Carbonization Behavior of Polyimide Films with Various Chemical Structures

M. INAGAKI,[1]* T. IBUKI,[2]† and T. TAKEICHI[2]

[1]Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo, 060 Japan and [2]Materials Science, Toyohashi University of Technology Tempaku-cho, Toyohashi, 441 Japan

SYNOPSIS

Six kinds of polyimide films with different molecular structures were synthesized and carbonized up to 1100°C. The carbonization behavior of polyimides was followed by measuring the changes in weight, size, and electrical conductivity. Pyrolysis gases evolved on the way to carbonize up to 1000°C were analyzed by gas chromatography.

All films showed appreciable shrinkage and became a black color above 500°C. No cracks and pores were observed on the films heated up to 1100°C, even under the scanning electron microscope. A large weight decrease of 35–50% was observed in a narrow temperature range from 500 to 650°C, which seemed to be due to the departure of CO groups as either CO or CO_2. An additional weight decrease occurred gradually above 800°C, due to N_2 departure. A remarkable increase of electrical conductivity along the film surface, more than 2 orders, was observed with the increase in heat-treatment temperature. The polyimide film with a flat molecular structure (PMDA/PPD) gave the highest conductivity: 3.7×10^2 S/cm.

INTRODUCTION

Polyimides have been developed as thermoresistant polymers and have been proposed to have a wide variety of applications.[1] In relation to high-temperature use, their thermal behavior, such as glass transition and pyrolysis, is important and has been studied by different authors.[2] The carbon materials as the products of complete pyrolysis of polyimides have attracted the most attention mainly because of the following reasons: (1) They are carbonized without any change in shape, even though the shrinkage by pyrolysis is not so small, being 20–40% in linear shrinkage, and (2) some of them give carbon films with high graphitizability,[3-6] which can be converted to graphite by high-temperature treatment.

Starting from a film of a polyimide and heating it to high temperatures such as 1000°C, we can get a carbon film without any cracks and pores. The carbonization of these polyimides seems to proceed in the solid state (solid-state carbonization) by expelling noncarbon atoms as different gases. Various thermosetting resins such as phenol and furfuryl-alcohol resins give solid carbons through solid-state carbonization, but usually they contain a large number of pores. Therefore, special attention, such as extremely slow heating, is necessary to avoid the formation of cracks and open pores due to shrinkage during carbonization.[7] The carbonization process of the commercially available polyimide films was studied by measuring the changes in weight, size, electrical conductivity, X-ray powder pattern, Raman spectrum, X-ray photoelectron spectrum, and gas chromatogram.[3,5,8-11] The carbon films obtained have relatively high electrical conductivity in the order of 10^2 S/cm.

The carbon materials that are prepared from most of thermosetting resins keep their amorphous nature, their small size of hexagonal carbon layers as basic structural units, their random stacking, and

their random orientation, mainly because there is no possibility for improvement of layer orientation during solid-state carbonization. To change them to graphite structure (graphitization), pressure as high as 10 kbar was experimentally shown to be needed during high-temperature treatment.[8]

However, in the case of the carbon films prepared from polyimides, "Kapton" (Du Pont) and "Novax" (Mitsubishi Kasei Co.) by high-temperature treatment, we have been able to get a high crystallinity of graphite, one comparable to highly oriented pyrolytic graphite (HOPG) and so-called kish graphite, the former being prepared by high-temperature and high-pressure treatment and the latter obtained by the precipitation of oversaturated carbon atoms in molten iron.[4-6] On the other hand, another polyimide "Upilex" (Ube Kousan Co.) was found to give a carbon film with much lower graphitizability.[12] From these experimental results, three factors determining the graphitizability of the resulting carbon film were deduced: (1) flatness of the precursor molecules, (2) their orientation along the film surface, and (3) simple release of noncarbon atoms during their pyrolysis.

In the present work, polyimides with different molecular structures were synthesized, particularly by taking account of the flatness of molecules, and the carbonization behavior of their polymers were followed. The electrical conductivity of the carbon films heated up to 1000°C is discussed from the flatness of the starting imide molecules.

