Analysis of Plasma Polymerization of Benzaldehyde

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SYNOPSIS

Plasma polymerization of benzaldehyde was investigated mainly by infrared spectroscopy. The solubility, wettability, and heat stability for the formed plasma polymer are discussed. Benzaldehyde was plasma-polymerized to yield films and/or powders. The products contained a large amount of carbonyl-containing groups, such as aromatic ketone, aliphatic ketone, α,β-olefinic ketone, and cyclic ketone. The chemical structures of formed polymer were strongly influenced by the plasma parameters and so were its solubility, surface wettability, and heat stability. The polymerization mechanism in plasma for benzaldehyde is discussed on the basis of the infrared analyses of the formed polymers at different plasma conditions.

INTRODUCTION

Technological applications of plasma polymerization in protective coating, insulating layers, and osmosis membranes have been successfully developed in the last two decades.[1-3] The polymer-forming process is different from that in common polymerization, such as ionic and radical. The physical property and chemical structures of plasma polymers are influenced by various conditions of the plasma polymerization, for example, the kind of monomer, existing gas, pressure in the plasma chamber, input high-frequency power, and position of the sample. Monomer molecules injected into the plasma chamber are activated by actions of plasma and fragmented into activated small fragments. Two fragments then are recombined to give a large molecule, and by repetition of fragmentation and recombination, polymer products are finally formed. It is rather difficult to characterize plasma polymers because of their insolubility. Elucidation of fragmentation and recombination mechanisms for plasma polymerization is difficult. Recently, infrared spectroscopy, ^{13}C-NMR in the solid state, pyrolysis mass spectroscopy, and gas condensate analysis have been used in structural studies on plasma-polymerized hydrocarbon, silane, and other organic compounds.[4-8]

We previously reported on the plasma polymerization of aldehyde monomer, propionic and butyl aldehyde,[9,10] which were poorly documented. In this study, we focused our attention on benzaldehyde. Owing to its relatively complex molecular constitution, this compound may fragment in plasma to more secondary products. These products can recombine to form more complex polymers than those produced from simple aldehyde monomers. This paper reports on our studies on the influence of plasma conditions on plasma polymerization for benzaldehyde. The chemical structure and some other properties of plasma-polymerized benzaldehyde (PPBA) are characterized.

EXPERIMENTAL

Plasma Polymerization

The reactor chamber is made of glass for plasma polymerization and is fitted with a monomer inlet, pressure gauge, vacuum system, and matching network for capacity coupling at a 13.56 MHz radio-frequency source and is schematically represented in Figure 1.

The plasma polymerization of benzaldehyde was carried out as follows: First, the reactor system was evacuated by a rotary pump through a cold trap with liquid nitrogen at a pressure of about 5×10^{-3} Torr. Second, argon gas was introduced into the reactor system three times; then, the monomer benzalde-
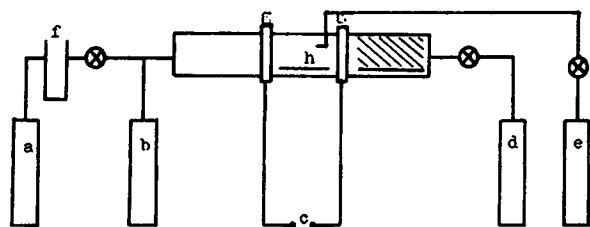
Figure 1   Plasma reactor system: (a) vacuum pump; (b) pressure gauge; (c) radio-frequency source; (d) argon gas; (e) benzaldehyde; (f) cold trap; (g) electrodes; (h) glass plates.

hyde was put into the reactor at a pressure of 2 $\times 10^{-2}$ to 6×10^{-2} Torr. Third, the radio-frequency power was fed (10–150 W), and then the glow discharge and polymerization of the monomer was initiated. All the plasma polymerization was conducted at a definite time of 30 min. The formed polymer PPBA film and/or powder were deposited onto the glass plates and the inner wall of the reactor chamber.

