe_3 \quad (21)$$

$$\text{IX}$$

$$Me_3Si-O-\overset{+}{SiMe_2} + \begin{matrix} O-SiMe_3 \\ | \\ SiMe_3 \end{matrix} \longrightarrow Me_3Si-O-SiMe_2-\overset{+}{O}-SiMe_3 \xrightarrow{-Me_3\overset{+}{Si}} Me_3Si-O-SiMe_2-O-SiMe_3 \quad (22)$$

$$\hspace{6cm} \begin{matrix} | \\ SiMe_3 \end{matrix}$$

$$\hspace{5.5cm} \text{X} \hspace{5cm} \text{B}$$
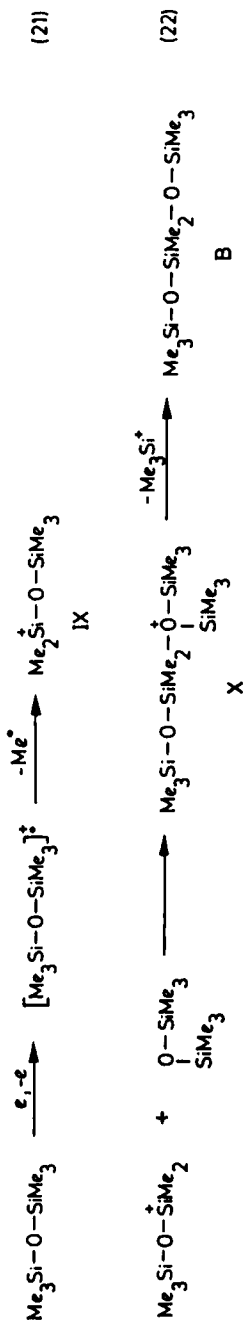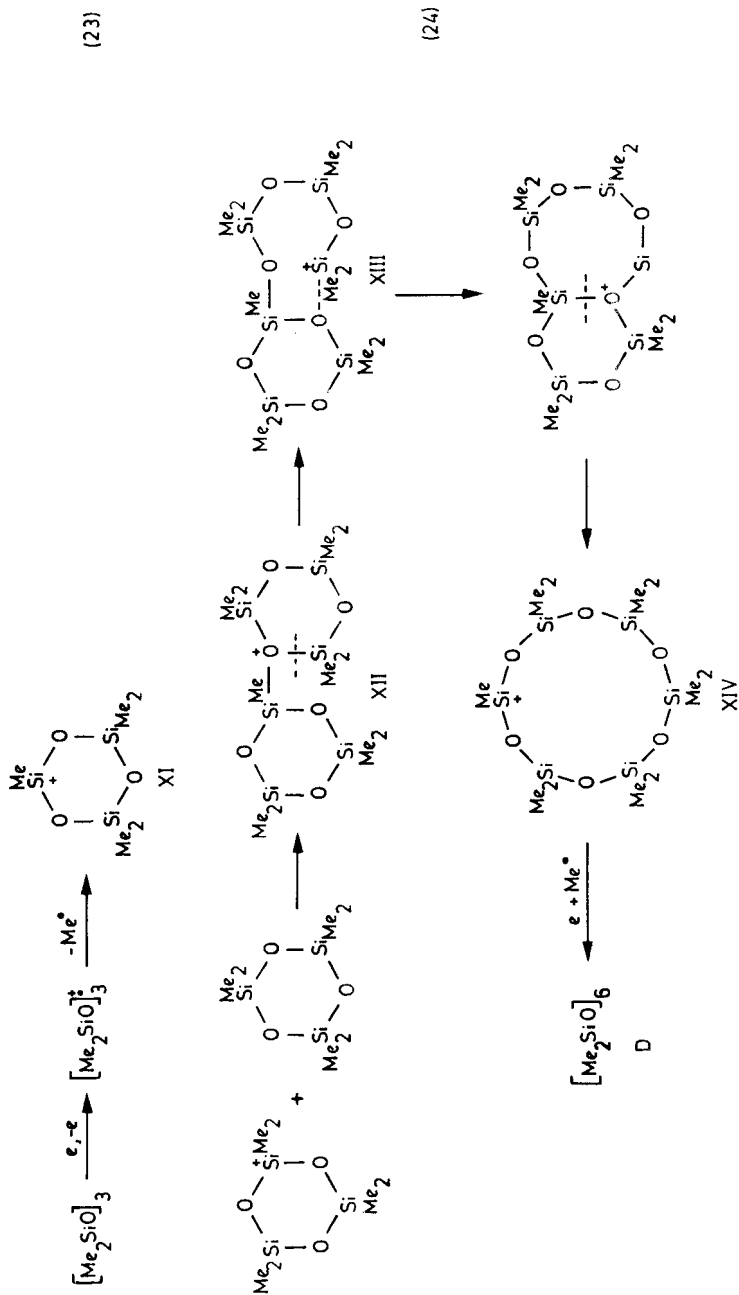
SCHEME 6.

