

Synthesis and Characterization of Novel Aromatic Polyamides from 1,4-Bis(4-aminophenyl)-2,3-diphenylnaphthalene and Aromatic Dicarboxylic Acids

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ABSTRACT: A new highly phenylated diamine, 1,4-bis(4-aminophenyl)-2,3-diphenylnaphthalene, was synthesized in two steps starting from 2,5-bis(4-nitrophenyl)-3,4-diphenylcyclopentadienone. New aromatic polyamides containing tetraphenylnaphthalene unit were prepared by low temperature solution polycondensation of this diamine with various aromatic dicarboxylic acid chlorides. These polyamides had inherent viscosities of 0.45–0.82 dl g⁻¹. Polyamides with *m*-phenylene moiety and flexible connecting group were soluble in various organic solvents such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone, but those with rigid symmetric structures were soluble in only hot *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone. The glass transition temperature of the polyamides ranged from 268 to 366°C, and the 10% weight loss temperatures were above 500°C in air.

KEY WORDS High Temperature Polymers / Soluble Aromatic Polyamides / 1,4-Bis(4-aminophenyl)-2,3-diphenylnaphthalene / Thermal Behavior /

Aromatic polyamides are high thermal stability coupled with high crystallinity and hence high temperature application especially as fibers.¹ However, most wholly aromatic polyamides are difficult to fabricate because of low solubility and high melting temperature. Several attempts have been made to improve the solubility by modifying the structure without losing their good thermal stability. Aromatic polyamides having phenyl-pendant structures such as tetraphenylthiophene,^{2–5} tetraphenylfuran,⁶ tetraphenylpyrrole,⁷ tetraphenylethylene,⁸ triphenylamine,⁹ triphenylphosphine,¹⁰ triphenylbenzene,¹¹ hexaphenylbenzene,¹² and tetraphenylquinquephenyl,¹³ have high thermal stability and high solubility. We conducted the synthesis of a new diamine monomer, 1,4-bis(4-aminophenyl)-2,3-diphenylnaphthalene and aromatic polyamides derived from it. This article deals with the synthesis and characterization of novel aromatic polyamides from this diamine and aromatic dicarboxylic acid chlorides. The properties of polyamides such as solubility and thermal behavior are also discussed.

EXPERIMENTAL

Materials

Isophthaloyl chloride (**IVa**), terephthaloyl chloride (**IVb**), 4,4'-biphenyldicarbonyl chloride (**IVc**), 4,4'-oxybiphenyl chloride (**IVd**), and 4,4'-sulfonyldibenzoyl chloride (**IVe**) were obtained commercially and purified by distillation under reduced pressure. *N,N*-Dimethylacetamide (DMAc) was purified by vacuum distillation over calcium hydride. 2,5-Bis(4-nitrophenyl)-3,4-diphenylcyclopentadienone (**I**)¹² and 2-phenyliodonobenzoate,¹⁴ a precursor for benzyne, were prepared as previously reported.

Monomer Synthesis

1,4-Bis(4-nitrophenyl)-2,3-diphenylnaphthalene (II). In a flask, 7.11 g (15 mmol) of compound **I** and 5.50 g (17 mmol) of 2-phenyliodonobenzoate were dissolved in 50 ml triethylene glycol dimethyl ether and the mixture was stirred at 210°C for about 10 min. The solution turned colorless, and was cooled to about 100°C and the solvent was evaporated under reduced pressure of 15–20 Torr. The residue was washed with methanol and dried under reduced pressure. The crude product was purified by silica gel column chromatography eluted by dichloromethane and hexane (4:1). mp 316–317°C. The yield was 5.40 g (69%). The IR spectrum (KBr) exhibited absorption bands at 1520 and 1350 cm⁻¹ (–NO₂), and 700 cm⁻¹ (naphthalene ring). ¹H NMR spectrum [δ in CDCl₃] showed signals at 6.80–6.90 (m, 10H), 7.40 and 8.14 (ABq, 8H, *J*=9 Hz), 7.47 (m, 2H), and 7.52 ppm (m, 2H). ¹³C NMR spectrum [δ in CDCl₃] exhibited peaks at 146.6, 139.1, 139.0, 137.1, 132.1, 131.2, 130.9, 127.1, 126.8, 126.4, 126.2, and 122.9 ppm.

Anal. Calcd for C₃₄H₂₂N₂O₄: C, 78.15%; H, 4.24%; N, 5.36%. Found: C, 78.21%; H, 4.28%; N, 5.35 %.