Product Analysis

After the polymer product deposition occurred for a desired time, generally there were two kinds of products, film and powder, formed between the electrodes and the right fraction of the reactor tube (the oblique line signed area in Fig. 1), respectively. The soluble fraction of PPBA (sol-PPBA) was extracted in benzene and separated from the insoluble fraction (insol-PPBA) by a Soxhlet extractor. Product analyses for PPBA samples were carried out mainly on an Analect RFX-65 FTIR spectrometer. The samples used for infrared measurement were prepared in KBr discs. Gel permeation chromatography was used to determine the molecular weight and molecular distribution of sol-PPBA with tetrahydrofuran as the solvent. The thermal property of PPBA was measured with a Shimadzu thermal analyzer DT-30 (N_2 protection, 5°C/min). Last, the contact angles of water and diiodomethane on the PPBA films deposited on the glass plates were measured at room temperature using an Erma contact angle meter G-1 with a goniometer.

RESULTS AND DISCUSSION

Polymer Deposition

The morphology of benzaldehyde plasma polymer PPBA was found to be intensively influenced by the

plasma conditions. When the monomer pressure was below 3.0×10^{-2} Torr, all the plasma-polymerized products were film that deposited mainly on the glass plate and the inner wall of the reactor tube between two electrodes. With an increase of the monomer pressure, the PPBA powder began to be found on the glass plates in the oblique line signed area shown in Figure 1. In our monomer pressure range of 3.0 $\times 10^{-2}$ to 6.0×10^{-2} Torr, the deposition rate of PPBA powder became larger with an increase of the monomer pressure. The color of the deposited PPBA films was also affected by the plasma parameters and changed from brown at 2.0×10^{-2} Torr to yellow at 5.0×10^{-2} Torr, for a constant power of 60 W. Meanwhile, the PPBA powders kept about the same color of light yellow for all plasma conditions.

Figures 2 and 3 show the effect of monomer pressure and glow discharge power on the deposition rate of PPBA films on the glass plates. The increase of monomer pressure leads to the increase of active species in plasma and the rate of plasma polymerization. Why did the deposition rate of PPBA film on the glass plates begin to decrease between two electrodes when the monomer pressure is above 4 $\times 10^{-2}$ Torr? This will be discussed in the following section. Figure 3 shows that in the small discharge power range the concentration of high-energetic species become greater with the increase of power as also do the plasma polymerization and deposition rate. When the discharge power is more than 40 W, the deposition rate remains roughly unchanged. This
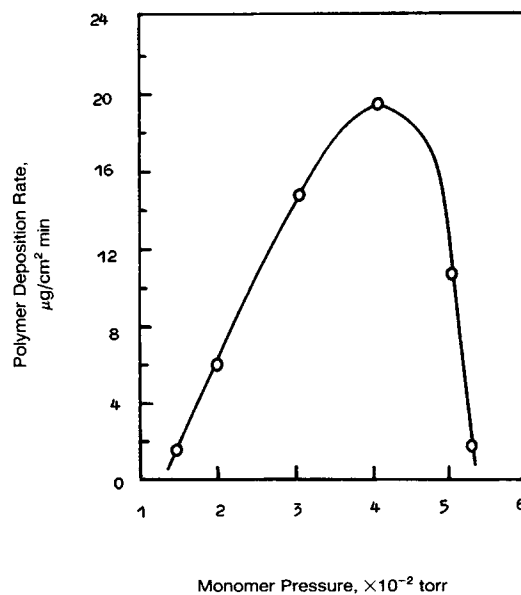
Figure 2   PPBA film deposition rate in plasma polymerization at 60 W.
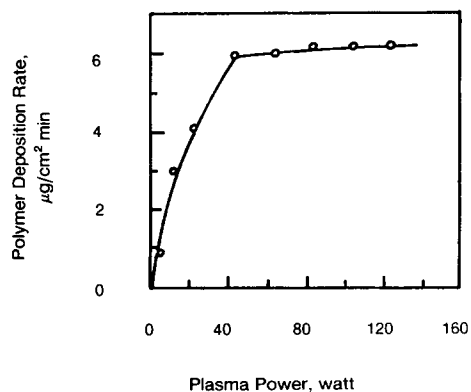
Figure 3 PPBA film deposition rate in plasma polymerization at 2.0×10^{-2} Torr.

