

# Preparation of Polyimide Powder

HIROSHI INOUE,<sup>1,\*</sup> TADAO MURAMATU,<sup>1</sup> YOSHIKAZU SASAKI,<sup>1</sup> and TOSHIO OGAWA<sup>2</sup>

<sup>1</sup>Polymer Laboratory (UBE), Corporate Research & Development, UBE Industries, Ltd., 1-22-32, Nishihon-machi, Ube, Yamaguchi 755, and <sup>2</sup>Department of Materials Science and Engineering, Faculty of Engineering, Kanazawa Institute of Technology, 7-1, Ohgigaoka, Nonoichi, Ishikawa 921, Japan

## SYNOPSIS

A polyimide powder was prepared from 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA). Polyimide powder having low molecular weight was prepared by imidizing low-molecular-weight polyamic acid. The molecular weight of this polyimide powder increased on heating in a solid state. The molecular weight increased with the decrease of crystallinity of polyimide. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Aromatic polyimides have been used in all fields—film, varnish, engineering plastics, and so on—in recent years. Engineering plastics of polyimide are generally made of polyimide powder by sintering in a process similar to that applied in powder metallurgy. Polyimide powders have been made from polyamic acids by chemical conversion<sup>1</sup> or by amine-catalyzed thermal conversion<sup>2</sup> (Fig. 1). These processes involve the formation of high-molecular-weight precursor polymer, a polyamic acid solution of which is generally extremely viscous. These studies have shown that the toughness of coalesced polyimide powders depends to a large degree on the molecular weight of the precursor polyamic acid. Thus, to produce higher molecular weight polyimides, it is necessary to handle the very viscous solution or else reduce the solids level of polyamic acid in the solution.<sup>3</sup>

It is known that the drop of molecular weight and the embrittlement of certain films at intermediate (150–200°C) stage of cure occurs in the case of film prepared from two-step polymerization.<sup>5–8</sup> Since the polyamic acid in the solution is heated to 150–200°C to prepare polyimide powder, it is presumed that the drop of molecular weight of polyamic acid occurs in a similar manner. If the molecular weight of polyamic acid dropped by heating to 150–200°C, the

precursor polyamic acid must not have higher molecular weight. We used soluble polyimide from 3,3',4,4'-biphenyl tetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA)<sup>4</sup> and examined the change of molecular weight in the process for preparing polyimide powder.<sup>9</sup>

## EXPERIMENTAL

### Preparation of Polyimide Powder

BPDA of 15.92 g (0.054 mol), ODA of 10.84 g (0.054 mol), and *N*-methyl-2-pyrrolidone (NMP) of 241 g were placed in a three-neck flask with a stirrer, thermometer, and reflux condenser that had a vessel for receiving water. The concentration of monomers was 10 wt %. The content was stirred at 30°C for 6 h. The resultant polyamic acid had an inherent viscosity ( $\eta_{inh}$ ) of 2.89 dL/g. Triethylamine of 27.4 g (0.27 mol) was mixed with the resultant polyamic acid solution. The mixture was stirred at 30°C for 2.5 h and raised gradually to 150°C. The yellow polyimide was precipitated from the mixture. Further, the mixture was raised to the boiling point of NMP, while water and triethylamine were removed from that by distillation. The mixture was kept at this temperature for 5 h. The product was separated by filtration and washed with NMP and acetone followed by drying in a vacuum oven at 140°C. The yield of the product was 94% of the theoretical amount.

\* To whom correspondence should be addressed.

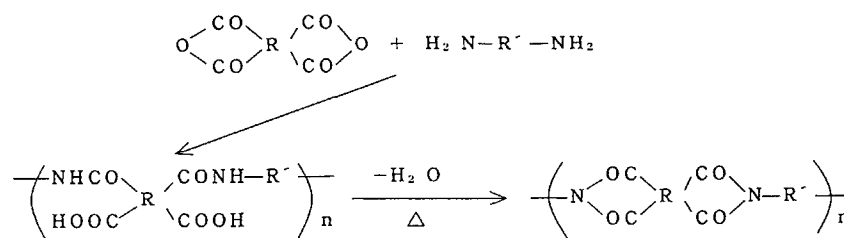


Figure 1 Scheme of two-step polymerization.

