

# Studies on Plasma Polymerization of Hexamethyldisiloxane in the Presence of Different Carrier Gases

JIANGLIN FANG,<sup>1</sup> HONG CHEN,<sup>2</sup> XUEHAI YU,<sup>2</sup>

<sup>1</sup> Center of Materials Analysis, Nanjing University, Nanjing 210093, People's Republic of China

<sup>2</sup> Department of Polymer Science and Engineering, Nanjing University, Nanjing 210093, People's Republic of China

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**ABSTRACT:** Plasma polymerization of hexamethyldisiloxane(HMDSO) in the presence of different carrier gases such as H<sub>2</sub>, He, N<sub>2</sub>, Ar, and O<sub>2</sub> was carried out using an inductively coupled electrodeless glow discharge. The polymerization kinetics showed that the monomer HMDSO plasma-polymerized at different rates from low to high for the carrier gases H<sub>2</sub>, He, N<sub>2</sub>, Ar, and O<sub>2</sub> in that order. The products were studied using FTIR, electron spectroscopy for chemical analysis, and elemental analysis. The results indicated that HMDSO molecules underwent different degrees of fragmentation in plasma polymerization for different carrier gases and radio frequency (RF) powers. The polymer deposition rate and the structures of products were mainly dependent on molecular fragmentation, which varied with carrier gas and imposed RF power. O<sub>2</sub> and H<sub>2</sub> gases can incorporate in the plasma polymers to form products containing more oxygen or hydrogen components, while other gases such as N<sub>2</sub> have no detectable component in products. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1434–1438, 2001

**Key words:** plasma polymerization; electrodeless glow discharge; hexamethyldisiloxane; carrier gases

## INTRODUCTION

Plasma polymerization refers to the formation of polymeric materials under the influence of plasma (partially ionized gas), a phenomenon that has been studied by many authors.<sup>1–4</sup> The films produced by plasma polymerization are usually insoluble, pinhole free, and adhere well to substrates. Polymer formation in glow discharge is a very complex phenomenon, and the elucidation of reactions involved in the process is far behind the extent of technical exploitation of the process. Consequently, most research in this area has been of an empirical and correlation-finding

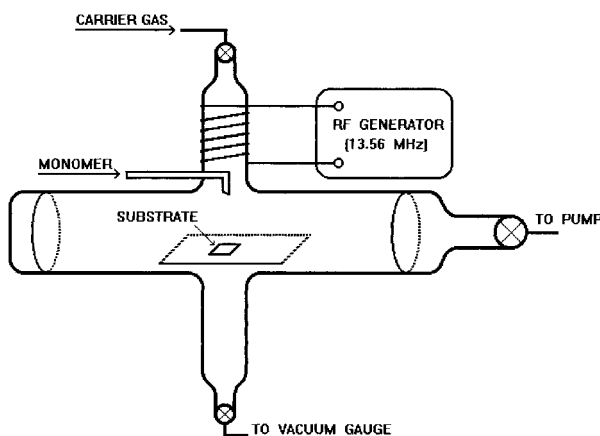
nature. Yasuda<sup>5</sup> proposed that plasma polymerization proceeds through a gradual propagation process—through continual cycle initiation, combination, and reinitiation, macromolecules will finally be formed. In our early studies,<sup>6</sup> four organodisiloxanes with different functional groups were polymerized by means of an inductively coupled electrodeless glow discharge. Through the determination of monomer polymerization kinetics and the studies of its products, it was shown that there were different degrees of monomer fragmentation for different functional groups in the polymerization process.

Although gases such as helium and argon are commonly used in plasma polymerization, few studies had been published on the effects of carrier gases on the monomer molecular fragmentation. Since monomer molecular fragmentation in

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Correspondence to: X. Yu.

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**Figure 1** Plasma polymerization apparatus.

plasma polymerization is affected by the gas composition of the system, five different gases— $H_2$ , He,  $N_2$ , Ar, and  $O_2$ —were chosen as carrier gases in the current work with monomer hexamethyldisiloxane (HMDSO) in a plasma system. These carrier gases are nonpolymer-forming gases and have different sensitivities to imposed radio frequency (RF) power, producing different numbers of electrons and different molecular ions. Through determination of monomer polymerization kinetics and studies of polymer products, we observed the effects of these carrier gases on polymerization rate, monomer molecular fragmentation, and product structures. Our explanation of how the new Si—H bonds are formed in nonpolymer-forming carry gases could provide important information for how polymeric materials are formed during plasma polymerization.

