

# GC/MS and PGC/MS Analyses of Plasma Polymerization for Benzaldehyde

QIANG ZHAO,\*† YUFEN ZHU, MINXI CAI, MANDAN XIE, and XUESHU LIU

Guangzhou Institute of Chemistry, Academia Sinica, People's Republic of China

## SYNOPSIS

Gas chromatography/mass spectrometry studies of gas condensates in plasma and pyrolysis products of plasma polymer for benzaldehyde were made. Both products' analyses indicate the significant presence of benzyl and carbonyl groups in plasma polymer samples. Infrared measurements were also used to correlate the structures suggested by GC/MS results. A radical mechanism, which involved hydrogen abstraction, aldehyde group abstraction, and benzyl fragmentation under plasma activation, was proposed. The highly crosslinked and branched structures of the plasma polymer were attributed to the subsequent reactivity of free radicals, formed as a result of the scission of the chemical bonds in the benzaldehyde molecules.

## INTRODUCTION

In past decades, investigation of plasma polymerization of organic compounds has increased significantly. Knowledge of the mechanism of plasma polymerization is of interest from both practical and theoretical viewpoints. The composition of gas condensates in plasma polymerization seems to be of particular importance, since the condensates contain intermediate polymerization products. Streitweiser and Ward,<sup>1</sup> in 1962, used a gas chromatography (GC) technique to study the composition of formed organic compounds in plasma of toluene. Recently, with the development of the gas chromatography/mass spectrometry (GC/MS) combined technique, it has been possible to study the separation and identification of gas condensates in plasma and to study the structure of plasma polymerized organosilicone<sup>2</sup> and fluoro-carbon.<sup>3</sup> The gas condensates can be resolved by GC and analyzed by MS. Therefore the GC/MS combined technique appears to be promising for this purpose. In a departure from the above trend of investigation, pyrolysis products' analysis has also been used to determine the structure of plasma polymers, such as plasma polymerized

ethylene,<sup>4</sup> benzene, *p*-xylene,<sup>5</sup> *n*-octane,<sup>6</sup> toluene,<sup>7</sup> and organosilicone.<sup>8,9</sup> Fragmentation patterns of the polymeric materials provide information about their chemical structures and the reaction mechanism involved in their formation.

This article applies the GC/MS technique to a study on the gas condensates of plasma polymerization and pyrolysis products of plasma polymerized samples for benzaldehyde. The method of polymerization in plasma has been extensively described.<sup>10</sup> Samples have been characterized with infrared spectra, thermogravimetric analysis, and contact angle data. The plasma-polymerized products exhibit a significantly different structure as compared with the benzaldehyde monomer. A large number of carbonyl groups, which included aliphatic ketone, aromatic ketone,  $\alpha$ - $\beta$ -olefinic ketone, and cyclic ( $\geq 7$ ) ketone, existed in the chemical structure of plasma-polymerized benzaldehyde (PPBA) samples. In this investigation, the GC/MS data on the plasma polymerization for benzaldehyde are further correlated with infrared measurements. Based on these results, an overall mechanism of plasma polymerization is discussed.

\* Present Address: Department of Chemistry, Texas Tech University, Lubbock, Texas 79409.

† To whom correspondence should be addressed.

## EXPERIMENTAL

The reactor system for the preparation of plasma polymerized benzaldehyde was described previ-

ously.<sup>10</sup> For the preparation of PPBA samples, a 13.56 MHz radio frequency glow discharge, with capacitive coupling, was used in a discharge tube. The benzaldehyde monomer pressure and plasma power were  $5 \times 10^{-2}$  torr and 60 watts, respectively. The gas condensates were collected in a trap that was cooled in liquid nitrogen. The samples of PPBA were scraped from the glass substrate in the discharge tube.

GC/MS examination was carried out for the low boiling point compounds in plasma gas condensates of benzaldehyde. After the plasma process was finished, the trapped products were collected and then injected into a Jeol JMA-2000 gas chromatograph/JMS-D300 double focusing mass spectrometer, equipped with a JMA-2000 data system. The following conditions were used: carrier gas: helium; injection port temperature: 250°C; column: SE-30 fused-silica capillary (25 m  $\times$  0.25 mm); column temperature: room temperature held for 5 min, then programmed at 5°C/min to 230°C; electron energy: 70 eV; ionization current: 300  $\mu$ A; ion source temperature: 250°C; interface temperature: 250°C. Some components of the gas condensates, which had not been detected by GC/MS due to high boiling point temperature, were identified at a high performance liquid chromatograph (Waters 244 ALC/GPC) by using retention time on a  $\mu$ Bondapak C18 (3 m  $\times$  3.9 mm) column, coincident with pure standard compounds. The solvent system was methanol-water (60 : 40, v/v) at a flow rate of 0.6 mL/min.

