High-Strength–High-Modulus Polyimide Fibers I. One-Step Synthesis of Spinnable Polyimides

TAKAHO KANEDA, TOSHIO KATSURA, KANJI NAKAGAWA, and HIROSHI MAKINO, *Chiba Research Laboratory of Ube Industries, Ltd., 8 Minami Kaigan, Goi, Ichihara-City Chiba,* and MASAO HORIO*, *Department of Polymer Chemistry, Kyoto University, Kyoto, 606 Japan*

Synopsis

Polyimides with aromatic links are synthesized usually in two steps, but a series of aromatic polyimides with large molecular weights sufficient to produce strong fibers were prepared in one step by the reaction of 3,3', 4,4'-biphenyltetracarboxylic dianhydride (BPDA) with various aromatic diamines. The one-step polycondensation was possible even when BPDA was replaced to some extent by pyromellitic dianhydride, which is a basic component in the conventional two-step method. The copolyimides based on BPDA and mixtures of aromatic diamines were also synthesized in similar manner. For the one-step polycondensation, phenol and some of its derivatives were found to be suitable solvents, while the typical solvent employed in the two-step method, such as N-methyl-2-pyrrolidone, could not be used because of the precipitation of low-molecular weight polyimides. p-Hydroxybenzoic acid proved to be a very efficient accelerator for the conversion of polyamic acids to polyimides.

INTRODUCTION

The heat-resistant products of polyimides with aromatic links in the molecular chains were made commercially available in the mid-1960s by the invention of two-step polycondensation technique.[1-8] The first step consists in acylation of diamine with tetracarboxylic dianhydride in an organic solvent and yields the soluble intermediate polymer (i.e., polyamic acid). Films, fibers, or powders are made from this precursor polymer. In the second step, the polyamic acid, formed into the desired shapes, is converted into polyimide by dehydration and cyclization effected by dehydrating agents,[3-5] heating,[1,2,6-8] or by the combination of chemical and thermal treatments.[6,7] As a rule, the commercial products of polyimides, represented by KAPTON®,[9] are manufactured by this two-step conversion technique.

Recently, it has been found that the soluble polyimides with large molecular weights sufficient to form strong films and fibers can be produced in a single step, when 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA)[10] is allowed to react in a phenolic solvent with aromatic diamines such as 4,4'-diaminodiphenyl ether.[11] The conversion to polyimides is completed in the solution without producing precipitation.[11] Polyimide films or fibers can be produced directly by casting or spinning of this solution, as is the case for the manufacture of UPILEX®.[12]

The higher solubility of polyimides based on BPDA may be due to the

* Correspondence should be addressed to this author.

CCC 0021-8995/86/013133-17$04.00

presence of a single bond between two benzene rings of BPDA, which makes the polyimide molecules more flexible than the chains based on pyromellitic dianhydride (PMDA). In the present study, the polyimides in which BPDA is the main constituent of dianhydrides are prepared by the one-step polycondensation process. Three series of polymides based on BPDA are synthesized for spinning into fibers.

Series I. o-Tolidine (3,3'-dimethyl-4,4'-diaminobiphenyl) (OTOL) is a diamine component and BPDA is a main component of dianhydrides. A part of BPDA can be replaced by PMDA within a limit of 50 mol%. Higher replacement gives rise to the precipitation of resulting polyimide in the course of polycondensation and makes it impossible to prepare a high-molecular weight polymer. The polyimides of this series are denoted, for instance, by BPDA/PMDA(6/4)-OTOL, and so forth. The figures in parentheses show the molar ratio.

Series II. 3,4'-Diaminodiphenyl ether (DADE) is used as a diamine component, instead of OTOL of Series I. A part of BPDA can be replaced by PMDA, as in the case of Series I, but the replacement is limited to 30 mol%, because at higher replacement the polymer deposits before a desired molecular weight is reached. The polyimides of this series are denoted, for instance, by BPDA/PMDA(7/3)-DADE, and so forth.

Series III. The diamine component is DADE or the mixtures of DADE and 1,4-phenylenediamine (DABZ), BPDA being the common dianhydride component. Since DABZ has no flexible bond like PMDA, the maximum content of DABZ in the mixtures of diamines is limited to 50 mol%. The polyimides of this series are denoted, for instance, by BPDA-DADE/DABZ(8/2), and so forth.

The monomeric units constructing the molecular chains of polyimides of three series are given by the structural formulae in Figure 1.

SYNTHESIS

The conditions of synthesis and the inherent viscosities of the polyimides of Series I are listed in Table I. The symbol P-I means the polyimides of Series I. The polyimides are numbered from 1 to 7 in decreasing order of BPDA/PMDA molar ratio.

The result of one-step polycondensation depends largely on the solvent. Needless to say, the solvent should be inert to the monomers and the polymers. Furthermore, it should have powerful solvent action both on the monomers and on the polymers. Particularly, the solvent should exhibit a strong dissolving power to polyimides with high molecular weights. Otherwise, the polyimide deposits from the reaction mixture before it grows to maturity and the one-step preparation fails for the want of solvent action. As a result of a series of experiments, some of the phenolic substances were found to be useful solvents in this regard. For the evaluation of solvents, BPDA/PMDA(6/4)-OTOL was synthesized in various solvents and the inherent viscosities of resulted polyimides were measured. Here, the inherent viscosity is a good indication of molecular weight of polymer and serves as an index of the suitability of solvent. Table II shows the inherent viscosities of polyimides prepared with various solvents. The polyimides were synthe-

