Preparation and Properties of Aromatic Polyamides from 2,2′-Bis(*p*-aminophenoxy)biphenyl or 2,2′-Bis(*p*-aminophenoxy)-1,1′-Binaphthyl and Aromatic Dicarboxylic Acids

GUEY-SHENG LIOU, MASAKI MARUYAMA, MASA-AKI KAKIMOTO, and YOSHIO IMAI*

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

SYNOPSIS

New aromatic diamines having kink and crank structures, 2,2′-bis(*p*-aminophenoxy)biphenyl and 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl, were synthesized by the reaction of *p*-fluoronitrobenzene with biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl, respectively, followed by catalytic reduction. Biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing aromatic polyamides having inherent viscosities of 0.44–1.18 and 0.26–0.88 dL/g, respectively, were obtained either by the direct polycondensation or low-temperature solution polycondensation of the diamines with aromatic dicarboxylic acids (or diacid chlorides). These polymers were readily soluble in a variety of organic solvents including *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide, *m*-cresol, and pyridine. Transparent, pale yellow, and flexible films of these polymers could be cast from the DMAc or NMP solutions. These aromatic polyamides containing biphenyl and binaphthyl units had glass transition temperatures in the range of 215–255 and 266–303°C, respectively. They began to lose weight at ca. 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′-biphthyl • aromatic polyamides • solubility • thermal behavior

INTRODUCTION

It is well known that wholly aromatic polyamides (aramids) are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties.[1] Fabrication of most aramids, however, was extremely difficult because of their high melting temperatures or softening temperatures and their limited solubility in organic solvents.[1] Recently, new processable engineering plastics possessing moderately high glass transition temperatures and good solubility in organic solvents have been required in practical use, and a number of soluble high temperature aramids[2–8] as well as thermoplastic aramids[9] have been reported. One of the approaches to improve their processability is the introduction of bulky, rigid, and unsymmetrical units into the polymer backbone. We have already reported that the biphenyl-2,2′-diyl-containing polyamides derived from 2,2′-bibenzoic acid and various aromatic diamines increased solubility in various organic solvents with retention of moderately high thermal stability.[10] We also synthesized a series of biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing polyarylates derived from biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl, and various aromatic diacid chlorides,[11,12] and found that the 1,1′-binaphthyl-2,2′-diyl-containing polyarylates had higher glass transition temperatures (T_g) by ca. 50°C and better solubility than the biphenyl-2,2′-diyl-containing polyarylates. However, only a limited number of 1,1-binaphthyl-containing aromatic polyamides have been reported. Such examples are the aramids derived from 2,2′-diamino-1,1′-binaphthyl and terephthaloyl chloride, and from 1,1′-binaphthyl-2,2′-dicarbonyl chloride and *p*-phenylenediamine, which were characterized as chiral stationary phases for the direct separation of

* To whom all correspondence should be addressed.

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 31, 2499–2506 (1993)
 CCC 0887-624X/93/102499-08

enantiomers by high-performance liquid chromatography.[13,14] In this case, however, the polyamides were obtained with low viscosity values due to the steric hindrance of these binaphthyl monomers.

To avoid the steric hindrance, thereby leading to the formation of higher molecular weight polyamides, a new kinked and cranked aromatic diamine, 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl was synthesized in the present study. The structurally related aromatic diamine, 2,2′-bis(*p*-aminophenoxy)biphenyl, was also prepared for comparison. These two monomers were used to prepare novel aromatic polyamides either by the direct polycondensation or by the low-temperature solution polycondensation with various aromatic dicarboxylic acids or diacid chlorides.

EXPERIMENTAL

Materials

Reagent-grade aromatic dicarboxylic acids such as isophthalic acid (**IIIa**), terephthalic acid (**IIIb**), 2,6-naphthalenedicarboxylic acid (**IIIc**), 4,4′-biphenyldicarboxylic acid (**IIId**), 4,4′-oxydibenzoic acid (**IIIe**), 4,4′-sulfonyldibenzoic acid (**IIIf**), and phenylindanedicarboxylic acid (**IIIg**) were used as received. Commercial isophthaloyl chloride (**IVa**) and terephthaloyl chloride (**IVb**) were purified by distillation under reduced pressure before use. Other aromatic diacid chlorides were prepared by the reaction of the corresponding aromatic dicarboxylic acids with thionyl chloride in the presence of a few drops of dimethylformamide (DMF) as a catalyst. 2,6-Naphthalenedicarbonyl chloride (**IVc**) and 4,4′-biphenyldicarbonyl chloride (**IVd**) were purified by sublimation,[15,16] while 4,4′-oxydibenzoyl chloride (**IVe**) and 4,4′-sulfonyldibenzoyl chloride (**IVf**) were purified by distillation.[17]

N-Methyl-2-pyrrolidone (NMP), pyridine, and triphenyl phosphite were purified by distillation over calcium hydride. Lithium chloride was dried at 200°C under vacuum, and reagent-grade propylene oxide was used as received.

