Preparation and Properties of Aromatic Polyimides from 2,2′-Bis(*p*-aminophenoxy)biphenyl or 2,2′-Bis(*p*-aminophenoxy)-1,1′-binaphthyl and Aromatic Tetracarboxylic Dianhydrides

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SYNOPSIS

New aromatic polyimides containing a biphenyl-2,2′-diyl or 1,1′-binaphthyl-2,2′-diyl unit were prepared by a conventional two-step method starting from 2,2′-bis(*p*-aminophenoxy)biphenyl or 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl and aromatic tetracarboxylic dianhydrides. The polyimides having inherent viscosities of 0.69–0.99 and 0.51–0.59 dL/g, respectively, were obtained. Some of these polymers were readily soluble in a variety of organic solvents including *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide, and pyridine. Transparent, flexible, and pale yellow to brown films of these polymers could be cast from the DMAc or NMP polyamic acid solutions. These aromatic polyimides containing biphenyl and binaphthyl units had glass transition temperatures in the range of 200–235 and 286–358°C, respectively. They began to lose weight around 380°C, with 10% weight loss being recorded at about 470°C in air. © 1993 John Wiley & Sons, Inc.

Keywords: 2,2′-bis(*p*-aminophenoxy)biphenyl • 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl • aromatic polyimides • solubility • thermal behavior

INTRODUCTION

The past decade of research on aromatic polyimides has been exemplified by attempts to improve the processing characteristics of these relatively intractable polymers due to insolubility in organic solvents and their extremely high glass transition, softening, or melting temperatures.[1,2] The excellent thermal and chemical stability of the wholly aromatic polyimides is generally attributed to the structural features of the polymers including the inert nature of the cyclic imide and aromatic groups. The initial method of overcoming intractability of the polyimides is the utilization of the polyamic acid stage, which could be fabricated into certain end-use forms by virtue of its good solubility in certain aprotic solvents. Subsequent cyclodehydration of the polyamic acid results in the polyimide form.

One of the successful approaches to increase solubility and processability of polyimides without sacrificing their high thermal stability is the introduction of bulky, pendant groups into the polymer backbone. Some organic-soluble polyimides have been demonstrated by using highly phenylated aromatic diamines such as 2,5-bis(*p*-aminophenyl)-3,4-diphenylthiophene,[3] 3,4-bis(*p*-aminophenyl)-2,5-diphenylfuran,[4] 3,4-bis(*p*-aminophenyl)-2,5-diphenylpyrrole,[5] and 4,4′-diaminotriphenylamine.[6] Our recent studies revealed that highly kinked and cranked aromatic diamines, 2,2′-bis(*p*-aminophenoxy)biphenyl (BBDA) and 2,2′-(*p*-aminophenoxy)-1,1′-binaphthyl (BNDA), were effectively used to prepare novel soluble aromatic polyamides through the polycondensation with aromatic diacid chlorides.[7] Therefore, these diamines, BBDA and BNDA, would be potential monomers for producing soluble aromatic polyimides with retention of high thermal stability.

This article deals with the synthesis of new soluble aromatic polyimides containing kink and crank

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Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 31, 3273–3279 (1993)

CCC 0887-624X/93/133273-07

biphenyl-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl units by the polymerization of BBDA and BNDA with aromatic tetracarboxylic dianhydrides through a conventional two-step method. The characteristics of polyimides such as solubility and thermal behavior are also discussed.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (**IIIa**), 3,3′,4,4′-biphenyltetracarboxylic dianhydride (**IIIb**), 4,4′-oxydiphthalic anhydride (**IIIc**), 4,4′-carbonyldiphthalic anhydride (**IIId**), and 4,4′-hexafluoroisopropylidenediphthalic anhydride (**IIIf**, supplied by Central Glass Co., Japan), were purified by sublimation. 4,4′-Sulfonyldiphthalic anhydride (**IIIe**, supplied by New Japan Chemical Co.), was used without further purification.

2,2′-Bis(*p*-aminophenoxy)biphenyl (**I**) and 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl (**II**) were prepared by the condensation of *p*-fluoronitrobenzene with biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl, respectively, followed by catalytic reduction of the dinitro compounds in dimethylformamide according to the previously reported procedure.[7]

N-methyl-2-pyrrolidone (NMP) and *N,N*-dimethylacetamide (DMAc) were purified by distillation over calcium hydride.