## EXPERIMENTS

### Plasma System and Plasma Polymerization

The plasma system was essentially the same as reported elsewhere.<sup>7</sup> As shown in Figure 1, the apparatus was equipped with a radio frequency (RF) (13.56 MHz) power generator by means of inductively coupling electrodeless glow discharge. A glass tubular reactor 9 cm in diameter and 4 cm in length was evacuated from the right side by a rotary vacuum pump via a cold trap. The pressure in the system was monitored by a vacuum gauge. Carrier gas and monomer vapor were introduced separately from two inlet positions. Under the coupling coil was a glass plate (10 cm in length), on which was placed a microscope cover slide ( $2.0$

$\times 2.0$  cm<sup>2</sup>). The rate of monomer polymerization could be determined by weight increment per unit time and area (mg cm<sup>-2</sup> min<sup>-1</sup>).

First, the system was evacuated to a pressure of less than 0.01 mmHg; carrier gas was then continually introduced into the reactor through a valve to maintain system pressure at 0.10 mmHg; then monomer HMDSO vapor was injected via a valve to make system pressure 0.20 mmHg; and, finally, RF power was imposed, and plasma polymerization was carried out.

### Infrared Spectroscopy

Samples for infrared spectroscopy (IR) were scraped from slides and were incorporated into KBr disks. The IR spectra were obtained on a Nicolet 170 SX FTIR spectrometer from 4000 cm<sup>-1</sup> to 400 cm<sup>-1</sup>.

### ESCA Spectra

Measurements of ESCA (electron spectroscopy for chemical analysis) spectra were made on polymers deposited on slides. The spectra were obtained using a VG ESCALAB MK-II electron spectrometer with an X-ray gun operating at 15 KV and 10 mA. The pressure in the spectrometer during measurements was less than  $10^{-7}$  torr. The Au (4f) line (BE = 84.0 eV) was used as the internal standard for binding energy calibration. The C1s, O1s, and Si2p core level spectra were used to determine the relative components of C, O, and Si atoms in samples.

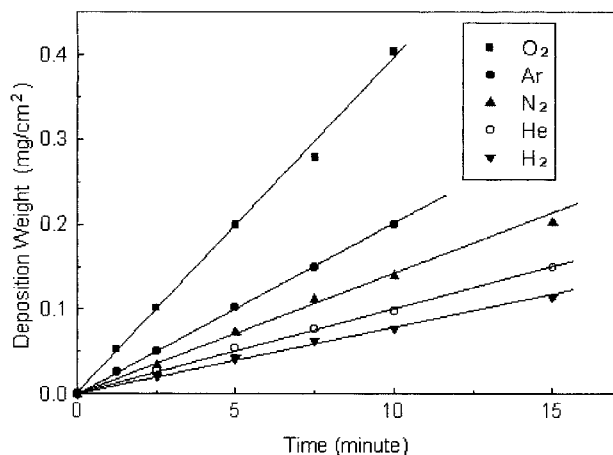
### Elemental Analysis

Samples scraped from the slides were measured on a PerkinElmer 240C elemental analyzer to determine the amount of carbon and hydrogen in plasma polymers.

## RESULTS AND DISCUSSION

### Polymerization Rates

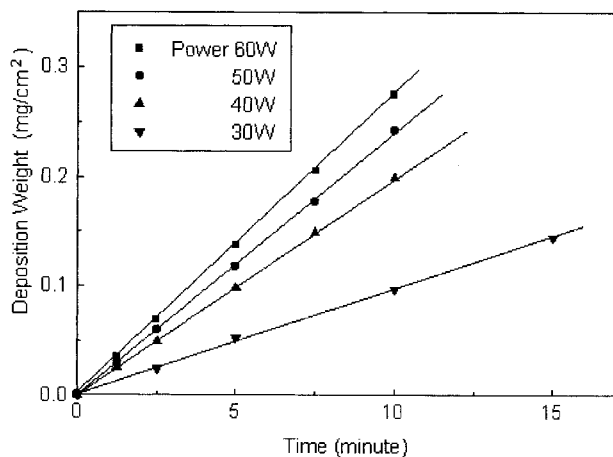
Figure 2 shows the plasma polymer depositions of HMDSO for the carrier gases  $H_2$ , He,  $N_2$ , Ar, and  $O_2$  in that order. Here the RF power was 40 W. The weight of deposited polymer increased linearly with reaction time. The slopes of these lines represent the values of the monomer polymerization rate (mg cm<sup>-2</sup> min<sup>-1</sup>). It can be seen that the rate of monomer HMDSO polymerization varied



