Spectroscopic Study on Chemical Structure of Plasma-Polymerized Hexamethyldisiloxane

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Synopsis

A plasma-polymerized material was produced from hexamethyldisiloxane vapor by a glow-discharge polymerization technique. Spectroscopic interpretation of the chemical structure of the polymerized hexamethyldisiloxane was studied by spectroscopic means such as IR, XPS, and NMR. The plasma polymer was barely soluble in the usual organic solvents, although it contained a small amount of the monomer and its oligomers. The IR spectrum indicated that the polymer consisted of Si—CH_3, Si—O, Si—CH_2, and Si—H groups. The surface of the polymer was found to retain structural units similar to the monomer from the XPS measurement. On the other hand, the ^{13}C and ^{29}Si high-resolution, solid-state NMR measurements revealed that the plasma polymer was highly crosslinked with a variety of conformations and a number of O atoms surrounding a Si atom. Results from the XPS and NMR spectra suggested that the bulk of the polymer was more oxidized than the surface layer; Si atom was preferentially oxidized. A hypothetical chemical structure was proposed for the polymerized hexamethyldisiloxane.

INTRODUCTION

A polymeric material can be deposited on a substrate placed in the glow discharge of an organic vapor. This material will take several forms: powder, thin film, and oil, or their combination, depending on the plasma polymerization conditions. The plasma polymerization technique is considered a unique method of preparation of these polymeric films and the application of this technique to several fields has been studied by various researchers.[1-6]

The polymeric films produced by these processes usually have highly branched and crosslinked chemical structures and are difficult to dissolve in the usual organic solvents. Structural interpretations of the plasma polymerized materials were made by IR, XPS, and NMR spectroscopy and the hypothetical structures deduced were compared by pyrolysis mass spectra and elemental analyses.[7-11]

In the present article the chemical structure of a plasma polymerized film prepared from hexamethyldisiloxane was investigated by elemental analysis, GPC, IR, XPS, and solid-state NMR spectra.

EXPERIMENTAL

Material

The organic compound used in the plasma polymerization was hexamethyldisiloxane (Wako Pure Chem. Ind.) of extra pure grade and without further purification.

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Plasma Polymerization

A schematic diagram of the reactor for the plasma polymerization is shown in Figure 1. A bell-jar type aluminium chamber, 26 cm in diameter and 26 cm high, was installed in vertical position and the system was evacuated to 10^{-3} torr(0.133 Pa) with a vacuum pump. Vapor of hexamethyldisiloxane was supplied from the bottom of the chamber. Plasma excitation was produced by loading a radio-frequency (RF) generator operating at 13.56 MHz and tuning the RF power achieved by a matching network. The glow-discharge polymerization was initiated by input power of 100 W, whereas the total pressure in the plasma chamber was 0.1 torr(13.3 Pa). The plasma-polymerized film was deposited onto aluminium foil placed on the inside wall of the chamber.

IR Measurement

IR measurement of the plasma-polymerized film formed from hexamethyldisiloxane on aluminium foil was made on a JEOL JIR-40X FT-IR spectrophotometer by the attenuated total reflection method.

XPS Measurement

X-ray photoelectron spectra of the plasma-polymerized film prepared from hexamethyldisiloxane on aluminium foil were recorded on a DuPont-Shimadzu ESCA-650B spectrometer with an Mg K_α photon source. The O_{1s}, C_{1s}, and Si_{2p} XPS spectra of the polymer were measured without gold decoration. The chemical shifts of their XPS spectra were calibrated by evaporation of$Au_{4f\,7/2}$ on that film level at 83.8eV.