Polymer Synthesis

Polyimide VIIa *from* II *and* IIIa *by Two-Step Method*

To a solution of 1.171 g (2.5 mmol) of **II** in 10 mL of NMP, 0.545 g (2.5 mmol) of **IIIa** was added at once at 0–5°C under nitrogen. The solution was stirred at that temperature for 1 h and then at 20–25°C for 5 h. About a half volume of the reaction solution was poured into 300 mL of methanol. The precipitated polymer was collected by filtration and dried under vacuum at room temperature. The inherent viscosity of polyamic acid **VIa** was 0.64 dL/g, measured at a concentration of 0.5 g/dL in DMAc at 30°C.

The polyamic acid film was obtained by casting from the reaction solution onto a glass plate and drying at room temperature overnight under vacuum. The polyamic acid in the form of film was converted to polyimide **VIIa** by successive heating under vacuum at 100°C for 1 h, 200°C for 1 h, and then 300°C for 1 h. The inherent viscosity of **VIIa** was 0.58 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C. The infrared (IR) spectrum of **VIIa** (film) exhibited absorptions at 1779, 1717, 1367, and 725 cm^{-1}, characteristic of the imide group.

Other polyimides were prepared by analogous procedure.

Measurements

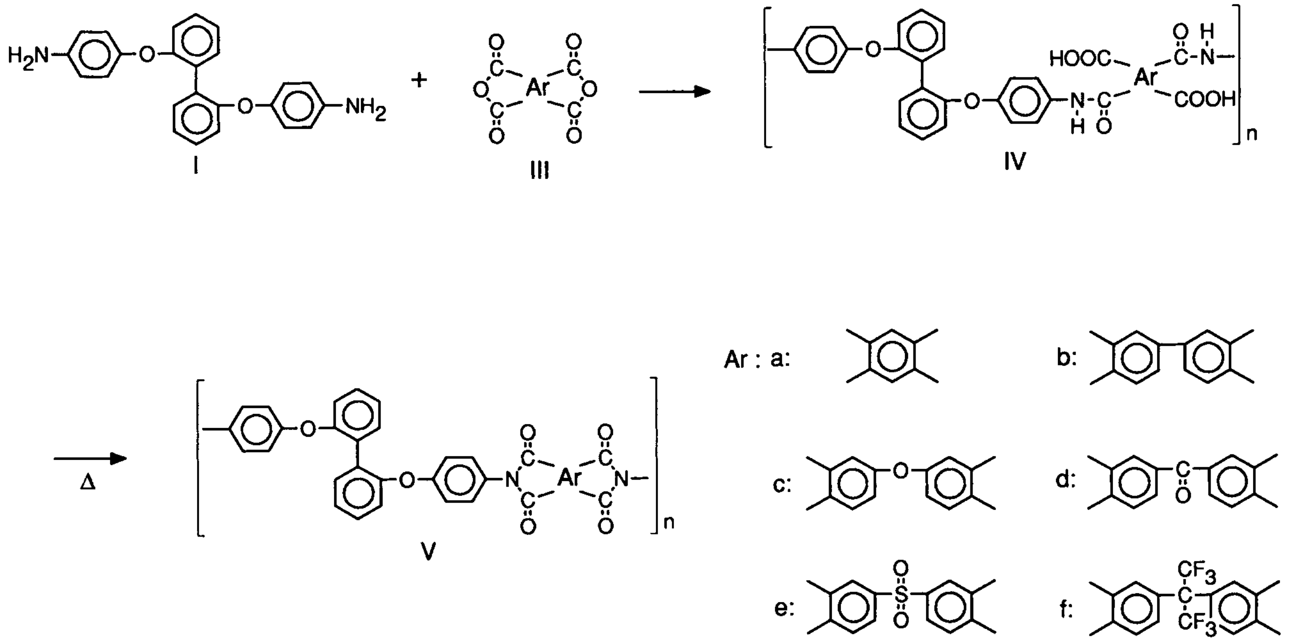
IR spectra were recorded on a JASCO FT/IR-5000 Fourier transform spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with DSC-41M and TGA-40M Shimadzu thermal analyzers, respectively. Wide-angle x-ray diffraction patterns were obtained at room temperature on a Rigakudenki RU-200 apparatus with nickel-filtered CuKα radiation (50 kV, 180 mA). Tensile properties were determined from stress–strain curves obtained with a Toyo Baldwin Tensilon UTM-III-20, and measurements were performed at room temperature using film specimens (about 0.1 mm thick, 1.0 cm wide, and 5.0 cm gauge length) at an elongation rate of 20%/min.

