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Plasma Reaction Behaviors of Carbon Disulfide and Carbon Dioxide in Glow Discharges

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ABSTRACT

Reaction behaviors of carbon disulfide and carbon dioxide in plasma were investigated and compared. It was found that carbon disulfide is very reactive in plasma to produce dark brown filmy polymers, but carbon dioxide does not give polymeric products at all. The difference in plasma behaviors of the two monomers can be attributed to the roles of sulfur and oxygen in the monomers. There is also some discussion on the spectroscopic data of carbon disulfide polymers.

INTRODUCTION

Plasma polymerization has some characteristics in its polymerization manner as well as in the properties of the products. Compared to usual vinyl and condensation polymerizations, it does not necessarily need special functional groups for polymerizations, but almost all volatile hydrocarbons can polymerize in plasma to give filmy or in some cases powdery products with cross-linked structure. In other words, the products are not constituted of the unit structural groups existing in the initial monomers. It may be stated that the radically or ionically activated species in plasma are the functional groups for polymerization. Therefore, the elemental composition and the composition ratio of the monomer seem to play rather important roles in the reaction behavior and also in the chemical and physical properties of the resulting polymers.

In this study, carbon disulfide and carbon dioxide, which have similar chemical structures with different elements (sulfur and oxygen), were investigated for their reaction behaviors in plasma.

It has been observed that carbon disulfide polymerizes in plasma to give dark brown products [1]. There are some assumptions about the chemical structures of the polymer, and the results of elemental analyses suggest that the polymers are carbon-rich compared to the original monomer.

EXPERIMENTAL

Carbon disulfide, CS_2 (MW = 76.1), was purified by distillation with phosphorous pentoxide to remove water. Carbon dioxide was reagent grade and was used as supplied.

The procedure of plasma reaction was similar to the one previously reported [2]. Glow discharges were generated at a frequency of 13.56 MHz. Pressure in the system was monitored with a Pirani gauge located between the reaction chamber and Dry-Ice traps. At first, the reaction system was evacuated and the pressure was reached at less than 1.0 μmHg. The fully degassed carbon disulfide or carbon dioxide was introduced into the chamber at a certain pressure through needle valves. Monomer gas was dispersed through a monomer inlet of about 18 cm in length with many small holes which was designed to produce more uniform deposition of polymers (when they are formed). In this apparatus, the after-glow region, which is 20-50 cm distant from the center of the RF coil, is used for plasma reaction. One of the merits of the after-glow method is that the heat increase during glow discharges can be depressed.

RESULTS AND DISCUSSION

Reaction in Glow Discharges

When vaporized carbon disulfide was exposed to glow discharges, the pressure was decreased steeply with applied discharge power (Fig. 1). Here, the initial pressures measured before discharge were 30, 60, and 85 μmHg, and the flow rates of the monomer were 0.5, 2.4, and 6.2 cm^3 (STP)/min, respectively, under these pressures. The pressures reached plateau at certain wattages; for example, 50 W for the 6.2 cm^3 (STP)/min rate. Pressure in such flow systems is related to the amount of gaseous particles formed. In case of carbon disulfide, the activated species in the plasma state are CS_2^+, CS^+, etc. [3]. The

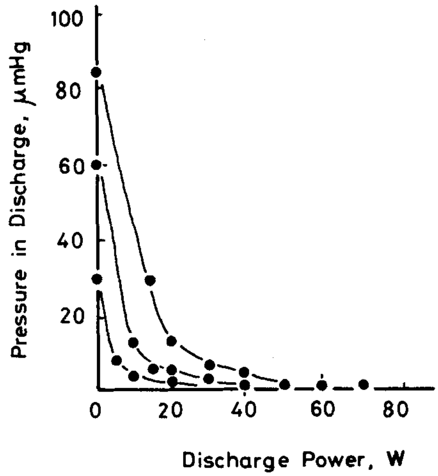

FIG. 1. Pressure in glow discharges of carbon disulfide at various discharge power. The initial pressure is 30, 60, and 85 μmHg.

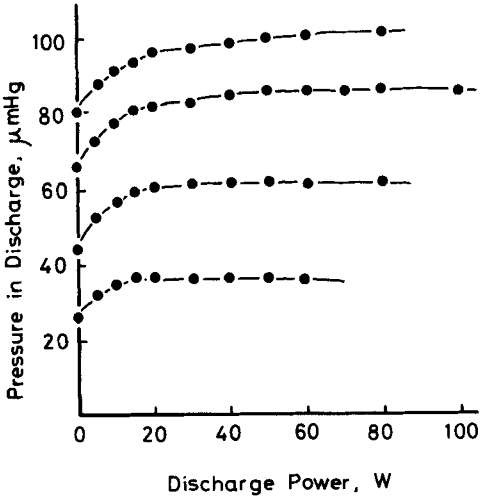

FIG. 2. Pressure in glow discharges of carbon dioxide at various discharge power. The initial pressure is 25, 45, 65, and 80 μmHg.

