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Thermal Decomposition of Plasma-Polymerized Organosilicon Thin Films

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ABSTRACT

Thermal decomposition of plasma-polymerized hexamethylcyclotrisilazane (PP-HMCTSN) thin films was studied by using various techniques. Pyrolysis-gas chromatography investigation of thermal decomposition products and IR examination of the polymer films showed that methylsilyl groups present in the monomer were highly susceptible to form disilymethylene and disilyethylene cross-linkages under plasma conditions. A three-stage mechanism of the thermal decomposition found by thermogravimetry proved a great complexity of the thermal reactions which occur during this process and, in turn, provided strong evidence for a very complex structure of plasma polymer. Electron microscopy investigation revealed a marked effect of the thermal decomposition process on the film microstructure. The trend observed in the morphological changes was consistent with kinetics of this process. The high temperature thermal treatment reduced the organic content of polymer film, correspondingly increasing its inorganic character. Films produced with this process were of unusually interesting properties, displaying strong adhesion to metal substrates and high resistance to corrosive agents.

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INTRODUCTION

Our recent studies have shown that the chemical structure of plasma-polymerized organosilicon thin films can be modified selectively by controlled pyrolytic process used either as a posttreatment [1] or combined with the polymerization step, i.e., as a deposition onto the heated substrate [2]. Films produced with the contribution of this process tend to be highly cross-linked with increasing inorganic character. They showed a high temperature stability, a strong adhesion to wide range of metal substrates, and an outstanding chemical resistance to aggressive environments. These interesting properties suggest the possibility of useful applications of such films; for example, as coatings for the passivation of metals [3].

In view of these promising results, the present work has been devoted to a more complex study on the thermal decomposition of plasma polymer films deposited from hexamethylcyclotrisilazane. The use of cyclic monomers in contrast to those of linear structure seems to be particularly advantageous due to the smaller number of methyl groups contained in the cyclic molecule. This is of importance for the production of films with low organic structural content.

The study was carried out by using various analytical methods including pyrolysis-gas chromatography combined techniques, infrared spectroscopy, thermogravimetry, and electron microscopy. The effect of thermal treatment on the properties of the film was also reported.

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EXPERIMENTAL

Polymerization Procedure

Plasma polymerizations were carried out in the electrode stationary system described previously [4]. The apparatus incorporates a vacuum bell jar containing two parallel stainless steel electrodes spaced 3 cm apart, each having a surface area of 50 cm^2. Polymer films were deposited in an audio frequency glow discharge generated at 20 kHz. Other discharge parameters used were as follows: initial pressure of monomer, $p = 0.3$ torr; current density, $j = 1$ mA/cm^2 and discharge duration, $t = 30$ s. The thickness of the polymer films deposited under these conditions was found to be 1.5 μm. Films of lower thickness were obtained by decreasing the discharge duration. The current density in some experiments was varied from 0.4 to 2.7 mA/cm^2, maintaining the remaining discharge parameters as above.

Pyrolysis-Gas Chromatography (PGC)

Polymer samples of about 0.2 mg removed from the electrodes were pyrolyzed in argon at 750°C for 15 s by using a Jeol pyrolyzer

unit, Model PL 723. The gaseous products of pyrolysis were fed directly to the injection part of a Jeol, Model JGC 1100, gas chromatograph, equipped with a flame ionization detector and a 1 m × 3 mm stainless steel separation column filled with a 5A 60/80 mesh molecular sieve. The column was heated from 40 to 270°C using linear heating rate of 10°/min. The areas under peaks in chromatograms were measured on a Takeda Riken, Model TR-2215 A, electronic integrator. The separated products were analyzed using a LKB, Model 2091, mass spectrometer equipped with a PDP11 computer. For their identification the retention time coincidence with pure standard compounds were also used.

Sampling of Reaction Products

The gaseous products of plasma reaction were sampled from the interelectrode region directly after glow discharge to the ampule of about 50 cm^3 in capacity, which was attached to the reactor through a stopcock. Prior to sampling, the ampule was evacuated to a pressure of less than 10^{-5} torr and the products were sucked into the ampule by opening the stopcock. The content of the ampule was then injected to a gas chromatograph and analyzed as described previously. The composition of sampled products was considered to be quantitatively the same as in the reactor.

Infrared Spectroscopy (IR)

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

Thermogravimetric Analysis (TGA)

The measurements were carried out in high vacuum (10^{-5} torr) by means of a Mettler thermobalance, Thermoanalyzer. Polymer samples not exceeding 8 mg were heated with a constant rate of 2°/min. The weight loss was recorded within the range from room temperature to 800°C.

Transmission Electron Microscopy (TEM)

The examinations were carried out with the films having the initial thickness of 600 Å, deposited on a 10-μm thick copper foil. The film samples were subjected to vacuum pyrolysis at 10^{-5} torr and at 800°C for various periods of time. The films were separated from the substrate by their immersion in a 30% aqueous solution of nitric acid

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until the copper foil was completely dissolved and then they were washed with distilled water. Film samples prepared in this way were placed on the microscopy mesh and examined directly in a Tesla, Model BS-500, transmission electron microscope.

Contact Angle Measurement

Samples for the measurement of the contact angle were prepared by depositing approximately 1 μm thick films onto polished stainless steel plates. The measurements were performed with two standard liquids: water and methylene iodide by using a PZO goniometer eye-piece. The contact angle was measured at room temperature with a drop of 20 μL. Reproducibility of measurements was better than $\pm 2°$ in most cases. The contact angle data were analyzed to calculate the dispersion contribution (γ_s^d) and the polar contribution (γ_s^p) according to a surface energy model reported by Owens et al. [5].

Materials

Hexamethylcyclotrisilazane (HMCTSN) monomer (PCR Research Chemicals Inc.) was purified by rectification in vacuum and then its purity was tested by gas chromatography. Water and methylene iodide were triply distilled before the contact angle measurements.