MATERIALS AND METHODS

Polyimides Synthesized

The molecular structures of the aromatic polyimides synthesized are summarized in Figure 1, together with their codes used in the present work. By reacting different anhydrides with equimolar aromatic diamines, respective polyamic acids were obtained as a solution of N-methyl-2-pyrrolidone (NMP) with a concentration of about 20 wt % by stirring for 24 h at room temperature in the flow of purified nitrogen gas. Pyromellitic dianhydride (PMDA), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), and hexafluoroisopropylidenebisphthalic anhydride (6FDA) were selected as anhydrides, and as aromatic diamine, 1,4-phenylenediamine (PPD), 4,4′-oxydianiline (ODA), and 4,4′-methylenedianiline (DDM) were used.

Each solution of polyamic acids thus prepared was spread out on a glass plate and dried at 80°C
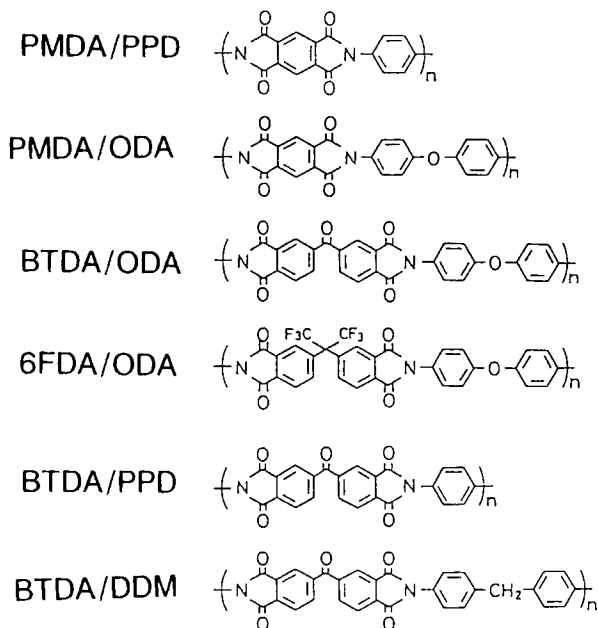
Figure 1 Molecular structure of the polyimides synthesized.

for 1 h and then at 150°C for 1 h. The partially imidized film was separated from the glass plate and then the imidization was completed at 350°C for 10 min without any constraint to the film, except for the PMDA/PPD film that was imidized on a glass plate. The polyimide films with thickness in the range of 20–50 μm were selected for further experiments.

The imide molecules consist of two constituent parts, as discussed in our previous paper[5] and called imide and bridging parts, even though the present naming is a little different from the conventional one in polymer science. In the present paper, the polyimide films prepared were named by using the names of the starting chemicals for each part; for example, BTDA/ODA means that the polyimide is synthesized from the reaction between BTDA and ODA, the former consisting of the imide part, and the latter, the bridging part. The sample PMDA/ODA in the present work has the same molecular structure as the commercially available polyimide film "Kapton."

Carbonization and Characterization

The polyimide films with thickness of about 20–50 μm were selected, in order to make the comparison of the experimental results with those on commercially available polyimide films easier. After cutting the film into a size of about 5 × 15 mm, it was car-

bonized between two alumina plates in the flow of nitrogen by heating to a temperature between 400 and 1100°C, with the heating rate of 400°C/h and holding at the temperature for 1 h.

The weight change was determined from the weights before and after heating. Since the weight of the original film is so small (about 0.02 g), the accuracy of the weight change determination was not very high, probably about ±3%.

Electrical conductivity was measured on a part of the carbonized films at room temperature by a conventional four-probe method. By using different current values of 0.1–20 mA, the average value of conductivity was determined on the film. The cross-sectional area and the distance between two probes for potential measurement were determined on each film specimen under a microscope.

Pyrolysis gases evolved were sampled at every 25°C above 350°C during heating a film specimen

Table I   Yield after the Carbonization at 1000°C and the Content of Carbon Atoms Belonging to Aromatic Rings in the Starting Polyimides

Sample Code	Yield after 1000°C (wt %)	Content of Aromatic Carbon Atoms (wt %)
PMDA/PPD	47.6	50.7
PMDA/ODA	59.3	56.5
GFDA/ODA	60.4	47.5
BTDA/PPD	62.1	54.8
BTDA/ODA	62.5	59.5
BTDA/DDM	63.3	59.5