result is the same as with the plasma polymerization for other monomers in a similar plasma reactor system.[11]

Chemical Structure of Plasma Polymers

With different plasma conditions, the PPBA films and/or powders were formed. Comparison of the infrared spectra of the monomer and plasma-polymerized film and powder products at 60 W and 5.0 $\times 10^{-2}$ Torr in Figure 4 shows the conversion of the monomer to the polymer. The primary nature of the aldehyde monomer is shown by two C—H stretching absorptions at 2817 and 2737 cm^{-1} and C=O stretching absorption at 1701 cm^{-1}. The other bands associated with the aldehyde group are several peaks in the 1000–1400 cm^{-1} region, such as 1203, 1286, 1311, and 1390 cm^{-1}. In Figure 4, none of the absorption in the infrared spectra of PPBA samples shows the existence of the aldehyde structure. The C=O stretching absorption for the monomer at 1701 cm^{-1} is replaced by the band at 1680 cm^{-1}, which indicates the formation of the aromatic ketone structure in the plasma polymer. The C—H stretching absorption for Ph—H of the monomer in the region of 3062 cm^{-1} becomes weak, and at the same time, the C—H stretching absorption for the —CH$_2$— structure in the region of 2924 cm^{-1} appears markedly for PPBA. The absorption at 1593 and 1454 cm^{-1} due to benzene ring vibration for benzaldehyde also becomes weak for polymers. The wavenumber values of them have shift a little, which is caused by the substitution changes of benzene rings. In addition, the absorptions in the 600–900 cm^{-1} region assigned to out-of-plane deformation of Ph—H also have obvious changes. The newly appeared peaks at 700 and 756 cm^{-1} indicate the ex-
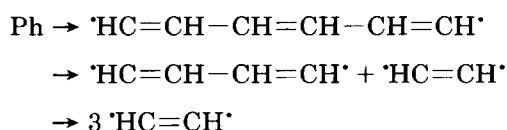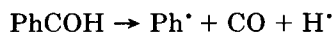
istence of a monosubstitution benzene ring in the PPBA chemical structure. The other newly appeared absorption at 1491 cm^{-1} associated with benzene-ring vibration also indicates the changes of substitution for the benzene ring in the plasma process.

In the glow-discharge area, the collision of free electrons with neutral gas molecules leads to the formation of a variety of species: atoms, free radicals, ions, and metastable compounds. The energy of the electrons in the range of 1–10 Ev is sufficient to break the primary convalent bonds found in organic compounds. Plasma polymerization is believed to be initiated by the free radicals and other chemically excited species in plasma with the monomer molecules.[12] Although electron energies are in the range sufficient for the rupture of any organic molecular bonds, it is not the fact that all the bonds in organic molecules are affected simultaneously and immediately. The rupture possibility of a weak bond is greater than that of a strong bond. For the benzaldehyde molecule, the hydrogen adjacent to the carbonyl group is the easiest to be affected by plasma for its weak bondage to carbonyl group. That could explain why there is no evidence in the infrared spectra to indicate the existence of an aldehyde group in the PPBA samples, even those produced
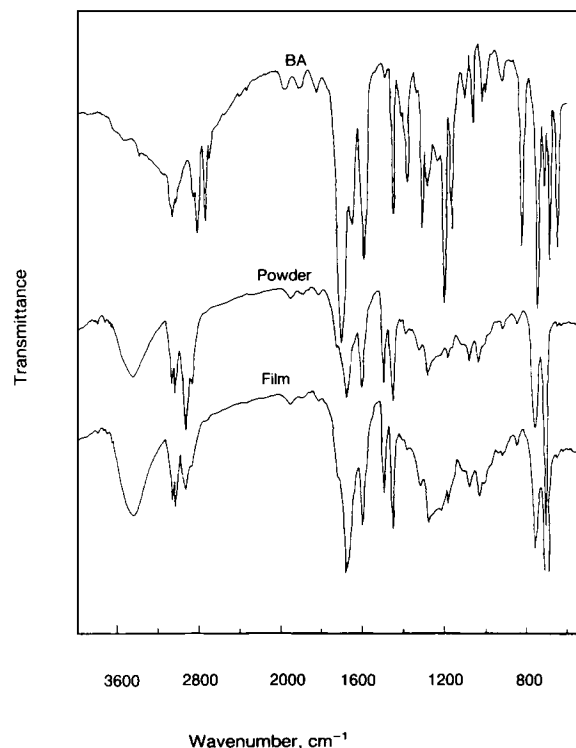
Figure 4 IR spectra for monomer and PPBA film and powder polymerized at 5.0×10^{-2} Torr and 60 W.