Series I

10 - N   10   N

Series II

10 - N   10,   N

Series III

10 - N   10   N

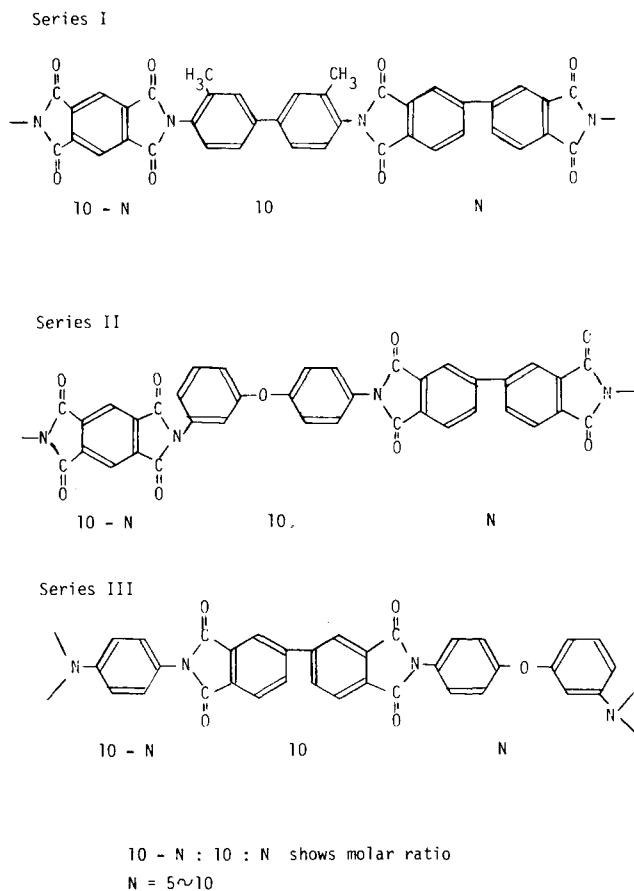10 - N : 10 : N   shows molar ratio

N = 5~10

Fig. 1. Structural formulae of monomeric units constructing polyimides of Series I, II, and III.

sized under the same conditions except for the solvents used. The solutions containing equimolar diamine (OTOL) and dianhydrides (BPDA/PMDA) with a total monomer concentration of 6 wt% were heated at 180°C for 11 h for polycondensation.

As can be deduced from Table II, phenol, p-chlorophenol, m-cresol, p-cresol, and 2,4-dichlorophenol are among the most suitable solvents, while o-chlorophenol and p-methoxyphenol cannot be used because low-molecular polyimide precipitates in the course of polycondensation. N-Methyl-2-pyrrolidone which is one of the typical solvents in use in the two-step method is also unsuitable for the same reason.

The catalytic formation of polyimides in the presence of carboxylic acids, such as formic acid, acetic acid, benzoic acid, and substituted derivatives of benzoic acid, is reported in a series of Russian literature.[13-16] The polyimides of Series I can be prepared without a catalyst within a reasonable time of reaction, as shown in Table I, but of interest is the effect of carboxylic acids on the synthesis of this type of polyimides. BPDA/PMDA(6/4)-OTOL was prepared with equal molarity of dianhydrides (BPDA/PMDA) and diamine (OTOL) in the presence of benzoic acid and some of its derivatives

TABLE I

Conditions of Synthesis and Inherent Viscosities of Polyimides of Series I

| Polyimide | Molar ratio of monomers | | | Solvent | Monomer concentration wt%[a] | Polycondensation | | η_{inh} dL/g |
	Diamine OTOL	Dianhydrides BPDA	PMDA			Temp. °C	Time h	
P-I,1	10	10	0	Phenol	10	185	5.5	2.74
P-I,2	10	9	1	Phenol	8	185	4.0	3.48
P-I,3	10	8	2	m- and p-Cresol (1:1)	10	185	9.0	3.63
P-I,4	10	7	3	p-Chlorophenol	10	195	7.0	5.26
P-I,5	10	6	4	Phenol	8	185	10.0	3.59
P-I,6	10	5	5	Phenol	12	185	2.3	3.32
P-I,7[b]	10	4	6	Phenol	8	185	4.0	2.32

[a] Percentage of total weight of monomers to weight of reaction mixture.
[b] Precipitation took place. This sample was not subjected to fiber spinning.

TABLE II
Inherent Viscosity of BPDA/PMDA(6/4)-OTOL Prepared in Different Solvents Under
Otherwise the Same Conditions

Solvent	η_{inh} dL/g	Notes
Phenol	3.06	Homogenous
p-Chlorophenol	2.88	"
m-Cresol	2.69	"
p-Cresol	3.34	"
2,4-Dichlorophenol	3.17	"
o-Chlorophenol	1.60	Precipitation
p-Methoxyphenol	1.84	"
N-Methyl-2-pyrrolidone	1.59	"

in a molar ratio, additive/OTOL = 2.5. The polycondensation was performed in phenol at 180°C for 2 h with a monomer concentration of 6 wt%. The inherent viscosities of resulted polyimides are listed in Table III.

It can be seen from the table that the carboxylic acids are really effective accelerators for the polycondensation. Most active is p-hydroxybenzoic acid. The ester is quite ineffective.

The catalytic effect is related to the dissociation constant or the acidity of carboxylic acid in such a manner that the inherent viscosity of resulting polyimide decreases with increased acidity of carboxylic acid.[16] For the preparation of polyimides containing six-membered imide rings, benzoic acid proved to be the most efficient catalyst and yielded the product with the biggest inherent viscosity. The substitution of benzoic acid with some groups, either electron donating or accepting, resulted in the reduction of catalytic effect.[15] Since the substituted derivatives used in this experiment have mostly smaller values of pK_a than that of unsubstituted benzoic acid, it follows that the increase in acidity of carboxylic acid leads to the reduction of inherent viscosity of polyimide. In our experiment, shown in Table III also, the inherent viscosity of polyimide decreases with decreased pK_a, namely with increase in acidity, in agreement with the results of studies quoted above.