In the pyrolysis gas chromatography/mass spectrometry work (PGC/MS), the polymer samples were taken in a curie point pyrolyzer and were preheated in the pyrolysis unit interface for some time

at 250°C with continuous helium flushing to remove residual low-molecular-weight organic compounds. The gaseous pyrolysis products were fed directly into the GC/MS system and were separated by means of a 2 m  $\times$  2 mm 3% SE-30 packed column, which was heated from 130°C to 230°C at a constant heating rate of 8°C/min, and a steady helium flow as carrier gas. The conditions of mass spectrometer for analyses of pyrolysis volatile products were the same as mentioned above.

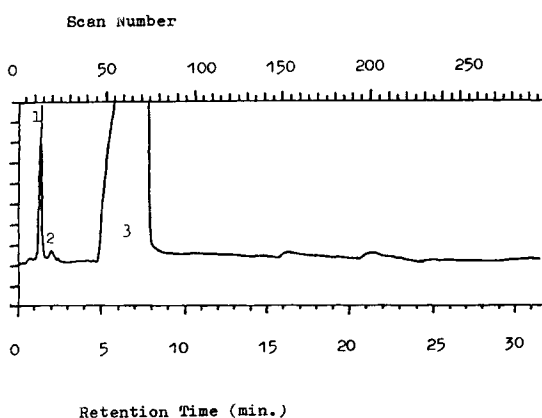
Infrared spectra of the polymer samples were run on an Analect RFX-65 FT-IR spectrometer with KBr pellets. The benzaldehyde monomer, a chemically pure reagent, was purified prior to plasma polymerization by vacuum rectification, and then its purity was tested by gas chromatography.

## RESULTS AND DISCUSSION

### GC/MS Examination of Gas Condensates

A gas chromatogram of the volatile products of low boiling point for plasma polymerization of benzaldehyde at 60 watts and  $5 \times 10^{-2}$  torr is shown in Figure 1. The products corresponding to the respective peak in the chromatogram were identified by a mass spectrometer with the aid of MS data in Ref. 11, and were found to be generally consistent with those of relevant organic compounds reported in the mentioned literature. A summary of the identification work, including the individual structural formulae and mol wt corresponding to the respective GC peak, is listed in Table I. The benzoic acid and diphenylketone in Table I were detected by high performance liquid chromatography, whose chromatogram is shown in Figure 2.

The data in Figure 1 indicate that benzene is the major product of benzaldehyde in plasma, which is attributed to the abstraction of aldehyde groups from benzaldehyde molecules. The benzene radicals formed in plasma can be further fragmented to produce unsaturated compounds with less than six carbon atoms. The absence of ethylene and ethynyl in the gas condensates is attributed to volatilization before sample injection into GC/MS system. The appearance of diphenylketone in the high performance liquid chromatogram is significant and indicated that benzoyl radicals formed in the benzaldehyde plasma. Benzoic acid is the oxidation product of benzaldehyde exposed to air before GC/MS analysis.



**Figure 1** Gas Chromatogram of gas condensates for benzaldehyde in plasma. (1) Ph, (2) PhCH<sub>3</sub>, (3) PhCHO.

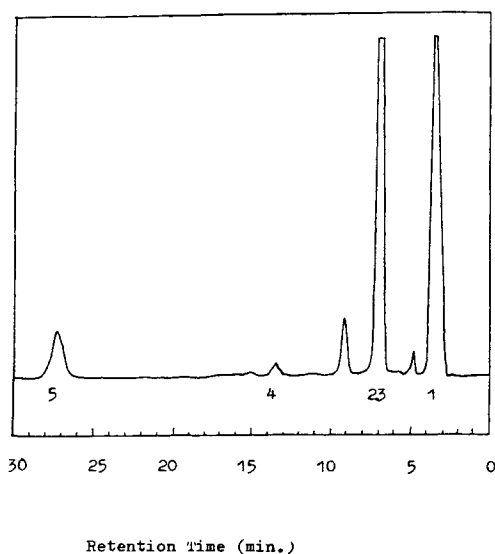
**Table I Identification of Gas Condensates for Benzaldehyde in Plasma**