at very low discharge power. Our past research on the plasma polymerization of aliphatic aldehyde monomers also showed the tendency of hydrogen abstraction from the aldehyde group.[9,10] At the same time of hydrogen abstraction, the fragmentation of the benzene ring and carbonyl abstraction occur with a great amount of radicals formed. The radicals formed react with other radicals and/or monomer molecules. Subsequently, the plasma polymers are formed. The fragmentation of benzaldehyde can be speculated upon as the result of plasma action, and one possible model is shown below:

$$PhCOH \rightarrow PhCO^{\bullet} + H^{\bullet}$$

$$PhCOH \rightarrow Ph^{\bullet} + CO + H^{\bullet}$$

$$Ph \rightarrow {}^{\bullet}HC{=}CH{-}CH{=}CH{-}CH{=}CH^{\bullet}$$

$$\rightarrow {}^{\bullet}HC{=}CH{-}CH{=}CH^{\bullet} + {}^{\bullet}HC{=}CH^{\bullet}$$

$$\rightarrow 3\ {}^{\bullet}HC{=}CH^{\bullet}$$

The proposed model is in accordance with the data of pyrolysis mass spectra and gas condensates analysis for benzaldehyde plasma polymerization, which will be discussed extensively in another paper of ours.

Figure 4 also shows some differences between the infrared spectra of PPBA film and powder produced at the same plasma condition. The relative absorption peaks associated with the benzene ring decrease more in intensity for PPBA powder compared with those for PPBA film. Also, the relative intensity of the C=O stretching absorption at 1680 cm⁻¹ are smaller for PPBA powder. These results indicate that a large number of free radicals and a more extensive fragmentation of the starting monomer yield further conversion of the intermediate species to a more modified structure for the resultant powder than for the film product. For the position of the monomer gas inlet, the instantaneous concentration of the monomer between two electrodes is greater than that in the oblique line signed area of Figure 1. The diffusion process from monomer inlet to the oblique line signed area for the monomer molecules make them suffer more fragmentation. It is not surprising to find a modified structure for the PPBA powder, with more aliphatic structure and fewer carbonyl groups. At a constant power, raising the monomer pressure above a definite value, the hydrogen abstraction from the aldehyde group for benzaldehyde depletes a large number of high-energetic particles between electrodes. The fragmentation of the benzene ring and the breakage of the carbonyl group begin to be difficult to occur in this

area. Therefore, the fragmentation of benzene ring and following polymerization process begin to emerge in the oblique line signed area of Figure 1. This assumption could explain the decrease of the film deposition rate at high monomer pressure, which was shown in Figure 2.