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RESULTS AND DISCUSSION

Pyrolysis-Gas Chromatography

PGC examination showed that the gaseous residue following thermal decomposition of PP-HMCTSN consists mostly of light hydrocarbons as methane, ethane, ethylene, and some amount of acetylene and propylene (Fig. 1). The formation of these products may be elucidated by taking into account our IR investigation reported previously [1]. It has been proved that thermal decomposition of PP-HMCTSN involves a rapid decay of $SiCH_3$, SiH, and NH groups due to the following reactions:

$$\equiv Si{-}CH_3 \longrightarrow \equiv Si^{\bullet} + {}^{\bullet}CH_3 \qquad (1)$$

$$\equiv Si{-}H \longrightarrow \equiv Si^{\bullet} + H^{\bullet} \qquad (2)$$

$$(\equiv Si)_2N{-}H \longrightarrow (\equiv Si)_2N^{\bullet} + H^{\bullet} \qquad (3)$$

The above process results in cross-linking of the polymer via formation of new Si–N bonds with tertiary nitrogen [1]:

$$(\equiv Si)_2N^{\bullet} + {}^{\bullet}Si\equiv \longrightarrow (\equiv Si)_3N \qquad (4)$$

The methyl and hydrogen radicals liberated due to Reactions (1), (2), and (3) may then be converted in the gaseous phase into numerous secondary products according to the following reactions [6]:

$$CH_3^{\bullet} + H^{\bullet} \longrightarrow CH_4 \qquad (5)$$

$$2CH_3^{\bullet} \longrightarrow C_2H_6 \qquad (6)$$

$$C_2H_6 + CH_3^{\bullet} \longrightarrow C_2H_5^{\bullet} + CH_4 \qquad (7)$$

$$C_2H_5^{\bullet} \longrightarrow C_2H_4 + H^{\bullet} \qquad (8)$$

$$C_2H_6 + H^{\bullet} \longrightarrow C_2H_5^{\bullet} + H_2 \qquad (9)$$

$$2C_2H_5^{\bullet} \longrightarrow C_2H_6 + C_2H_4 \qquad (10)$$

According to the kinetics data of these reactions [6], the formation of hydrogen, methane, and ethylene appears to be the most favorable process. This well explains the high content of methane and ethylene found in the decomposition products (Fig. 1); hydrogen was not detected in this study. Some amount of acetylene and propylene, as noted in Fig. 1, results from the thermal conversion of ethylene [6]. These results confirm our IR study [1] and indicate that abstraction of methyls from silicon is the dominating reaction during the thermal decomposition process.

To obtain more detailed information on the structure of PP-HMCTSN, the PGC examinations were carried out for polymer films deposited at various current densities, the rest of the polymerization parameters being constant. The PGC data were evaluated as the concentration ratios C_2H_6/CH_4 and C_2H_4/CH_4, these being the ratios of the gas chromatographic peak areas of the respective decomposition components. The ratios plotted as a function of current density are shown in Fig. 2. It is seen that the C_2H_4/CH_4 ratio rises with increasing current density whereas the C_2H_6/CH_4 ratio remains constant; the values at zero current density correspond to the respective ratios for monomer determined by PGC examination. Assuming that methane, ethane, and ethylene are formed as secondary decomposition products according to Reactions (5)-(10), their relative content in the gas phase under the same pyrolysis conditions will be independent of the number

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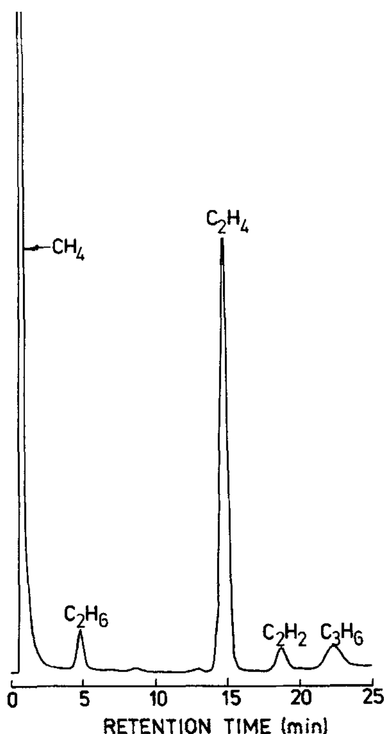

FIG. 1. Gas chromatogram of thermal decomposition products of PP-HMCTSN deposited at 0.3 torr, 1 mA/cm^2, 30 s. Pyrolysis temperature: 750°C, time: 15 s.

of methyl groups in the polymer and should remain constant. This is in good agreement with a distinct plateau in the C_2H_6/CH_4 curve (Fig. 2) observed within the whole density range under investigation. The rise of the C_2H_4/CH_4 ratio with increasing current density (Fig. 2) results from the increase in ethylene content. It follows that ethylene is formed not only through Reactions (8) and (10) but may also be evolved from the polymer as a primary decomposition product. The IR analysis of polymer films indicates the presence of ethylene linkages between silicons. The IR spectra will be discussed separately in the next section. Comparison of the relative bond energies of the Si–C (74 kcal/mol) and C–C (83 kcal/mol) bonds [7] indicates that the former will undergo thermal scission more readily than the latter. Thus ethylene may be evolved from the polymer through decomposition of disilylethylene links according to the simplified reaction

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$$\equiv Si-CH_2-CH_2-Si\equiv \longrightarrow 2(\equiv Si^{\bullet}) + C_2H_4 \qquad (11)$$

This reaction is confirmed by the results of other authors [8] who have studied thermal decomposition of poly-dimethyl-sil-ethylene-siloxane and poly-dimethyl-sil-propylene-siloxane. They have found the elimination of hydrocarbon segments located between silicons and subsequent evolution of ethylene and propylene, respectively.

Referring now to the C_2H_4/CH_4 curve shown in Fig. 2, it is noted that the rise of this ratio with current density results from the increase of disilyethylene linkages in the polymer structure. The extrapolation of the curve to zero current density exactly yields the C_2H_4/CH_4 value found for monomer. This value corresponds to the relative content of ethylene in the decomposition products produced via secondary Reactions (8) and (10).