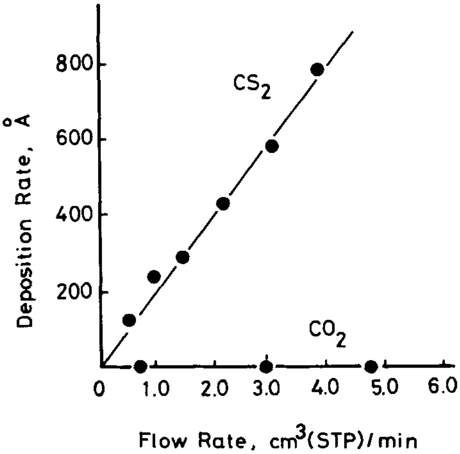

FIG. 3. Flow rate dependence of deposition rate of the carbon disulfide plasma polymer produced at the discharge power of 50 W.

pressure behavior in plasma suggests that these species are spontaneously consumed for polymerization, and the gaseous products are negligibly small in amount.

In contrast to this, the circumstances for carbon dioxide are quite different, and the pressure increases with discharge power (Fig. 2). The fragmented particles, reported as CO_2^+, CO^+, O_2^+, O^+, and C^+ [4], do not produce polymeric deposits but give mostly gaseous products.

It has been known that plasma reaction depends upon glow characteristics which are related to discharge power, monomer flow rate, molecular weight, etc. [5]. In the two gases, the plasma reaction of carbon disulfide can be carried out at much lower wattages. When the reaction was conducted at a certain flow rate (for example, 4.0 cm^3 (STP)/min), the discharge power necessary for full glow is 20 W for carbon disulfide and 45 W for carbon dioxide. One of the main reasons for the high polymerizability of carbon disulfide (or the necessity of lower power) in plasma reaction is that the activated species mostly participate in polymerization, and the gaseous by-products which will consume additional energy for keeping full glows are not formed. In other words, the applied power is used much more effectively in the reaction of carbon disulfide.

Polymer deposition rates were obtained and the flow rate dependence was examined (Fig. 3). Deposition rates were measured by the weight of polymers deposited per unit time. Discharge power employed was 50 W throughout the measurements. The power is high enough for the plasma reaction in the flow rate range as examined. It was found that the deposition rate increases linearly with the flow

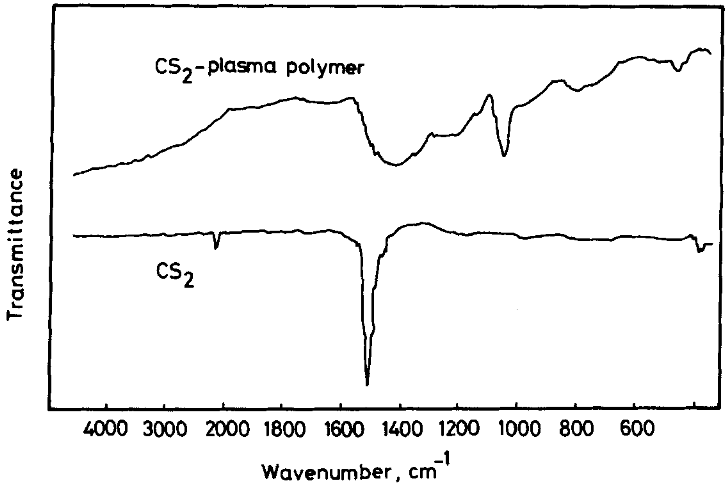

FIG. 4. Infrared spectra of carbon disulfide plasma polymer (on KBr disk) and the monomer.

rate in carbon disulfide. In contrast to this, carbon dioxide will not produce polymeric deposits at all by itself under any plasma conditions examined in this study.

At least two reaction processes are involved in the plasma reaction: activation of molecules and the following polymerization or fragmentation of the activated species. The plasma activation processes are more or less similar in the two monomers, but the reaction after activation is quite different. The difference may be attributable to the reactivity of sulfur and oxygen in the two monomers. Usually, carbonyl-containing compounds such as acetone and acrylic acid are poorly or hardly polymerizable in plasma. These monomers are considered to be fragmented more easily by decarbonylation and scissions of C—O bonds, and the resulting polymerization is hindered.

Structure of CS_2 Plasma Polymers

Carbon disulfide gives dark brown filmy products with a graphite-like appearance. In order to obtain some information on the chemical structure, IR and ESCA spectra were taken.