1,4-Bis(4-aminophenyl)-2,3-diphenylnaphthalene (III). A mixture of 5.23 g (10 mmol) of compound **II** and 0.3 g of 10% Pd/C in 50 ml of *N,N*-dimethylformamide was stirred at 70°C for 12 h under a hydrogen atmosphere. After Pd/C was removed by filtration, the solvent was evaporated under reduced pressure and the crude product was purified by distillation under reduced pressure (Glass tube oven). bp 330 °C (1 Torr). mp 279–280°C. The yield was 3.89 g (84%). The IR spectrum (KBr) exhibited absorption bands at 3450 and 3360 cm⁻¹ (–NH₂), and 695 cm⁻¹ (naphthalene ring). ¹H NMR spectrum [δ in CDCl₃] showed signals at 6.57 and 6.97 (ABq, 8H, *J*=8 Hz), 6.80–6.90 (m, 10H), 7.37 (m, 2H), and 7.73 ppm (m, 2H). ¹³C NMR spectrum [δ in CDCl₃] exhibited peaks at 144.4, 141.0, 139.1, 138.0, 132.5, 132.1, 131.3, 129.8, 127.1, 126.5, 125.6, 125.0, and 114.4 ppm.

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Anal. Calcd for $C_{34}H_{26}N_2$: C, 88.28%; H, 5.66%; N, 6.06%. Found: C, 88.22%; H, 5.62%; N, 6.12%.

Polymerization

A typical polycondensation is given below.

Polyamide Va from III and IVa. In a three necked flask, a solution of 0.693 g (1.5 mmol) of diamine **III** and 5 ml DMAc was chilled in a dry ice-acetone bath under nitrogen. To this, 0.304 g (1.5 mmol) of solid diacid chloride **IVa** was added all at once. The mixture was stirred at 4°C in ice-water bath. The polymerization proceeded as the solid was dissolved. After stirring at the temperature for 5 h, the reaction mixture was poured into 400 ml methanol, and dried at 100°C under vacuum. The yield was 0.86 g (97%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.53 dl g⁻¹ at a concentration of 0.5 g dl⁻¹ at 30°C. The IR spectrum (Film) exhibited absorption bands at 3380 cm⁻¹ (N-H) and 1660 cm⁻¹ (C=O).

Anal. Calcd for $(C_{42}H_{28}N_2O_2)_n$: C, 85.11%; H, 4.76%; N, 4.73%. Found: C, 84.75%; H, 4.70%; N, 4.68%.

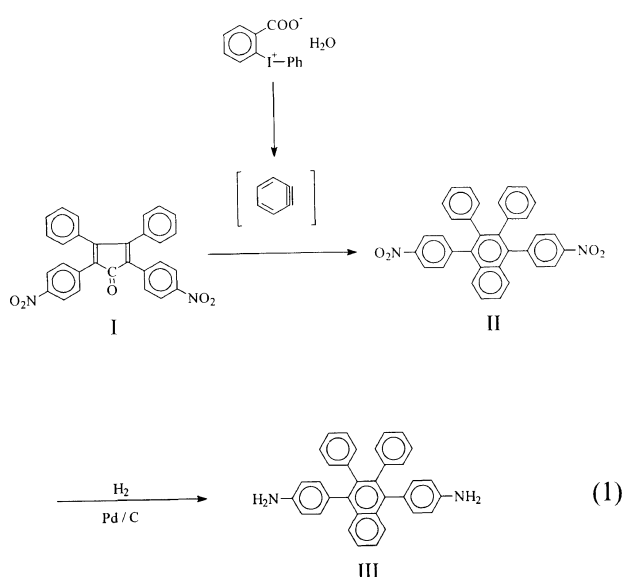
Measurements

¹H and ¹³C NMR spectra and IR spectra were recorded on a JNM-GSX-400 FT-NMR spectrometer and a Shimadzu Spectro Photometer IR 435, respectively. X-Ray diffraction measurement was made with a Rigaku RAD-B System. Differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis were a Rigaku Thermal Analysis Station TAS 100 and TG 8110, respectively, at a heating rate of 10°C min⁻¹ in air and nitrogen.

RESULTS AND DISCUSSION

Monomer Synthesis

A new aromatic diamine having tetraphenyl-naphthalene structure, 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene (**III**), was synthesized in two steps starting from 2,5-bis(4-nitrophenyl)-3,4-diphenylcyclopentadienone (**I**) according to eq 1.