Monomer Synthesis

2,2′-Bis(p-aminophenoxy)biphenyl (BBDA) I

2,2′-Bis(*p*-nitrophenoxy)biphenyl (BBDN) was prepared by the condensation of *p*-fluoronitrobenzene with biphenyl-2,2′-diol. In a three-neck flask equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser, were placed 7.45 g (40 mmol) of biphenyl-2,2′-diol, 11.30 g (80.1 mmol) of *p*-fluoronitrobenzene, and 13 g (94 mmol) of dry potassium carbonate, 80 mL of NMP, and 40 mL of toluene. The mixture was stirred at around 140°C for 6 h under nitrogen to facilitate dehydration. After the toluene had been removed, the reaction was carried out with stirring at 160–170°C for 12 h. The reaction mixture was filtered, and then poured into 5 L of water. The brown precipitate was collected by filtration and dried under vacuum. The product was purified by recrystallization from ethanol to afford 9.78 g (57% yield) of yellow needles; mp 159–160°C. The infrared (IR) spectrum (KBr) exhibited absorptions at 1578 and 1346 cm^{-1} (NO_2). The ^{13}C-nuclear magnetic resonance (NMR) spectrum (DMSO-d_6) showed peaks δ at 163.72, 152.83, 143.30, 133.38, 131.38, 130.89, 127.15, 126.83, 121.95, and 118.38 ppm.

ANAL. Calcd for $C_{24}H_{16}N_2O_6$: C, 67.29%; H, 3.76%; N, 6.54%. Found: C, 67.10%; H, 3.61%; N, 6.54%.

I (BBDA) was synthesized according to modification of the Herz's method[18] by the catalytic reduction of the dinitro compound BBDN. A mixture of 12.25 g (30 mmol) of BBDN and 1.3 g of 10% palladium on carbon in 300 mL of 1,4-dioxane was stirred at 40°C under hydrogen until the theoretical amount of hydrogen was consumed. The time taken to reach this stage was ca. 30 h. The solution was filtered, and the filtrate was evaporated to remove the solvent. The product obtained after drying under vacuum was purified by recrystallization from ethanol to afford 5.33 g (51% yield) of yellow needles; mp 158–159°C. The IR spectrum (KBr) showed absorptions at 3368 and 3416 cm^{-1} (N—H). The ^1H-NMR spectrum (DMSO-d_6) showed peaks δ at 6.5–7.5 (16H, aromatic), and 4.6 ppm (4H, amino group). The ^{13}C-NMR spectrum (DMSO-d_6) showed peaks δ at 157.76, 147.69, 146.28, 132.84, 129.92, 129.59, 122.93, 122.01, 117.24, and 116.27 ppm.

ANAL. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24%; H, 5.47%; N, 7.60%. Found: C, 77.97%; H, 5.40%; N, 7.70%.

2,2′-Bis(p-aminophenoxy)-1,1′-binaphthyl (BNDA) II

2,2′-Dihydroxy-1,1′-binaphthyl was prepared by the oxidative coupling reaction of β-naphthol in solid state.[19] A mixture of 5.0 g of β-naphthol (35 mmol) and 19.0 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) (70 mmol) was finely powdered by using an agate mortar and a pestle. The mixture was then placed in a flask and allowed to react at 50°C for 2 h. The product was obtained by treating the

reaction mixture with dilute hydrochloric acid, and purified by recrystallization from toluene to give 3.0 g (60% yield) of pale pink needles; mp 217–218°C (lit.[19] mp 218–219°C).