### Preparation of Film from Polyimide Solution

Polyimide powder of 3.6 g and *p*-chlorophenol (PCP) of 36 g were introduced into a flask, and the mixture was kept at 110°C with stirring for about 30 min. The polyimide solution was spread on a glass plate at 50°C to form a film. The film was kept at 140°C under 1 mmHg to solidify the film by evaporating away PCP from the film. Thereafter, the film was raised to 300°C after 1 h and kept at this temperature for 1 h. The final film had a thickness of about 35 μm.

### Solubility of Polyimide Powder

The solubilities of polyimide powder were examined using several phenol solvents for measuring the inherent viscosity of a polyimide powder. The polyimide powder of 2 g was added to a phenol solvent of 20 g and was heated with stirring at the temperature of 110°C for 30 min. The solution was cooled to 50°C and the insoluble part of polyimide powder was separated by filtration and washed with NMP and acetone followed by drying in a vacuum oven at 140°C. The weight of the polyimide powder was measured. The solubilities are shown in Table I. Among them, *p*-chlorophenol was most recommendable due to a relatively lower melting point. We decided to use PCP as the solvent for polyimide powder.

Table I Solubility of Polyimide Powder

Solvent	Solubility at 110°C (%)
<i>p</i> -Chlorophenol	> 10
4-Bromophenol	> 10
3-Chloro-6-hydroxytoluene	> 10
<i>o</i> -Chlorophenol	3.2
<i>m</i> -Cresol	0.8
<i>o</i> -Cresol	0.7
Phenol	0.3

### Analysis

Inherent viscosity ( $\eta_{inh}$ ) was determined by the following method. In the case of a polyamic acid, the polymer was dissolved at a concentration of 0.5 g in 100 mL of NMP. The  $\eta_{inh}$  was measured at 30°C. In the case of a polyimide powder and film, the polymer was dissolved at a concentration of 0.5 g in 100 mL of PCP at 70°C. The  $\eta_{inh}$  was measured at 50°C. Wide-angle X-ray diffraction (WAXD) measurements were conducted on an X-ray diffractometer (Model 2038), supplied by Rigaku Denki K.K. The  $\text{CuK}_\alpha$  radiation source was operated at 40 kV and 40 mA. WAXD measurements were performed in transmission geometry.

## RESULTS AND DISCUSSION

The preparation processes of polyimide powder are shown in Figure 2. An NMP solution of a polyamic acid was prepared from BPDA and ODA. The final concentration of polyamic acid was 10% by weight, which showed 2.89 dL/g in  $\eta_{inh}$ . The solution was mixed with triethylamine (5 equivalents per mole of polyamic acid). The mixture was stirred at 30°C for 2.5 h and gradually raised to 200°C with stirring after 1.5 h and kept at this temperature for 3 h. The triethylamine began to reflux at about 125°C, and

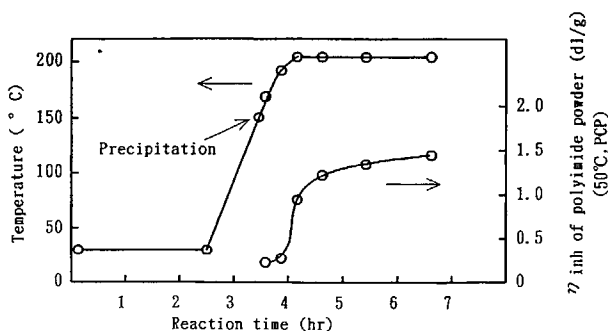
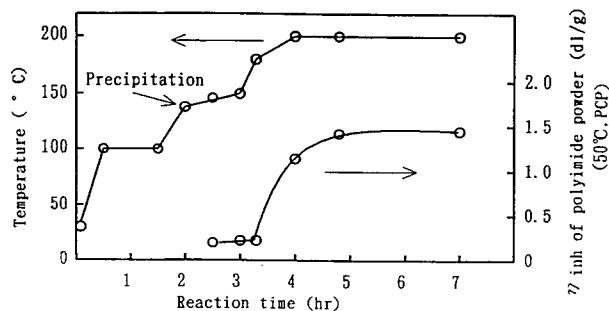


Figure 2 Formation of polyimide powder from polyamic acid with triethylamine.