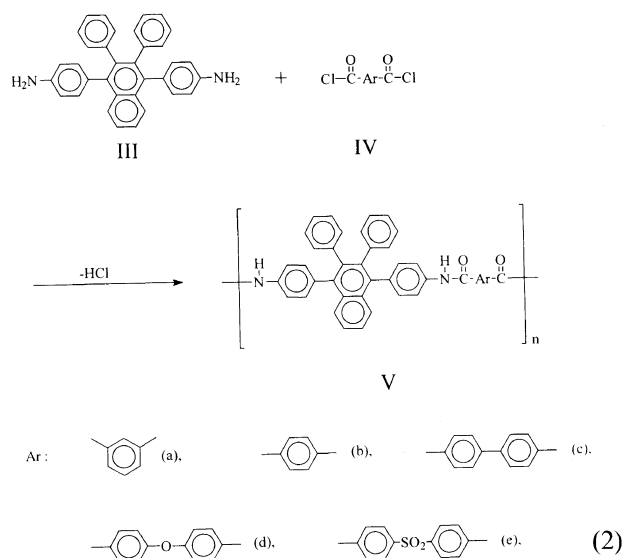


Compound (**I**) was reacted with the intermediate benzyne generated by heating 2-phenyliodonobenzoate to yield 1,4-bis(4-nitrophenyl)-2,3-diphenyl-naphthalene (**II**) in 69%. Reaction conditions were the same as those of Beringer *et al.* for the preparation of 1,2,3,4-tetra-phenyl-naphthalene.¹⁴ Subsequent hydrogenation of the dinitro compound using Pd/C as catalyst afforded 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene in 84% yield.

Chemical structures were confirmed by IR and NMR spectra, and elemental analysis. In the synthesis of compound **II**, the disappearance of the characteristic carbonyl band at 1715 cm⁻¹ was observed on the IR spectrum together with the appearance of resonances at 7.47 ppm and 7.52 ppm due to protons connected with naphthalene ring on the ¹H NMR spectrum. Compound **III** showed IR absorption at 3450 and 3360 cm⁻¹ characteristic of amino group. The ¹³C NMR spectrum of **III** exhibited 13 peaks due to symmetry, indicating the formation of the postulated diamine. Elemental analysis of all the compounds was also in good agreement with calculated results for the proposed structures.

Polymer Synthesis

Aromatic polyamides containing tetraphenyl-naphthalene unit were prepared by the temperature solution polycondensation of 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene (**III**) with various aromatic dicarboxylic acid chlorides (**IVa–IVe**) in DMAc (eq 2). Most polycondensations proceeded in a homogeneous solution, except for polymerization with **IVb** and **IVc** where precipitation of the polymers occurred during reaction because of low solubility of polymer **Vb** and **Vc** in DMAc.



The results of synthesis of the aromatic polyamides are summarized in Table I. Inherent viscosities of the polymers were in the range of 0.45–0.82 dl g⁻¹, and most polyamides gave films by casting from the DMAc solutions. IR spectra of these polymers showed characteristic amide absorption bands at around 3360 cm⁻¹ (N-H) and 1660 cm⁻¹ (C=O), which confirmed the formation of the proposed polyamides.

Table I. Synthesis of aromatic polyamides^a

Diacid chloride	Polymer			Remarks ^c
	Code	Yield %	η_{inh}^b dl g ⁻¹	
IVa	Va	97	0.53	S
IVb	Vb	96	0.45	P
IVc	Vc	92	0.63	P
IVd	Vd	95	0.74	S
IVe	Ve	94	0.82	S

^a Polymerization was carried out with 1.5 mmol of each monomer in 5.0 ml DMAc at 4°C for 5 h under nitrogen. ^b Measured at 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C. ^c Appearance of the polymerization system: S, homogeneous solution; P, polymer precipitation.

Table II. Solubility of aromatic polyamides

Solvent	Polymer				
	Va	Vb	Vc	Vd	Ve
<i>N</i> -Methyl-2-pyrrolidone	++	+	+	++	++
<i>N,N</i> -Dimethylacetamide	++	+	+	++	++
<i>N,N</i> -Dimethylformamide	++	-	-	++	++
<i>m</i> -Cresol	++	-	-	++	+
Pyridine	++	-	-	+	+

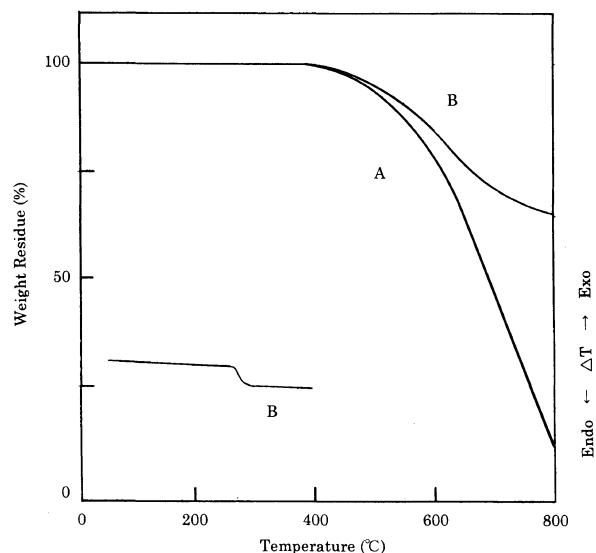
^a Solubility: ++, soluble at room temperature; +, soluble on heating; -, insoluble.