Order	Scan Number	Molecular Weight	Structure
1	8	50	HC≡C—C≡CH
2	8	52	HC≡C—HC=CH
3	10	18	H <sub>2</sub> O
4	13	78	Ph
5	20	92	PhCH <sub>3</sub>
6	63	106	PhCHO
7	153	154	Ph—Ph
8	—	122	PhCOOH
9	—	182	PhCOPh

### PGC/MS Examination of Plasma Polymerized Product

In the PGC/MS experiment, the polymer samples were pyrolyzed at 770°C for five seconds. The temperature is sufficiently high to cause cleavage of chemical bonds, thus producing a variety of low-molecular-weight molecules and radicals. The volatile pyrolysis products formed were separated in the GC column and were identified by mass spectrometer. The identification results for pyrolysis products are shown in Table II. The composition of pyrolysis products includes aromatic hydrocarbon, aromatic aldehyde, some acetone, and carbon dioxide. Many of these have also been detected previ-

ously in the PGC/MS analyses of plasma polymerized benzene, xylene,<sup>5</sup> and toluene.<sup>7</sup> It is well known that the interpretation of pyrolysis chromatograms, in terms of the polymer structure, is difficult. The major appearance of benzene and toluene in the chromatogram is strong evidence for presence of a significant number of phenyl structures in PPBA samples. The aliphatic hydrocarbons, such as butadiene and ethenyl ethynyl, which were found in gas condensates, disappear from the pyrolysis products of PPBA samples. This disappearance further suggests that the chemical structure of the PPBA samples consists of a large number of benzyl rings linked by ethylene and aliphatic ketone. The presence of acetone, benzaldehyde, and benzaethanal in the pyrolysis products is also suggested. It is interesting that the toluene/benzene ratio for pyrolysis products is about 1, which is much more than the value for gas condensates of benzaldehyde in plasma (Figs. 1 and 3).



**Figure 2** High performance liquid chromatogram of gas condensates for benzaldehyde in plasma. Species are identified as follows: (1) PhCOOH, (2) Ph, (3) PhCHO, (4) PhCOPh, (5) Ph—Ph.

**Table II Identification of Pyrolysis Products of PPBA Sample**

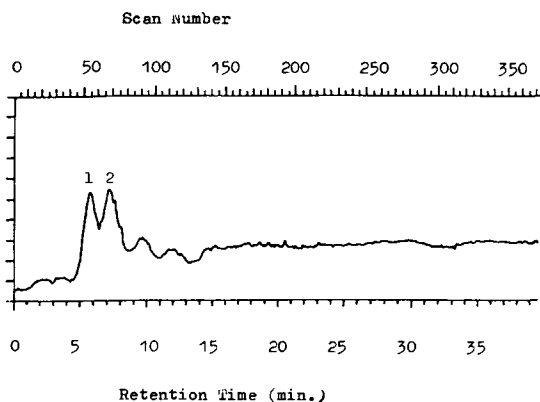
Order	Scan Number	Molecular Weight	Structure
1	20	44	CO <sub>2</sub>
2	55	78	Ph
3	68	92	PhCH <sub>3</sub>
4	90	104	PhCH=CH <sub>2</sub>
5	90	106	PhCH <sub>2</sub> CH <sub>3</sub>
6	95	58	CH <sub>3</sub> COCH <sub>3</sub>
7	112	106	PhCHO
8	112	120	PhCH <sub>2</sub> CHO
9	140	116	PhCH <sub>2</sub> CH=CH
10	140	118	CH <sub>3</sub> PhCH=CH <sub>2</sub>
11	140	120	CH <sub>3</sub> PhCH <sub>2</sub> CH <sub>3</sub>
12	280	168	CH <sub>3</sub> Ph—Ph

