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Rigid-Rod Polyamides and Polyimides Derived from 4,3″-Diamino-2′,6′-diphenyl- or Di(4-biphenylyl)-*p*-terphenyl and 4-Amino-4″-carboxy-2′,6′-diphenyl-*p*-terphenyl

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ABSTRACT: 4,3″-Diamino-2′,6′-diphenyl- or di(4-biphenylyl)-*p*-terphenyl (**3a** or **3b**) and 4-amino-4″-carboxy-2′,6′-diphenyl-*p*-terphenyl (**6**) were synthesized through pyrylium salts and used for the preparation of rigid-rod polyamides and polyimides. The polymers were characterized by inherent viscosity, elemental analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR, UV−vis, X-ray, differential scanning calorimetry (DSC), thermomechanical analysis (TMA), thermal gravimetric analysis (TGA) isothermal gravimetric analysis, and moisture absorption. They were amorphous. All polyamides as well as the polyimide derived from **3b** and benzophenonetetracarboxylic dianhydride dissolved in polar aprotic solvents and H_2SO_4 98%. Polyamide prepared from **6** showed blue fluorescence in dimethylformamide solution. The T_gs of polyamides ranged from 235 to 285 °C. The polymers possessed excellent thermooxidative stability with no weight loss up to 379−417 °C in air.

Introduction

Rigid-rod polymers are well accepted as heat-resistant materials with high mechanical strength, giving easily lyotropic solutions.[1−3] However, they present usually infusibility and limited solubility, properties which decrease their processability and restrict further applications. To overcome this problem, various monomers carrying pendent groups have been polymerized or copolymerized leading to polymers with enhanced solubility.[4−37]

Soluble, rigid-rod polyamides and polyimides have been synthesized in our laboratory derived from aromatic diamines of *p*-terphenyl[38] or biphenyl[39] containing phenyl pendent groups. More recently, we have prepared soluble, blue- light-emitting, rigid-rod polyamides and polyimides starting from an aromatic diamine of *p*-quinquephenyl carrying phenyl or 4-biphenylyl pendent groups.[40]

The present investigation describes the synthesis and characterization of a new series of rigid-rod polyamides and polyimides prepared from a diamine of *p*-terphenyl bearing phenyl or 4-biphenylyl pendent groups at 2′ and 6′ positions as well as from an analogous amino acid. The monomers were synthesized by a convenient method through pyrylium salts from widely used and inexpensive starting materials.

Characterization Methods. Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16PC FT-IR spectrometer with KBr pellets. ^{1}H-NMR (400 MHz) and ^{13}C-NMR (100 MHz) spectra were obtained using a Bruker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. UV−vis spectra were recorded on a Beckman DU-640 spectrometer with spectograde DMF. DSC and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA and isothermal gravimetric analysis (IGA), and the weight loss comparisons were made between comparable specimens. Dynamic TGA measurements were made at a heating rate of 20 °C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. TMA was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 20 °C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted in duplicate. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing powder of polymer for 3 min under 5−7 kpsi at ambient temperature. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 mL in DMAc or concentrated H_2SO_4 at 30 °C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard Model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

To determine the equilibrium water absorption, polymer samples were previously conditioned at 120 °C in an oven for 12 h. They were subsequently placed in a desiccator where 65% r.h. (relative humidity) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20 °C and were periodically weighed.

Reagents and Solvents. 3-Nitrobenzaldehyde, 4-phenylacetophenone, and 4-carboxybenzaldehyde were recrystallized from 95% ethanol. Acetophenone was distilled under vacuum. 4-Nitrophenylacetic acid so-

