

Synthesis and Characterization of Novel Aromatic Polyamides from 3,4-Bis(4-aminophenyl)-2,5-diphenylthiophene and Aromatic Dicarboxylic Acids

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ABSTRACT: A new highly phenylated diamine, 3,4-bis(4-aminophenyl)-2,5-diphenylthiophene, was synthesized in three steps starting from 4'-nitrodeoxybenzoin. New aromatic polyamides containing tetraphenylthiophene unit were prepared by the low temperature solution polycondensation of this diamine with various aromatic dicarboxylic acid chlorides. These polyamides had inherent viscosities of 0.20—0.35 dl g⁻¹ and were generally soluble in various organic solvents such as *N,N*-dimethylacetamide, *N*-methyl-2-pyrrolidone, and dimethyl sulfoxide. The glass transition temperatures of the polyamides ranged from 285 to 327°C, and the 10% weight loss temperatures were observed above 530°C in nitrogen.

KEY WORDS High Temperature Polymers / Soluble Aromatic Polyamides
/ 3,4-Bis(4-aminophenyl)-2,5-diphenylthiophene / Thermal Behavior /

Aromatic polyamides are well known to have high thermal stability coupled with high crystallinity and hence found high temperature applications especially as fibers for many years.¹ However, most wholly aromatic polyamides are difficult to fabricate because of their less solubility and high melting temperatures. Several attempts have been made to improve the solubility by modifying the structure without losing their good thermal stability.^{2,3} We also have found that the aromatic polyamides having phenyl-pendant structures such as tetraphenylthiophene,⁴⁻⁶ tetraphenylfuran,⁷ tetraphenylpyrrole,⁸ tetraphenylethylene,⁹ triphenylamine,¹⁰ and triphenylphosphine,¹¹ have high thermal stability and good solubility in various organic solvents. In continuation to our studies on the synthesis of high temperature polymers, we aimed at the synthesis of a new diamine monomer, 3,4-bis(4-

aminophenyl)-2,5-diphenylthiophene, and the resultant aromatic polyamides. This article deals with the synthesis and characterization of novel aromatic polyamides from this diamine and various aromatic dicarboxylic acid chlorides. The properties were compared with those of the structurally related polyamides derived from the isomeric diamine, 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene.⁵

EXPERIMENTAL

Materials

Isophthaloyl chloride (**IVa**), terephthaloyl chloride (**IVb**), 4,4'-biphenyldicarbonyl chloride (**IVc**), 2,6-naphthalenedicarbonyl chloride (**IVd**), 4,4'-oxybiphenoyl chloride (**IVe**), and 4,4'-sulfonyldibenzoyl chloride (**IVf**) were obtained commercially and purified by distillation under reduced pressure. *N*-methyl-2-

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pyrrolidone (NMP) was purified by vacuum distillation with calcium hydride.

Monomer Synthesis

3,4-Bis(4-nitrophenyl)-2,5-diphenylthiophene (II). 1,2-Bis(4-nitrophenyl)-1,2-dibenzoyl-ethane (I) was prepared in 75% yield by the oxidative coupling of 4'-nitrodeoxybenzoin using sodium ethoxide and iodine according to the method reported previously.⁷

In a flask, 39.0 g (81 mmol) of compound I and 40.5 g (97 mmol) of 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, Lawesson's reagent, were dissolved in 200 ml of dry toluene and the mixture was refluxed for 5 h. After cooling, the precipitate was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The crude product was recrystallized from acetic acid to afford yellow prisms; mp 231–232°C. The yield was 32.5 g (83%). The IR spectrum (KBr) exhibited an absorption band at 1444 cm⁻¹ (thiophene ring) with no carbonyl absorption. The ¹³C NMR spectrum (δ in CDCl₃) showed peaks at 146.9, 142.9, 141.3, 136.5, 132.9, 131.8, 129.4, 128.8, 128.3, and 123.5 ppm.

Anal. Calcd for C₂₈H₁₈N₂O₄S: C, 70.28%; H, 3.79%; N, 5.85%; S, 6.70%. Found: C, 70.19%; H, 3.66%; N, 5.78%; S, 6.55%.