NMR Measurement

The JEOL FX-200 (^{13}C frequency 50 MHz) with an attachment for the CP/MAS method[12] was used for the measurement of the ^{13}C and ^{29}Si high-

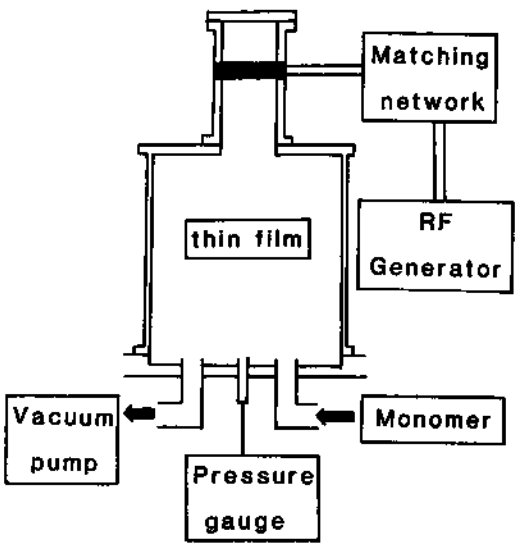

Fig. 1. Schematic diagram of the apparatus for plasma polymerization.

resolution, solid-state NMR spectra of the plasma-polymerized hexamethyldisiloxane scraped off with a knife from the inside wall of the plasma chamber. The chloroform extracted from the polymer by a Soxhlet extractor were subjected to ^{13}C-NMR spectroscopy by using JEOL FX-90Q in deuteriochloroform.

Elemental Analysis

The plasma polymer deposited onto the inside wall of the chamber was provided by elemental analysis. The C and H contents of the plasma polymer were determined by using a Yanagimoto CHN corder MT-3. The Si content of the polymer was determined by atomic absorption analysis. The residual C,H, and Si in the polymer was evaluated as the O content.

Molecular Weight

The molecular weight of the chloroform extracts of the polymer was measured by a JASCO GPC TRIROTAR standardized by polystyrene.

RESULTS AND DISCUSSION

Infrared Spectroscopy

The polymer prepared by glow-discharge polymerization normally has an irregular and amorphous structure and it is difficult to determine the total structure of the plasma polymer. Main functional groups included in the plasma polymer can be evaluated qualitatively by referring to the IR spectrum of the polymer. Figure 2 illustrates the IR spectrum of the plasma-polymerized film prepared from hexamethyldisiloxane on aluminium foil. On this spectrum the main absorptions appear at 2960 cm^{-1} (CH_3 stretching), 2900 cm^{-1} (CH_2 stretching), 2123 cm^{-1}(Si—H stretching), 1259 cm^{-1}(Si—CH_3 sym. deformation), 1200–1000 cm^{-1}(Si—O—C, Si—O—Si stretching), 840 cm^{-1}(Si—CH_2 sym. rocking), and 800 cm^{-1}(Si—CH_2 asym.

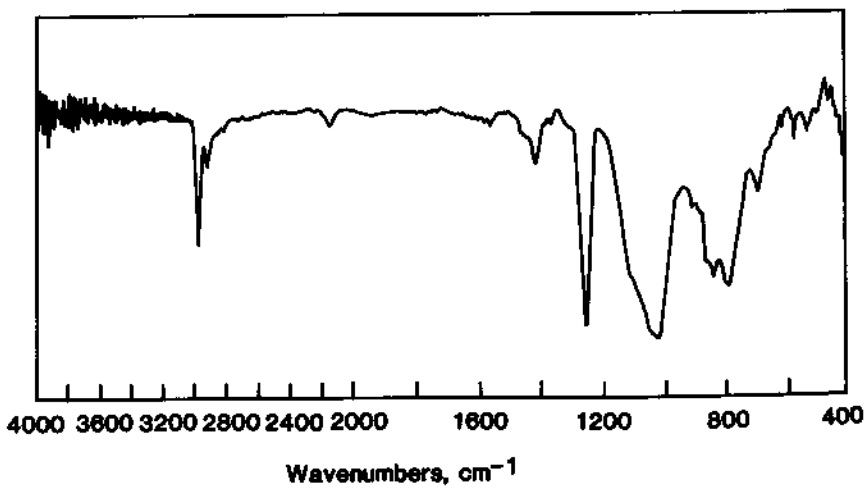

Fig. 2. IR spectrum of plasma-polymerized film prepared from hexamethyldisiloxane.

rocking).[13] The polymer deposited onto aluminium foil consists mainly of Si—CH_3, Si—O, Si—CH_2, and Si—H groups.