2,2′-Bis(*p*-nitrophenoxy)-1,1′-binaphthyl (BNDN) was synthesized by the condensation of 2,2′-dihydroxy-1,1′-binaphthyl with *p*-fluoronitrobenzene. A mixture of 1.92 g (80 mmol) of sodium hydride in 80 mL of DMSO was stirred at room temperature. To the mixture 11.45 g (40 mmol) of 2,2′-dihydroxy-1,1′-binaphthyl and 11.29 g (80 mmol) of *p*-fluoronitrobenzene were added. The mixture was heated with stirring at 100°C for 12 h, and then precipitated into 2 L of cold water. The product was filtered and recrystallized from a mixture of benzene and hexane. The yield was 12.68 g (60%) of pale yellow crystalline powder; mp 196–197°C. The IR spectrum (KBr) exhibited absorptions at 1584 and 1342 cm^{-1} (NO_2). The ^{13}C-NMR spectrum (DMSO-d_6) showed peaks δ at 163.50, 150.99, 143.19, 134.58, 132.19, 129.70, 128.62, 126.88, 126.50, 123.63, 121.46, and 118.43 ppm.

ANAL. Calcd for $C_{32}H_{20}N_2O_6$: C, 72.72%; H, 3.81%; N, 5.30%. Found: C, 72.85%; H, 3.61%; N, 5.22%.

II (BNDA) was synthesized by the catalytic reduction of dinitro compound BNDN in dimethylformamide according to the same procedure as that described above. A 50 mmol scale reaction was carried out, and the yield was 85%. Pure BNDA was obtained by sublimation as pale yellow needles; mp 318–320°C. The IR spectrum (KBr) exhibited absorptions at 3374 and 3460 cm^{-1} (N—H). The ^1H-NMR spectrum (DMSO-d_6) showed peaks δ at 6.5–8.0 (20H, aromatic), and 4.9 ppm (4H, amino group).

ANAL. Calcd for $C_{32}H_{24}N_2O_2$: C, 82.03%; H, 5.16%; N, 5.98%. Found: C, 82.30%; H, 5.10%; N, 5.83%.

Polymer Synthesis

Polyamide Va from I and IIIa by Direct Polycondensation Method

A mixture of 0.737 g (2.0 mmol) of **I,** 0.332 g (2.0 mmol) of **IIIa,** 0.25 g of lithium chloride, and 1.24 g (4 mmol) of triphenyl phosphite in 1.0 mL of pyridine and 4 mL of NMP was heated with stirring at 100°C for 3 h under nitrogen. The reaction mixture was poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with hot methanol, and dried 100°C under vacuum. The polymer weighed 1.10 g (98%) and had an inherent viscosity of 0.59 dL/g, measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C. The IR spectrum (film) exhibited absorptions at 3306 cm^{-1} (N—H) and 1661 cm^{-1} (C=O).

Other aramids were synthesized by a similar procedure.

Polymer Va from I and IVa by Low-Temperature Solution Method

A solution of 0.737 g (2.0 mmol) of **I** in 5 mL of NMP was cooled to −25–−30°C on a dry ice–acetone bath. After that 0.7 mL of propylene oxide was added to the mixture, then 0.407 g (2.0 mmol) of **IVa** was added. The mixture was stirred at −10°C for 1 h and then 20–25°C for 5 h under nitrogen. The solution thus obtained was poured into 300 mL of methanol. The precipitated polymer was collected by filtration, washed well with hot methanol, and dried at 100°C under vacuum. The yield of the polymer was 1.11 g (98%) and the inherent viscosity was 0.90 dL/g in concentrated sulfuric acid.

Other aramids were prepared by analogous procedure.

