Preparation and Properties of New Soluble Aromatic Polyamides from 2,2′-Bis(4-aminophenyl)biphenyl and Aromatic Dicarboxylic Acids

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ABSTRACT: New biphenyl-2,2′-diyl-containing aromatic polyamides having a crank and twisted noncoplannar structure were synthesized in inherent viscosities of 0.39–1.42 dL/g by the low-temperature solution polycondensation of 2,2′-bis(4-aminophenyl)biphenyl, prepared in four steps starting from 2-aminobiphenyl, with various aromatic dicarboxylic acid chlorides. These polyamides were readily soluble in a variety of solvents including *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone (NMP), *m*-cresol, and pyridine. Transparent, pale-yellow, and flexible films could be cast from the NMP solutions of the polyamides. The aromatic polyamides had glass transition temperatures in the range of 284–320°C, and began to lose weight around 400°C, with 10% weight loss being recorded at about 500°C in air. © 1998 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 36: 2029–2035, 1998

Keywords: 2,2′-bis(4-aminophenyl)biphenyl; aromatic polyamides; solubility; thermal behavior

INTRODUCTION

Wholly aromatic polyamides (aramids) such as poly-*m*-phenyleneisophthalamide and poly-*p*-phenyleneterephthalamide are characterized as highly thermally stable polymers with a favorable balance of physical and chemical properties, and are great importance in industrial applications.[1,2] However, these aramids are generally intractable and lack the properties essential for fabrication into useful forms due to their high melting or high glass transition temperatures and their limited solubility in organic solvents.

We have demonstrated approaches to make high-temperature aromatic polymers soluble while maintaining their high thermal stability.[3,4] One of the effective approaches to improve solubility of aramids is the introduction of bulky pendant phenyl groups along the polymer backbone.[5–16] Recently, in continuation of these studies, we are interested in the potential usefulness of biphenyl-2,2′-diyl unit having crank and twisted structure. We have already reported that the aramids derived from 2,2′-bibenzoic acid,[17] 2,2′-bis(4-aminophenoxy)biphenyl,[18] and 2,2′-bis(4-carboxyphenoxy)biphenyl[19] had improved solubility with retention of moderately high thermal stability. In additon, the aramids having no ether connecting group obtained from 2,2′-bibenzoic acid were found to have higher glass transition temperatures by about 60°C than the corresponding aramids with flexible ether linkage from 2,2′-bis(4-aminophenoxy)biphenyl or 2,2′-bis(4-carboxyphenoxy)biphenyl.

To get more insight into the effect of flexible ether connecting group on the properties of aramids, an aromatic diamine having bulky, crank,

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and twisted noncoplannar structure without ether linkage, 2,2′-bis(4-aminophenyl)biphenyl, was synthesized in the present study. The new aramids were prepared by the low-temperature solution polycondensation of the aromatic diamine with various aromatic dicarboxylic acid chlorides, and their properties were compared with those of the corresponding ether-bearing aramids derived from 2,2′-bis(4-aminophenoxy)biphenyl.[18]

EXPERIMENTAL

Materials

Commercial isophthaloyl chloride (**2a**) and terephthaloyl chloride (**2b**) were purified by distillation under reduced pressure before use. The other aromatic dicarboxylic acid chlorides were prepared by the reaction of the corresponding aromatic dicarboxylic acids with thionyl chloride in the presence of a few drops of *N,N*-dimethylformamide (DMF) as a catalyst.[18] 2,6-Naphthalenedicarbonyl chloride (**2c**) and 4,4′-biphenyldicarbonyl chloride (**2d**) were purified by sublimation, while 4,4′-oxydibenzoyl chloride (**2e**) and 4,4′-sulfonyldibenzoyl chloride (**2f**) were done by distillation.

N-Methyl-2-pyrrolidone (NMP) was purified by distillation over calcium hydride. Reagent grade propylene oxide was used as received.