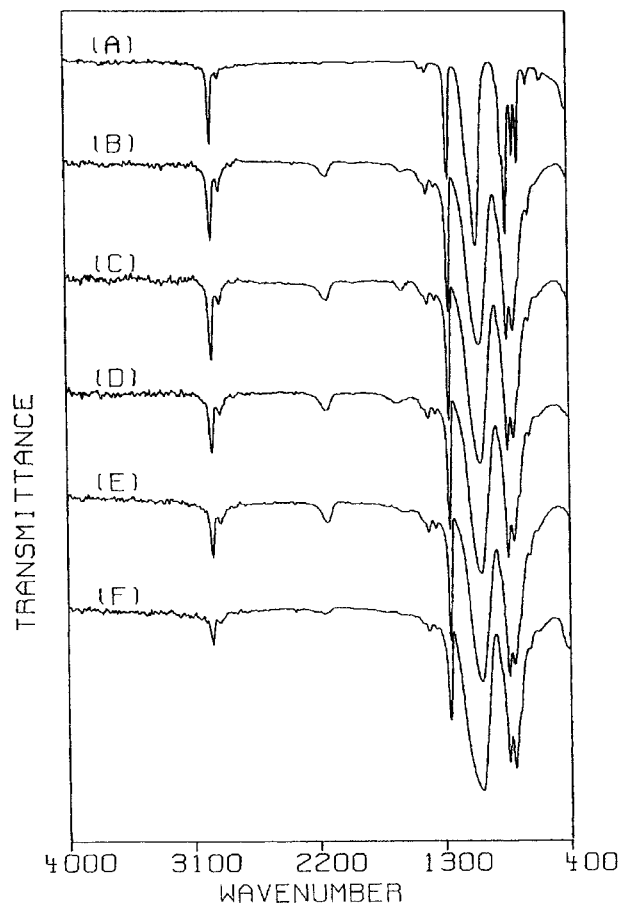
**Figure 2** Plots of polymer deposition weight versus deposition time at RF power of 40 W for carrier gases  $H_2$ , He,  $N_2$ , Ar, and  $O_2$ .

from low to high with the different carrier gases in this order:  $H_2$ , He,  $N_2$ , Ar,  $O_2$ . The degree of monomer molecular fragmentation varied with the different carrier gases and resulted in different polymerization rates. This conclusion was proven by IR analysis.

Figure 3 expresses HMDSO plasma polymerization depositions with Ar as the carrier gas at 30 W, 40 W, 50 W, and 60 W RF powers. As the power increased, the deposition rate also increased. An easy explanation is that the higher polymerization rate was a result of the higher degree of monomer molecular fragmentation during a period of higher RF power.



**Figure 3** Plots of polymer deposition weight versus deposition time for Ar carrier gas at RF powers of 30 W, 40 W, 50 W, and 60 W.



**Figure 4** IR Spectra of (A) monomer and its plasma polymers at an RF power of 40 W for carrier gases: (B)  $H_2$ , (C) He, (D)  $N_2$ , (E) Ar, and (F)  $O_2$ .

### IR Spectra

Figure 4 shows the IR spectra of plasma polymers of HMDSO separately with the  $H_2$ , He,  $N_2$ , Ar, and  $O_2$  carrier gases (all at RF power of 40 W). Their products were very similar to crosslinking poly(dimethylsiloxane). The positions of the major peaks in the spectra and their assignment to specific groups are shown in Table I.<sup>8</sup> In plasma

**Table I** Infrared Frequencies and Band Assignments

Frequency ( $cm^{-1}$ )	Band Assignment
2950–2850	C—H
2150–2100	Si—H
1260	Si— $CH_3$
1150–1000	Si—O—Si, Si—O—C
840, 830	Si—C