To study the effect of the plasma parameters on the chemical structure of PPBA, the monomer pressure was varied at 2.0×10^{-2} and 5.0×10^{-2} Torr, keeping the plasma power constant at 20 W. This in effect decreases the energy input per unit mass of monomer. Figure 5 shows the infrared spectra of the PPBA films at different monomer pressure, which have remarkable differences. There are obvious absorptions in relation to the benzene ring structure for PPBA film at 5.0×10^{-2} Torr, while there was no marked evidence for PPBA film at 2.0×10^{-2} Torr. More olefinic structure yielded at low monomer pressure than at high monomer pressure, which was indicated by the more intensive C=C stretching absorption at 1633 cm⁻¹ in the spectrum of PPBA film at 2.0×10^{-2} Torr. More interesting in Figure 5 is the difference of the C=O stretching absorption of PPBA films at 2.0×10^{-2} and 5.0×10^{-2} Torr. The aromatic ketone characterized by the absorption at 1680 cm⁻¹ is the main existing formation of carbonyl groups for PPBA film at 5.0×10^{-2} Torr. According to the wavenumber value and shape of the C=O stretching absorption, the PPBA film at 2.0×10^{-2} Torr may include several kinds of carbonyl groups, such as aliphatic ketone (1714 cm⁻¹), aromatic ketone (1680 cm⁻¹), α,β-olefinic ketone (1675 cm⁻¹), and cyclic ($\geq$ 7) ketone
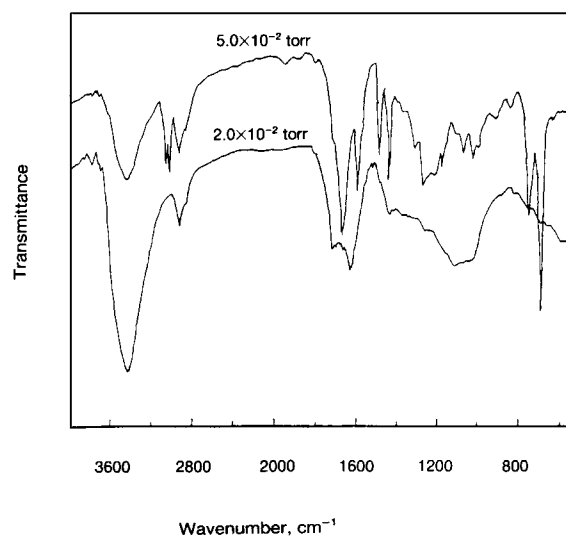
Figure 5 IR spectra for PPBA films at 20 W as a function of monomer pressure.

(1703 cm^{-1}). The percentage of each kind of carbonyl group is very difficult to obtain from the received infrared spectra of the PPBA samples.

To gain further insight into the effect of the plasma parameters on the chemical structure of PPBA samples, the plasma power was varied from 20 to 120 W, keeping the monomer pressure at 2.0 × 10^{-2} Torr. Figure 6 shows the infrared spectra of PPBA film polymerized at different wattages. At the low monomer pressure of 2.0 × 10^{-2} Torr, the benzene rings of the monomer molecules are found to be ruptured even at a small plasma power of 20 W. As the plasma power was raised from 20 to 60 W or above, the absorptions related to the benzene ring cannot be observed, which indicated the complete fragmentation of the benzene ring for benzaldehyde. The C=O stretching absorption of the aldehyde group for the monomer was also replaced by absorption of other carbonyl formations that may include several different kinds of carbonyl groups for its peak variance with various wattages. The carbonyl group for PPBA at 20 W existed considerably with aliphatic ketone for its strongest absorption at 1714 cm^{-1}. As the plasma power increased to 60 W, the C=O stretching absorption had no obvious changes except its relative intensity in comparison with the C=C stretching absorption at 1633 cm^{-1}, which was caused by the carbonyl abstraction from monomer molecules with the increase of plasma power. When the plasma power was further raised to 120 W, the wavenumber value of carbonyl

Figure 6 IR spectra for PPBA films at 2.0 × 10^{-2} Torr as a function of plasma power.

stretching absorption shifted to 1703 cm^{-1} and, meanwhile, its peak shape became narrow, which indicated probably only one kind of carbonyl formation, cyclic ketone,[7] existed in the chemical structure of PPBA samples at 120 W. The high-plasma power increases the number of chemically excited species and the electron energy, which will result in PPBA samples with more cross-linking. It is not a surprise that the carbonyl groups of the PPBA sample at 120 W exist mainly in the aliphatic cyclic structures.