Monomer Synthesis

2-Amino-4′-nitrobiphenyl

In a three-necked flask equipped with a mechanical stirrer, a dropping funnnel, and a thermometer were placed 11.0 g (65 mmol) of 2-aminobiphenyl and 300 mL of concentrated sulfuric acid. The mixture was stirred at room temperature, giving the solution. Then the flask was placed in an ice-salt bath and cooled to a temperature between 0°C and −5°C. To the stirred solution, a mixture of 7.5 mL of concentrated sulfuric acid and 3.0 mL of fuming nitric acid was added dropwise, while the temperature was kept below 0°C. The addition required about 1 h, and the stirring was continued further for 45 min. The solution was poured onto 1 kg of crushed ice, and neutralized carefully with aqueous sodium hydroxide. The product was collected by filtration, dried, and recrystallized from ethanol, affording 7.46 g (54%) of orange needles, m.p. 155.5–157.5°C (lit.[20] m.p. 156–158.5°C). The infrared (IR) spectrum (KBr) exhibited absorption bands at 3458 and 3386 (NH_2), and 1506 and 1347 cm^{-1} (NO_2). The ^{13}C-nuclear magnetic resonance (NMR) spectrum (DMSO-d_6) showed peaks δ at 146.6, 146.5, 145.9, 128.2, 128.0, 127.6, 123.1, 118.9, and 116.0 ppm.

2-Iodo-4′-nitrobiphenyl

A mixture of 10.71 g (50 mmol) of 2-amino-4′-nitrobiphenyl and 200 mL of 2 *M* hydrochloric acid was cooled in an ice bath. To the stirred solution was added 12.1 g (175 mmol) of sodium nitrite all at once, and the solution was stirred for 2 h. To this was added an aqueous solution of 33.2 g (200 mmol) of potassium iodide dropwise with stirring, and the stirring was continued at room temperature for 3 days until completion of the reaction. The crude product thus precipitated was collected and dried. This was then dissolved in benzene and washed with an aqueous potassium hydroxide. After removal of most of the benzene, the concentrated benzene solution was subjected to silica-gel column chromatography using benzene as an eluent, and the product was isolated. This was further purified by recrystallization from ethanol, giving 7.23 g (45%) of pale yellow needles, m.p. 99–101°C (lit.[21] m.p. 100–101.5°C). The IR spectrum (KBr) exhibited absorption bands at 1516 and 1350 cm^{-1} (NO_2). The ^{13}C-NMR spectrum (DMSO-d_6) showed peaks δ at 149.96, 146.77, 143.84, 139.40, 130.57, 130.08, 129.86, 128.56, 123.15, and 97.74 ppm.

ANAL. Calcd for $C_{12}H_8INO_2$: C, 44.33%; H, 2.48%; I, 39.03%; N, 4.31%. Found: C, 44.34%; H, 2.19%; I, 39.14%; N, 4.24%.

2,2′-Bis(4-nitrophenyl)biphenyl

A 5.88 g (92.5 mmol) portion of copper powder, activated just before use by the treatment with disodium *N,N,N′,N′*-ethylenediaminetetraacetate, was added to 5.0 g (15.4 mmol) of 2-iodo-4′-nitrobiphenyl, and the mixture was heated with stirring at 230°C for 8 h under nitrogen atmosphere. After cooling, the solidified mass was extracted with benzene. The extract was concentrated until the crystals began to separate, affording 1.93 g (63%) of yellow needles, m.p. 296–297°C (lit.[21] m.p. 290°C). The IR spectrum (KBr) exhibited absorption bands at 1514 and 1347 cm^{-1} (NO_2).

ANAL. Calcd for $C_{24}H_{16}N_2O_4$: C, 72.72%; H, 4.07%; N, 7.07%. Found: C, 72.65%; H, 3.77%; N, 7.12%.