of about 0.08 g up to 1000°C, with a heating rate of 200°C/h in the flow of helium, and then examined with gas chromatography. An activated carbon column at 75°C and a thermal conductivity detector were used. The volume of the evolved gas was determined from the peak area of each gas in the gas chromatogram observed by referring to the standard
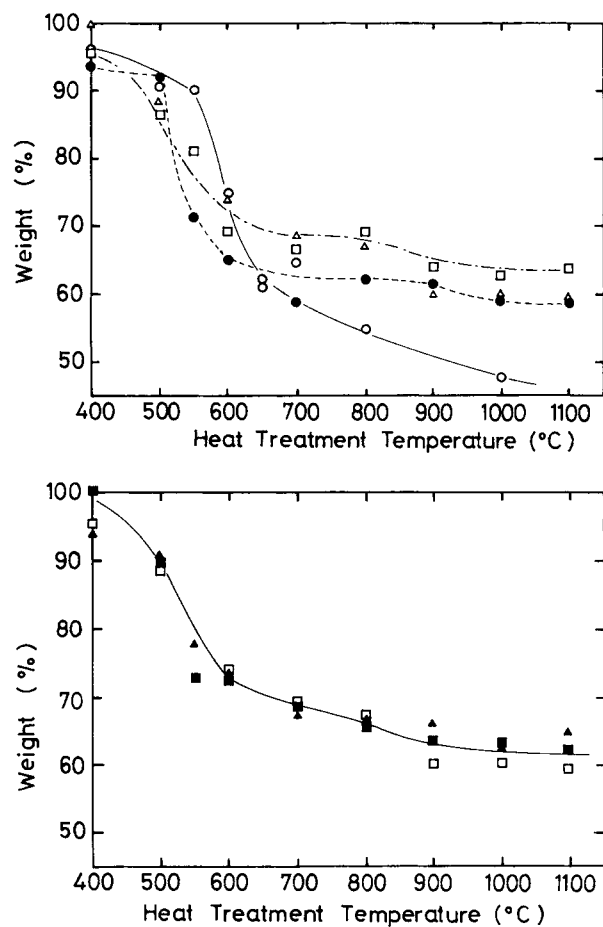
Figure 2   Changes of weight with heat-treatment temperature on the polyimides: (O) PMDA/PPD; (●) PMDA/ODA; (□) BTDA/ODA; (△) 6FDA/ODA; (▲) BTDA/PPD; (■) BTDA/DDM.
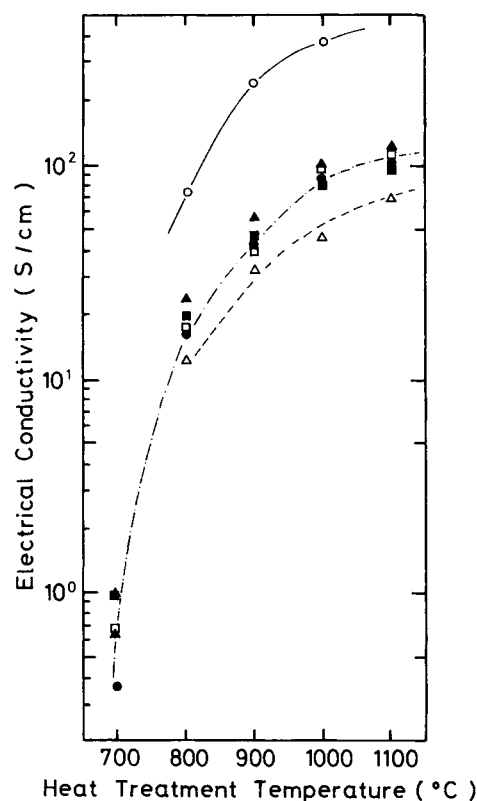

Figure 3   Changes of electrical conductivity at room temperature with heat-treatment temperature on the polyimides films: (O) PMDA/PPD; (●) PMDA/ODA; (□) BTDA/ODA; (△) 6FDA/ODA; (▲) BTDA/PPD; (■) BTDA/DDM.

gases and was expressed as the volume per 1°C increment and per 1 g of starting polyimide.

RESULTS AND DISCUSSION

Each film obtained by heating above 500°C showed appreciable shrinkage and became black, but no cracks and pores were observed even under the scanning electron microscope.