3,4-Bis(4-aminophenyl)-2,5-diphenylthiophene (III). To a mixture of 20.0 g (0.04 mol) of compound II in 200 ml of glacial acetic acid, a solution of 99.5 g (0.44 mol) of stannous chloride dihydrate in 100 ml of concentrated hydrochloric acid was added all at once. The mixture was refluxed for 5 h. After it had been cooled, an aqueous sodium hydroxide solution was added to the resulting suspension with vigorous stirring in order to make a strongly alkaline mixture (pH 11–12). The solid thus obtained was filtered, washed repeatedly with water, and dried. It was recrystallized from toluene to give white needles; mp 246–247°C. The yield was 12.4 g (71%). The IR spectrum (KBr) exhibited absorption bands at 3446 and

3364 cm⁻¹ (N–H). The ¹H NMR spectrum [δ in dimethyl sulfoxide (DMSO)-*d*₆] showed signals at 6.30–6.47 (d, 4H, aromatic ortho to NH₂), 6.58–6.71 (d, 4H, aromatic *meta* to NH₂), and 7.18–7.33 ppm (m, 14H, other aromatic). The ¹³C NMR spectrum (δ in DMSO-*d*₆) exhibited peaks at 148.2, 141.8, 137.3, 135.6, 132.2, 129.7, 129.5, 128.1, 124.8, and 114.8 ppm.

Anal. Calcd for C₂₈H₂₂N₂S: C, 80.35%; H, 5.30%; N, 6.69%; S, 7.66%. Found: C, 80.56%; H, 5.37%; N, 6.52%; S, 7.44%.

Polymerization

A typical example of the polycondensation is given below.

Polyamide Vb from III and IVb

In a three neck flask, a solution of 1.046 g (2.5 mmol) of diamine III and 5.0 ml of NMP was chilled in a dry ice–acetone bath under nitrogen. To this, 0.508 g (2.5 mmol) of solid diacid chloride IVb was added all at once. Then the mixture was stirred at 4°C in an ice–water bath. The polymerization proceeded as the solid dissolved. After stirring at that temperature for 5 h, the reaction mixture was poured into 400 ml of methanol. The precipitated polymer was collected, washed thoroughly with methanol, and dried at 100°C under vacuum. The yield was 1.340 g (97%). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.23 dl g⁻¹, measured 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 1657 cm⁻¹ (C=O).

Anal. Calcd for (C₃₆H₂₄N₂O₂S)_n: C, 78.81%; H, 4.41%; N, 5.11%; S, 5.84%. Found: C, 78.49%; H, 4.53%; N, 5.21%; S, 5.61%.

Measurements

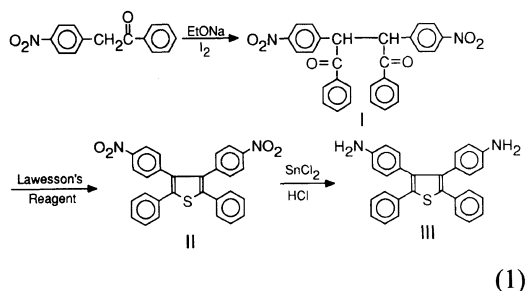
IR spectra were recorded on a JASCO FTIR-5000 spectrophotometer. ¹H NMR (90 MHz) and ¹³C NMR (22.6 MHz) spectra were obtained on a JEOL C60-HL spectrom-

eter. Wide angle X-ray diffraction patterns were obtained for film specimens on a Rigaku Denki XG X-ray diffraction apparatus with nickel-filtered Cu-K_α radiation (35 kV, 200 mA). Differential thermal analysis (DTA), thermogravimetry (TG), and differential scanning calorimetry (DSC) were performed with Shimadzu thermal analyzers DTA-40, TGA-40M, and DSC-41M, respectively, and the measurements were made at a heating rate of 10°C min⁻¹ in air or nitrogen.

RESULTS AND DISCUSSION

Monomer Synthesis

A new aromatic diamine having bulky pendant phenyl groups, 3,4-bis(4-aminophenyl)-2,5-diphenylthiophene (**III**), was synthesized in three steps starting from 4'-nitrodeoxybenzoin according to eq 1.