2,2′-Bis(4-aminophenyl)biphenyl (1)

A mixture of 1.40 g (3.53 mmol) of 2,2′-bis(4-nitrophenyl)biphenyl and 5.6 g of sodium sulfide in 70 mL of ethanol and 30 mL of water was refluxed for 3 h. After removal of the solvents by evaporation, the residue was washed with water and dried under vacuum. The crude product was purified by distillation under reduced pressure, affording 0.93 g (78%) of yellowish-white solid, m.p. 165–167°C (lit.[21] m.p. 163–164°C). The IR spectrum (KBr) exhibited absorption bands at 3445 and 3370 cm^{-1} (NH_2). The ^{13}C-NMR spectrum (DMSO-d_6) showed peaks δ at 146.82, 140.75, 139.56, 131.22, 129.48, 128.24, 126.88, 125.53, and 113.12 ppm.

ANAL. Cacld for $C_{24}H_{20}N_2$: C, 85.68%; H, 5.99%; N, 8.33%. Found: C, 85.21%; H, 5.78%; N, 8.51%.

Polymer Synthesis

Polymer 3a *from* 1 *and* 2a

A solution of 0.841 g (2.5 mmol) of aromatic diamine **1** in 5.0 mL of NMP was cooled to −25 to −30°C on a dry ice-acetone bath. To the mixture 0.5 mL of propylene oxide and 0.508 g (2.5 mmol) of diacid chloride **2a** were added successively. The mixture was stirred at −10°C for 1 h and then at 20–25°C for 5 h under nitrogen. The viscous solution thus formed 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 1.12 g (96%) and the inherent viscosity was 0.41 dL/g, measured at a concentratioin of 0.5 g/dL in concentrated sulfuric acid at 30°C. The IR spectrum (film) exhibited characteristic amide absorption bands at 3308 (N—H) and 1669 cm^{-1} (C═O).

The other aramids were prepared by an analogous procedure.

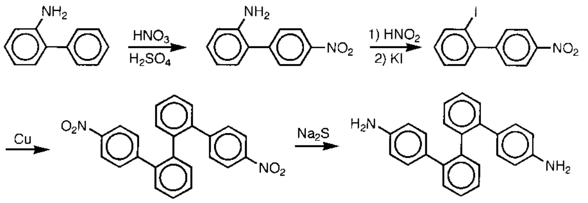
Measurements

IR and ^{13}C-NMR spectra were recorded on a JASCO FT/IR-5000 spectrophotometer and a JEOL FX-90Q spectrometer, respectively. 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 Rigaku-dennki 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 50 mm thick, 5.0 mm wide, and 5.0 cm gauge length) at an elongation rate of 20%/min.

RESULTS AND DISCUSSION

Monomer Synthesis

The aromatic diamine monomer, 2,2′-bis(4-aminophenyl)biphenyl, used for the preparation of new aramids were synthesized according to Scheme 1 in four steps starting from 2-aminobiphenyl.



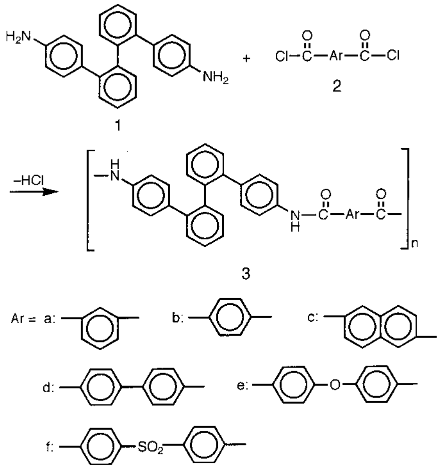
Scheme 1.

2-Amino-4′-nitrobiphenyl was prepared in a 54% yield by the nitration of 2-aminobiphenyl according to the reported procedure.[20] Then the synthetic route of 2,2′-bis(4-aminophenyl)biphenyl reported by Sako[21] was adopted here, starting from 2-amino-4′-nitrobiphenyl in three steps. The Sandmeyer reaction of 2-amino-4′-nitrobiphenyl with nitrous acid, followed by the treatment with potassium iodide, produced 2-iodo-4′-nitrobiphenyl in a 45% yield. Then 2-iodo-4′-nitrobiphenyl was subjected to the Ullmann coupling with copper powder to give 2,2′-bis(4-nitrophenyl)biphenyl in a 63% yield. Finally, the reduction of 2,2′-bis(4-nitrophenyl)biphenyl with sodium sulfide afforded 2,2′-bis(4-aminophenyl)biphenyl in a 78% yield.