In relation to the mechanism of catalytic effect of carboxylic acids on polyimide formation, reference must be made first to the report describing that the acylation of aromatic amines by acid anhydride is eminently accelerated by carboxylic acids such as acetic acid, monochloroacetic acid,

TABLE III
Effect of Carboxylic Acids on Inherent Viscosity of BPDA/PMDA(6/4)-OTOL. pK_a Values
of Carboxylic Acids are Given

Carboxylic acids	η_{inh} dL/g	pK_a
p-Hydroxybenzoic acid	4.83	4.48
Benzoic acid	3.21	4.19
Salicylic acid	2.64	2.97
Methyl salicylate	0.92	—
No additive	0.93	—

trichloroacetic acid, and benzoic acid.[17] The kinetic study published later on the acylation of aniline with phthalic anhydride shows that the rate of reaction of amic acid formation is remarkably enhanced by benzoic acid.[18] In accordance with the results of these studies, it is assumed that carboxylic acids accelerate the formation of polyamic acid by facilitating the cleavage of anhydride rings to react with aromatic diamine.[14,16] However, this assumption based on the formation of small-molecular acylated compounds is not without dispute, because a series of experiments on the formation of polyimide in the presence of p-hydroxybenzoic acid brings about a different result, as will be illustrated below.

BPDA/PMDA(6/4)-OTOL was prepared according to three different methods, with the equimolar mixture of diamine (OTOL) and dianhydrides (BPDA/PMDA) using p-chlorophenol as a solvent. The total content of monomers in the solution was 6 wt%. In the first experiment, p-hydroxybenzoic acid was added to the mixture from the beginning so as to make the CO_2H/OTOL molar ratio 1.25. In the second experiment, p-hydroxybenzoic acid was added in the same molar ratio to the mixture after the polyamic acid had been produced, and the third experiment was performed without p-hydroxybenozic acid throughout.

Each experiment was done on the same scheme. The reaction mixture was heated primarily at 60°C for 2 h to produce the polyamic acid. The product at this stage was separated from a weighed aliquot of reaction mixture. The precipitation of the product took place quantitatively when the mixture was poured into a large quantity of methanol. The inherent viscosity and infrared (IR) spectrum of this primary product were measured. Then, the rest of mixture was heated up to 180°C and kept at this temperature for 2 h and the product was precipitated from another aliquot of mixture in the same manner as above, and the inherent viscosity of precipitate was measured. The heating at 180°C continued for an additional 2 h and the product was precipitated from the remainder of mixture, and the inherent viscosity and IR spectrum were measured on this final product.

The inherent viscosities of the products at various stages of reaction are plotted in Figure 2. Curves A, B, and C refer to the results of the first, the second, and the third experiment, respectively.

Figures 3 and 4 reproduce the IR spectra of the primary and the final product, respectively.

The IR spectrum of the primary product (Fig. 3) exhibits the strong absorption of well known Amide-I, II, and III bands at wave numbers of 1,650, 1,520 and 1,300 cm^{-1}, respectively, but the bands due to cyclic imide groups, marked with arrows on the chart, are very weak. The spectrum indicates, therefore, that the primary product consists mostly of the polyamic acid, and the content of the polyimide is very little, if any. On the other hand, the spectrum of the final product (Fig. 4) shows no absorption at the wave numbers at which Amide-I, II, and III bands appeared, but exhibits, as marked on the chart, strong bands at 1,770 and 1,718 cm^{-1} which are assigned to the stretch vibration of C=O linkages of cyclic polyimide groups and a strong band at 1,370 cm^{-1} which is due to the C-N stretch vibration of cyclic polyimide groups.[19,20] It can be deduced from the spectra that the primary product obtained at 60°C is mostly the polyamic acid and the final
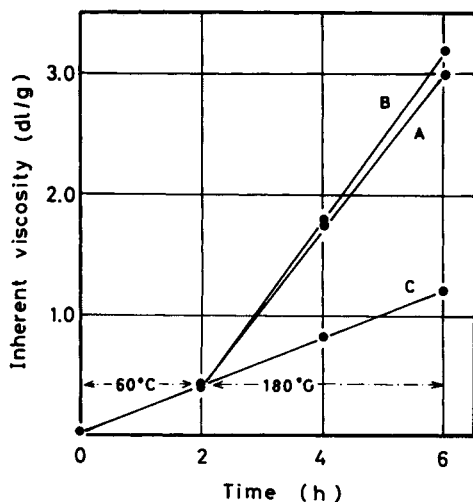
Fig. 2.   Inherent viscosities of products at various stages in synthesis of BPDA/PMDA(6/4)-OTOL. A: p-Hydroxybenzoic acid was present from the beginning. B: p-Hydroxybenzoic acid was added after reaction mixture had been heated at 60°C for 2 h. C: No catalyst throughout.

product, generated by heating at 180°C, consists almost purely of the polyimide.