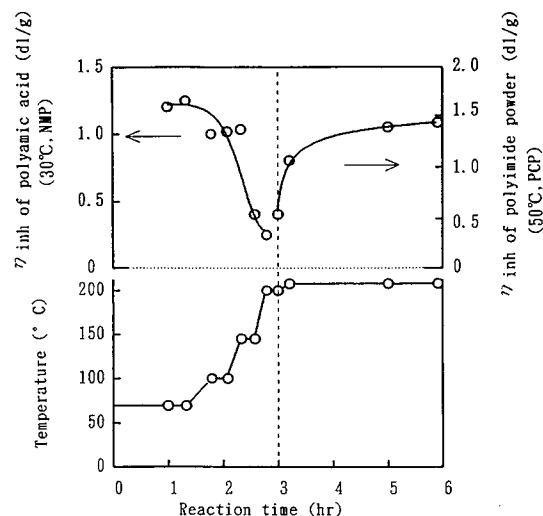
**Figure 3** Formation of polyimide powder from polyamic acid with triethylamine.

yellow polyimide began to precipitate at about 150°C. About 10-mL aliquots of the solution containing polyimide powder were withdrawn. The polyimide powder was separated by means of filtering and washed with NMP and acetone and dried. The precipitated powder was so fine that it was difficult to filter. The particle size of the powder was increased to a few microns by heating the suspension, and the powder was separated by filtering. As shown in Figure 2, the  $\eta_{inh}$  values of the powders increase with the time of heating. It is apparent that the polymerization also proceeds in the solid state like powder, similar to that in the film state.<sup>5,6,12</sup>

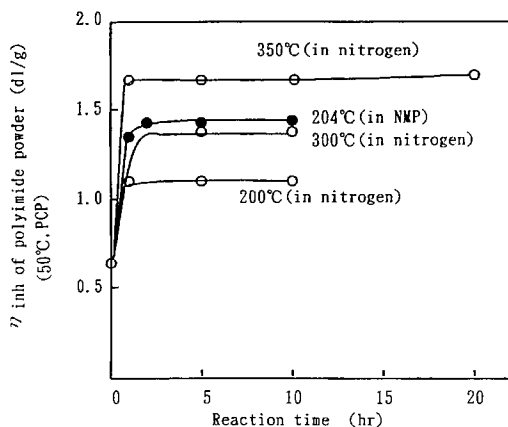
Next, the influence of a degree of polymerization of the polyamic acid was examined. The degree of polymerization of the polyamic acid used in the aforementioned example was relatively high. Then we examined the degree of polymerization of polyimide powder in the case of a low degree of polymerization of polyamic acid. As shown in Figure 3, the mixture was raised to 100°C with stirring after BPDA, ODA, and NMP were introduced into a vessel. The mixture was dissolved after a while and maintained at 100°C for 1 h. The  $\eta_{inh}$  of the polyamic acid at this stage was 1.09 dL/g. Triethylamine was added to the mixture. The solution was gradually raised to 150°C after 30 min, and yellow polyimide began to precipitate. The  $\eta_{inh}$  of this polyimide powder was 0.19 dL/g just after the precipitation. The mixture was kept at this temperature for 1 h. The  $\eta_{inh}$  of the polyimide powder after 1 h was almost the same as the first precipitation. The temperature was raised to 200°C after 1 h, and the precipitate was maintained at this temperature. As shown in Figure 3, the  $\eta_{inh}$  of the powder increased with the temperature. The  $\eta_{inh}$  of polyimide powder after 1 h at 204°C was 1.42 dL/g. The  $\eta_{inh}$  after 3 h was the same as that after 1 h. The  $\eta_{inh}$  is thought to level off at a certain value. In spite of using the polyamic acid that has a low molecular

weight in this experiment, the  $\eta_{inh}$  was almost the same as that with a high molecular weight, as shown in Figure 2. This result means that a polyamic acid does not convert into a polyimide powder keeping the same molecular weight. Namely, it suggests that a polyamic acid depolymerizes to lower molecular weight and then imidizes to polyimide powder. This powder may convert to a higher molecular weight polyimide by heating.