The chemical structures of all the synthesized compounds were confirmed by the good agreement of the melting points with those reported in the literatures[20,21] and of the elemental analysis values with the calculated values. In addition, the IR and ^{13}C-NMR spectra also supported the formation of the desired compounds having the proposed structures.

Polymer Synthesis

The low-temperature solution polycondensation of aromatic diamines with aromatic dicarboxylic acid chlorides is a convenient method for the preparation of aramids on a laboratory scale.[22] New biphenyl-2,2′-diyl-containing aramids **3a–3f** were prepared from aromatic diamine **1** and various aromatic diacid chlorides **2a–2f** by the low-temperature solution polycondensation in NMP in the presence of propylene oxide as an acid acceptor (Scheme 2), and the results are summarized in Table I.



Scheme 2.

Most of the polycondensations proceeded homogeneously giving the viscous aramid solutions, except those for the preparation of aramids **3b** and **3c**, where gelation occurred during the polymerizations. Nevertheless, a series of aramids **3a–3f** were obtained almost quantitatively with inherent viscosities of 0.39–1.42 dL/g, indicative of moderate to high molecular weights.

Table I. Synthesis of Aramids

Code	Yield (%)	η_{inh}[a] (dL/g)	Elemental Analysis[b] (%) C	H	N
3a	96	0.41	83.02	4.71	6.12
			(82.38)	(4.75)	(6.00)
3b	93	0.79[c]	81.40	4.62	5.90
			(82.38)	(4.75)	(6.00)
3c	99	1.10[c]	82.75	4.30	5.45
			(83.70)	(4.68)	(5.42)
3d	100	1.42	84.75	4.74	5.12
			(84.11)	(4.83)	(5.16)
3e	97	1.28	81.43	4.72	4.99
			(81.70)	(4.69)	(5.01)
3f	95	0.39	74.48	4.00	4.59
			(75.23)	(4.32)	(4.62)

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

[b] The data in parentheses are the calculated values.

[c] Soluble fraction in concentrated sulfuric acid.

Table II. Solubility of Aramids[a]

Solvent[b]	Polymer **3a**, **3d**	**3b**, **3c**, **3e**	**3f**
NMP	++	±	++
DMAc	++	±	++
Pyridine	++	±	++
m-Cresol	++	±	±
DMSO	−	−	−

[a] Solubility: (++) soluble at room temperature, (±) partly soluble, and (−) insoluble.

[b] DMAc: *N,N*-dimethylacetamide, and DMSO: dimethyl sulfoxide.

The formation of the aramids was confirmed by means of elemental analysis and IR spectroscopy. The elemental analysis values of these aramids agreed well with the calculated values for the proposed structures (Table I). The IR spectra of the polymers showed characteristic amide absorption bands near 3310 (N—H) and 1670 cm^{-1} (C═O).

Polymer Characterization

The qualitative solubility of the aramids is summarized in Table II. Aramids **3a** and **3f** having an *m*-phenylene linkage and sulfone connecting group, respectively, were highly soluble in a variety of polar solvents including NMP, DMAc, pyridine, and *m*-cresol. It is interesting to note that aramid **3d**, despite bearing a symmetrical and rigid biphenyl-4,4′-diyl unit, had excellent solubility in these solvents. On the other hand, aramids **3b** and **3c** only partly dissolved in the above organic solvents due to having symmetrical and rigid *p*-phenylene and naphthalene-2,6-diyl units, respectively. The poor solubility of aramid **3e** possessing ether linkages is puzzling and cannot be explained at this stage. Thus, the solubility of aramids was moderately improved by the introduction of bulky, cranked, and twisted biphenyl-2,2′-diyl component into the polymer backbone.