Properties of Plasma Polymers

The plasma polymer PPBA had different solubility with different plasma conditions. The plasma-polymerized film at 2.0 × 10^{-2} Torr and 20 W was insoluble, whereas the film and powder products formed at 5.0 × 10^{-2} Torr and 60 W were partially soluble in benzene, tetrahydrofuran, and other solvents. The percentage of both the sol-PPBA and the insol-PPBA were different for the PPBA film and powder products at a definite plasma conditions. For the PPBA samples polymerized at 5.0 × 10^{-2} Torr and 60 W, the soluble percentage of film and powder products were 87.1 wt % and 44.0 wt %, respectively. Generally, the insolubility of plasma polymers is due to the highly cross-linked nature typical of the plasma polymers.[13] The different solubility indicates that the film product has less cross-linking than does the powder product. Figure 7 demonstrates the comparison of the infrared spectra between the soluble and insoluble fraction of PPBA film. The sol-PPBA fraction is found to have more preservation of the benzene ring, more retention of carbonyl groups, and less appearance of aliphatic structures. The weight-average molecular weight of the sol-PPBA powder at 5.0 × 10^{-2} Torr and 60 W was calculated as 6.9 × 10^3 with a calibration curve of GPC. The molecular weight value corresponds to other known plasma polymers.[14]

The plasma polymers PPBA with different amounts of carbonyl groups and benzene rings are expected to have different wettability. The wettability values obtained on glass plates during various plasma processes are given in Figure 8 by the measurement of contact angles. The wettability values did not change significantly whether the chemically active sample surface was left in argon for 1 day or quenched in air after the plasma polymerization. The "U" curves in Figure 8 show that the wettability values of PPBA films increase and then decrease with the variance of the plasma power from 20 to 150 W. Generally, the wettability value is affected
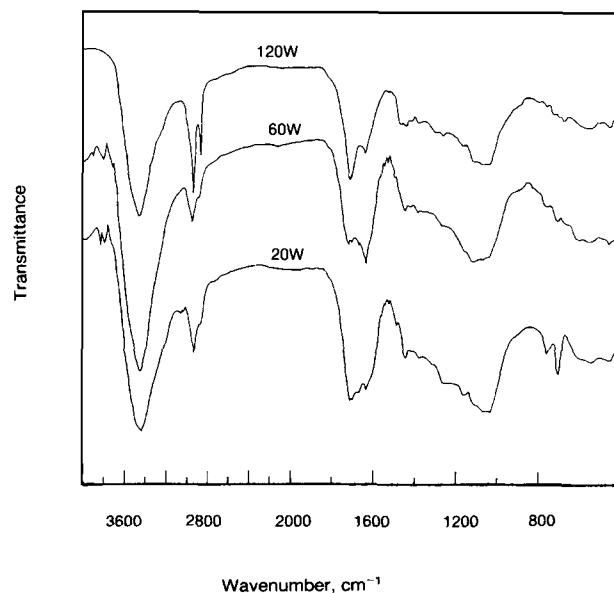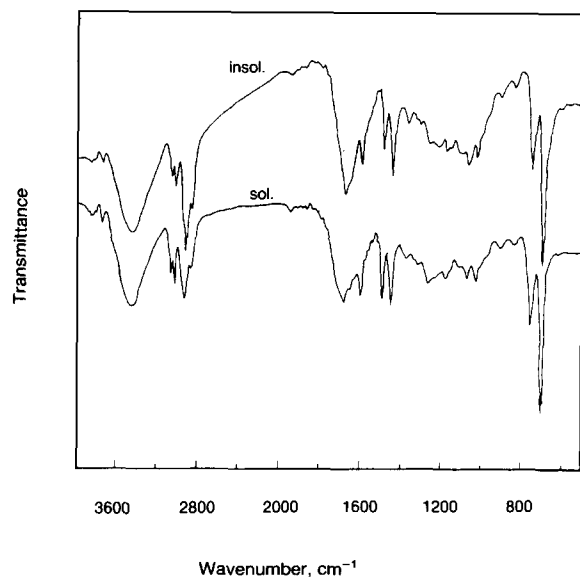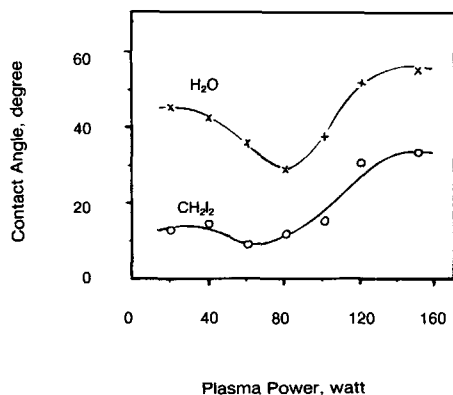
Figure 7 IR spectra for sol-PPBA and insol-PPBA films polymerized at 5.0 × 10⁻² Torr and 60 W.