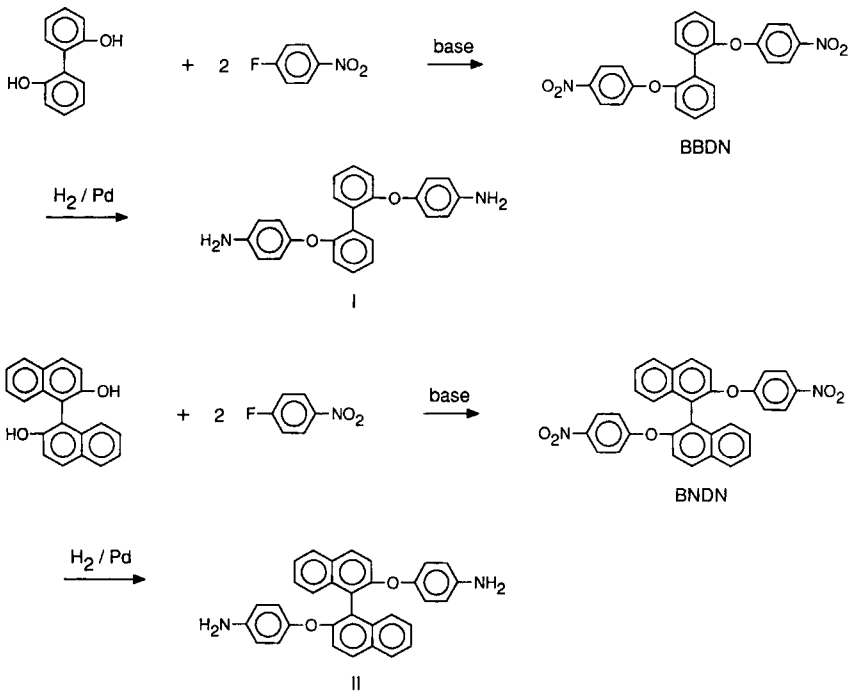
Measurements

IR spectra were recorded on a JASCO FT/IR-5000 Fourier transform spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed with Shimadzu thermal analyzers DSC-41M and TGA-40M, 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-II-20, and measurements were performed at room temperature using solution-cast 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

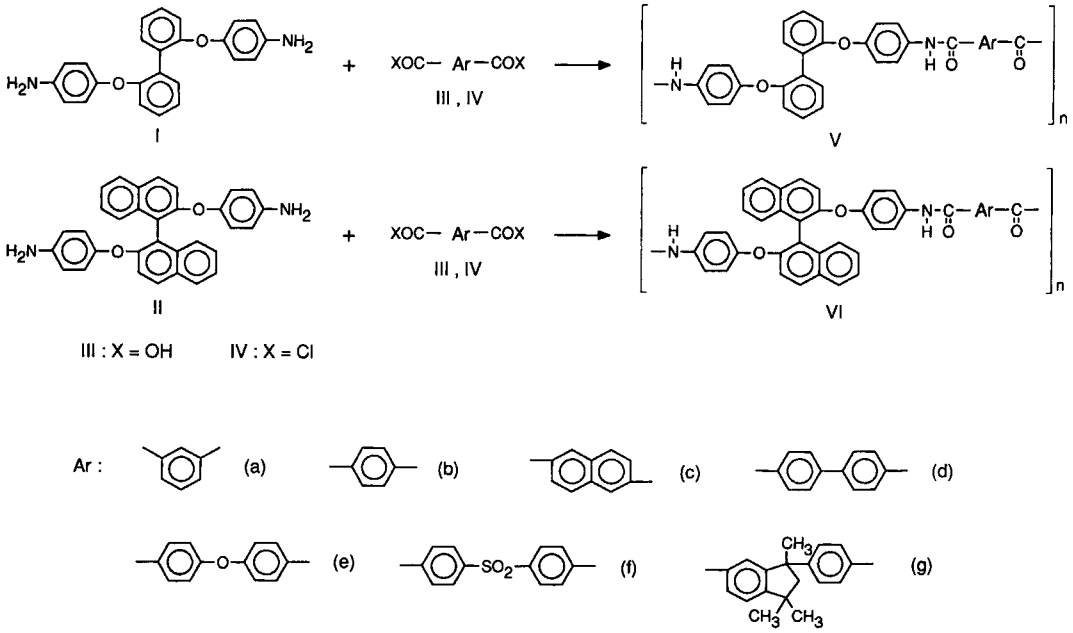
Monomer Synthesis

New polymer-forming diamines, 2,2′-bis(*p*-aminophenoxy)biphenyl (BBDA) **I** and 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl (BNDA) **II,** were successfully synthesized from biphenyl-2,2′-diol and 2,2′-dihydroxy-1,1′-binaphthyl, respectively, as starting materials according to synthetic Scheme 1. Thus, these diamines were obtained by the reaction of *p*-fluoronitrobenzene with the bisphenols, followed by catalytic reduction.



Scheme 1.

The chemical structures of all synthesized compounds were conformed by means of elemental analysis, and IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopic techniques. Concerning the synthesis of diamines **I** and **II**, the disappearance of characteristic nitro stretching bands at around 1345 and 1580 cm^{-1} on the IR spectra revealed completion of the reduction of dinitro compounds BBDN and BNDN. The elemental analyses of all of these compounds were also in good agreement with the calculated values for the proposed structures. The ^{13}C-NMR spectra of BBDN and **I** exhibited exactly 10 peaks due to



Scheme 2.