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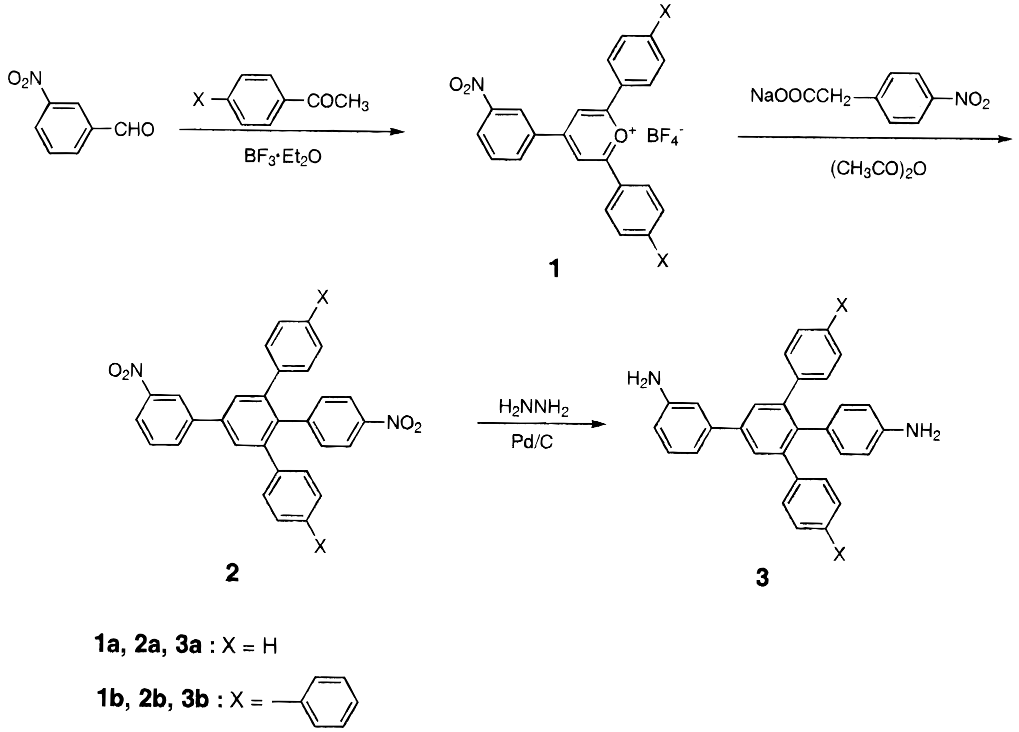
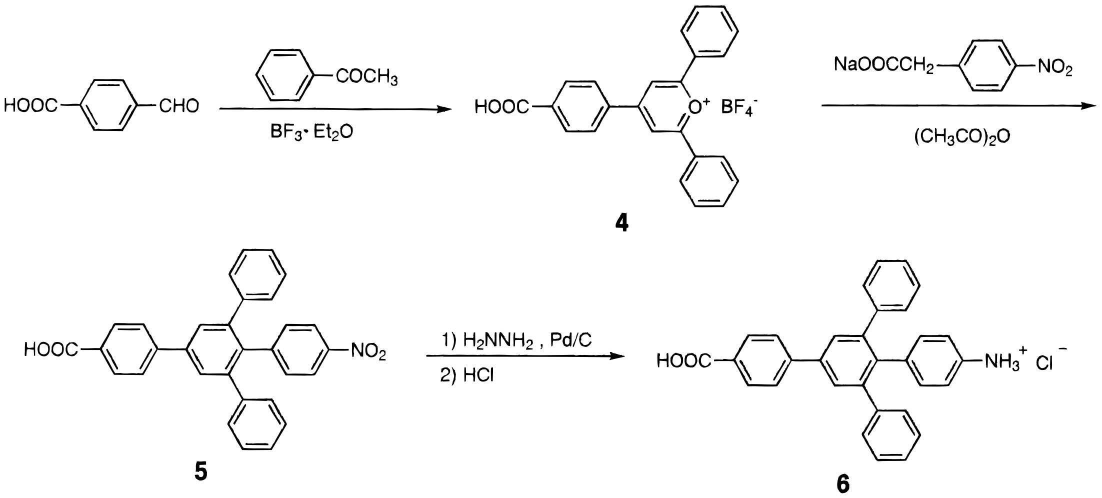
Scheme 1



Scheme 2



dium salt was prepared by reacting equimolar amounts of 4-nitrophenylacetic acid with aqueous sodium hydroxide. Terephthaloyl chloride was recrystallized from *n*-hexane. Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Toluene and dimethylacetamide (DMAc) were dried by distillation over sodium or CaH_2, respectively. Boron trifluoride etherate, hydrazine hydrate, and acetic anhydride were used as supplied.