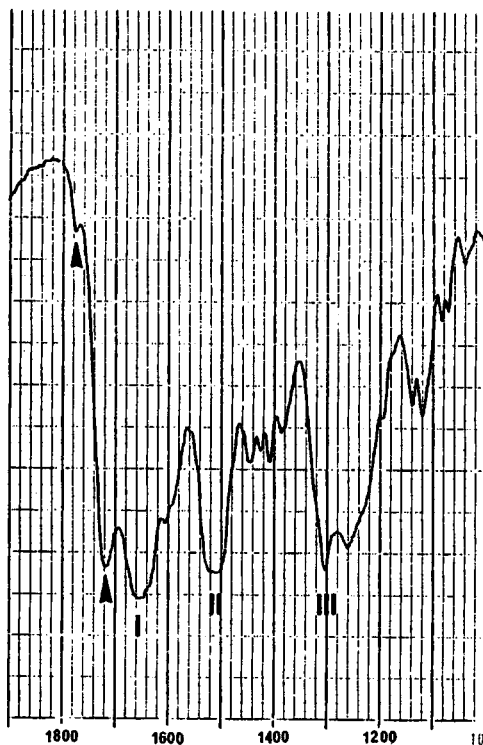Now, the comparison of three curves, A, B, and C, in Figure 2 indicates that the polyamic acid is produced in quite the same manner either from

Fig. 3.   IR spectrum of product obtained from reaction mixture heated at 60°C for 2 h.
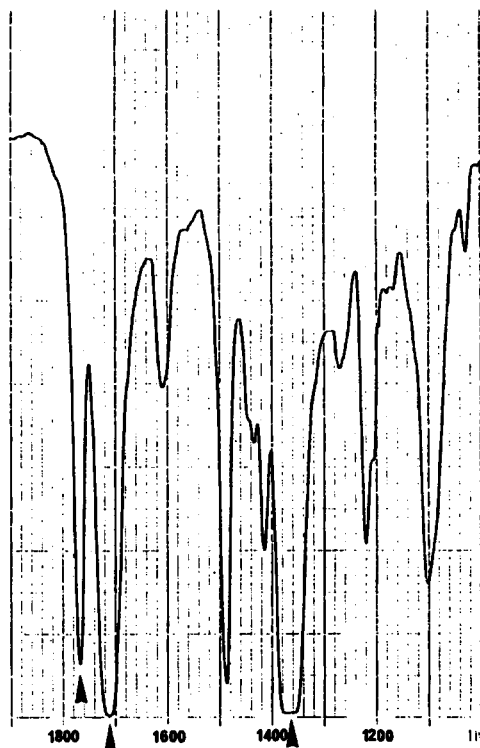
Fig. 4. IR spectrum of product obtained from reaction mixture heated at 180°C for 4 h after it had been heated at 60°C for 2 h.

the reaction mixture containing p-hydroxybenzoic acid (Curve A) or from the reaction mixtures free from p-hydroxybenzoic acid (Curves B and C). Therefore, the assumption that the carboxylic acid accelerates the formation of polyamic acid is not plausible. It can be seen, on the contrary, that p-hydroxybenzoic acid strongly accelerates the later stage of reaction that takes place at 180°C, as deduced from the comparison of Curves A and B with C. It is interesting to see that the p-hydroxybenzoic acid which was present from the first and the p-hydroxybenzoic acid that was added after the polyamic acid had been produced, have practically the same accelerating effect on the conversion of polyamic acid to polyimide, as can be deduced from the similarity between Curves A and B. This means that carboxylic acid is effective on the reaction of cyclodehydration of polyamic acid to convert it into polyimide, in contrast to the published opinion that the catalytic effect is attributable to the acceleration of polyamic acid formation.

It is reported that the catalytic effect of carboxylic acid is weakened when the CO_2H/diamine molar ratio exceeds an optimum value.[13,15,16] According to the literature, the optimum molar ratio differs greatly in different types of polyimides. For instance, for the catalytic effect of benzoic acid, optimum CO_2H/diamine molar ratios of 2.5 and 0.65 are reported with respect to the preparations of two different polyimides.[13,15] Contrary to these findings, the inherent viscosities of BPDA/PMDA(6/4)-OTOL polyimides prepared from reaction mixtures with added p-hydroxybenzoic acid in molar ratios

of CO_2H/OTOL ranging from 0.1 to 20 increase steadily with increase in the molar ratio, although the rate of increase slows down at high contents of p-hydroxybenzoic acid. The result is graphically shown in Figure 5 which plots the inherent viscosity against the molar ratio of p-hydroxybenzoic acid/OTOL.

The conditions of preparation of polyimides of Series II are tabulated in Table IV together with the inherent viscosities of the resulted polyimides. The polyimides of this series are denoted by P-II and numbered from 1 to 5 in decreasing order of BPDA/PDMA molar ratio. The polyimides of Series II with large inherent viscosities, sufficient to make strong fibers could be formed only in the presence of accelerators, because DADE reacted with BPDA and PMDA less actively than OTOL. It was found by the experiments that p-hydroxybenzoic acid is a good accelerator for the preparation of polyimides of Series II. Even in the presence of this accelerator, however, the reaction mixtures with BPDA/PMDA molar ratios of 6/4 and 5/5 produced only low-molecular polyimides which were precipitated from the solution in the course of polycondensation. Therefore, the polyimides made from these reaction mixtures could not be submitted to the spinning tests. Only the polyimides made from the reaction mixtures with BPDA/PMDA molar ratios of 9/1, 8/2, and 7/3 were subjected to the fiber spinning.

The polyimides of Series III were synthesized under the conditions shown in Table V. The polyimides are denoted by P-III and numbered from 1 to 7 in decreasing order of DADE/DABZ molar ratio. The inherent viscosities of the polyimides are listed in the last but one column of this table. As in the case of the polyimides of Series II, the presence of p-hydroxybenzoic acid was necessary for the preparation of the products with sufficiently large inherent viscosities.