Polymer Characterization

Table II lists qualitative solubility of the tetraphenyl-naphthalene containing aromatic polyamides. Polymer **Va** with *m*-phenylene moiety as well as polymer **Vd** and **Ve** having flexible connecting groups was more soluble than the other polymers (**Vb** and **Vc**) with rigid symmetric structures, and dissolved in *N*-methylpyrrolidone (NMP), DMAc, and *N,N*-dimethylformamide even at room temperature. Polyamides, **Vb** and **Vc**, with rigid symmetric structure were soluble only in hot NMP and DMAc. All polymers were entirely insoluble in methanol, acetone, chloroform and tetrahydrofuran. The solubility of the tetraphenyl-naphthalene-based polyamides was lower than that of aromatic polyamides having similar phenyl-pendant structures such as tetraphenylthiophene,²⁻⁵ tetraphenylfuran,⁶ tetraphenylpyrrole,⁷ tetraphenylethylene,⁸ triphenylamine,⁹ and triphenylphosphine,¹⁰ previously reported soluble in NMP at room temperature. The rigid terphenyl structure without hetero-atom in the tetraphenyl-naphthalene may cause the low solubility.

X-Ray diffraction studies indicated that these polyamides, even **Vb** and **Vc**, which had rigid symmetric structure, were amorphous. The amorphous nature of these polymers was not reflected by solubility.

The thermal behavior of the polyamides was evaluated by TG and DSC. Figure 1 shows typical DSC and TG curves of polyamide **Va**. The glass transition temperatures (T_g) and 10% weight loss temperature (T_{10}) are summarized in Table III. The present polyamides had relatively high T_g in the range of 268–366°C. Polyamides **Vb** and **Vc** having rigid symmetric structures had higher T_g than the polymers (**Va**, **Vd**, and **Ve**) with unsymmetric

**Figure 1.** DSC and TG curves for polyamide **Va** at heating rate of 10°C min⁻¹ in (A) air and (B) nitrogen.**Table III.** Thermal behavior of aromatic polyamides

Polymer	T_g^a °C	T_{10}^b		Char yield ^c %
		In air °C	In nitrogen °C	
Va	268	509	550	64
Vb	366	504	545	65
Vc	353	503	538	60
Vd	300	526	552	62
Ve	335	490	530	55

^a Determined by DSC in nitrogen at a heating rate of 10°C min⁻¹.

^b Temperature at which there was 10% weight loss by TG at heating rate of 10°C min⁻¹. ^c Char yield in nitrogen at 800°C by TG.

ones and flexible connecting group.

None of the present polyamides lost weight below 400°C in air or nitrogen, and T_{10} in air and nitrogen were ranged from 514–536°C and 520–544°C, respectively, indicating high thermal stability. More than 60% weight was retained even at 800°C in nitrogen for the polyamides. Based on T_{10} , the tetraphenyl-naphthalene-based polyamides had as high thermal stability as tetraphenylthiophene-based polyamide,¹⁵ the most thermally stable polymer in the aromatic polyamide with similar phenyl pendant structure.

CONCLUSION

We synthesized a new highly phenylated diamine, 1,4-bis(4-aminophenyl)-2,3-diphenyl-naphthalene, which was subsequently used for the polycondensation with aromatic dicarboxylic acid chlorides to obtain aromatic polyamides. The polyamides were soluble in polar organic solvents, such as *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone, and had high glass transition temperatures and high thermal stability.

REFERENCES

1. P. E. Cassidy, "Thermally Stable Polymers," Dekker, New York, N. Y., 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. Y. Imai and M. Kakimoto, *Polym. Plast. Technol. Eng.*, **28**, 371 (1989).
5. H.-J. Jeong, A. Kobayashi, M. Kakimoto, and Y. Imai, *Polym. J.*, **26**, 99 (1994).
6. H.-J. Jeong, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem. Ed.*, **28**, 3293 (1990).
7. H.-J. Jeong, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem. Ed.*, **29**, 767 (1991).
8. M.-L. Xie, Y. Oishi, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem. Ed.*, **29**, 55 (1991).
9. Y. Oishi, H. Takado, M. Yoneyama, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem. Ed.*, **28**, 1763 (1990).
10. M. Yamashita, M. Kakimoto, and Y. Imai, *J. Polym. Sci., A, Polym. Chem. Ed.*, **31**, 1513 (1993).
11. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 1236 (1998).
12. Y. Sakaguchi and F. W. Harris, *Polym. J.*, **24**, 1147 (1992).
13. I. K. Spiliopoulos and J. A. Mikroyannidis, *Macromolecules*, **31**, 515 (1998).
14. F. M. Beringer and S. J. Huang, *J. Org. Chem.*, **29**, 445 (1964).
15. Y. Imai, *High Perform. Polym.*, **7**, 337 (1995).