Table I. Synthesis of Polyamides[a]

Polymer Code	η_{inh} of Polymer[b] (dL/g)		Elemental Analysis			
	Method A	Method B		C (%)	H (%)	N (%)
Va	0.59	0.90	Calcd:	77.10	4.45	5.62
			Found:	75.94	4.73	5.99
Vb	0.50	1.18	Calcd:	77.10	4.45	5.62
			Found:	77.62	4.63	5.66
Vc	0.48	0.67	Calcd:	78.82	4.41	5.11
			Found:	77.59	4.32	4.94
Vd	0.76	0.71	Calcd:	79.43	4.56	4.87
			Found:	80.69	4.59	5.00
Ve	0.59	1.09	Calcd:	77.28	4.44	4.74
			Found:	76.10	4.58	4.97
Vf	0.56	0.91	Calcd:	71.46	4.10	4.39
			Found:	70.25	4.25	4.44
Vg	0.44	—	Calcd:	80.47	5.52	4.27
			Found:	79.67	5.57	4.17
VIa	0.50	0.30	Calcd:	80.25	4.38	4.68
			Found:	79.10	4.38	4.83
VIb	0.32	0.67	Calcd:	80.25	4.38	4.68
			Found:	79.13	4.34	4.72
VIc	0.34	0.88	Calcd:	81.46	4.35	4.32
			Found:	80.30	4.11	4.56
VId	0.52	0.68	Calcd:	81.88	4.48	4.15
			Found:	80.80	4.50	4.25
VIe	0.43	0.66	Calcd:	79.98	4.38	4.06
			Found:	78.65	4.52	4.27
VIf	0.36	0.63	Calcd:	74.78	4.09	3.79
			Found:	73.56	3.86	3.88
VIg	0.26	—	Calcd:	82.52	5.33	3.70
			Found:	80.98	5.25	3.94

[a] Method A: Polymerization was carried out with 2.0 mmol of the diacid, 2.0 mmol of the diamine, 0.25 g of lithium chloride, and 1.24 g of triphenyl phosphite in 1.0 mL pyridine and 4 mL of NMP with stirring at 100°C for 3 h under nitrogen. Method B: Polymerization was carried out with 2.0 mmol of the diacid chloride, 2.0 mmol of the diamine, and 0.7 mL of propylene oxide in 5 mL of NMP with stirring at −10°C for 1 h and then 20–25 °C for 5 h under nitrogen.

[b] Inherent viscosity was measured at a concentration of 0.5 g/dL in concentrated sulfuric acid at 30°C.

Table II. Solubility of Polyamides[a]

Solvent	Polymer					
	Va, Vf, Vg, VIa, VIe, VIf, VIg	**VIc**	**VIb**	**Vb, Vc, Ve**	**VId**	**Vd**
Conc. Sulfuric acid	++	++	++	++	++	++
N-Methyl-2-pyrrolidone	++	++	++	++	++	++
Dimethylacetamide	++	++	++	++	−	−
Dimethylformamide	++	++	++	−	−	−
Dimethyl sulfoxide	++	++	++	−	+	−
m-Cresol	++	+	−	−	−	−
Pyridine	++	+	−	−	−	−
Methanol	−	−	−	−	−	−
Acetone	−	−	−	−	−	−

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

symmetry and were consistent with the calculated values, while those of BNDN and **II** showed only 12 and 13 peaks, respectively, owing to overlapping of some peaks.

Polymer Synthesis

The direct polycondensation of aromatic diamines with dicarboxylic acids using a mixture of triphenyl phosphite and pyridine as a condensing agent,[20] as well as the low-temperature solution polycondensation of aromatic diamines with diacid chlorides,[21] are convenient methods for the preparation of polyamides on a laboratory scale. New biphenyl-2,2′-diyl- and 1,1′-binaphthyl-2,2′-diyl-containing aramids **V** and **VI** were prepared from aromatic diamines **I** and **II** with aromatic dicarboxylic acids **IIIa–IIIg** by the direct polycondensation (Scheme 2), and the results are summarized in Table I. All the polymerizations proceed in homogeneous solution, and aromatic polyamides **V** and **VI** were obtained in almost quantative yields with inherent viscosities of 0.44–0.76 and 0.26–0.52 dL/g, respectively.