Preparation of Starting Materials (Schemes 1 and 2). 4-(3-Nitrophenyl)-2,6-diphenylpyrylium tetrafluoroborate (**1a**) and 4-(4-carboxyphenyl)-2,6-diphenylpyrylium tetrafluoroborate (**4**) were synthesized and characterized previously.[39]

4-(3-Nitrophenyl)-2,6-di(4-biphenylyl)pyrylium tetrafluoroborate (1b). 3-Nitrobenzaldehyde (5.00 g, 33.01 mmol) and 4-phenylacetophenone (12.84 g, 66.02 mmol) were dissolved in toluene (25 mL) by slight heating. Boron trifluoride etherate (9.98 mL, 97.22 mmol) diluted with toluene (5 mL) was added portionwise to the stirred solution at room temperature, and it was refluxed for 3 h. The dark red solution was concentrated under reduced pressure, and the residue was stirred with warm 1,4-dioxane. The red solid obtained was filtered off, washed with 1,4-dioxane, and dried to afford **1b** in 58% yield (11.39 g). It was recrystallized from acetic acid. Mp: 299−301 °C. IR (KBr, cm^{-1}): 1620, 1604, 1494, 1460 (aromatic and pyrylium structure); 1536, 1348 (NO_2); 1054 (br, BF_4^-). ^1H-NMR (DMSO-d_6): δ 8.85−8.30 (m, 4H, aromatic meta to O^+ and ortho to NO_2); 7.95−7.25 (m, 20H, other aromatic).

4,3″-Dinitro-2′,6′-diphenyl-*p*-terphenyl (2a). A mixture of **1a** (4.57 g, 10.36 mmol), 4-nitrophenylacetic acid sodium salt (1.70 g, 20.72 mmol), and acetic anhydride (10 mL) was stirred and refluxed for 3 h. It was cooled at about −10 °C overnight, and the yellow

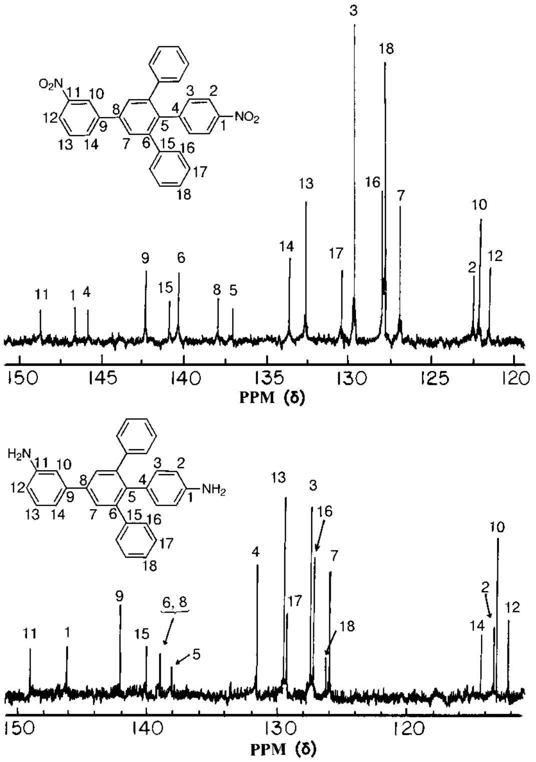


Figure 1. ^{13}C-NMR spectra of compounds **2a** (upper) and **3a** (lower) in DMSO-d_6 solution.

solid precipitate was filtered off, washed with methanol, and dried to afford **2a** (4.40 g, 90%). A purified sample was obtained by recrystallization from acetic acid. Mp: 144−145 °C. IR (KBr, cm^{-1}): 1598, 1516 (aromatic); 1527, 1346 (NO_2). ^{1}H-NMR (DMSO-d_6): δ 8.61 (s, 1H, aromatic at position 2″); 8.33−8.24 (m, 3H, aromatic at positions 3, 5, and 4″); 7.89−7.76 (m, 6H, aromatic at positions 2, 6, 3′, 5′, 5″, and 6″); 7.23−7.18 (m, 10H, other aromatic). The ^{13}C-NMR spectrum is shown in Figure 1.