To clarify the process of powder formation, the following experiment was carried out, as shown in Figure 4. BPDA and ODA were introduced into NMP, and the mixture was dissolved with stirring at 70°C. The  $\eta_{inh}$  of the polyamic acid was 1.16 dL/g when the mixture was dissolved. As a  $\eta_{inh}$  of a polyamic acid polymerized at 30°C is around 3.0 dL/g, the  $\eta_{inh}$  of that at 70°C is considerably lower. Then the temperature was raised to 100°C, and the  $\eta_{inh}$  of the polyamic acid dropped slowly. When the temperature was raised to 145°C, the  $\eta_{inh}$  of that dropped rapidly. Since triethylamine was not used in this experiment, the precipitation began at 190°C. The  $\eta_{inh}$  dropped to 0.27 dL/g just before the precipitation. The absorption of imide group of 1770  $\text{cm}^{-1}$  was already observed by infrared analysis of the solution at 145°C. This absorption intensity became maximum just before the precipitation at 190°C, but the absorption of the amide group of 1540  $\text{cm}^{-1}$  was still observed at 190°C. The presence of both the imide and amide groups shows that a partially imidized polyamic acid or a soluble polyimide of low molecular weight were prepared. When the proportion of imide group in polyamic acid became larger or the molecular weight of polyimide became larger,



**Figure 4** Formation of polyimide powder from polyamic acid without triethylamine.



**Figure 5**  $\eta_{inh}$  as a function of cure temperature for thermally staged powders.

the polymer was thought to become insoluble in NMP and to precipitate. The absorption of the imide group of  $1770\text{ cm}^{-1}$  was observed in the filtrate just after the precipitation. This result means that the low-molecular-weight polyimide is present in the NMP solution. The absorption of the imide group was not observed in the filtrate of the suspension after heating at  $204^\circ\text{C}$  for 2 h. This result shows that the molecular weight of soluble polyimide became larger or the proportion of imidization in a partially imidized polyamic acid became larger and precipitated from the solution.

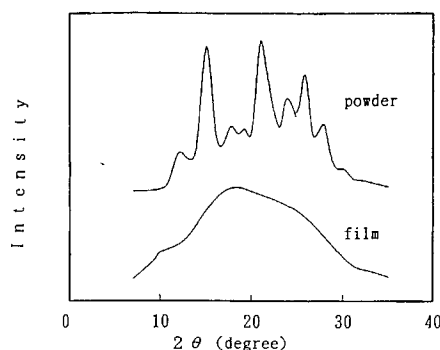
The polymerization of polyimide powder in solid state was studied in detail (Fig. 5). The powder just after precipitation was heated in NMP or nitrogen atmosphere for 10–20 h, and the  $\eta_{inh}$  values of powders were measured. The  $\eta_{inh}$  increases from  $0.64\text{ dL/g}$  to  $1.38\text{ dL/g}$  or  $1.68\text{ dL/g}$ , respectively, by remaining at 200 or  $350^\circ\text{C}$  in a nitrogen atmosphere for 1 h. The  $\eta_{inh}$  of the powder on further heating did not increase, and it leveled off at a certain value. The degree of polymerization is dependent on the temperature, but not on the time. The  $\eta_{inh}$  remaining at  $204^\circ\text{C}$  in NMP became larger than that remaining at  $200^\circ\text{C}$  in a nitrogen atmosphere. This result suggests that the molecular chain heated in NMP is more mobile than that in a nitrogen atmosphere, because NMP would act as a plasticizer.

In this manner, the polymerization in the solid state seems to be influenced by the condition of the solid state. For example, the difference in the crystallinity or the orientation of polymer will influence the degree of polymerization in the solid state. Some polyimide powders are known to be higher in crystallinity.<sup>10</sup> On the other hand, the crystallinity or the orientation of the polyimide film from BPDA/ODA is known to be low because of the flexible ether