SCHEME 7.

23) and the reaction of primary cation XI with the monomer molecule (Reaction 24). As one can see, the latter step leads toward formation of the intermediate dimeric cation XII which can subsequently disso- ciate by ring opening to form cyclic-linear structure XIII with the ac- tive site on the end of its linear fragment. This structure may in- volve various rearrangements resulting from attachment of the active linear fragment to different oxygen atoms from a cyclic part as in the case of HMCTSN. Reaction (24), however, describes the case where the attachment of the active linear fragment to one of the two equiva- lent oxygens 2 or 6 is assumed to take place. The reaction results in formation of the cyclic cation XIV with a doubly expanded ring with re- spect to the monomer. Then cation XIV is deactivated to the neutral Product D.

The reactions of OMCTSO presented in Scheme 8 exemplify forma- tion of the oligomers by ring contraction and expansion processes that can take place in one stage. The primary cation XV produced in the first step (Reaction 25) undergoes reaction with the monomer molecule to form the intermediate bicyclic cation XVI (Reaction 26) which then converts by ring opening to cyclic-linear structure XVII. The rearrangement of the latter structure by Reaction (26) involves formation of the cyclic neutral Product A and the cyclic cation XVIII with the rings being contracted and expanded by one dimethylsiloxy unit, respectively, as compared to the monomer. Deactivation of cation XVIII yields the neutral Product C.

By inspecting Table 1, one can note substantial differences in the ring size of the products from HMCTSO and OMCTSO. The former monomer appears to produce oligomers with larger rings than those from the latter monomer. This is due to their different reac- tivities that are assumed to increase with the ring strain energy. The literature data [35] show the ring strain energy of HMCTSO (2.5 kcal/ mol) to be ten times higher than that of OMCTSO (0.24 kcal/mol). This marked difference may account for the stronger tendency of HMCTSO toward the ring expansion process as shown by the results from Table 1.

Finally, it should be emphasized that although there is no direct proof for the proposed ionic mechanisms, they seem to explain forma- tion of the observed oligomeric structures more reasonably than the assumed radical mechanism.

Overall Mechanism of Polymerization

Although a number of the kinetic models describing plasma polym- erization [36-40] were based on the assumption of the radical mechan- ism for elementary plasma reactions, the contribution of the ionic mechanism to this process cannot be ignored totally. The most im- portant problem that remains open is the contribution of a particular mechanism to the overall polymerization process. This seems to de- pend not only on the plasma conditions but also on the monomer sus-

(25)

(26)

SCHEME 8.

ceptibility to undergo homolytic and heterolytic bond-breaking reactions. However, at the present state of the art a quantitative description of the plasma polymerization process in terms of both radical and ionic mechanisms is difficult to accomplish and only its qualitative picture may be discussed.