4,3″-Dinitro-2′,6′-di(4-biphenylyl)-*p*-terphenyl (2b). A mixture of **1b** (9.00 g, 15.17 mmol), 4-nitrophenylacetic acid sodium salt (2.49 g, 30.34 mmol), and acetic anhydride (20 mL) was stirred and refluxed for 3 h. It was cooled at about −10 °C, and methanol (20 mL) was added. The yellow solid precipitate was filtered off, washed with methanol, and dried to afford **2b** (8.23 g, 87%). It was recrystallized from acetic acid. Mp: 172−174 °C. IR (KBr, cm^{-1}): 1598, 1484 (aromatic); 1518, 1346 (NO_2). ^{1}H-NMR (DMSO-d_6): δ 8.54 (s, 1H, aromatic at position 2″); 8.21−8.12 (m, 3H, aromatic at positions 3, 5, and 4″); 7.84−7.46 (m, 6H aromatic at positions 2, 6, 3′, 5′, 5″, and 6″ as well as 8H aromatic at positions 2, 3, 5, and 6 of side biphenyls); 7.35−7.21 (m, 10H, aromatic at positions 2″, 3″, 4″, 5″, and 6″ of side biphenyls).

4,3″-Diamino-2′,6′-diphenyl-*p*-terphenyl (3a). Hydrazine hydrate (5 mL) was added dropwise to a mixture of **2a** (3.50 g, 7.42 mmol), 95% ethanol (20 mL), and a catalytic amount of 10% palladium on activated carbon at the boiling temperature. The mixture was refluxed overnight, and **2a** was dissolved during this period. It was subsequently filtered, and the filtrate was cooled at 0 °C. The whitish solid obtained was filtered off, washed with water, and dried to afford **3a** (2.29 g, 75%). It was recrystallized from ethanol 70%. Mp: 226−227 °C. Anal. Calcd for $C_{30}H_{24}N_2$: C, 87.35; H, 5.86; N, 6.79. Found: C, 86.72; H, 5.80; N, 6.82. IR (KBr, cm^{-1}): 3412, 3347 (N−H stretching); 1621 (N−H deformation); 1606, 1518, 1424 (aromatic); 1276 (C−N stretching). ^{1}H-NMR (DMSO-d_6): δ 7.50 (s, 1H, aromatic at positions 3′ and 5′); 7.23−7.00 (m, 10H, aromatic of side phenyls); 6.91, 6.90, 6.79 (t, 3H, aromatic at positions 2″, 5″, and 6″); 6.60 (s, 1H, aromatic at position 4″); 6.49, 6.47 (d, 2H, aromatic at positions 2 and 6); 6.22, 6.20 (d, 2H, aromatic at positions 3 and 5); 4.75 (br, 4H, NH_2). The ^{13}C-NMR spectrum is shown in Figure 1.