X-Ray Photoelectron Spectroscopy

XPS investigation of the surface characterization of the plasma polymer provides invaluable information about its surface chemical structure. O_{1s}, C_{1s}, and Si_{2p} XPS spectra of the plasma-polymerized film formed from hexamethyldisiloxane are shown in Figure 3. The O_{1s} spectrum has a peak centered at 531.4 eV (Si—O group) and the C_{1s} spectrum centered at 283.9 eV can be assigned to Si—CH_3 or Si—CH_2 group. The Si_{2p} core level spectrum of the polymer has a peak centered at 101.2 eV and shows that the surface of the polymer contains a Si(—CH_3)$_3$(—O—) or Si(—CH_2—)$_3$(—O—) group similar to the monomer.[14] The atomic ratio of C:Si:O of the polymer was 65:20:15, estimated from the peak areas with correction by experimentally determined instrument sensitivity factors C = 1.00, Si = 1.045, O = 0.349. This atomic ratio is close to the C:Si:O of the monomer, which is 60:20:10. On the other hand, the C:Si:O calculated from the results of elemental analysis of the polymer was 38:20:29. This result suggests that the bulk of the polymer has a chemical structure different from that of its surface. It is possible to confirm this hypothesis by other spectroscopic information concerning the bulk of the polymer.

The Oligomers in the Plasma Polymer

The plasma polymer formed from hexamethyldisiloxane was scraped off the inside wall of the chamber with a knife and collected polymer was packed into a filter paper thimble placed in a Soxhlet extractor and extracted with acetone, chloroform, and methanol. However, the polymer was barely soluble, although it contained a small amount of the monomer and its oligomers. The chloroform extracts obtained were 2.5% of the weight of the polymer.

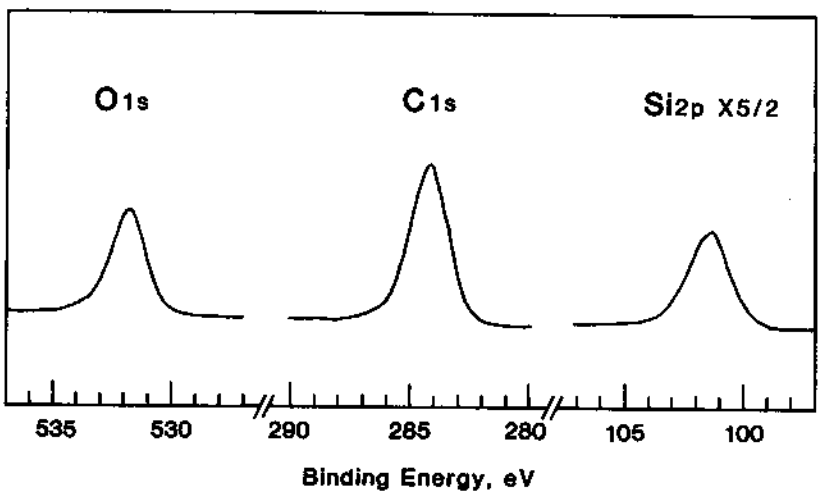

Fig. 3. XPS spectra of plasma-polymerized film prepared from hexamethyldisiloxane.

The molecular weight of the extracts was about 2000 measured by GPC. The ^{13}C-NMR spectrum of the extracts is shown in Figure 4. The main two peaks in the ^{13}C-NMR spectrum of the extracts are indicated at $-0.22 \sim 1.69$ and 29.5 ppm. The signals at 29.5 and $-0.22 \sim 1.69$ ppm were assigned respectively to the Si—CH_2 and Si—CH_3 groups and no signals of the O—CH_2 group at $40 \sim 60$ ppm were observed. It appears that the molecular structure of the extracts is similar to the chemical structure of the monomer; that is a Si(—CH_3)$_3$(—O—)-type chemical structure.