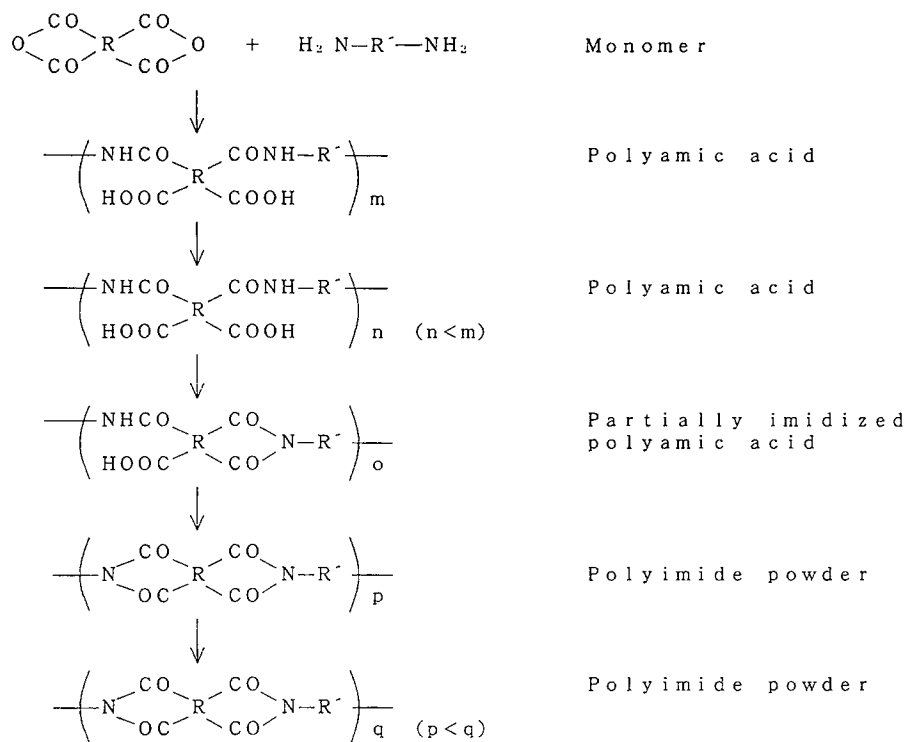
**Table II** Change of  $\eta_{inh}$  of Films from BPDA/ODA

Heating Condition	$\eta_{inh}$ (dL/g) ( $50^\circ\text{C}$ , PCP)
(Polyimide powder)	0.64
rt – $300^\circ\text{C}$ , 60 min	2.62
rt – $300^\circ\text{C}$ , 60 min $300^\circ\text{C}$ , 60 min	3.49

linkage of ODA.<sup>11</sup> If the degree of polymerization in solid state is correlated with the crystallinity of polymer, the increase in the  $\eta_{inh}$  of the film on heating is expected to be larger than that of the powder.<sup>12</sup> Consequently, we studied the change of the  $\eta_{inh}$  of the films from the solution of dissolved powder on curing (Table II). The  $\eta_{inh}$  of the polyimide powder used was  $0.64\text{ dL/g}$ . This powder was dissolved in *p*-chlorophenol, and then the films were prepared from the solution. The film increased from  $30^\circ\text{C}$  to  $300^\circ\text{C}$  after 1 h, and the  $\eta_{inh}$  increased to  $2.62\text{ dL/g}$  and finally reached  $3.48\text{ dL/g}$ , when the film was heated at  $300^\circ\text{C}$  for 1 h. When the powder was kept at  $300^\circ\text{C}$  in nitrogen for 2 h, the  $\eta_{inh}$  was  $1.43\text{ dL/g}$ . There is a large difference in the  $\eta_{inh}$  values between the film and the powder. It is thought that the crystallinity of polyimide powder is higher than that of the film. The transmission WAXD patterns of the powder and the film are shown in Figure 6. The film is almost amorphous, and the crystallinity of the film is low. The crystallinity of the powder is definitely higher than that of the film. Then intermolecular restriction in the powder is higher than that in the film, and it makes the polymer chain in powder less mobile. As a result, the increase of the  $\eta_{inh}$  of powder in solid state is not large.



**Figure 6** Wide-angle X-ray diffraction (WAXD) patterns of polyimide film and powder (transmission).



**Figure 7** Process of formation of polyimide powder.

## CONCLUSIONS

The processes of formation of the polyimide powder from BPDA/ODA were studied. The powder precipitated from the polyamic acid solution on heating. The  $\eta_{inh}$  of the powder was low just after precipitation. The  $\eta_{inh}$  of this powder increased on heating the suspension, but the increase of the  $\eta_{inh}$  leveled off at a certain value. When the polyamic acid solution is heated, both depolymerization to low molecular weight and imidization occur. A partially imidized polyamic acid or a soluble polyimide of low molecular weight is formed, and the proportion of the imide group in polyamic acid becomes larger or the molecular weight of polyimide becomes larger on heating. As a result, the polymer becomes insoluble in NMP. This powder converted to higher molecular weight polyimide on heating (Fig. 7). The molecular weight of polyimide prepared decreases with an increase in crystallinity.

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