**Table II IR Absorption Ratios A(Si—H)/A(Si—CH<sub>3</sub>) in Plasma Polymers at RF Power 40 W for Different Carrier Gases**

Carrier Gas	H <sub>2</sub>	He	N <sub>2</sub>	Ar	O <sub>2</sub>
A(Si—H)/A(Si—CH <sub>3</sub> )	0.20	0.28	0.32	0.33	0.13

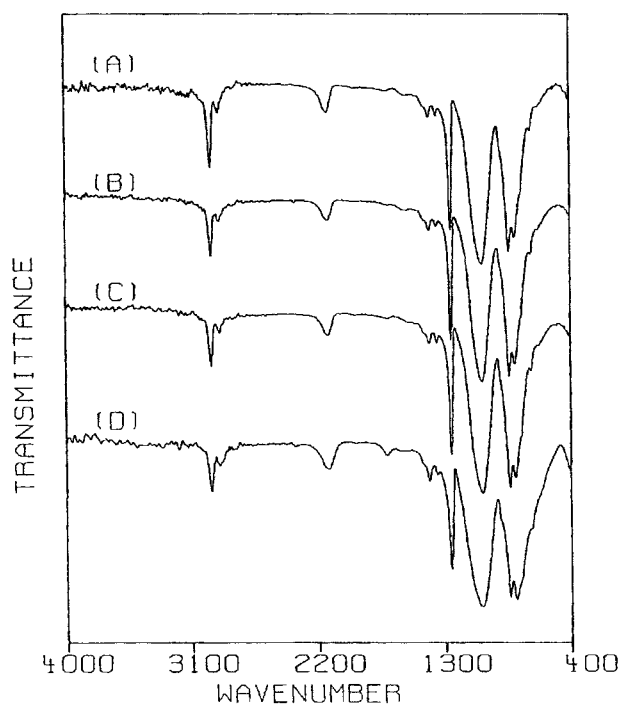
polymers there appeared a new Si—H bond (absorption at 2150–2100 cm<sup>-1</sup>) as a result of the molecular fragmentation Si—CH<sub>3</sub> (absorption at 1260 cm<sup>-1</sup>) breaking to detach the —CH<sub>3</sub> group and then combining with hydrogen formed from the breaking of the C—H bond.<sup>6</sup> The strength of absorption of the Si—H bond varied with different carrier gases, indicating a different degree of monomer molecular fragmentation during formation of crosslinking polymer products. The absorption of C—H (2950–2850 cm<sup>-1</sup>) and Si—CH<sub>3</sub> (1260 cm<sup>-1</sup>) bonds also expresses the structural changes in the products. Although the Si—H bond absorption increased, the absorption of the C—H and Si—CH<sub>3</sub> bonds decreased according to the following order of carrier gases: H<sub>2</sub> < He < N<sub>2</sub> < Ar < O<sub>2</sub>. We use the absorption peak area ratios A(Si—H)/A(Si—CH<sub>3</sub>) to characterize this

**Table III IR Absorption Ratios A(Si—H)/A(Si—CH<sub>3</sub>) in Plasma Polymers for Ar Carrier Gas at Different Powers**

RF Power (W)	30	40	50	60
A(Si—H)/A(Si—CH <sub>3</sub> )	0.30	0.33	0.44	0.53

molecular fragmentation of the Si—CH<sub>3</sub> and C—H bonds, as shown in Table II. The ratio increased according to the order of carrier gases indicated above, which is the same polymerization rate order, except for carrier gas O<sub>2</sub>, as discussed in the previous section, in which it was shown that the higher polymerization rate resulted from a higher degree of monomer molecular fragmentation. Here, for O<sub>2</sub> gas, though there was a higher fragmentation, the product polymer possessed a lesser amount of the Si—H group. It was probably due to the oxidation of the Si—CH<sub>3</sub> group after detaching from the —CH<sub>3</sub> group in the O<sub>2</sub> gas plasma system, which can be demonstrated by the broader absorption peak at 1150–1000 cm<sup>-1</sup> because of the absorption of the Si—O—C group at a higher wavenumber. ESCA and EA measurements from the latter also would indicate that its plasma polymers contained a greater oxygen component. For the plasma polymerization system with H<sub>2</sub> as the carrier gas, there were more hydrogen atoms in the system because of the carrier gas and the C—H cracking, but the amount of Si—H in the product structure was not high. It was concluded that the amount of Si—H depended only on the fragmentation of the Si—CH<sub>3</sub>.