These organo-soluble aramids **3a**, **3d**, and **3f** gave transparent, pale-yellow, and flexible films by casting from NMP solutions. Among them, the film obtained from aramid **3d** was particulaly

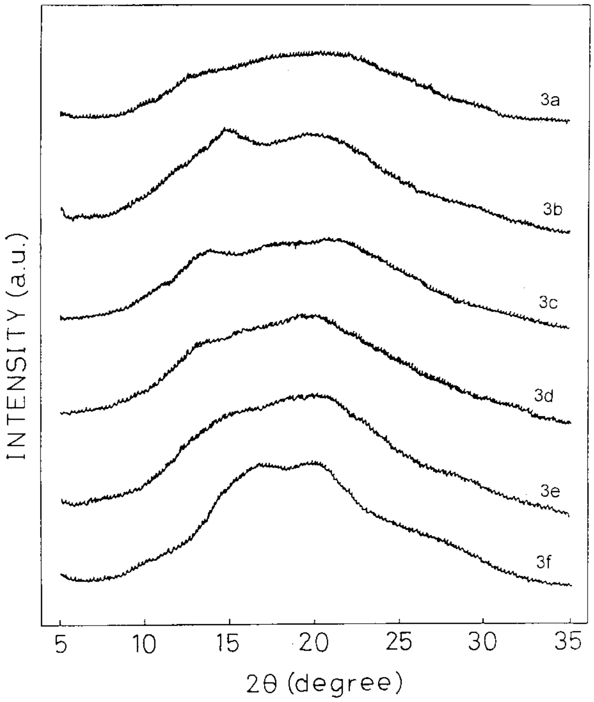


Figure 1. X-ray diffraction diagrams of aramids.

tough and flexible with good quality, and had a tensile strength of 162 MPa, an elongation at break of 6.4%, and a tensile modulus of 5.8 GPa.

Figure 1 shows the X-ray diffraction diagrams of the aramids. Aramids **3b** and **3c** composed of a symmetrical and rigid backbone had low degree of crystallinity, whereas the other aramids were practically amorphous. This could be attributed to the incorporation of bulky biphenyl-2,2′-diyl unit along the polymer main chain. In addition, these results are very similar to the facts that the structurally related aramids derived from 2,2′-bis(4-aminophenoxy)biphenyl and terephthalic or 2,6-naphthalenedicarboxylic acid,[18] as well as the aramid from 2,2′-bis(4-carboxyphenoxy)biphenyl and *p*-phenylenediamine,[19] had a fair degree of crystallinity.

The thermal behavior of the aramids was evaluated by means of DSC and TG. Figure 2 depicts typical DSC and TG curves of aramid **3a**, and the thermal behavior data are summarized in Table III. The glass transition temperatures (T_g) of all the aramids, except for polymer **3b,** which, with a low degree of crystallinity had no T_g, were observed in the range of 284–320°C, depending on the structure of the diacid components used. The T_g values decreased in the order of **3d** > **3c** > **3f** > **3e** > **3a** with decreasing rigidity and symmetry of the polymer backbone. All the aramids were stable up to 400°C in both air and nitrogen atmospheres, and the temperatures at 10% weight loss were above 505°C on the TG curves.

The properties of the new aramids were compared with those of the structurally related aramids derived from 2,2′-bis(4-aminophenoxy)biphenyl and the corresponding aromatic dicarboxylic acids.[18] Table IV summarizes the comparison of the properties of the two sets of aramids. It is reasonable that the present aramids derived from 2,2′-bis(4-aminophenyl)biphenyl had less solubility than the corresponding ether-containing aramids from 2,2′-bis(4-aminophenoxy)biphenyl. Regarding the thermal properties, the T_g values of the present aramids were about 60°C higher than those of the corresponding ether-bearing aramids. This is attributable to the difference of rigidity between the biphenyldiyl and oxydiphenylene backbone structure. In addition, the 10% weight loss temperatures of the new aramids were some 50°C higher than those of the ether-containing aramids due to the stability difference between the two functional groups.