Infrared Spectroscopy

To confirm the results obtained from the PGC experiments, the polymer films were analyzed using infrared spectroscopy. The

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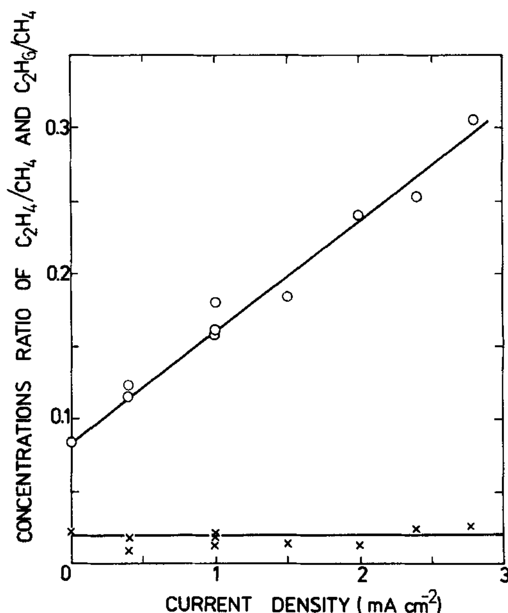

FIG. 2. Concentrations ratio of C_2H_4/CH_4 (o) and C_2H_6/CH_4 (x) in gaseous pyrolyzate of PP-HMCTSN as a function of discharge current density.

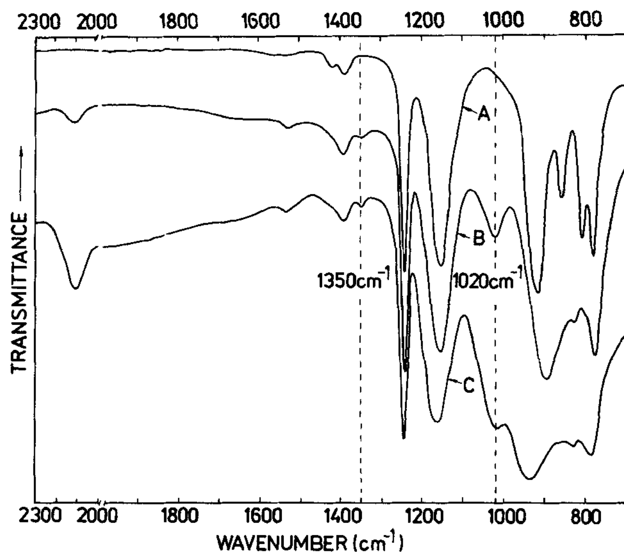

FIG. 3. IR spectra of PP-HMCTSN films deposited at 0.3 torr, 30 s at various discharge current density: (A) monomer spectrum, (B) 1 mA/cm^2, (C) 2 mA/cm^2.

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infrared spectra of PP-HMCTSN films are shown in Fig. 3. For comparison, there is also shown a spectrum of monomer. Since a detailed description of these spectra has already been published elsewhere [1, 9, 10], their discussion here will be confined only to several absorption bands important for the scope of this work.

Referring to Fig. 3, it is noted that the spectrum of polymer film (Fig. 3B) exhibits a new absorption band at 1020 cm^{-1} which is absent in the monomer spectrum (Fig. 3A). This band may be assigned to ω ($-CH_2-$) vibration in disilymethylene or disilyethylene bonds [11]. The presence of these groups can also be recognized by a weak but distinctive band appearing at 1350 cm^{-1} (Fig. 3B) which originates from $\delta_s(-CH_2-)$ vibration [11]. The marked broadening of the band at 1020 cm^{-1} may be due to a strong overlapping effect of absorptions corresponding to $\omega(-CH_2-)$ vibration in disilymethylene and disilyethylene bonds and may prove the presence of both bonds in the polymer. In the spectrum of polymer film deposited at a higher current density (Fig. 3C), there is seen a distinct rise in the intensity of the discussed bands which results from the increased content of $\equiv Si-CH_2-Si\equiv$ and $\equiv Si-CH_2-CH_2-Si\equiv$ linkages in the polymer structure.

More convincing results for formation of these bonds were obtained by an additional experiment with use of hexamethyldisilane (HMDS) as a model monomer containing only $Si-CH_3$ and Si–Si structural units. It may be expected that HMDS will polymerize under plasma condi-

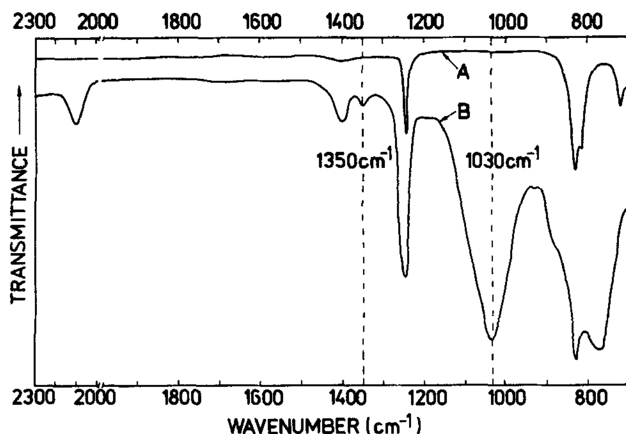

FIG. 4. IR spectra of HMDS monomer (A) and its plasma polymer (B) deposited at 0.6 torr, 1 mA/cm^2, 30 s.

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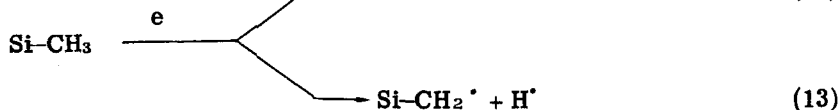
tions mainly by formation of $\equiv Si-CH_2-Si\equiv$ and $\equiv Si-CH_2-CH_2-Si\equiv$ bonds. The IR spectrum of polymer deposited from this monomer (Fig. 4B) clearly shows new absorption bands at 1350 cm^{-1} and 1030 cm^{-} which are absent in the monomer spectrum (Fig. 4A). The bands appear in similar regions as those observed in PP-HMCTSN spectra (Fig. 3B and C) except that here they are more intense. This provides strong evidence for the presence of the discussed bonds in the structure of both polymers investigated.