The IR spectra of plasma polymers of HMDSO for the Ar carrier gas at RF powers of 30 W, 40 W, 50 W, and 60 W are shown in Figure 5. Table III lists the IR absorption peak area ratios A(Si—H)/A(Si—CH<sub>3</sub>). With an increased RF power, the monomer molecules underwent a higher fragmentation and produced higher-degree crosslinking products. Here absorption at 1150–1000 cm<sup>-1</sup> became broader at a high RF power because of the

**Figure 5** IR Spectra of monomer HMDSO plasma polymers for Ar carrier gas at RF powers of: (A) 30 W, (B) 40 W, (C) 50 W, (D) 60 W.**Table IV Atomic Ratios in Plasma Polymers (RF Power 40 W) Measured by ESCA**

Carrier Gas	H <sub>2</sub>	He	N <sub>2</sub>	Ar	O <sub>2</sub>
C:Si	2.97	2.80	2.58	2.41	2.12
O:Si	0.99	1.00	0.98	0.99	1.72

**Table V Elemental Compositions and Atomic Ratios in Plasma Polymers Measured by EA**

Carrier Gas	Power (W)	Elemental Composition (wt %)		Atomic Ratio
		Carbon (C)	Hydrogen (H)	
H <sub>2</sub>	40	35.30	8.32	2.83
He	40	33.10	8.11	2.94
N <sub>2</sub>	40	31.17	7.87	3.03
Ar	40	30.86	8.02	3.12
O <sub>2</sub>	40	25.55	6.28	2.95
Ar	30	31.31	7.80	2.99
Ar	50	29.92	8.18	3.28
Ar	60	28.36	8.25	3.49

breaking of the Si—O—Si bond and its combining with a carbon group to form Si—O—C.

#### ESCA Spectra and Elemental Analysis

ESCA and EA were carried out on plasma polymers of monomer HMDSO separately for the carrier gases H<sub>2</sub>, He, N<sub>2</sub>, Ar and O<sub>2</sub>. Only C, Si, and O atoms were observed in ESCA spectra, and O1s (533.2 eV), C1s (284.5 eV), Si2p (101.9 eV) core-level spectra were used to define the relative atomic ratios in polymers. The results are shown in Table IV. The EA measurement results are listed in Table V, which suggest that the C atom components decreased in the order of the carrier gases—H<sub>2</sub>, He, N<sub>2</sub>, Ar, O<sub>2</sub>—confirming that the Si—CH<sub>3</sub> group in the monomer molecule cracked in increased order. In the polymer products for carrier gases of H<sub>2</sub>, He, N<sub>2</sub> and Ar, the O:Si atomic ratios were almost unchanged because of the relative stability of the Si—O bond. In the polymer products for O<sub>2</sub> carrier gas, there was a greater oxygen component, further evidence that O<sub>2</sub> gas participated in the polymer-forming processes, as described in IR spectra results. The polymer product for the H<sub>2</sub> carrier gas possessed a higher hydrogen component, which was consistent with the high absorption of C—H bond in IR

spectra mentioned above, and was also probably a result of the incorporation of hydrogen from the H<sub>2</sub> gas plasma. In Table V the atomic ratio H:C of some plasma polymers is larger than that of HMDSO (H:C = 3.0), further demonstrating a greater number of Si—H groups in some plasma polymers, as shown in the IR spectra.

#### CONCLUSIONS

1. Monomer HMDSO plasma polymerized at different rates from low to high for different carrier gases in the order of H<sub>2</sub>, He, N<sub>2</sub>, Ar, O<sub>2</sub> and the polymerization rates depended mainly on molecular fragmentation, which varied with carrier gas and imposed RF power.
2. In the plasma polymerization of HMDSO, monomer molecules first split into fragments through the breaking of less stable chemical bonds: C—H and Si—CH<sub>3</sub> bonds instead of Si—O bonds.
3. O<sub>2</sub> and H<sub>2</sub> gases can incorporate into the plasma polymers to form products containing a greater oxygen or hydrogen component, while for other gas such as N<sub>2</sub> there is no detectable component in the products.

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