Based on the reaction schemes presented in an earlier section, the elementary plasma reactions of the silicon cationic species (generated in the initiation step) with the silazane and siloxane bonds can be illustrated schematically by

$$-\overset{|}{\underset{|}{Si}}{}^{+} + \overset{|}{\underset{|}{N}}H-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-\overset{+}{\underset{|}{N}}H-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-N-\overset{|}{\underset{|}{Si}}- + H^{+} \qquad (27)$$

$$\begin{array}{ccc} & | & | \\ & -Si- & -Si- \\ & | & | \end{array} \qquad \begin{array}{c} | \\ -Si- \\ | \end{array}$$

$$\longrightarrow -\overset{|}{\underset{|}{Si}}-NH-\overset{|}{\underset{|}{Si}}- + -\overset{|}{\underset{|}{Si}}{}^{+} \qquad (28)$$

$$-\overset{|}{\underset{|}{Si}}{}^{+} + \overset{|}{\underset{|}{O}}-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-\overset{+}{\underset{|}{O}}-\overset{|}{\underset{|}{Si}}- \longrightarrow -\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}} + -\overset{|}{\underset{|}{Si}}{}^{+} \qquad (29)$$

$$\begin{array}{cc} | & | \\ -Si- & -Si- \\ | & | \end{array}$$
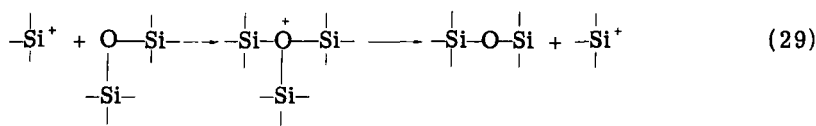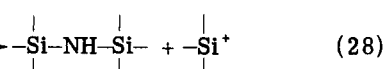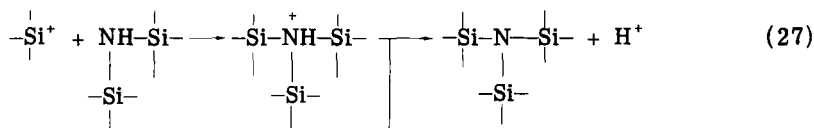
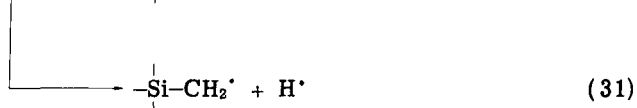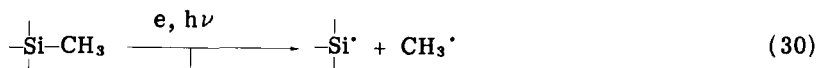These reactions account for the formation of new Si–N and Si–O bonds, respectively, and they are considered to occur in the gas phase as well as in the surface layer of the deposit. The possibility of two competitive steps for the reaction of silazane bond arises from the trifunctionality of the nitrogen atom. It is important to note that Reaction (27) may strongly contribute to the cross-linking process in the case of methylsilazanes. Reactions (28) and (29) play a substantial role in formation of the oligomers; however, they cannot produce cross-linking.

The relatively small polar bond components of the Si–C (12%) and C–H (4%) bonds [32] leads to an expectation of an intense homolytic decomposition of the methylsilyl groups under the impact of the electrons and highly energetic UV photons emitted from the plasma. The primary steps of this process may be described by

$$-\overset{|}{\underset{|}{Si}}-CH_3 \xrightarrow{\text{e, }h\nu} -\overset{|}{\underset{|}{Si}}{}^{\bullet} + CH_3{}^{\bullet} \qquad (30)$$

$$\longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2{}^{\bullet} + H^{\bullet} \qquad (31)$$

Reaction (30) seems to be more prevalent due to the lower energy of the Si–C bond (76 kcal/mol) compared with the C–H bond (99 kcal/mol) [33].