It should be noted that a similar type of bonding has been found in the solid-state polymerization of octamethylcyclotetrasiloxane initiated by silent discharge [12].

Mechanism of Cross-Linking

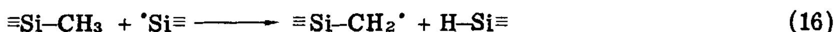
The presence of disilymethylene and disilyethylene bonds found by PGC and IR analyses in the polymer films proves that their formation is associated with a strong fragmentation of methylsilyl groups. The collisions of monomer molecules in the gas phase with a highly energetic plasma species such as electrons, ions, or photons involve Si–C and C–H bonds rupture. Assuming a radical mechanism for plasma polymerization [13, 14], the primary steps of this process may be described by



The lower energy of the Si–C bond as compared with the C–H bond [7] allows us to assume that Reaction (12) will be more prevalent. These reactions may also occur in the growing polymer by the impact of active plasma species on the film surface. The reactive structures thus formed may undergo a number of different secondary reactions according to the following simplified scheme [15]:

$$\equiv Si\text{–}CH_3 + CH_3^{\bullet} \longrightarrow \equiv Si\text{–}CH_2^{\bullet} + CH_4 \quad (14)$$

$$\equiv Si\text{–}CH_3 + H^{\bullet} \longrightarrow \equiv Si\text{–}CH_2^{\bullet} + H_2 \quad (15)$$

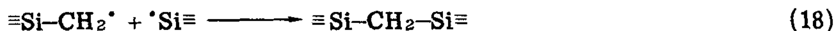


$$\equiv Si\text{–}CH_3 + {}^{\bullet}Si\equiv \longrightarrow \equiv Si\text{–}CH_2^{\bullet} + H\text{–}Si\equiv \quad (16)$$

$$2CH_3^{\bullet} \longrightarrow C_2H_6 \quad (17)$$

Reaction (16) is confirmed by the appearance of a distinct absorption band at 2100 cm^{-1} from SiH groups in the polymers spectra (Figs. 3 and 4).

The $\equiv Si^{\bullet}$ and $\equiv SiCH_2^{\bullet}$ active structures produced according to the above reactions scheme may subsequently be combined to form disily-hydrocarbon and disilane bonds in the polymer as follows:



$$\equiv Si\text{–}CH_2^{\bullet} + {}^{\bullet}Si\equiv \longrightarrow \equiv Si\text{–}CH_2\text{–}Si\equiv \quad (18)$$

$$2\,(\equiv Si\text{–}CH_2^{\bullet}) \longrightarrow \equiv Si\text{–}CH_2\text{–}CH_2\text{–}Si\equiv \quad (19)$$

$$2\,(\equiv Si^{\bullet}) \longrightarrow \equiv Si\text{–}Si\equiv \quad (20)$$

We emphasize that these processes strongly contribute to cross-linking in the polymer film. However, a quantitative evaluation of these links is difficult due to the extremely low quantity of deposited polymeric material and its almost complete insolubility in organic solvents.

It should be noted that a similar mechanism of cross-linking has been found in conventional polydimethylsiloxane subjected to high energy irradiation [16] and UV irradiation [17]. It was shown [16] that radiolysis of this polymer at room temperature produced $\equiv Si\text{–}CH_2\text{–}Si\equiv$, $\equiv Si\text{–}CH_2\text{–}CH_2\text{–}Si\equiv$, and $\equiv Si\text{–}Si\equiv$ cross-linkages at their contents ratios of 1.8:0.5:1.1, respectively. This proportion indicates that formation of $\equiv Si\text{–}CH_2\text{–}Si\equiv$ bonds proceeds more readily than $\equiv Si\text{–}CH_2\text{–}CH_2\text{–}Si\equiv$ bonds. This presumably results from the higher content of $\equiv Si^{\bullet}$ than $\equiv Si\text{–}CH_2^{\bullet}$ species. Similar trend may also be considered for the plasma polymerization.

Our recent IR [2] and PGC [18] investigations of plasma polymers

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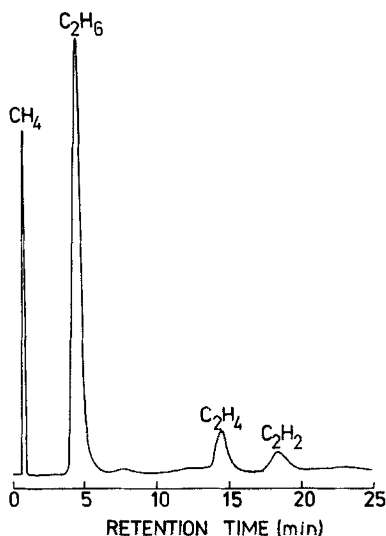

FIG. 5. Gas chromatogram of glow discharge products of HMCTSN formed at 0.3 torr, 1 mA/cm^2, 30 s.

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obtained from numerous methylsilicon monomers also indicated the presence of disilymethylene and disilyethylene cross-linkages in their structure. In view of these results, it may be concluded that the discussed mechanism of cross-linking appears to be a general feature of organosilicon monomers with methylsilyl structural units and plays a significant role in the polymer film growth. Moreover, the density data of plasma-polymerized methylsilicon films [19] strongly suggested that this type of cross-linking may even occur in the internal (adjacent to the substrate) layer of the growing film as a result of photochemical reactions initiated by energetic UV photons emitted from plasma which penetrate the deposit.