Figure 9 TGA curves for PPBA films at 60 W as a function of monomer pressure.

by variations in cross-linking density, chemical groups, and the texture on the surface of the plasma film. The wettability changes in Figure 8 may be explained as follows: At low plasma power, the fragmentation of the benzene ring makes a main contribution to the reduction of contact angles. With an increase of plasma power, the benzene are fragmented completely. The increase of the contact angle value is caused by the carbonyl abstraction from the chemical structure of plasma polymers PPBA that was revealed by infrared spectra, as shown in Figure 6.

Finally, the heat stability of the PPBA samples was measured by TGA (Fig. 9). Commonly, the

continuous evaporation of those fractions with low molecular weight may cause the poor base line in the TGA plots. But the plots in Figure 9 show no obvious weight loss observed at 200°C. The characteristic of PPBA of a good heat stability may be advantageous for the purpose of the surface treatment for fillers. The temperature of 200°C is beyond the modeling temperature of the common polymer materials such as PE, PP, PS, and PVC. Figure 9 shows the comparison of the heat stability for PPBA film at different monomer pressures. It is expected that with the decrease of monomer pressure the monomer molecules undergo increased fragmentation, as shown by the infrared spectra in Figure 5, and as a result, the thermal stability of the plasma polymers would be in that order which corresponds to the experimental curves of TGA in Figure 9. The residue of PPBA at 5.0 × 10⁻² Torr retained a small part (22 wt %) at 650°C. But the residue of PPBA at 2.0 × 10⁻² Torr is more stable, retaining 42 wt %. This observation can be explained by heat stability as a result of the increased cross-linking at low monomer pressure for PPBA plasma polymers.

CONCLUSION

Plasma polymerization of benzaldehyde was studied mainly by infrared spectroscopy that focused on the investigation of the chemical structure of PPBA samples as a function of the controllable plasma parameters. The solubility, surface, and heat properties of the formed PPBA polymers were discussed:

Figure 8 Contact angles for PPBA films at 3.0 × 10⁻² Torr as a function of plasma power.

1. Benzaldehyde is plasma-polymerized to yield films or and powders that have different chemical structures.
2. The formed PPBA samples include considerable carbonyl-containing structures, such as aliphatic ketone, α,β-olefinic ketone, aromatic ketone, and cyclic ketone, whose constitution is affected by the plasma conditions.
3. Some PPBA samples comprise two fractions, sol-PPBA and insol-PPBA, which also have different chemical structures.
4. The wettability and heat stability of PPBA are affected the same by the plasma conditions. The high-temperature stability for PPBA polymers provide the potential possibility of its application in the treatment of filler surfaces.

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