RESULTS AND DISCUSSION

Polymer Synthesis

The conventional two-step procedure starting from aromatic diamines and tetracarboxylic dianhydrides is a convenient method for the preparation of polyimides.[1,2] Biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing polyimides **V** and **VII** were synthesized by the two-step method starting from aromatic diamines **I** or **II** with aromatic tetracarboxylic dianhydrides **IIIa–IIIf** through the ring-opening polyaddition and subsequent thermal cyclodehydration (Schemes 1 and 2), and the results are summarized in Table I. All the ring-opening polyaddition in NMP at room temperature afforded polyamic acids **IV** and **VI** with inherent viscosities of 0.40–0.70 and 0.44–0.68 dL/g, respectively, suggesting the formation of moderate high molecular weight polymers. Transparent and flexible films of the polyamic acids could be obtained by casting from the resulting polymer solutions.

The thermal conversion to polyimides was carried out by successive heating of the polyamic acids in

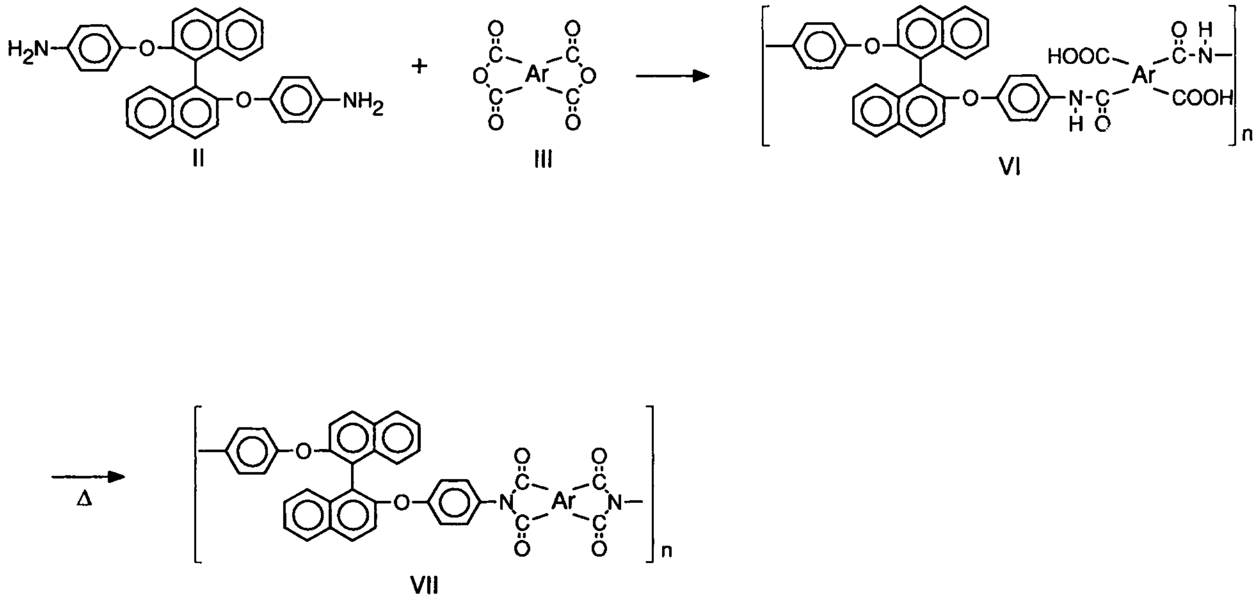


Scheme 1.

the form of films to 300°C under vacuum. The resultant polyimides **V** and **VII** having inherent viscosities of 0.69–0.99 and 0.51–0.59 dL/g, respectively, were successfully obtained. The formation of polyimides was confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these polyimides were in good agreement with the calculated values for the proposed structures (Table I). In the IR spectra, the polyimides showed characteristic imide absorptions at near 1780, 1720, 1370, and 725 cm^{-1}.