Nuclear Magnetic Resonance Spectroscopy

High-resolution, solid-state NMR studies by cross polarization (CP) and magic angle spinning (MAS) have provided qualitative as well as quantitative information about chemical structures.[15] Recent reports have described the use of ^{13}C and ^{29}Si solid-state NMR in the silylation of silica surfaces.[16-17]

Plasma-polymerized material is usually almost insoluble in most organic solvents. Consequently it is necessary to characterize the chemical structure of the plasma polymer by using high-resolution, solid-state NMR. The ^{13}C- and ^{29}Si-CP/MAS-NMR spectra are shown in Figure 5 and Figure 6, respectively. In the ^{13}C-CP/MAS-NMR spectrum the chemical shift of the distinct resonance at 1.5 ppm indicates that the methyl resonance and broad signals at $10 \sim 40$ ppm are attributed to methylene resonance. The observation in line broadening at $10 \sim 40$ ppm apparently depends on the continuous arrangement of the CH_2 group and the various conformations of the branched and crosslinked structure. The values of the relative concen-

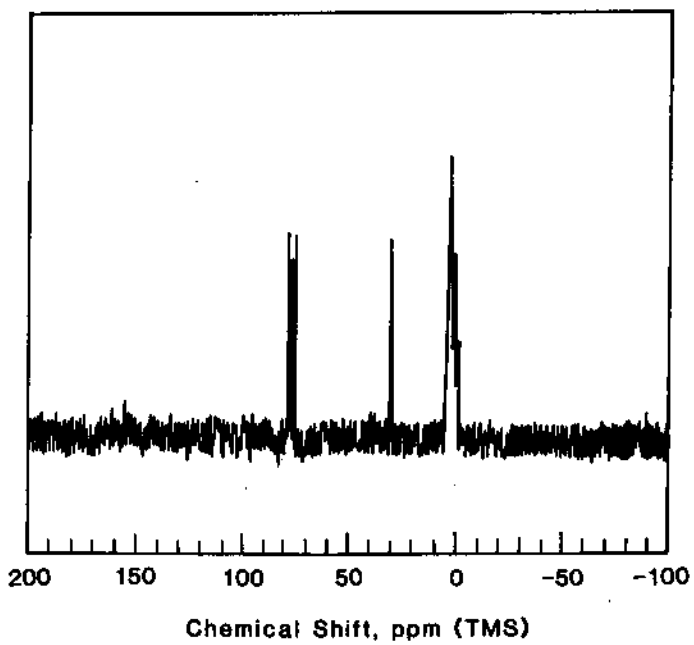

Fig. 4. ^{13}C-NMR spectrum of chloroform extracts from plasma-polymerized hexamethyldisiloxane in $CDCl_3$.

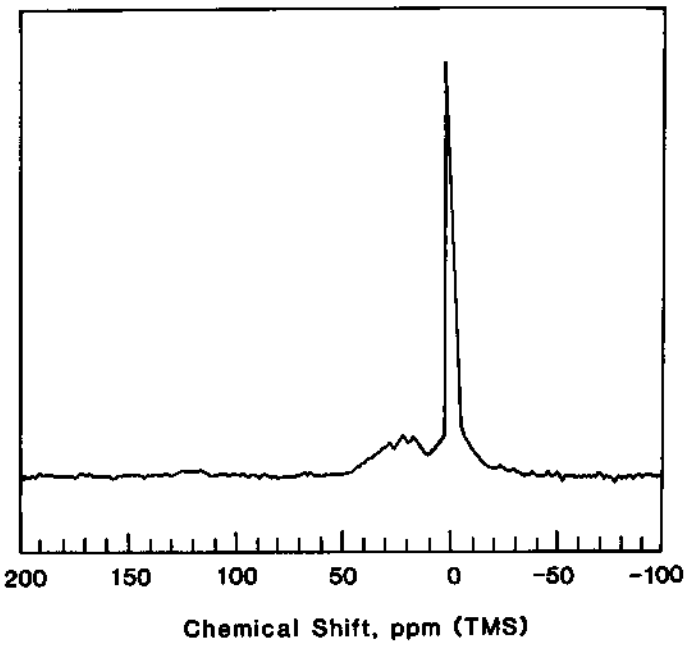

Fig. 5. ^{13}C-CP/MAS-NMR spectrum of plasma-polymerized hexamethyldisiloxane.