Composition of Glow Discharge Products

Fragmentation of methylsilyl groups following Reactions (12)-(15) and (17) should involve a liberation of hydrogen, methane, and ethane. To identify some of these fragmentation products, a gas chromatography investigation of the gas phase after glow discharge was carried out. A typical gas chromatogram of the gaseous residue following glow discharge in HMCTSN vapor, illustrated in Fig. 5, shows the presence of ethane as a main component and some amount of methane, ethylene, and acetylene. Ethane appears to be a secondary product of methyl combinations, and its high content, as is shown in Fig. 5, is

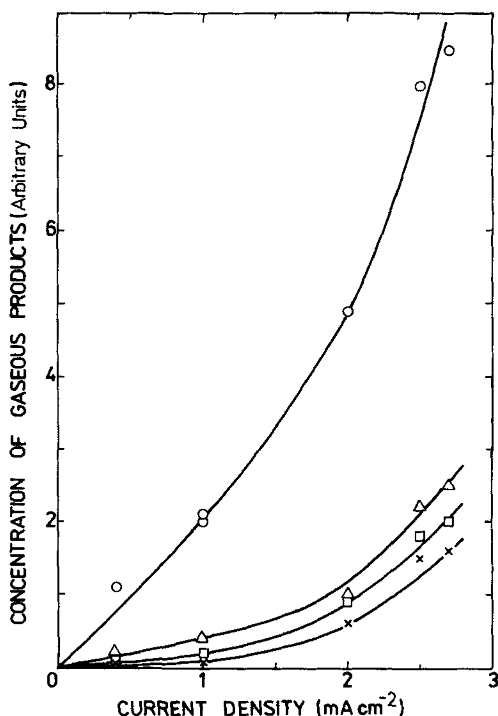

FIG. 6. Concentrations of glow discharge products of HMCTSN in arbitrary units as a function of discharge current density: (○) C_2H_6, (△) CH_4, (□) C_2H_4, (X) C_2H_2.

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strong evidence for the fragmentation of methylsilyl groups due to Reaction (12).

More detailed information on the fragmentation process of HMCTSN was obtained by the investigation of the composition of the glow discharge products as a function of discharge current density. It was found that this parameter had no effect on the qualitative composition of the glow discharge products; however, distinct quantitative changes were observed. To evaluate the composition of the gas phase, the concentration of each component was determined from the area under the respective gas chromatographic peak. Prior to the evaluation, the areas under the peaks were normalized using a response factor (reported in Ref. 20) for particular components. The concentrations of the glow discharge products expressed in arbitrary units are shown as a function of discharge current density in Fig. 6. It can be noted that concentrations of particular products rise with the current density. This may be explained by the increase in density of active plasma particles which cause an increase in monomer fragmentation and conversion

of the fragments into numerous secondary products. However, the sharpest increase noted for ethane results from the high concentration of methyls produced by the rupture of $\equiv$Si–CH_3 bonds (Reaction 12). Therefore, the combination of methyls to ethane (Reaction 17) may proceed more readily than their conversion into methane due to Reaction (14). This explains the lower rate of increase in methane concentration with current density (Fig. 6). A similar trend in the formation of gaseous products has also been observed for UV photolysis of methylsilazanes [21]. The photolysis products were found to consist of hydrogen, methane, and a large amount of ethane. This points out that UV radiation from plasma plays an important role in the monomer fragmentation and generation of active species.

The low concentrations found for ethylene and acetylene (Fig. 6) suggest that these products are formed by plasma conversion of ethane [22]. From the ethane and methane concentration curves, one can conclude that the increase of these products in the gas phase involves a rise of $\equiv Si^{\bullet}$ and $\equiv SiCH_2^{\bullet}$ active species (generated via Reactions 12 and 13, respectively) capable of producing disilymethylene and disilyethylene links in the polymer. This is evident in view of the PGC and IR data presented in the earlier sections which indicated a marked increase of these bonds in PP-HMCTSN with a rise in current density. However, the steeper slope noted for the ethane curve shows that the generation of $\equiv Si^{\bullet}$ species dominates here, and due to their high content, the formation of $\equiv$Si–CH_2–Si$\equiv$ bonds seems to be more favorable than $\equiv$Si–CH_2–CH_2–Si$\equiv$ bonds.

The effect of current density on the fragmentation of methylsilyl groups demonstrated by the increase in the gas phase of the secondary products of methyls reactions, may also be confirmed by the results of elemental analysis of PP-HMCTSN [9]. Carbon and hydrogen content in the polymer were found to decrease significantly with an increasing value of this parameter.

Thermogravimetric Analysis

The thermal decomposition process of PP-HMCTSN films was also examined quantitatively by using dynamic thermogravimetric measurements. To obtain thermograms with well-resolved decomposition stages, samples of plasma polymer were heated in vacuum at a relatively low (2°/min) heating rate. A representative thermogram for PP-HMCTSN is illustrated in Fig. 7. It follows from the TG curve that thermal decomposition of the polymer takes place in three distinct, separated stages. A rapid weight loss observed in the first stage proceeding at low temperatures up to 140°C is due to the volatilization of low molecular products whose presence in this polymer was testified to by gas chromatography and mass spectrometry studies [23, 24]. It was shown that PP-HMCTSN contains a small amount of monomer, its oxy derivative, octamethylcyclotetrasilazane, and bicyclic dimer. This is also consistent with the density data, reported

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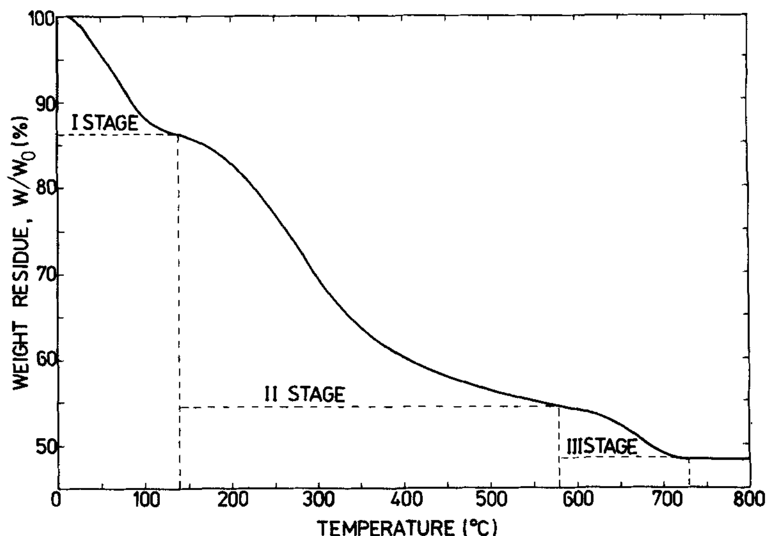