The IR spectrum of the polymer deposited on a KBr disk is shown and compared to that of the monomeric carbon disulfide (Fig. 4). It is suggested that the structure is quite different from that of the monomer. Although the spectrum peaks are broadened and complicated, some typical functional groups can be identified from the absorption

TABLE 1. Identification of Peak Bands in the IR Spectrum of Carbon Disulfide Plasma Polymer

Peak band (cm^{-1})	Identification
1400-1500	C=C
1350, 1200 (sh)	$-SO_2$
1030-1080 (s)	C=S and/or sulfoxide
1200	Thioketone

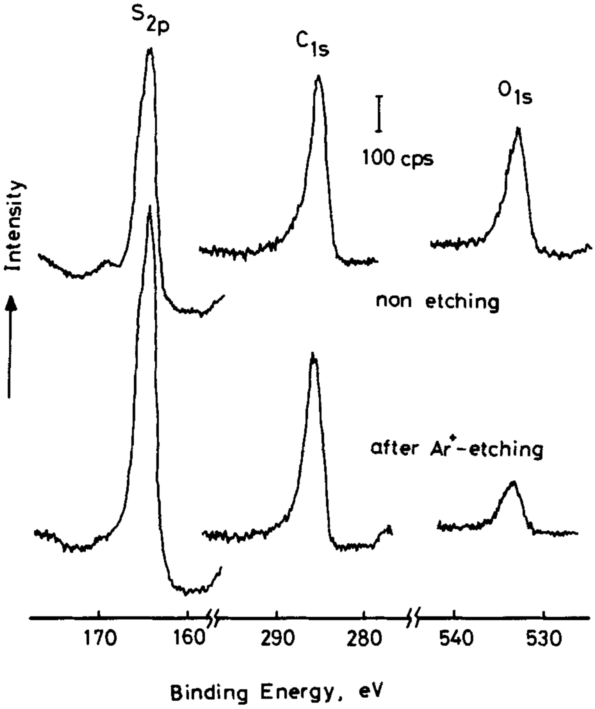

FIG. 5. ESCA spectra of carbon disulfide plasma polymer deposited under monomer inlet; as produced and after Ar^+-etching for 5 s.

TABLE 2. Peak Position and the Half-Width in the ESCA Spectra of CS_2 Plasma Polymers

Condition	Element	Peak position (eV)	Half-width (eV)
Under monomer inlet, nonetching	C	285.9	2.2
	S	163.7 (168.6 w)	2.3
	O	533.8	2.8
Under monomer inlet, Ar^+-etching	C	286.0	2.0
	S	163.7 (170.0)	2.3
	O	533.5	2.6
Under RF-coil, nonetching	C	286.0	2.0
	S	163.7 (168.7)	2.4
	O	533.4	2.4
Under RF-coil, Ar^+-etching	C	285.9	2.0
	S	163.8 (168.4)	2.4
	O	533.4	2.4

bands (Table 1). Here, sulfoxyl and sulfonyl groups are probably formed by oxidation in air after polymerization.

ESCA spectra were taken for the CS_2 polymers which were deposited about 500 Å in thickness on aluminum foil under the plasma condition, 60 μmHg of vapor pressure, and 50 W of discharge power. A spectrum was also taken of the polymer obtained just under a RF coil where the plasma glow is much stronger. Some typical spectra are shown in Fig. 5 for the polymer samples as produced and after Ar^+-etching in the ESCA apparatus. Some interesting features can be pointed out from the spectra. (1) Oxygen is observed around 533 eV in all samples besides carbon and sulfur. (2) In the peaks of sulfur, small subpeaks can be observed in a higher position around 170 eV, and they are identified as the oxidized sulfurs which become much smaller after Ar^+-etching.

Table 2 shows the peak positions and the peak width of the elements observed in the ESCA spectra. From the results it is suggested that these polymeric products have complicated structures and complicated circumstances in the valence bonds.

ESCA peaks were also used for the quantitative elemental analyses of the surface layers. The relative elemental intensities must be taken into consideration for this purpose, because the intensities change depending on the kind of elements. In this study, Wagner's

TABLE 3. Relative Elemental Ratio in CS_2 Plasma Polymers Estimated from the ESCA Peaks

Condition	Elemental ratio		
	C	S	O
Under monomer inlet, nonetching	1.0^a	0.97	0.25
Under monomer inlet, Ar^+-etching	1.0	1.39	0.12
Under RF-coil, nonetching	1.0	0.49	0.29
Under RF-coil, Ar^+-etching	1.0	0.47	0.14

[a] Carbon is taken as standard (1.0).

data of relative intensity, which are given as $C_{1s} = 0.24$, $O_{1s} = 0.61$, and $S_{2p} = 0.33$ [6], were used. The relative amount of elements can be given by dividing the peak areas by the relative intensities. The results are shown in Table 3. Here, the amounts of other elements are taken relative to carbon (1). It is interesting to note that sulfur is smaller in amount than is carbon in the monomer, and that the relative amount is changed depending on the plasma condition. The polymers formed in more vigorous condition under a RF coil contain less sulfur. The difference in the elemental ratio may suggest some difference in the reaction mechanism producing the polymers.

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