Recently Lawesson's reagent, 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane-2,4-disulfide, was used effectively in place of classic phosphorus pentasulfide as a sulfurizing agent for the synthesis of substituted thiophenes from 1,4-diketone compounds.¹² Here compound **I**, synthesized by the oxidative coupling of 4'-deoxybenzoin,⁷ was successfully converted by treating with Lawesson's reagent in refluxing toluene to 3,4-bis(4-nitrophenyl)-2,5-diphenylthiophene (**II**) in 83% yield. The subsequent reduction of the dinitro compound **II** with stannous chloride afforded diaminetetraphenylthiophene **III** in 71% yield.

The chemical structures of all the synthesized

compounds were confirmed by means of both IR and NMR spectra, and elemental analysis. Concerning the synthesis of compound **II**, the disappearance of the characteristic carbonyl band at 1660 cm⁻¹ was observed on the IR spectrum together with the appearance of an absorption band at 1444 cm⁻¹ due to thiophene ring. Compound **III** showed IR absorptions at 3446 and 3364 cm⁻¹ characteristic of amino group. The ¹³C NMR spectrum of compound **III** exhibited 10 peaks due to symmetry, indicative of the formation of the postulated diamine. The elemental analysis of all of these compounds were also in good agreement with the calculated values for the proposed structures.

Polymer Synthesis

New aromatic polyamides **V** containing tetraphenylthiophene unit were prepared by the low temperature solution polycondensation of diaminetetraphenylthiophene **III** with various aromatic dicarboxylic acid chlorides **IVa—IVf** in NMP [eq 2].

The results of synthesis of the aromatic polyamides are summarized in Table I. The inherent viscosities of the polymers were in the

Table I. Synthesis of aromatic polyamides^a

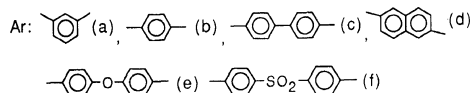
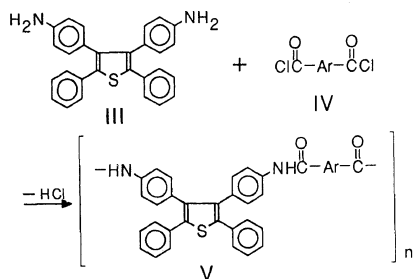
Diacid chloride	Polymer			Remarks ^c
	Code	Yield	η_{inh}^b	
		%	dl g ⁻¹	
IVa	Va	99	0.20	S
IVb	Vb	82	0.20	P
IVc	Vc	89	0.33	S
IVd	Vd	95	0.35	S
IVe	Ve	86	0.27	S
IVf	Vf	90	0.30	S

^a Polymerization was carried out with 2.5 mmol of each monomer in 5.0 ml of NMP at 4°C for 5 h under nitrogen.

^b Measured at a concentration of 0.5 g dl⁻¹ in concentrated sulfuric acid at 30°C.

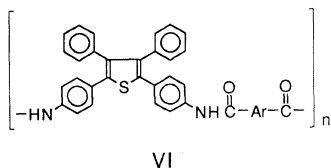
^c Appearance of the polymerization mixture: S, homogeneous solution; P, polymer precipitation.

range of 0.20–0.35 dl g⁻¹, and hence these polyamides gave brittle films by



(2)

casting from the NMP solutions. Most of the polycondensations proceeded in homogeneous solution, except the polymerization with **IVb** where precipitation of the polymer occurred during the course of the reaction because of low solubility of polymer **Vb** in NMP. On the whole, this diaminotetraphenylthiophene afforded the polymers with relatively low viscosity values, compared with polyamides **VI** having inherent viscosities of around 1.0 dl g⁻¹ derived from the isomeric diamine, 2,5-bis(4-aminophenyl)-3,4-diphenylthiophene.⁵ The reason is unclear yet, but may be attributed partly to the steric hindrance of diamine **III** with V-shaped narrow angle between two aminophenyl groups. The IR spectra of these polymers showed characteristic amide absorption bands at around 3360 cm⁻¹ (N–H) and 1657 cm⁻¹ (C=O), which confirmed the formation of the proposed polyamides.