FIG. 7. Thermogram of PP-HMCTSN deposited at 0.3 torr, 1 mA/ cm^2, 30 s.

previously [19], which revealed the existence of a heterogeneous film structure. The plasma organosilicon films were found to be composed of a dense, highly cross-linked phase, and a thin oligomeric surface layer.

In the second stage of decomposition, proceeding within a higher temperature range of 140 to 580°C (Fig. 7), the largest weight loss is noted. On the basis of our previous IR investigation [1] and PGC examination carried out at these temperatures, this stage may be attributed to the scissions of $\equiv Si-CH_3$, $\equiv Si-(CH_2)_2-Si\equiv$, $\equiv Si-H$, and $(\equiv Si)_2N-H$ bonds. The weight loss is associated with the evolution of hydrogen, methane, ethane, and ethylene produced via Reactions (5)-(11). This elimination of hydrogen- and carbon-containing groups involves formation of $(\equiv Si)_3N$ bonds in the polymer according to Reaction (4).

The appearance of a TG curve in the third stage of decomposition within the temperature range of 580-730°C is more difficult to explain. The small weight loss observed in this stage may presumably result from dehydrogenation of $\equiv Si-CH_2-Si\equiv$ linkages retained in the polymer residue and their transformation into Si–C inorganic bonds. This interpretation agrees well with the results of IR analysis of the residue collected after TGA measurement. The IR spectrum of this sample was similar to that presented elsewhere [10] and showed no absorption bands to be assigned to C–H bonds. A very intense and broad band appeared within the 1000-800 cm^{-1} range and was characteristic of

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inorganic material. A marked broadening of this band seemed to be due to overlapping of absorptions from Si–C and Si–N inorganic bonds formed by thermal decomposition.

In general, the TGA data presented here prove the great complexity of reactions occurring during thermal decomposition of PP-HMCTSN. The three well-resolved stages found in this process provide evidence for the very complex structure of plasma polymer as documented by IR and PGC investigations.

Transmission Electron Microscopy

In view of the evident changes in the chemical structure of PP-HMCTSN films involved in their thermal decomposition [1], it was interesting to establish the effect of this process on the morphological structure of the film. For this purpose, the TEM technique was used. Films deposited onto copper foil were heated in vacuum at 800°C. This drastic temperature was chosen from the TG curve (Fig. 7) to attain a deep decomposition of plasma polymer film.

TEM micrographs of PP-HMCTSN films obtained after various periods of their vacuum heat-treatment and untreated film are shown in Fig. 8. The roughness observed in the untreated film (Fig. 8a) presumably results from a nonuniform etching by nitric acid of the film surface adjacent to the substrate, which may occur during dissolving of the copper substrate. It can be seen in Fig. 8b that a 30-s heat treatment involves a marked change in morphology of the film structure. The microporosity in the film is produced by a vigorous evolution of the gaseous products of thermal decomposition found by PGC investigations. The rapid change in film structure agrees with the kinetic data which indicated that the sharpest decrease in organic group content takes place at the initial stage of pyrolysis [1]. The microporosity is seen to decay completely with increase in heating time (Fig. 8c), and the structure of the film becomes almost uniform. Some fine roughness present in the film seems to be reproduced by the substrate since its surface structure (Fig. 8d) is similar to that noted in the film. The latter change in film morphology is due to thermally induced cross-linking reactions taking place during this stage of pyrolysis [1]. This process is associated with the increase of inorganic structural content in the film and gives a marked rise to its density. This is consistent with the trend in morphological changes noted in Fig. 8c.

Effect of Thermal Treatment on Film Properties

The structural changes of PP-HMCTSN films involved in thermal treatment were also exhibited by a significant variation in their physical and chemical properties.