It is interesting to see throughout the experiments that p-hydroxybenzoic acid which has not yet been referred to in the literature is a good accelerator for the polyimide formation. Figure 6 depicts the effect of p-hydroxybenzoic
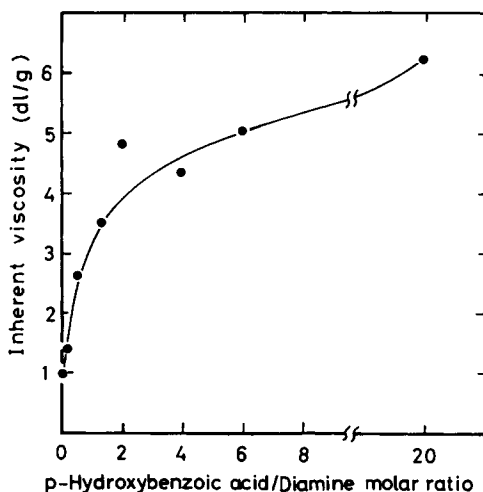

Fig. 5.   Inherent viscosity of BPDA/PMDA(6/4)-OTOL prepared in the presence of p-hydroxybenzoic acid as a function of p-hydroxybenzoic acid/diamine molar ratio.

TABLE IV
Conditions of Synthesis and Inherent Viscosities of Polyimides of Series II

Polyimide	Molar ratio of monomers			Solvent	Monomer concentration wt%	P-HBA[a] CO_2H/ DADE molar ratio	Polycondensation		η_{inh} dL/g	Notes
	Diamine	Dianhydrides					Temp. °C	Time h		
	DADE	BPDA	PMDA							
P-II,1	10	9	1	Phenol	5.0	2.5	175	69	2.13	h[b]
P-II,2	10	8	2	Phenol	5.0	2.0	175	43	2.25	h
P-II,3	10	7	3	Phenol	6.0	2.5	175	30	1.96	t[c]
P-II,4[e]	10	6	4	Phenol	5.0	2.5	175	70	0.73	ppt[d]
P-II,5[e]	10	5	5	Phenol	5.0	2.5	175	132	0.53	ppt

[a] p-Hydroxybenzoic acid
[b] Reaction mixture was homogeneous.
[c] Reaction mixture became turbid.
[d] Precipitation took place.
[e] Were not subjected to fiber spinning.

TABLE V
Conditions of Synthesis and Inherent Viscosities of Polyimides of Series III

Polyimide	Molar ratio of monomers			Solvent	Monomer concentration wt%	P-HBA[a] CO$_2$H/ BPDA molar ratio	Polycondensation		η_{inh} dL/g	Notes
	Diamines		Dianhydride				Temp. °C	Time h		
	DADE	DABZ	BPDA							
P-III,1	10	0	10	Phenol	6.0	2.0	175	70	2.63	h[b]
P-III,2	9	1	10	Phenol	7.0	2.0	175	45	2.11	h
P-III,3	8	2	10	Phenol	6.0	2.0	175	19	2.36	h
P-III,4	7	3	10	Phenol	6.0	2.5	175	32	2.81	h
P-III,5	6	4	10	Phenol	5.0	2.0	175	66	2.37	h
P-III,6	5	5	10	Phenol	5.0	2.0	175	63	2.27	t[c]
P-III,7[e]	4	6	10	Phenol	5.0	2.0	175	120	2.26	ppt[d]

[a] p-Hydroxybenzoic acid
[b] Reaction mixture was homogeneous.
[c] Reaction mixture became turbid.
[d] Precipitation took place.
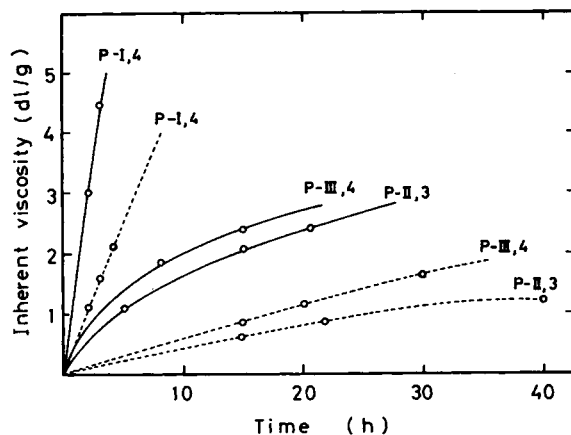[e] Was not subjected to fiber spinning.

Fig. 6. Effect of p-hydroxybenzoic acid on inherent viscosities of BPDA/PMDA(7/3)-OTOL (P-I,4), BPDA/PMDA(7/3)-DADE (P-II,3), and BPDA-DADE/DABZ(7/3) (P-III,4). Solid lines: p-Hydroxybenzoic acid/diamine(s) molar ratio 2.5. Broken lines: No catalyst.

acid on the production of typical polyimides of Series I, II, and III. In the figure, the inherent viscosities are plotted against the time of reaction. The solid lines show the inherent viscosities of polyimides prepared in the presence of p-hydroxybenzoic acid in a CO_2H/diamine(s) molar ratio of 2.5, and the broken lines show the inherent viscosities of polyimides prepared in the absence of p-hydroxybenzoic acid. All of the polyimides were prepared in phenol with equimolar mixtures of dianhydride(s) and diamine(s) at 180°C. The concentration of monomers was 6 wt% in total. It can be seen in Figure 6 that the rate of reaction of polyimide formation can be arranged in decreasing order: Series I > Series III > Series II. Only the polyimides of Series I can be prepared without accelerator.

EXPERIEMTAL

Polyimides

Preparation of BPDA/PMDA(6/4)-OTOL [An Example of the Polyimides of Series I. (Ref. P-I,5 in Table I.)]