4,3″-Diamino-2′,6′-di(4-biphenylyl)-*p*-terphenyl (3b). It was prepared as a yellowish solid in 81% yield by hydrogenation of **2b** according to the procedure described for **3a**. A purified sample was obtained by recrystallization from 1,2-dichloroethane. Mp: 189−191 °C. Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33; H, 5.71; N, 4.96. Found: C, 88.46; H, 5.64; N, 4.94. IR (KBr, cm^{-1}): 3388, 3212 (N−H stretching); 1618 (N−H deformation); 1597, 1518, 1486 (aromatic); 1278 (C−N stretching). ^{1}H-NMR (DMSO-d_6): δ 7.67−7.53 (m, 2H aromatic at positions 3′ and 5′ of terphenyl as well as 8H aromatic at positions 2, 3, 5, and 6 of side biphenyls); 7.46−7.25 (m, 10H, aromatic at positions 2′, 3′, 4′, 5′, and 6′ of side biphenyls); 7.04−6.95 (t, 3H, aromatic at positions 2″, 5″, and 6″ of terphenyl); 6.60, 6.58 (d, 3H, aromatic at positions 2, 6, and 4″ of terphenyl); 6.29, 6.27 (d, 2H, aromatic at positions 3 and 5 of terphenyl); 5.00, 4.71 (d, 4H, NH_2). ^{13}C-NMR (DMSO-d_6): δ 148.29, 145.69, 140.96, 140.58, 139.38, 138.87, 138.51, 137.36, 136.92, 130.96, 129.33, 128.56, 128.01, 126.60, 126.43, 125.58, 125.52, 125.21, 124.89, 113.64, 112.63, 112.51, 111.54.

4-Nitro-4″-carboxy-2′,6′-diphenyl-*p*-terphenyl (5). A mixture of **4** (4.00 g, 9.09 mmol), 4-nitrophenylacetic acid sodium salt (1.49 g, 18.18 mmol), and acetic anhydride (15 mL) was stirred and refluxed for 3 h. It was cooled at about −10 °C overnight, and the yellow solid precipitate was filtered off, washed with methanol, and dried to afford **5** (2.24 g, 52%). A purified sample was obtained by recrystallization from acetic acid. Mp: >300 °C. IR (KBr, cm^{-1}): 3190−2650 (O−H stretching); 1688 (C=O); 1598 (aromatic); 1518, 1346 (NO_2); 1424, 1290 (C−O stretching and O-H deformation). ^{1}H-NMR (DMSO-d_6): δ 12.50 (s, 1H, COOH); 8.06, 8.04 (d, 2H, aromatic at positions 3 and 5); 7.98, 7.96 (d, 2H, aromatic at positions 3″ and 5″); 7.88−7.77 (m, 6H, aromatic at positions 2, 6, 3′, 5′, 2″, and 6″); 7.23−7.17 (m, 10H, other aromatic). ^{13}C-NMR (DMSO-d_6): δ 166.96, 146.67, 145.75, 143.14, 142.17, 140.44, 139.06, 136.71, 132.59, 130.31, 129.90, 129.62, 127.80, 127.07, 126.84, 122.08.

4-Amino-4″-carboxy-2′,6′-diphenyl-*p*-terphenyl Hydrochloric Salt (6). Hydrazine hydrate (5 mL) was added dropwise to a mixture of **5** (2.00 g, 4.22 mmol), 95% ethanol (15 mL), and a catalytic amount of 10% palladium on activated carbon at boiling temperature. The mixture was refluxed overnight and filtered. The filtrate was cooled at 0 °C, and concentrated hydrochloric acid was added. The whitish solid precipitate was filtered off, washed thoroughly with water, and dried to afford **6** (1.59 g, 80%). It was recrystallized from 1,2-dichlorobenzene. Mp: 244−246 °C. Anal. Calcd for $C_{31}H_{24}NO_2Cl$: C, 77.90; H, 5.06; N, 2.93. Found: C, 77.18; H, 5.09; N, 2.88. IR (KBr, cm^{-1}): 3386−2600 (O−H stretching and NH_3^+ stretching); 1692 (C=O); 1610 (NH_3^+ deformation); 1516, 1489 (aromatic); 1268 (C−N stretching). ^{1}H-NMR (DMSO-d_6): δ 8.05, 8.03 (d,