The active radical species thus generated may undergo a variety of secondary reactions according to the following reactions [41]:

$$-\overset{|}{\underset{|}{Si}}-CH_3 + \overset{|}{\cdot Si}- \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2{}^{\cdot} + H-\overset{|}{\underset{|}{Si}}- \tag{32}$$

$$-\overset{|}{\underset{|}{Si}}-CH_3 + CH_3{}^{\cdot} \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2{}^{\cdot} + CH_4 \tag{33}$$

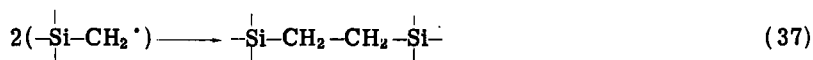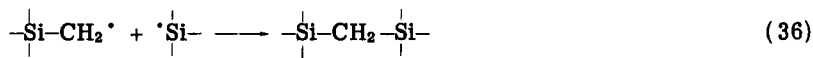$$-\overset{|}{\underset{|}{Si}}-CH_3 + H^{\cdot} \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2{}^{\cdot} + H_2 \tag{34}$$

$$2CH_3{}^{\cdot} \longrightarrow C_2H_6 \tag{35}$$
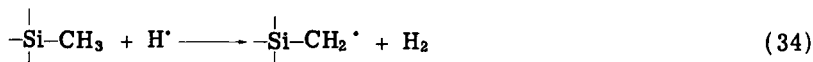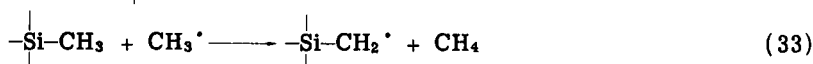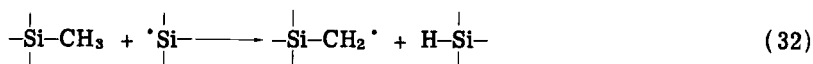
Reaction (32) is evidently confirmed by the results of MS and IR analyses and accounts for the presence of Si–H groups in some of the oligomeric products (Table 1) and in polymer films as revealed by the IR spectra (Fig. 9). The formation of light hydrocarbons following Reactions (33) and (35) was proved by gas chromatographic analysis of the gas phase after glow discharge. A typical gas chromatogram of the gaseous residue following glow discharge, presented in Fig. 10, shows the presence of ethane as a main component and some amount of methane and ethylene. The latter component seems to originate mainly from plasma conversion of ethane. The high concentration of ethane found in the gaseous plasma products for all investigated monomers proves that abstraction of methyl groups from silicon atoms is a basic plasma reaction of methylsilicones. It is important to mention that reactions similar to those presented above have been observed for a number of the methylsilazanes when subjected to UV irradiation [42]. This points out that UV radiation from plasma may play a substantial role in the generation of active species.

The Si' and SiCH$_2$' radical structures produced via Reactions (30)-(34) may subsequently recombine to form disilymethylene (DSM) and disilyethylene (DSE) bonds, respectively:

$$-\overset{|}{\underset{|}{Si}}-CH_2{}^{\cdot} + \overset{|}{\cdot Si}- \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2-\overset{|}{\underset{|}{Si}}- \tag{36}$$

$$2(-\overset{|}{\underset{|}{Si}}-CH_2{}^{\cdot}) \longrightarrow -\overset{|}{\underset{|}{Si}}-CH_2-CH_2-\overset{|}{\underset{|}{Si}}- \tag{37}$$

The presence of these bonds in the polymers was proved earlier by IR data. However, their quantitative evaluation is difficult due to the extremely low quantity of deposited polymeric material and its almost complete insolubility in organic solvents. Some information on the content of DSE links in the polymers can be obtained by pyrolysis/gas chromatography (P/GC) examinations. A representative pyrogram of
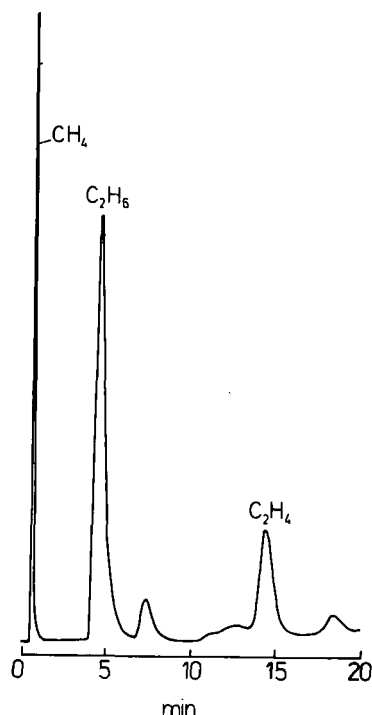
FIG. 10. Gas chromatogram of the glow discharge products of HMDSN.