Polymer Characterization

The solubility behavior of the polyimides was studied qualitively, and the results are shown in Table II.



Scheme 2.

Table I. Synthesis of Polyimides[a]

Polyamic Acid		Polyimide					
					Elemental Analysis		
Code	η_{inh}[b] (dL/g)	Code	η_{inh}[c] (dL/g)		C (%)	H (%)	N (%)
IVa	0.70	**Va**	—	Calcd:	74.18	3.30	5.08
				Found:	74.28	3.22	5.11
IVb	0.58	**Vb**	0.77	Calcd:	76.67	3.54	4.47
				Found:	77.08	3.43	4.52
IVc	0.40	**Vc**	0.87	Calcd:	74.76	3.45	4.36
				Found:	74.60	3.24	4.47
IVd	0.43	**Vd**	—	Calcd:	75.23	3.39	4.28
				Found:	75.26	3.22	4.38
IVe	0.42	**Ve**	0.69	Calcd:	69.56	3.21	4.06
				Found:	69.76	3.09	4.03
IVf	0.46	**Vf**	0.99	Calcd:	66.50	2.86	3.61
				Found:	65.96	2.79	3.69
VIa	0.64	**VIIa**	0.58	Calcd:	77.53	3.41	4.30
				Found:	76.84	3.27	4.17
VIb	0.68	**VIIb**	0.56	Calcd:	79.33	3.60	3.85
				Found:	79.17	3.27	3.89
VIc	0.44	**VIIc**	0.53	Calcd:	77.62	3.53	3.77
				Found:	77.35	3.51	3.82
VId	0.55	**VIId**	0.55	Calcd:	77.98	3.47	3.71
				Found:	78.42	3.07	3.78
VIe	0.64	**VIIe**	0.59	Calcd:	72.90	3.31	3.54
				Found:	71.82	2.86	3.42
VIf	0.55	**VIIf**	0.51	Calcd:	69.87	2.99	3.20
				Found:	70.08	2.70	3.23

[a] Polymerization was carried out with 2.5 mmol of each monomer in 10 mL NMP at 0–5°C for 1 h, then at room temperature for 6 h under nitrogen atmosphere. Polyimide was obtained by heating polyamic acid at 100°C for 1 h, 200°C for 1 h, and then 300°C for 1 h under vacuum.

[b] Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

[c] Measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

Table II. Solubility of Polyimides[a]

	Polymer					
Solvent	**VIIe, VIIf**	**VIIc**	**Vc, Ve, Vf**	**VIIb, VIId, Vb**	**VIIa**	**Va, Vd**
Conc. sulfuric acid	++	++	++	++	++	−
N-methyl-2-pyrrolidone	++	++	++	−	−	−
Dimethylacetamide	++	++	++	−	−	−
Dimethylformamide	++	++	++	−	−	−
Pyridine	++	++	++	−	−	−
Dimethyl sulfoxide	++	+	−	−	−	−
m-Cresol	+	+	−	+	−	−
Acetone	−	−	−	−	−	−

[a] (++) Soluble at room temperature, (+) soluble on heating, (−) insoluble.