A four-necked 300-ml flask equipped with a stirrer, nirogen inlet, and outlet tubes and a reagent inlet tube was purged with dry nitrogen and charged with 5.9999 g (0.0204 mole) of BPDA, 2.9665 g (0.0136 mole) of PMDA, and 186.1 g of phenol. The flask was warmed at 60°C in an oil bath with stirring for 1 h. To the mixture was added 7.2176 g (0.0340 mole) of OTOL and the contents of flask were stirred for 2 h at 60°C. The total weight of the reactant monomers (i.e., BPDA, PMDA and OTOL), amounted to 8% of the weight of solution. Next, the bath was warmed gradually up to 185°C over about 1 h. As the temperature increased, the mixture in the flask turned to the homogeneous solution with a light brown color. The heating continued for 10 h with stirring in the flow of nitrogen, by which the water liberated by polycondensation was removed. The viscosity of the solution

increased with time, but there no precipitation took place throughout the entire stage of reaction. Then, the solution was allowed to cool and poured into a large quantity of methanol in which the polyimide deposited as a yellow product. The precipitate was separated by filtration, washed, and pulverized in methanol with the aid of a powerful blender. The polyimide powder was filtered off again and vacuum dried at 100°C. A 100% yield of polymer with an inherent viscosity of 3.59 dL/g was obtained.

$C_{27.6}H_{16.4}N_2O_4$
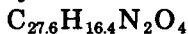
Calc.	C 75.33	H 3.76	N 6.37	O 14.54
Found	C 75.07	H 3.83	N 6.15	O 14.95

The IR spectrum is similar to that shown in Figure 4 and exhibits the bands characteristics of cyclic imide groups, but no band of amide groups is seen.

Preparation of BPDA/PMDA(7/3)-DADE [An Example of the Polyimides of Series II (Ref. P-II,3 in Table IV)]

The same flask as described above was charged with 5.1489 g (0.0175 mole) of BPDA and 1.6359 g (0.0075 mole) of PMDA and 176.1 g of phenol. The flask was warmed at 60°C to dissolve the dianhydrides. To the solution was added 5.0061 g (0.0250 mole) of DADE, and the mixture was stirred for 1.5 h. At this point, 8.6250 g (0.0625 mole) of *p*-hydroxybenzoic acid was added. The total weight of reactant monomers is 6% of the total weight of solution and the *p*-hydroxybenzoic acid/DADE molar ratio is 2.5. Next, the contents of the flask were warmed to 175°C over about 1 h and kept at this temperature for 30 h with stirring under the flow of dry nitrogen. The solution became turbid on heating, but no precipitation took place. The polyimide was separated in the same way as in the preceding case. The yield was quantitative and the inherent viscosity was 1.96 dL/g

$C_{26.2}H_{12.8}N_2O_5$
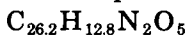
Calc.	C 72.24.	H 2.96	N 6.43	O 18.37
Found	C 72.51	H 3.09	N 6.43	O 17.97

The IR spectrum of the polyimide is shown in Figure 7. The strong bands characteristic of aromatic polyimidies are seen at 1,770, 1,718 and 1,370 cm^{-1}, as was the case with BPDA/PMDA(6/4)-OTOL, while the bands characteristic of aromatic amides are missing.

Preparation of BPDA-DADE/DABZ(7/3) [An Example of the Polyimides of Series III (Ref. P-III,4 in Table V)]

BPDA, 7.3555 g (0.0250 mole), was dissolved in 174.2 g of phenol in the same flask as described before. To the solution was added DADE, 3.5025 g (0.0175 mole), and DABZ, 0.8111 g (0.0075) mole). After the mixture had been stirred at 60°C for 1.5 h, *p*-hydroxybenzoic acid, 8.6250 g (0.0625 mole), was added. The total weight of BPDA, DADE, and DABZ in the solution is 6% of the weight of solution and the *p*-hydroxybenzoic acid/BPDA molar ratio is 2.5. The temperature was raised up to 175°C in about 1 h, and the reaction mixture was kept at this temperature for 32 h with stirring under the flow of dry nitrogen to complete the conversion to polyimide. The solution was homogeneous throughout the entire period of heating. The polyimide was separated in the same manner as stated previously. The yield
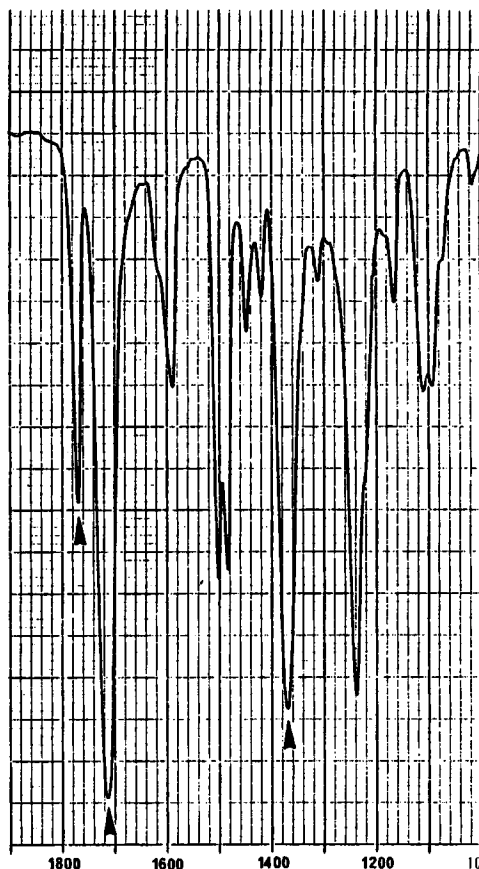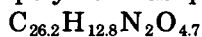
Fig. 7.   IR spectrum of BPDA/PMDA(7/3)-DADE.

of polymer was quantitative and the inherent viscosity was 2.81 dL/g

$C_{26.2}H_{12.8}N_2O_{4.7}$

Calc.	C 73.04	H 3.00	N 6.50	O 17.45
Found	C 73.22	H 3.12	N 6.53	O 17.13

Figure 8 shows the IR spectrum of BPDA-DADE/DABZ(7/3). The strong bands characteristic of aromatic polyimides are present at 1,770, 1,718, and 1,370 cm^{-1}, as was the case for two previous examples of polyimides. The bands assignable to aromatic polyamide groups are missing.