the investigated polymers, as exemplified in Fig. 11, shows that the pyrolysis products contain mainly methane and ethylene and some amount of ethane. Most recently we have found [7] that ethylene originates not only from secondary thermal reactions of the remaining components but also a considerable amount evolves directly from the $Si-CH_2-CH_2-Si$ structural units in the polymer by thermal scission of the $Si-C$ bonds. This accounts for the high content of ethylene in the pyrolysis products as can be noted in Fig. 11. To obtain more precise information on the pyrolysis products, the gas chromatographic data were evaluated as the concentration ratios C_2H_4/CH_4 and C_2H_6/CH_4, these being the ratios of the gas chromatographic peak areas of the respective components. The ratios for particular plasma polymers are listed in Table 2. As can be seen, the C_2H_4/CH_4 ratio varies substantially whereas the C_2H_6/CH_4 ratio remains almost constant, independent of the polymer. This indicates that the relative ethylene content, in contrast to that of ethane, evidently depends on the polymer structure. According to our previous finding [7], it will
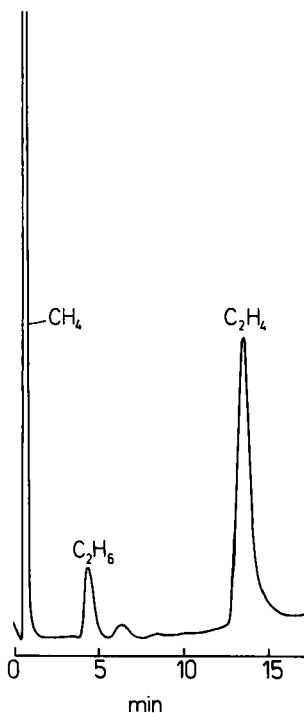
FIG. 11.   Gas chromatogram of the pyrolysis products of PP-HMDSN.

increase with the concentration of DSE bonds in the polymer. Thus, the higher ethylene content found for plasma polymers of methylsilox-anes (Table 2) proves that this group of monomers produces more DSE links than that of methylsilazanes. This agrees reasonably with the fact that methylsilazanes can easily undergo an additional linking via Si–N bonds with tertiary nitrogen (Reaction 27), and therefore this strongly competetive process may markedly reduce the formation of DSE and also DSM links. This effect is revealed even more distinctly by the data obtained for both silazane polymers. Over twice the lower ethylene content noted for PP-HCTSN undoubtedly is due to the larger number of –NH– units in HMCTSN (with respect to HMDSN) and the re-sulting intense formation of Si–N rather than DSE links. A very close ethylene content observed for siloxane polymers independent of their structure accounts for nearly the same capability of methylsiloxanes toward the formation of DSE links.

It has been found that a type of bonding similar to that described by Reactions (36) and (37) appears in conventional polydimethylsiloxane

TABLE 2. Relative Contents of Gaseous Pyrolysis Products of
Plasma Polymers from Methylsilazane and Methylsiloxane Monomers,
and Relative Pressure Increase in Reactor after Glow Discharge