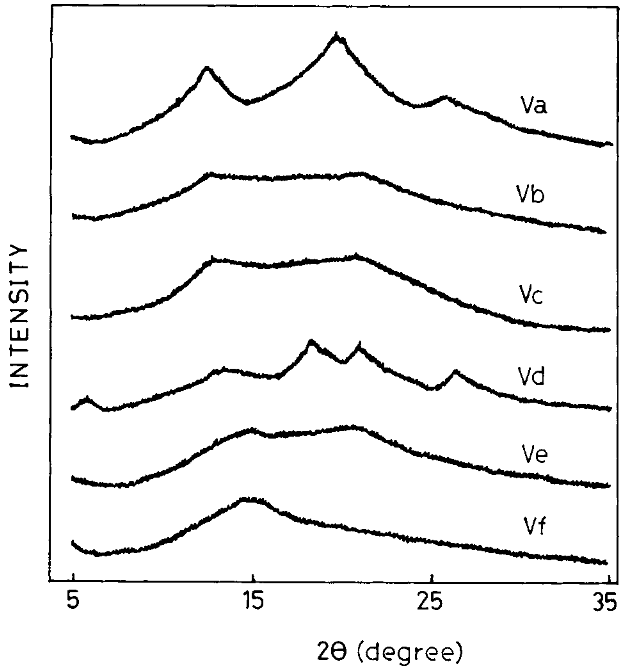


Figure 1. X-ray diffraction diagrams of polyimides V.

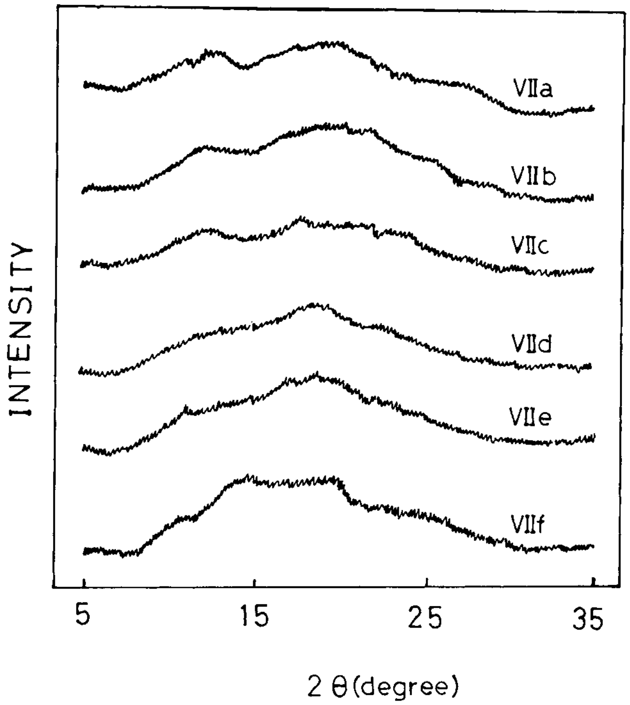


Figure 2. X-ray diffraction diagrams of polyimides VII.

Polyimides **Vc, Ve, Vf, VIIc, VIIe,** and **VIIf** were highly soluble in organic solvents such as NMP, DMAc, dimethylformamide, and pyridine. Thus, the solubility of polyimides was greatly improved by the introduction of a bulky, kinked, and cranked biphenyl-2,2′-diyl or 1,1′-binaphthyl-2,2′-diyl unit into the polymer backbone. The solubility studies also revealed that polyimides **VII** had better solubility than polyimides **V** in some organic solvents, in which the bulky effect of the binaphthyl structure was greater than that of the biphenyl.

The x-ray diffraction studies (Figs. 1 and 2) re-

Table III. Thermal Properties of Polyimides

Polymer	T_g[a] (°C)	T_d[b] (°C) In Air	T_d[b] (°C) In Nitrogen	T_{10}[b] (°C) In Air	T_{10}[b] (°C) In Nitrogen
Va	—	440	460	545	560
Vb	230	430	435	545	570
Vc	200	415	435	530	550
Vd	225	400	405	510	550
Ve	235	395	405	510	505
Vf	235	420	435	525	540
VIIa	358	420	430	535	565
VIIb	307	400	400	555	580
VIIc	290	400	400	535	570
VIId	286	420	450	510	555
VIIe	294	390	410	480	525
VIIf	292	380	440	490	555

[a] Determined by DSC at a heating rate of 20°C/min in nitrogen.

[b] T_d and T_{10} are temperatures of initial decomposition and 10% weight loss, respectively, measured by TG at a heating rate of 10°C/min.