The changes of relative weight with heating temperatures for the polyimides are shown in Figure 2. All polyimides show a remarkable weight decrease in a narrow temperature range from 500 to 650°C and a gradual decrease above 800°C. In Figure 2(a), the polyimides having the same bridging part ODA, except PMDA/PPD, are compared, and those having the same imide part, in Figure 2(b). The yield from polyimides after the carbonization up to 1100°C depends strongly on the structure of the im-
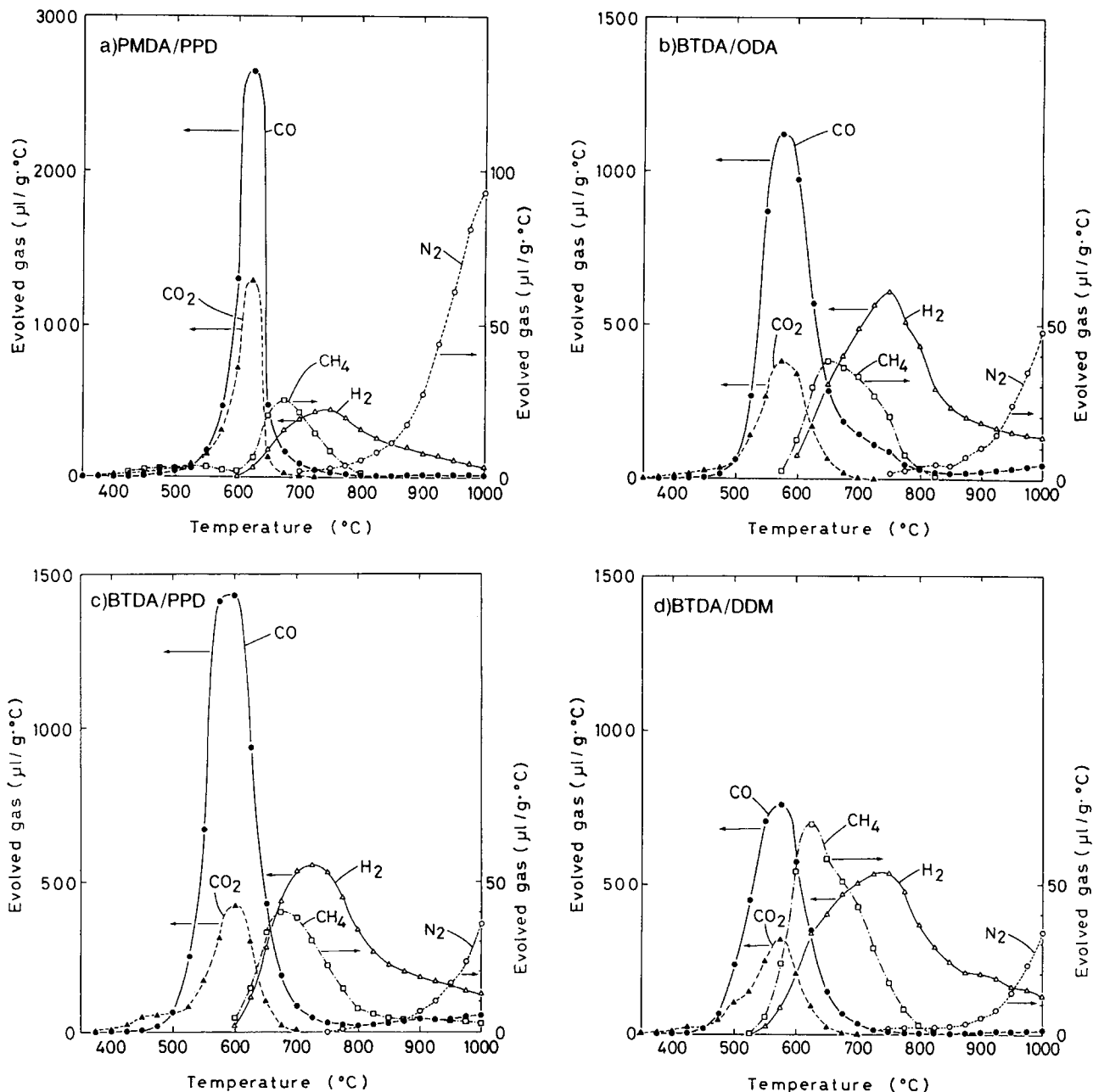
Figure 4   Changes of decomposition gases measured by a gas chromatograph with heat-treatment temperature.

ide part; the polyimides that have the same bridging part show quite different yields, but those with the same imide part, show almost the same yield.

The films PMDA/PPD, PMDA/ODA, and BTDA/ODA showed a little scattering in experimental points around 700–800°C, but it seemed to be due to low accuracy in weight determination.