trations of the CH_2 and CH_3 groups are anticipated to be responsible for the gross structure of the polymer. The CH_2:CH_3 ratio which was 15:23 suggests a quick guide to a highly branched and crosslinked structure of plasma-polymerized hexamethyldisiloxane. On the other hand, plasma-polymerized hexamethyldisiloxane exhibits several signals in the ^{29}Si-CP/MAS/NMR spectrum. The chemical shifts of these signals are compared to

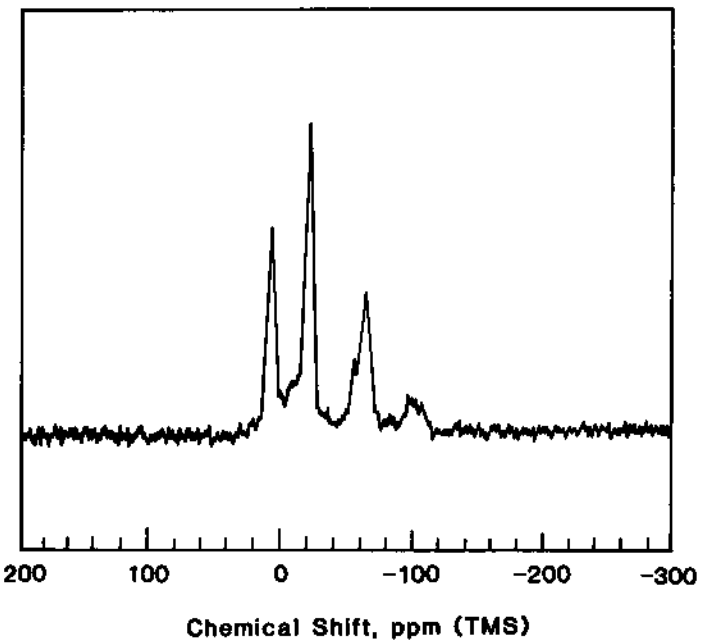

Fig. 6. ^{29}Si-CP/MAS-NMR spectrum of plasma-polymerized hexamethyldisiloxane.

TABLE I
The Results of IR, XPS, Elemental, and NMR Analyses of Plasma-Polymerized Hexamethyldisiloxane

IR	Si—CH_3(1259 cm^{-1}), Si—O(1200–1000 cm^{-1}), Si—CH_2(840–800 cm^{-1}), Si—H(2123 cm^{-1})
	C:Si: O
(Monomer)	60:20:10
XPS	65:20:15
Elemental analysis	38:20:29
^{13}C-NMR	CH_2:CH_3 = 15:23
^{29}Si-NMR[a]	A:M:D:T:Q = 1:4:8:5:2

[a] A unit:Si (—CH_3)$_4$ type.
M unit:Si (—CH_3)$_3$(—O—) type.
D unit:Si (—CH_3)$_2$(—O—)$_2$ type.
T unit:Si (—CH_3)(—O—)$_3$ type.
Q unit:Si (—O—)$_4$ type.