Scratch and abrasion qualitative tests showed a progressive

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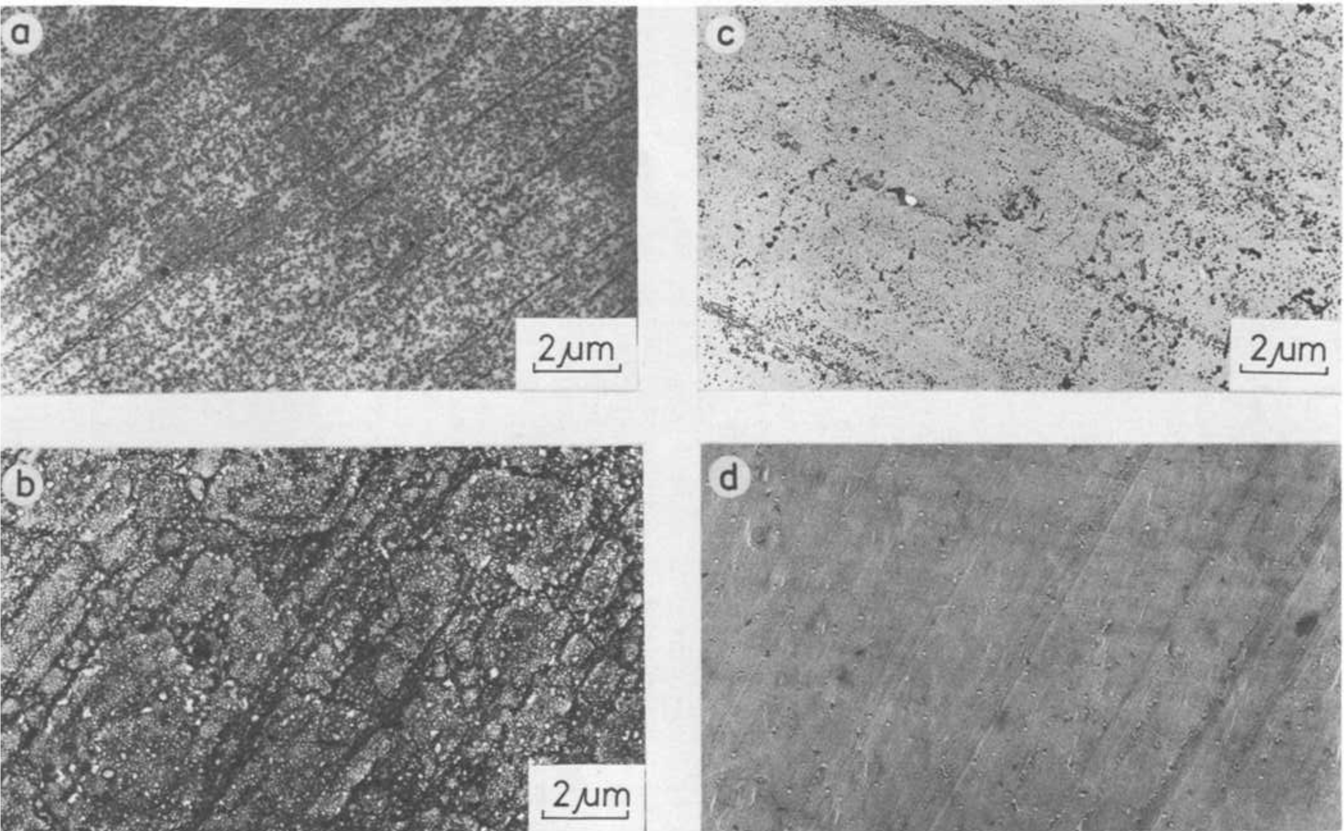

FIG. 8. TEM micrographs of PP-HMCTSN film following various durations of thermal treatment in vacuum at 800°C: (a) untreated film, (b) 0.5 min, (c) 3 min, (d) carbon replica of substrate.

TABLE 1. Effect of Vacuum Heat Treatment on Surface Energy of Plasma-Polymerized Hexamethylcyclotrisilazane Film

Treatment conditions		Surface energy (erg/cm^2)			% Energy increase		
Temperature (°C)	Time (h)	γ_s^d	γ_s^p	γ_s^a	γ_s^d	γ_s^p	γ_s
Untreated film		30.1	5.3	35.4	0	0	0
600	2	34.3	7.2	41.5	14	36	17
800	0.5	38.4	7.8	46.2	28	47	31

$^a\gamma_s = \gamma_s^d + \gamma_s^p$.

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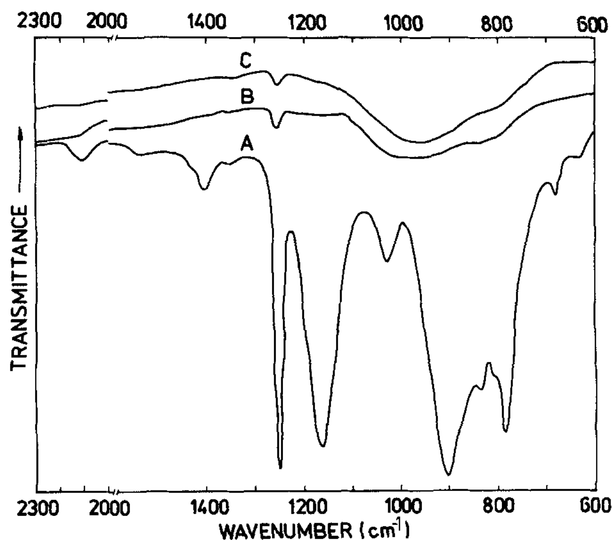

FIG. 9. Infrared ATR spectra of PP-HMCTSN film following various conditions of thermal treatment in vacuum: (A) untreated film; (B) 600°C, 2 h; (C) 800°C, 0.5 h.

hardening of the film and an increase of its adhesion to the metal substrates with treatment time. The pyrolyzed films were found to be colorless, glassy materials which adhered tenaciously to a wide range of metal substrates such as carbon steel, stainless steel, copper, and brass.

Examinations of the film surface by contact angle measurements showed a strong effect of thermal treatment on the surface free energy. The dispersion (γ_s^d) and polar (γ_s^p) contributions to the surface energy (γ_s) evaluated from the contact angle data for untreated film and subjected to a vacuum thermal treatment are listed in Table 1. The conditions of treatment, as specified in Table 1, were chosen to produce films with an extremely low content of organic groups. This may be shown by the IR spectra in Fig. 9 which indicate a decay of SiH (2100 cm^{-1}), $SiCH_3$ (1410 and 1260 cm^{-1}), and NH (1160 cm^{-1}) groups in the polymer films treated under these conditions (Figs. 9B and C). Data in Table 1 clearly indicate that the structural changes produced by thermal treatment markedly increase the dispersion and polar contributions of the surface energy. The increase of the dispersion contribution may be due to the rise in density of film resulting from thermal cross-linking. The density value was found to vary from 1.2 g/cm^3 for untreated film to nearly 2 g/cm^3 for film treated at 800°C. It is evident that the distance between the elements of the polymer structure decreases with increasing density, and this gives rise to the dispersion forces since they are proportional to the inverse sixth power of this distance [25]. The increase noted in the polar component of surface energy is considered to be due mainly to the rise in concentration of Si–N bonds which are produced in the pyrolyzed film according to Reactions (1)-(4). The presence of these bonds is proved by the appearance in the IR spectra (Figs. 9B and C) of a very intense and broad absorption band in the range 1000-800 cm^{-1}, which is similar to that of silicon nitride [26]. However, a marked broadening of this band indicates that absorption from Si–C inorganic bonds may also fall in this region.