Polymer Characterization

Table II lists qualitative solubility of the

Table II. Solubility of aromatic polyamides^a

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

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

tetraphenylthiophene-containing aromatic polyamides **V**. All the polymers were soluble in NMP, *N,N*-dimethylacetamide, and dimethyl sulfoxide, but entirely insoluble in methanol, acetone, and chloroform. Polymer **Va** with *m*-phenylene moiety as well as polymers **Ve** and **Vf** having flexible connecting groups were more soluble than the other polymers (**Vb**, **Vc**, and **Vd**) with rigid symmetric structures, and dissolved even in *m*-cresol and pyridine. Polyamides **VI** having isomeric structure (the arylene moiety (Ar) for polymer **VI** corresponds individually to that for polymer **V**) showed similar solubility behavior to the present polyamides **V**. The solubility of these two tetraphenylthiophene-based polyamides was better than that of the tetraphenylfuran- and tetraphenylpyrrole-containing polyamides.^{7,8}

The thermal behavior of these polyamides **V** and **VI** was evaluated by means of DTA, TG, and DSC. Figure 1 shows typical DTA and TG curves of polyamide **Va**, and the glass transition temperatures (T_g) and 10% weight loss temperatures (T_{10}) are summarized in Table III. The present polyamides **V** had relatively high T_g values in the range of 285–327°C. In general, polyamides **Vb** and **Vc** having rigid symmetric structures had higher T_g values than polymers **Va** with unsymmetric one. On the whole, the T_g values were almost comparable to those of the isomeric polyamides **VI** (304–317°C), and even to those of tetraphenylfuran- and tetraphenylpyrrole-con-

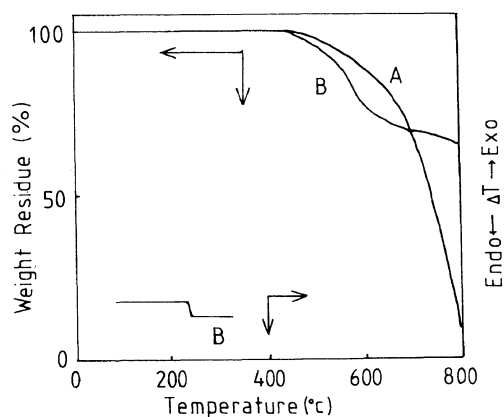


Figure 1. DTA and TG curves for polyamide **Va** at a heating rate of $10^{\circ}\text{C min}^{-1}$ in (A) air and (B) nitrogen.

Table III. Thermal behavior of aromatic polyamides

Polymer	T_g^a °C	T_{10}^b		Char yield ^c %
		In air	In nitrogen	
		°C	°C	
Va	293	565	535	64
Vb	323	510	565	65
Vc	321	505	545	62
Vd	299	530	560	64
Ve	285	510	540	60
Vf	327	490	530	57
VIa	304	490	500	39
VIb	314	500	530	55
VIc	—	535	540	58
VI d	—	505	565	78
VIe	306	495	515	49
VI f	317	475	510	59

^a Determined by DSC in nitrogen at a heating rate of $10^{\circ}\text{C min}^{-1}$.

^b Temperature at which 10% weight loss was recorded by TG at a heating rate of $10^{\circ}\text{C min}^{-1}$.

^c Char yield in nitrogen at 800°C .

taining polyamides.^{7,8}

All the present polyamides **V** did not lose weight below 400°C in air or nitrogen, and the T_{10} values in air and nitrogen were in the range of 490 – 565°C and 530 – 565°C , respectively, indicating high thermal stability. In addition, more than 60% weight was retained even at 800°C in nitrogen for these polyamides. The

thermal stability with respect to T_{10} values was somewhat higher than that of the isomeric polyamides **VI**. On the basis of T_{10} values in air or nitrogen, these tetraphenylthiophene-based polyamides had higher thermal stability than the tetraphenylfuran- and tetraphenylpyrrole-containing polyamides.^{7,8} This is attributable to difference in inherent thermal stability between these five-membered heterocyclic rings as discussed previously.⁸

CONCLUSION

We have synthesized the new aromatic diamine having bulky pendant phenyl groups, 3,4-bis(4-aminophenyl)-2,5-diphenylthiophene, which was subjected to polycondensation with aromatic dicarboxylic acid chlorides giving new aromatic polyamides. These polyamides were soluble in various organic solvents, and had high glass transition temperatures as well as high thermal stability.

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