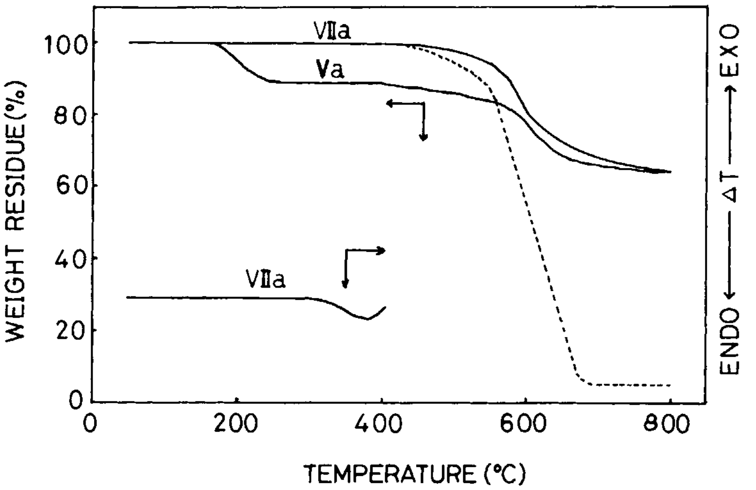


Figure 3. TG curves for polyamic acid **VIa** and polyimide **VIIa**: (· · ·) in air, and (—) in nitrogen, at a heating rate of 10°C/min. DSC curve of polyimide VIIa at a heating rate of 20°C/min.

vealed that polyimides **Va** and **Vd** had a fair degree of crystallinity, whereas all of the other polymers were amorphous. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, and this could be attributed to the introduction of a bulky biphenyl-2,2′-diyl or 1,1′-binaphthyl-2,2′-diyl unit along the polymer backbone.

The thermal behavior of the polymers was evaluated by DSC and TG. Figure 3 shows typical DSC and TG curves of polymer **VIIa,** and the thermal behavior data of the polymers are given in Table III. The glass transition temperatures (T_g) of polymers **V** and **VII** were observed in the range of 200–235 and 286–358°C, respectively, depending on the structure of dianhydride component, and decreased with decreasing rigidity of the polymer backbone. The T_gs of polyimides **VII** derived from **II** were ca. 60–70°C higher than those of the corresponding polyimides **V** derived from **I** due to the difference of rigidity between binaphthyl and biphenyl units. All the polymers were stable up to 380°C in both air and nitrogen atmospheres, and the temperatures at 10% weight loss were above 480°C on the TG curves. No obvious difference in thermal stability was observed between the biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing polyimides.

The mechanical properties of the aromatic polyimides films prepared by the two-step method are summarized in Table IV. The tensile strength, elongation at break, and tensile modulus of polyimides **V** films were 64–109 MPa, 2.3–4.6%, and 2.4–2.9 GPa, respectively, while polyimides **VII** films were too brittle to be measured.

Table IV. Mechanical Properties of Polyimides

	Polymer			
	Vb	**Vc**	**Ve**	**Vf**
Tensile strength (MPa)	109	94	64	80
Elongation at break (%)	3.6	4.6	2.3	3.3
Tensile modulus (GPa)	2.6	2.4	2.9	2.6

CONCLUSION

The introduction of bulky, kinked, and cranked biphenyl-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl units into the polyimide backbone improved solubility of the polymers in various organic solvents. Polyimide **VIIa** derived from 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl and pyromellitic dianhydride had glass transition temperature of 358°C, and polymers **VIIc, VIIe,** and **VIIf** also had T_gs near 300°C, with excellent solubility in various organic solvents. Thus, these polyimides are considered to be new promising processable high-temperature polymeric materials.

REFERENCES AND NOTES

1. M. I. Bessonov, M. M. Koton, V. V. Kudryavtsev, and L. A. Laius, *Polyimides: Thermal Stable Polymers,* Plenum, New York, 1984.
2. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., *Polyimides,* Chapman and Hall, New York, 1990.
3. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci. Polym. Chem. Ed.,* **22,** 2189 (1984).
4. H.-J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **29,** 39 (1991).
5. H.-J. Jeong, M. Kakimato, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **29,** 1691 (1991).
6. Y. Oishi, M. Ishida, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **30,** 1027 (1992).
7. G. S. Liou, M. Maruyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **31,** 2499 (1993).

Received February 19, 1993
Accepted May 19, 1993