A series of aramids **V** and **VI** could also be obtained readily by the low-temperature solution polycondensation of the diamines with various aromatic diacid chlorides **IVa–IVf** in NMP in the presence of propylene oxide as an acid acceptor (Scheme 2). Table I summarizes the results of the polymerization. Aramids **Va–Vf** and **VIa–VIf** with inherent viscosities of 0.67–1.18 and 0.30–0.88 dL/g, respectively, were successfully obtained by the low-temperature solution polycondensation. This method afforded the aramids having higher inherent viscosities compared with the polymers by the direct polycondensation.

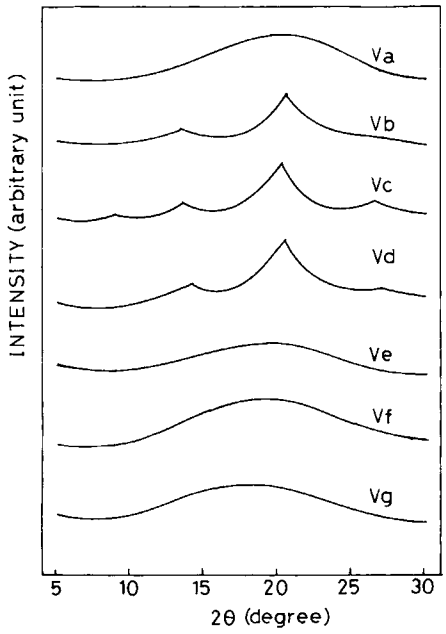


Figure 1. X-ray diffraction diagrams of polyamides **V**.

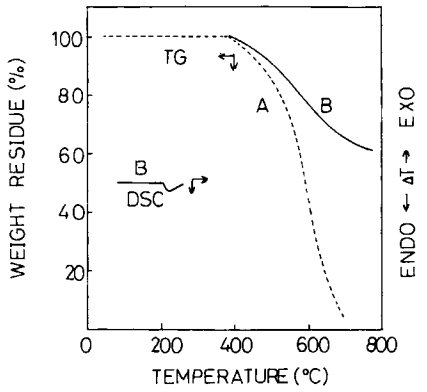


Figure 2. DSC and TG curves for polyamide **Va:** (A) in air, and (B) in nitrogen. DSC heating rate = 20°C/min, and TG heating rate = 10°C/min.

The formation of aramids was confirmed by elemental analysis and IR spectroscopy. The elemental analysis values of these aramids were in good agreement with the calculated values for the proposed structures (Table I). The IR spectra of the polymers showed characteristic amide absorptions near 3300 cm^{-1} (N—H) and 1660 cm^{-1} (C=O).

Table III. Thermal Properties of Polyamides

Polymer Code	T_g[a] (°C)	T_d[b] (°C)		T_{10}[b] (°C)	
		In Air	In N_2	In Air	In N_2
Va	215	375	370	465	505
Vb	—	405	410	445	515
Vc	—	395	400	465	515
Vd	—	405	410	480	555
Ve	220	390	410	465	520
Vf	240	420	410	500	515
Vg	255	390	410	500	495
VIa	277	390	390	500	520
VIb	300	390	400	510	540
VIc	290	385	385	480	525
VId	—	390	400	505	530
VIe	266	370	385	470	495
VIf	290	380	400	480	505
VIg	303	385	400	480	500

[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.

Table IV. Mechanical Properties of Polyamides

	Polymer							
	Va	**Ve**	**Vf**	**VIa**	**VIb**	**VIc**	**VIe**	**VIf**
Tensile strength (MPa)	104	100	78	64	75	95	78	70
Elongation at break (%)	4.4	5.8	4.2	3.6	3.8	4.4	4.2	3.6
Tensile modulus (GPa)	3.0	2.6	2.9	2.2	2.5	2.6	2.2	2.6

Polymer Characterization

Table II shows the solubility behavior of the aramids. All the polyamides except polymer **Vd** and **VId** were highly soluble in polar aprotic solvents such as DMAc, NMP, and dimethyl sulfoxide, some of them dissolved in *m*-cresol and even in less polar pyridine. Polymer **Vd** and **VId** dissolved only in NMP due to having symmetrical and rigid biphenylylene diacid component. Thus, the solubility of aramids was greatly improved by the introduction of 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 polyamides **VI** had better solubility than polyamides **V** in many organic solvents, in which the bulky effect of the binaphthyl structure is greater than that of the biphenyl.