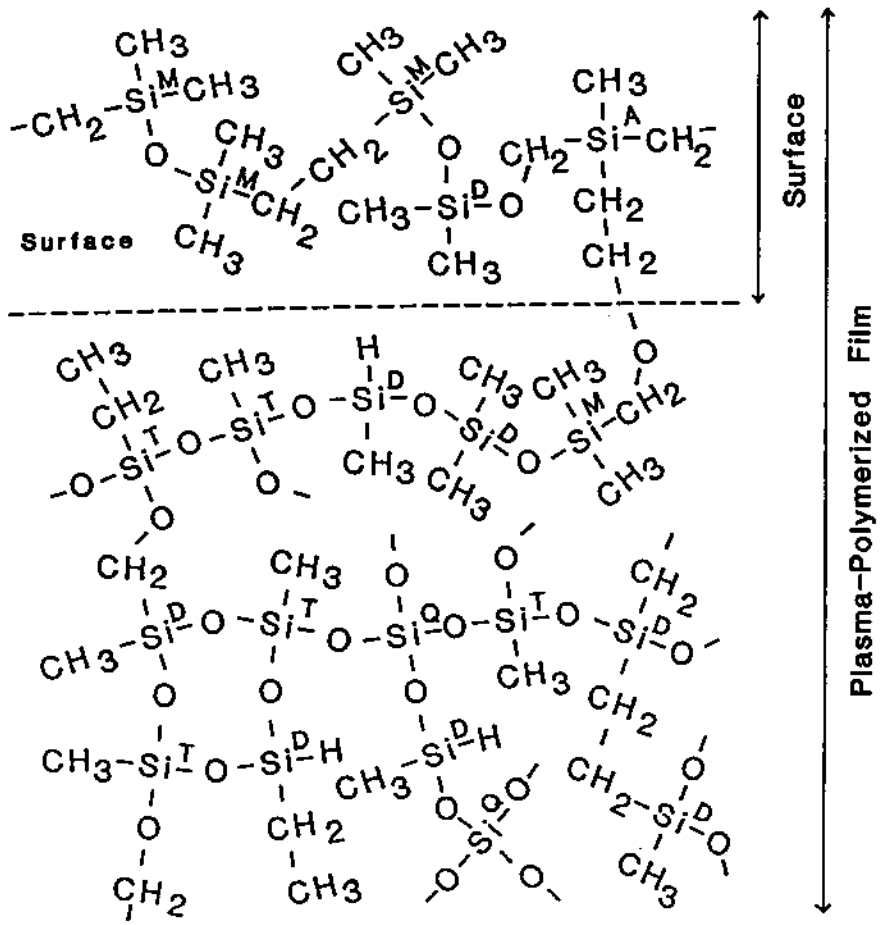

Fig. 7. Hypothetical structure of plasma-polymerized film prepared from hexamethyldisiloxane.

data on the literature obtained from the ^{29}Si—NMR spectra of organosilicic compounds.[18-19] Signals of 0,7, $-10 \sim -30$, $-58 \sim -66$, and $-99 \sim -109$ ppm are dependent on the number of O atoms surrounding the Si atom and are assigned respectively to the Si(—CH_3)$_4$ type (A unit), Si(—CH_3)$_3$(—O—) type (M unit), Si(—CH_3)$_2$(—O—)$_2$ type (D unit), Si(—CH_3)(—O—)$_3$ type (T unit), and Si(—O—)$_4$ type (Q unit).

Hypothetical Chemical Structure

The results of IR, XPS, elemental, and NMR analyses of plasma-polymerized hexamethyldisiloxane are listed in Table I.

Figure 7 shows a hypothetical chemical structure of plasma-polymerized film prepared from hexamethyldisiloxane. The relative composition of the A:M:D:T:Q unit in Figure 7 is approximately 1:4:8:5:2, which was evaluated from the peak areas of the ^{29}Si-CP/MAS-NMR spectrum of the polymer. The difference in structure between the surface and bulk of the plasma-polymerized film suggests that the ablation of the CH_2 and CH_3 groups and crosslinking reactions in electrical discharges occurred in the oxygenation of the bulk of the polymer. The ^{29}Si-CP/MAS-NMR spectrum of the plasma polymer reveals that the oxidation of the Si atom in particular occurred in plasma-polymerized hexamethyldisiloxane.

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