Materials

Dianhydrides

BPDA. The industrial product of 3,3',4,4'-biphenyltetracarboxylic dianhydride (Ube Industries, Ltd.) was used without further purification. T_m 302-306°C. A sharp peak is seen at 304°C in DSC curve (Itatani et al.,[21] T_m 295-308°C).

$C_{16}H_6O_6$
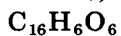
Calc.	C 65.32	H 2.05	O 32.63
Found	C 65.30	H 2.00	O 32.70

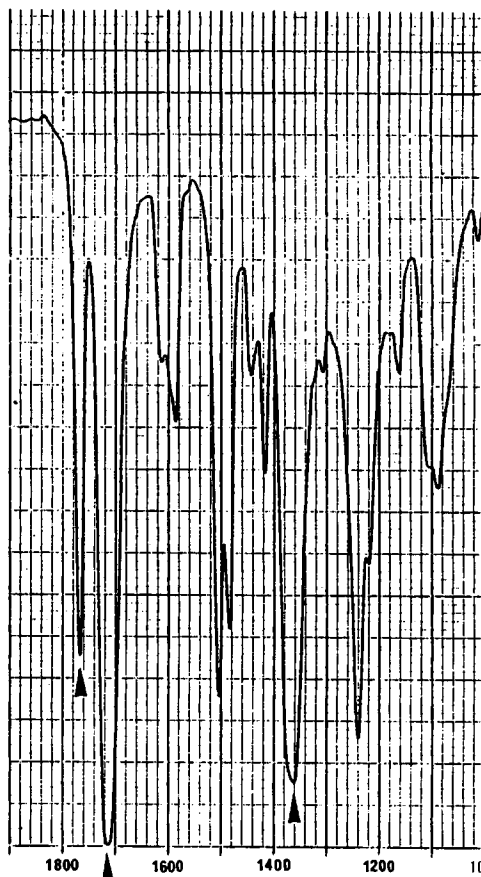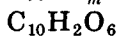**PMDA.** Commerically available pyromellitic dianhydride (Tokyo Kasei

Fig. 8.   IR spectrum of BPDA-DADE/DABZ(7/3).

Co., EP-grade) was purified by sublimation at 240°C/1 mmHg. Yield about
100%. T_m 274.2-275.6°C (Merck Index, T_m 276°C).
$C_{10}H_2O_6$

|			
Calc.	C 55.07	H 0.92	O 44.01
Found	C 54.90	H 0.98	O 44.12

Diamines

OTOL. Commercially available o-tolidine (Kanto Kagaku Co., special
grade) was recrystallized twice from ethanol. Yield 72.6%. T_m 127.4-129.6°C
(Merck Index, T_m 129-131°C).
$C_{14}H_{16}N_2$
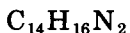
|			
Calc.	C 79.21	H 7.60	N 13.19
Found	C 79.19	H 7.67	N 13.14

DADE. 3,4'-Diaminidiphenyl ether for industrial use (Wakayama Seika
Kōgyo Co.) was purified by distillation at 220-225°C/1 mmHg. T_m 83.0-83.4°C
$C_{12}H_{12}N_2O$
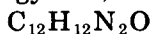
Calc.	C 71.98	H 6.04	N 13.99	O 7.99
Found	C 71.72	H 6.00	N 14.00	O 8.28

DABZ. Commercially available p-phenylenediamine (Yoneyama Yaku-

hin Co., EP grade) was distilled at 180°C/30 mmHg using a Vigreux column. The forerun and residue on distillation were rejected. Yield about 90%.

$C_6H_8N_2$
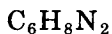
Calc.	C 66.64	H 7.46	N 25.90
Found	C 66.75	H 7.29	N 25.96

Solvents

Phenol. Commercially available phenol (Tokyo Kasei Co., special grade) was distilled under atmospheric pressure. The distillate collected in a narrow range of temperatures from 183.2°C to 183.7°C was used. The forerun and residue on distillation, about 10% of the whole, were rejected.

pChlorophenol. The distillate collected at 102.3–102.8°C/10 mmHg from a commercial reagent (Tokyo Kasei Co., special grade) was used.

o-Chlorophenol. Commerically available o-chlorophenol (Tokyo Kasei Co., Ep grade) was distilled at 76.1–78.0°C/23–26 mmHg.

2,4-Dichlorophenol. Commercially available reagent (Tokyo Kasei Co., special grade) was distilled under a reduced pressure of 20 mmHg and the distillate collected at 79.0-80.5°C was used.

o-Cresol. Commerically available o-cresol (Tokyo Kasei Co., special grade) was distilled under normal pressure and distillate was collected at temperature ranging from 191.5 to 192.9°C.

m-Cresol. The distillate collected at 113°C/31 mmHg from commercially available reagent (Tokyo Kasei Co., special grade) was used.

p-Cresol. The distillate collected at 86.0°C/18 mmHg from commercially available reagent (Tokyo Kasei Co., special grade) was used.

p-Methoxyphenol. Commercially available reagent (Tokyo Kasei Co., special grade) was distilled at 111.7-112.2°C/4 mmHg.