The x-ray diffraction studies (Fig. 1) revealed that polyamides **Vb, Vc,** and **Vd** had a fair degree of crystallinity, whereas all of the other polymers were completely amorphous. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, and this could be attributed to the introduction of 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 means of DSC and TG. Figure 2 shows typical DSC and TG curves of polymer **Va,** and the thermal behavior data of the polymers are given in Table III. The glass transition temperatures (T_g) of polymers **V** and **VI** were observed in the 215–255 and 266–303°C range, respectively, depending on the structure of diacid component, and decreased with decreasing rigidity and symmetry of the polymer backbone. The T_gs of aramids **VI** derived from **II** were about 50°C higher than those of the corresponding aramids **V** derived from **I** due to the difference of rigidity between binaphthyl and biphenyl units. All the polymers were stable up to 370°C in both air and nitrogen atmospheres, and the temperatures at 10% weight loss were above 450°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 polyamides.

The mechanical properties of the solution cast films of the polyamides from the NMP solutions are given in Table IV. The tensile strength, elongation at break, and tensile modulus of polyamides **V** films were 78–104 MPa, 4.2–5.8%, and 2.6–3.0 GPa, and polyamides **VI** films were 64–95 MPa, 3.6–4.4%, and 2.2–2.6 GPa, respectively.

CONCLUSION

The introduction of bulky, kinked, and cranked biphenyl-2,2′-diyl and 1,1′-binaphthyl-2,2′-diyl units into the polyamide backbone improved solubility of the polymers in various organic solvents. Aramids **VI** derived from 2,2′-bis(*p*-aminophenoxy)-1,1′-binaphthyl had glass transition temperatures above 300°C, high thermal stability, and excellent solubility in organic solvents, compared with aramids **V** from 2,2′-bis(*p*-aminophenoxy)biphenyl. Thus, these aramids are considered to be promising soluble high-temperature polymeric materials.

REFERENCES AND NOTES

1. P. E. Cassidy, *Thermally Stable Polymers,* Dekker, New York, 1980.
2. M. Kakimoto, Y. S. Negi, and Y. Imai, *J. Polym. Sci. Polym. Chem. Ed.,* **23,** 1787 (1985).
3. Y. Imai, N. N. Maldar, and M. Kakimoto, *J. Polym. Sci. Polym. Chem. Ed.,* **23,** 1797 (1985).
4. C.-P. Yang, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **27,** 3895 (1989).
5. Y. Oishi, H. Takado, M. Yoneyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **28,** 1763 (1990).
6. H.-J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **28,** 3293 (1990).
7. M.-L. Xie, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.,* **29,** 55 (1991).

8. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **29,** 767 (1991).
9. D. J. Sikkema, *Chemtech,* **20,** 688 (1990).
10. G. S. Liou, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **29,** 995 (1991).
11. G. S. Liou, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **30,** 2195 (1992).
12. G. S. Liou, M. Kakimoto, and Y. Imai, *Prepr. 62th Chem. Soc. Jpn. Fall Mtg.*, **2,** 896 (1991).
13. R. C. Schulz, and R. H. Jung, *Makromol. Chem.*, **116,** 190 (1968).
14. Y. Tamai, Y. Matsuzaka, S. Oi, and S. Miyano, *Bull. Chem. Soc. Jpn.*, **64,** 2260 (1991).
15. M. Matsuoka, M. Ishisaka, T. Kitao, and K. Konishi, *Nippon Kagaku Kaishi,* 603 (1974).
16. T. S. Work, *J. Chem. Soc.*, 1315 (1940).
17. H. Manami, M. Nakazawa, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci. Part A: Polym. Chem.*, **28,** 465 (1990).
18. R. Herz, *Chem. Ber.*, **23,** 2538 (1890).
19. F. Toda, K. Tanaka, and S. Iwata, *J. Org. Chem.*, **54,** 3007 (1989).
20. N. Yamazaki, M. Matsumoto, and F. Higashi, *J. Polym. Sci. Polym. Chem. Ed.*, **13,** 1373 (1975).
21. P. W. Morgan. *Condensation Polymer by Interfacial and Solution Methods,* Interscience, New York, 1965.

Received September 25, 1992
Accepted February 9, 1993