The yields observed on the polyimides, except 6FDA/ODA, after the carbonization up to 1100°C were almost comparable to the calculated content of carbon atoms belonging to aromatic rings in the starting polyimide molecules, as shown in Table I. For 6FDA/ODA, yield higher by 13% than the content of aromatic rings was obtained, which seemed to be due to the presence of sp^3 carbon atom in the imide part.

In Figure 3, the electrical conductivity along the film surface at room temperature was plotted as a function of carbonization temperature on different polyimide films. The increase in conductivity with carbonization is very remarkable, more than 2 orders, for each film.

The films derived from PMDA/PPD have rather high conductivity up to 3.7×10^2 S/cm, of which the original polyimide does not have bend in the molecule. Three films containing the same imide part derived from BTDA but with different bridging parts have almost the same conductivity. The film PMDA/ODA, which has a little bend in the bridging part, gives a little higher conductivity than do these three films. The film 6FDA/ODA, which contains the sp^3 carbon atom in the imide part, gives appreciably low conductivity, i.e., the lowest values among the films used in the present work, after high-temperature carbonization. The C—C bond with sp^3 orbitals, which gives three dimensional conformation to the molecule, seems to be broken at relatively low temperature, but also gives some disturbance in the molecular orientation formed in the stage of the starting polyimide. This might be the reason for low electrical conductivity along the film surface and probably also for higher carbon yield after 1000°C than that expected from the content of aromatic rings.

The changes of the evolved gases with heating up to 1000°C are shown for five polyimide films, PMDA/PPD, PMDA/ODA, BTDA/ODA, BTDA/PPD, and BTDA/DDM, in Figure 4. For all polyimide films, large amounts of CO and CO_2 are evolved in a narrow temperature range of 500–650°C, corresponding to the abrupt weight decrease in the same temperature range (Fig. 2). Above 600°C, CH_4 and H_2 start to be released and show maximum evolution at around 700°C and 750–

800°C, respectively. For BTDA/DDM, which contains methylene groups and of which oxygen content is relatively small in comparison with other polyimides, the evolved amounts of CO and CO_2 are relatively small and that of CH_4 is relatively large. Above 800°C, the evolution of N_2 is observed for all polyimide films, which seems to cause the gradual weight decrease (Fig. 2) and also the rapid increase in electrical conductivity (Fig. 3).

For PMDA/ODA and BTDA/ODA, the evolution profile of CO shows a tail above 700°C. In contrast, three other polyimides shown in Figure 4 do not show such a tailing phenomenon, suggesting the release of etheric oxygen in the bridging part from ODA.

REFERENCES

1. A. K. St. Clair and T. L. St. Clair, *Polym. Eng. Sci.,* **22,** 9 (1982); P. M. Hergenrother, *CHEMTECH,* **August,** 496 (1984).
2. C. E. Sroog, *J. Polym. Sci. Macromol. Rev.,* **11,** 161 (1976); D. A. Scola, in *31st National SAMPE Symposium,* **31,** 1844 (1986); P. M. Hergenrother, *Polym. J.,* **19,** 73 (1987).
3. A. Buerger, E. Fitzer, M. Heim, and B. Terwiesch, *Carbon,* **13,** 149 (1975).
4. Y. Hishiyama, S. Yasuda, A. Yoshida, and M. Inagaki, *J. Mater. Sci.,* **23,** 3722 (1988).
5. M. Inagaki, L. J. Meng, T. Ibuki, and Y. Hishiyama, *Carbon,* to appear.
6. Y. Hishiyama and M. Inagaki, *J. Mater. Res.,* to appear.
7. T. Noda, M. Inagaki, and S. Yamada, *J. Non-Cryst. Solids,* **1,** 285 (1969).
8. M. Inagaki, *Tanso,* **1987**(129), 68 (1987).
9. C. Z. Hu and J. D. Andrade, *J. Appl. Polym. Sci.,* **30,** 4409 (1985).
10. C. Z. Hu, J. D. Andrade, and P. Dryden, *J. Appl. Polym. Sci.,* **35,** 1149 (1988).
11. M. Inagaki, S. Harada, T. Sato, T. Nakajima, Y. Horino, and K. Morita, *Carbon,* **27,** 253 (1988).
12. M. Inagaki, K. Sakamoto, and Y. Hishiyama, *J. Mater. Res.,* **6,** 1108 (1991).