### IR Examination of Plasma Polymerization Product

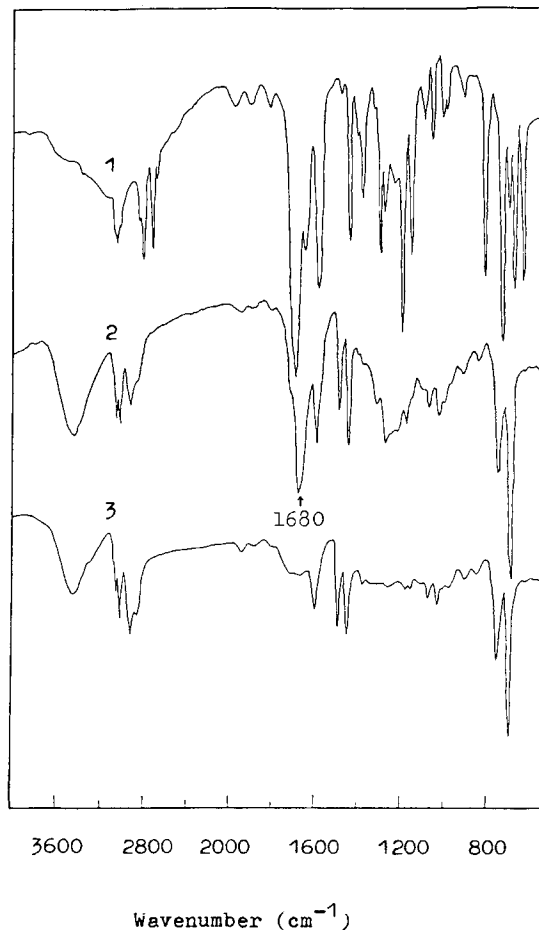
A comparison of the infrared spectra of the monomer and plasma polymerized sample at 60 watts and  $5 \times 10^{-2}$  torr is shown in Figure 4. The primary absorptions of aldehyde monomer at 2817 and 2737  $\text{cm}^{-1}$  (C—H stretching) and 1701  $\text{cm}^{-1}$  (C=O stretching) disappear completely in the infrared spectrum of the PPBA sample. A strong peak at 1680  $\text{cm}^{-1}$  indicates the formation of aromatic ketone in PPBA structure. The C—H stretching for Ph—H for the monomer at 3062  $\text{cm}^{-1}$  becomes weak, and at the same time the C—H stretching for the —CH<sub>2</sub>— structure at 2924  $\text{cm}^{-1}$  appears to be significant. In order to understand further the chemical structure for PPBA samples, a plasma polymerized Benzene sample (PPB) was prepared at 60 watts and  $1 \times 10^{-2}$  torr, and its infrared spectrum is also shown in Figure 4. The major difference in the infrared spectra for PPBA and PPB is a strong C=O stretching absorption. It seems that PPBA is the result of PPB with a large number of carbonyl groups incorporated between its phenyl ring and aliphatic carbon or another phenyl ring.

### Plasma Polymerization Mechanism

The compound suggested by GC/MS and PGC/MS techniques testifies to the following reactive fragments, presumably with radical centers: Ph· and PhCO·, resulting from the fragmentation of the monomer molecules in plasma. Fragmentation and recombination of relevant radicals, and their reaction with neutral molecules in plasma, explain well the formation of the low-molecular-weight prod-

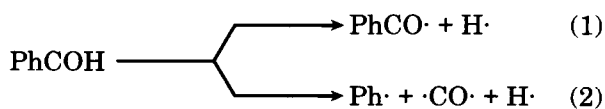


**Figure 3** Gas chromatogram of volatile pyrolysis products for polymerized benzaldehyde sample. (1) Ph, (2) PhCH<sub>3</sub>.



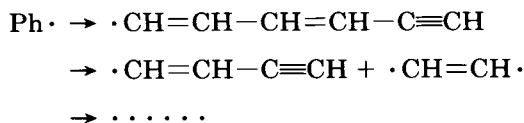
**Figure 4** Infrared spectra of (1) benzaldehyde, (2) plasma polymerized benzaldehyde, and (3) plasma polymerized benzene.

ucts in gas condensates. Based on the experimental results, we conclude that the structures of PPBA include the units of —Ph—Ph—, —Ph—CH<sub>2</sub>—Ph— and —Ph—CO—Ph—, etc. Assuming a radical mechanism for plasma polymerization,<sup>12,13</sup> the primary steps of benzaldehyde in plasma may be described by:



The lower energy of the CO—H bond, as compared with C—CO bond, allows us to assume that the reaction 1 will be more prevalent. The strong C=O stretching peak in the PPBA's infrared spectrum also suggests this. The reactive radicals formed in

the above reactions may undergo fragmentation according to the following simplified scheme:



The above reactions were partly confirmed by the appearance of the distinct C—H absorption at  $2924\text{ cm}^{-1}$  in the infrared spectrum for PPBA and the appearance of ethynyl products in plasma gas condensates.

The radical formed by secondary fragmentation of benzaldehyde may subsequently react with benzyl radicals, benzoyl radicals, and neutral molecules. Finally, polymer products are formed. These reactions contribute a complicated structure to PPBA samples. The pyrolysis products of PPBA sample also correspond to the above mechanism.

A series of samples, polymerized under different plasma conditions, leads to different benzyl ring and carbonyl group concentrations for PPBA.<sup>10</sup> The GC/MS and PGC/MS analyses at different plasma conditions should yield more information about the mechanism of plasma polymerization and the structural features of these new samples.

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