N-Methyl-2-pyrrolidone. Commercially available reagent (Tokyo Kasei Co., special grade) was dehydrated with molecular sieves and distilled at 65.0°C/5 mmHg. The forerun and residue were rejected. Yield about 90%. Stored in a closet purged with dry nitrogen.

Additives Used as Accelerators

Benzoic acid. Commercially available benzoic acid (Kanto Kagaku Co., special grade) was recrystallized from ethanol. Yield 76.5%. T_m 121.6-122.6°C.

p-Hydroxybenzoic Acid. Commercially available p-hydroxybenzoic acid (Tokyo Kasei Co., special-grade) was recrystallized from ethanol. Yield 73.3%. T_m 213.5-214.3°C.

Salicylic Acid. Commercially available salicylic acid (Kanto Kagaku Co., special grade) was recrystallized from water. Yield 39%. T_m 156.2-158.1°C.

Methyl Salicyclate. Commercial reagent (Tokyo Kasei, Co., EP grade) was distilled at 81.5-82.0°C/5 mmH. The forerun and residue on distillation, about 10% of the whole, were rejected.

Inherent Viscosity

The relative viscosity (η) was measured with a capillary viscometer of Cannon-Fenske type on solution containing 0.5 g of polyimide in 100 ml of 100% sulfuric acid at 30°C. For the samples of polyamic acid, dimethyl

sulfoxide was used in place of sulfuric acid. Inherent viscosity (η_{inh}) defined as $\ln\eta/c$ is reported in deciliter per gram.

IR Spectrum

Films of polyimides 10-20 μm in thickness were prepared from the solution in p-chlorophenol and mounted on Hitachi, Infrared Spectrophotometer, 260-50. For the samples of polyamic acid, films were made from the solution in dimethyl sulfoxide.

References

1. G. M. Bower and L. W. Frost, *J. Polymer Sci.*, A1, 3135 (1963).
2. W. M. Edwards, U. S. Pat. 3,179,614 (1965) to E. I. du Pont de Nemours and Co.
3. A. L. Endrey, U. S. Pat. 3,179,630 (1965) to E. I. du Pont de Nemours and Co.
4. A. L. Endrey, U. S. Pat. 3,179,631 (1965) to E. I. du Pont de Nemours and Co.
5. A. L. Endrey, U. S. Pat. 3,179,632 (1965) to E. I. du Pont de Nemours and Co.
6. A. L. Endrey, U. S. Pat. 3,179,633 (1965) to E. I. du Pont de Nemours and Co.
7. W. M. Edwards, U. S. Pat. 3,179,634 (1965) to E. I. du Pont de Nemours and Co.
8. O. E. Sroog, A. L. Endrey, S. V. Abramo, C. E. Berr, W. M. Edwards, and K. L. Oliver, *J. Polymer Sci.*, A 3, 1373 (1965).
9. E. I. du Pont de Nemours and Co.
10. Polyimides based on BPDA are referred to in a series of Russian literture. N. A. Adrova, M. M. Koton, and E. M. Moskvina, *Doklady An SSSR*, 165, 1069 (1965); N. A. Adrova, M. I. Bessonov, L. A. Laius, and A. P. Rudakov, "Polyimides," Israel Program for Scientific Translation, Ltd., (1969); S. V. Vinogradova, Ya. S. Vygodskii, and V. V. Korshak, *Vysokomol. Soed.*, A 12, 1987 (1970).
11. Y. Sasaki, H. Inoue, I. Sasaki, H. Itatani, and M. Kashima, Ger. Offen, 2,945,139 (1980); U. S. Pat. 4,290,936 (1981); Brit. 2,037,305 (1981); JP Kokai Tokkyo Koho 56-38324 (1981) to Ube Industries, Ltd.
12. Ube Industries, Ltd.
13. V. V. Korshak, S. V. Vinogradova, Ya. S. Vygodskii, and S. V. Gerashchenko, Ger. Offen, 2,461,350 (1976), *Chem. Abstr.*, 85, 109176t (1979).
14. S. V. Vinogradova, Ya. S. Vygodskii, N. A. Churochkina, and V. V. Korshak, *Vysokomol. Soed.*, Ser. B, 19(2), 93 (1977)
15. V. V. Korshak, S. V. Vinogradova, and Ya. S. Vygodskii, *Faserforsch. Textiltech.*, 28(9), 439 (1977)
16. B. A. Zhubanov, G. I. Boiko, and R. F. Mukhamedova, *Izv. Akad. Nauk Kaz. SSR, Ser. Khim.*, 2, 53 (1981)
17. L. M. Litvinenko and D. M. Aleksandrova, *Ukr. Khim. Zh.*, 27, 634 (1961).
18. A. I. Sadovnikov and L. V. Kuritsyn, *Izv. Vyssh. Uchebn. Saved., Khim. Khim. Technol.*, 25(3), 275 (1982).
19. T. Nishizaki and A. Fukami, *Kogyokagaku Zasshi* (J. Chem. Soc., Japan, Ind. Chem. Sec.), 66, 382 (1963).
20. T. Nishizaki and A. Fukami, *Kogyokagaku Zasshi* (J. Chem. Soc., Japan, Ind. Chem. Sec.), 67, 474 (1964).
21. H. Itatani and H. Yoshimoto, *J. Org. Chem.*, 38, 76 (1973).