Monomer	Relative content of pyrolysis products		Pressure increase, $\% \Delta P/P_0$
	C_2H_4/CH_4	C_2H_6/CH_4	
Hexamethyldi-silazane	0.85	0.06	26
Hexamethylcyclo-trisilazane	0.40	0.05	33
Hexamethyldi-siloxane	1.20	0.06	23
Hexamethylcyclo-trisiloxane	1.15	0.05	6
Octamethylcyclo-tetrasiloxane	1.16	0.06	9

when it is subjected to UV irradiation [43] and high energy irradiation
[44], and involves an intense cross-linking in this polymer. Moreover,
quantitative evaluation has shown that radiolysis of hexamethyldisiloxane
[45], octamethyltrisiloxane [19], and polydimethylsiloxane [44] produce
Si–CH₂–Si and Si–CH₂–CH₂–Si links at contents ratio of (1.8-2):(0.5-0.7),
respectively. This ratio indicates that Si–CH₂–Si links are formed more
readily than Si–CH₂–CH₂–Si links. This presumably results from the
higher content of Si˙ than of Si–CH₂˙ radical species involved in this
process. A similar trend may also be assumed for plasma polymeriza-
tion.

In view of these data, it is concluded that formation of DSM and DSE
links is a general feature of organosilicon monomers with methylsilyl
structural units, and this process, among other reactions, strongly con-
tributes to the growth of the polymer network. Furthermore, our den-
sity data of methylsilazane and methylsiloxane plasma polymers [5] sug-
gest that this type of cross-linking may even occur in the internal (adja-
cent to the substrate) layer of the growing film as a result of photochemi-
cal reactions initiated by energetic UV photons from plasma which pene-
trate the deposit.

The contribution of the particular elementary reactions to the overall
polymerization process should be in close relation to the pressure
change in the reaction system following glow discharge. The pressure
was found to increase in the case of each monomer investigated. This
trend is consistent with the fragmentation reactions presented above.

The pressure increase data evaluated as the ratio $\Delta P/P_0$, where ΔP

is the difference between the pressure after the discharge is finished
and its initial value P_0, are shown in Table 2. Distinct differences in
the pressure increase values as observed for silazane and siloxane
monomers evidently indicate their different fragmentations in plasma.

The higher $\Delta P/P_0$ values noted for silazane monomers may be ex-
plained by the additional fragmentation involved in hydrogen detach-
ment from the −NH− units according to Reaction (27). This is con-
firmed by comparing the data of both silazane monomers where $\Delta P/P_0$
appears to increase markedly with the number of −NH− units in the
monomer. The relatively low $\Delta P/P_0$ values observed for cyclic
siloxanes may be due to ring expansion reactions resulting in the for-
mation of a cyclic dimeric molecule (as noted for HMCTSO) or even
higher molecular weight cyclic products than those detected by GC/
MS analysis. This process can consequently reduce the pressure in-
crease arising from the fragmentation of methylsilyl groups.

CONCLUDING REMARKS

Our GC/MS studies have shown the presence of the oligomeric
phase in plasma-polymerized organosilicones which were found to
contain products with molecular weights mostly no higher than two
monomer units. The results strongly suggest that the oligomers may
be formed in the gas phase and then they are incorporated into the
growing polymer film.

MS structural data have revealed that formation of the oligomers
must proceed by Si−N and Si−O bond cleavage in silazane and siloxane
monomers, respectively. The high susceptibility of these bonds to
undergo heterolytic fission allows us to assume an ionic nature of the
primary active species involved in the oligomerization process. The
proposed ionic mechanism appears to explain the formation of the ob-
served oligomers more reasonably than the radical mechanism.

IR and PGC data have shown that methylsilyl structural units of
silazane and siloxane monomers are highly susceptible toward forma-
tion of disilymethylene and disilyethylene cross-links in the polymers.
This process is considered to proceed via homolytic fission of the
Si−C and C−H bonds in methylsilyl groups and subsequent recombina-
tion of the radical structures thus formed.

The basic difference in the plasma polymerization mechanism of
methylsilazanes and methylsiloxanes is that the former group of mono-
mers produces additional cross-linking via the Si−N bonds with ter-
tiary nitrogen. The intense hydrogen detachment from the −NH− units
involved in this process has been manifested by distinct differences in
pressure increases in the reaction systems noted for both groups of
monomers.

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