CONCLUSIONS

New soluble aramids having inherent viscosities up to 1.42 dL/g were readily synthesized by the low-temperature solution polycondensation of 2,2′-bis(4-aminophenyl)biphenyl with various aromatic dicarboxylic acid chlorides. The introduction of bulky, crank, and twisted noncoplannar biphenyl-2,2′-diyl unit without ether linkages into the aramid backbone increased glass transition tempera-

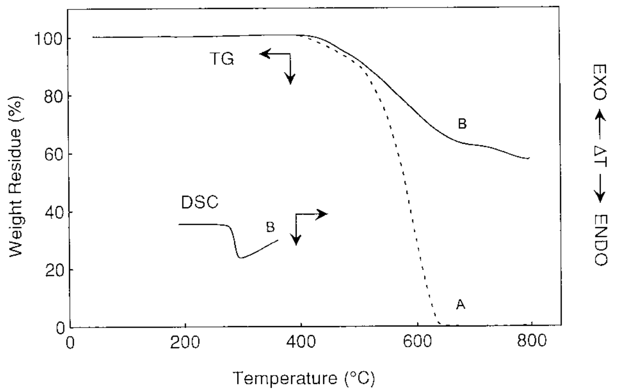


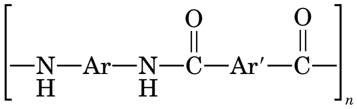
Figure 2. DSC and TD curves of aramid **3a**: (A) in air, and (B) in nitrogen. DSC and TG heating rate = 10°C/min.

Table III. Thermal Behavior of Aramids

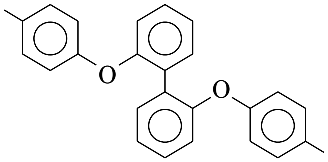
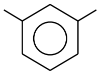
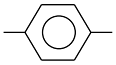
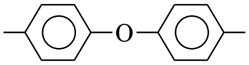
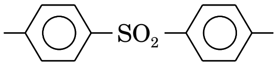
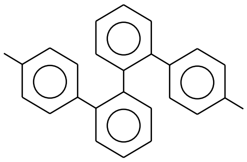
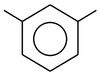
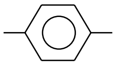
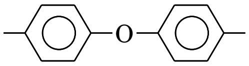
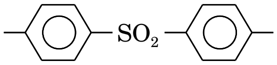
Polymer	T_g[a] (°C)	T_d[b] (°C)		T_{10}[b] (°C)	
		In Air	In Nitrogen	In Air	In Nitrogen
3a	284	400	400	510	525
3b	—	405	420	505	510
3c	315	410	415	510	515
3d	320	415	415	530	565
3e	287	410	420	505	510
3f	303	415	415	505	505

[a] Determined by DSC at a heating rate of 10°C/min in nitrogen.
[b] T_d (initial decomposition temperature) and T_{10} (10% weight loss temperature) determined by TG at a heating rate of 10°C/min.

Table IV. Comparison of Properties of Structurally Related Aramids



$$\left[-\underset{H}{N}-Ar-\underset{H}{N}-\overset{O}{\overset{\|}{C}}-Ar'-\overset{O}{\overset{\|}{C}}- \right]_n$$

Ar	Ar′	Solubility[a]			T_g (°C)	T_{10}[b] (°C)
		H_2SO_4	NMP	DMAc		
		++	++	++	215	465
		++	++	++	—	445
		++	++	++	220	465
		++	++	++	240	500
		++	++	++	284	510
		++	±	±	—	505
		++	±	±	287	505
		++	++	++	303	505

[a] Solubility: (++) soluble at room temperature and (±) partly soluble.
[b] T_{10}: 10% weight loss temperature in air.

tures up to 320°C and high thermal stability with retention of moderate solubility in organic solvents, compared with the aramids containing biphenyl-2,2′-diyl and ether connecting groups.

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