It should be noted that the increase in the surface energy observed for thermally treated films agrees reasonably with the improvement in their adhesion to the metal substrate, although types of interfacial bonding other than van der Waals cannot be excluded here. It is very likely that under such drastic treatment conditions, chemical bonding may also occur within the polymer-metal interface region.

Examination of the chemical properties indicated that the resistance of films to aggressive environments after their thermal treatment improved significantly. Passivation tests have shown that metal substrates coated with pyrolyzed films display outstanding stability to highly corrosive environments such as saline, acidic, or sulfur-rich media over a broad range of temperature.

It is interesting to note that plasma polymer films deposited from other organosilazanes, such as hexamethyldisilazane and cyclic

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methylsilazanes with four- and eight-membered rings, were found to form films of similar properties when pyrolyzed in vacuum. On the contrary to these results, however, the thermal treatment of plasma-polymerized organosiloxanes resulted in significant deterioration in film adhesion to the metal substrate and a strong peeling effect was observed even under milder conditions of treatment. This shows that organosilazanes appear to be particularly useful for the production of strongly adhered protective coatings for metals.

CONCLUSIONS

PGC and IR data have shown that methylsilyl structural units of monomer are highly susceptible under plasma conditions toward formation of disilymethylene and disilyethylene cross-linkages in the polymer film. This type of cross-linking, among other reactions, contributes to the growth of the polymer network and appears to be a general feature of organosilicon monomers with methylsilyl groups.

A three-stage mechanism of thermal decomposition documented by TGA data proves a great complexity of thermal reactions occur during this process and, in turn, indicates a very complex structure of plasma polymer. Abstraction of methyls and scission of Si–C bonds in the polymer network appear to be the dominating thermal reactions.

TEM investigation has shown the significant effect of thermal decomposition on the morphological structure of film. The trend in microstructural changes in consistent with the kinetics of thermal decomposition. A marked improvement of film adhesion to metal substrate resulting from thermal treatment agrees reasonably with the increase in surface energy evaluated by contact angle measurements.

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REFERENCES

[1] A. M. Wróbel and M. Kryszewski, in Plasma Polymerization (M. Shen and A. T. Bell, eds.), (ACS Symp. Ser., Vol. 108), American Chemical Society, Washington, D.C., 1979, Chap. 14.

[2] A. M. Wróbel, M. R. Wertheimer, and H. P. Schreiber, Paper Presented at IEEE International Conference on Plasma Science, Montreal, 1979; J. Macromol. Sci.–Chem., In Press.

[3] H. P. Schreiber, M. R. Wertheimer, and A. M. Wróbel, Paper Presented at International Conference on Metallurgical Coatings, Held by Vacuum Metallurgy and Thin Films Divisions of AVS, San Diego, California 1980; Thin Solid Films, In Press.

[4] A. M. Wróbel, M. Kryszewski, and M. Gazicki, Polymer, 17, 673 (1976).

[5] D. K. Owens and R. C. Wend, J. Appl. Polym. Sci., 13, 1741 (1969).

[6] K. J. Laidler and L. F. Loucks "The Decomposition and Isomerization of Hydrocarbons" in Comprehensive Chemical Kinetics, Vol. 5 (C. H. Bamford and C. F. H. Tipper, eds.), Elsevier, Amsterdam, 1972.
[7] C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960.
[8] M. Blazso, G. Garzo, T. Szekely, K. A. Andrianov, and L. M. Volkova, J. Organomet. Chem., 54, 105 (1973).
[9] A. M. Wróbel, M. Kryszewski, and M. Gazicki, Polymer, 17, 678 (1976).
[10] A. M. Wróbel and M. Kryszewski, J. Macromol. Sci.–Chem., A12, 1041 (1978).
[11] D. R. Anderson, "Infrared, Raman and Ultraviolet Spectroscopy", in Analysis of Silicones (A. L. Smith, ed.), Wiley-Interscience, New York, 1974.
[12] F. Denes, C. Ungurenasu, and I. Haiduc, Eur. Polym. J., 6, 1155 (1970).
[13] A. T. Bell, J. Macromol. Sci.–Chem., A10, 369 (1976).
[14] J. M. Tibbit, R. Jensen, A. T. Bell, and M. Shen, Macromolecules, 10, 647 (1977).
[15] H. Sakurai in Free Radicals, Vol. 2 (J. K. Kochi, ed.), Wiley-Interscience, New York, 1973, Chap. 25.
[16] A. A. Miller, J. Am. Chem. Soc., 82, 3519 (1960).
[17] A. D. Dellman, M. Landy, and B. B. Simms, J. Polym. Sci., A1, 7, 3375 (1969).
[18] A. M. Wróbel, In Preparation.
[19] A. M. Wróbel, M. R. Wertheimer, J. Dib, and H. P. Schreiber, J. Macromol. Sci.–Chem., A14, 321 (1980).
[20] W. A. Dietz, J. Gas Chromatogr., 5, 68 (1967).
[21] E. L. Zuzgov, N. N. Bubnov, E. A. Semenova, D. Ya. Zinkin, and V. V. Voevodsky, Kinet. Katal., 6, 229 (1965).
[22] H. Kobayashi, A. T. Bell, and M. Shen, Macromolecules, 7, 277 (1974).
[23] M. Gazicki, A. M. Wróbel, and M. Kryszewski, J. Appl. Polym. Sci., 22, 2013 (1977).
[24] M. Kryszewski, A. M. Wróbel, and J. Tyczkowski in Plasma Polymerization (M. Shen and A. T. Bell, eds.), (ACS Symp. Ser., Vol. 108), American Chemical Society, Washington, D.C., 1979, Chap. 13.
[25] F. London, Trans. Faraday Soc., 33, 8 (1937).
[26] W. A. Pliskin, J. Vac. Sci. Technol., 14, 1082 (1977).

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