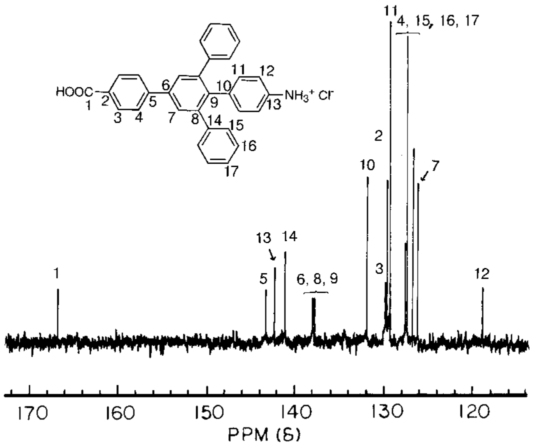
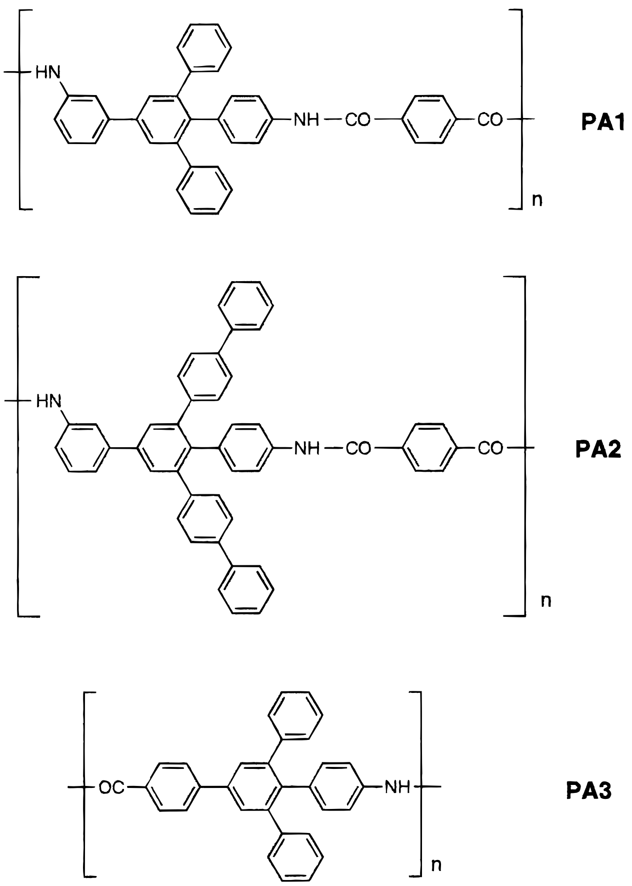


Figure 2. ^{13}C-NMR spectrum of compound **6** in DMSO-d_6 solution.

Chart 1



PA1

PA2

PA3

2H, aromatic at positions 3″ and 5″); 7.94, 7.92 (d, 2H, aromatic at positions 2″ and 6″); 7.70 (s, 2H, aromatic at positions 3′ and 5′); 7.24–7.16 (m, 10H, aromatic of side phenyls); 6.86, 6.84 (d, 2H, aromatic at positions 2 and 6); 6.79, 6.77 (d, 2H, aromatic at positions 3 and 5). The carboxylic and amine protons were unobserved. The ^{13}C-NMR spectrum is shown in Figure 2.

Preparation of Polyamides (Chart 1). Polyamides PA1 and PA2. A flask equipped with a dropping funnel and a magnetic stirrer was charged with a solution of **3a** (0.49 g, 1.19 mmol) in DMAc (9 mL) containing 5 wt % LiCl. Triethylamine (0.24 g, 2.38 mmol) was added to the solution. Terephthaloyl chloride (0.24 g, 1.19 mmol) dissolved in DMAc (5 mL) was added dropwise to the stirred solution at −15 °C under N_2. The mixture was subsequently stirred at this temperature for 6 h and then at room temperature overnight in a stream of N_2. It was poured into water, and the whitish solid precipitate was filtered off, washed with water was then with hot acetone, and dried to afford **PA1** (0.58 g, 81%).

Table 1. Yields, Inherent Viscosities, and Elemental Analyses of Polymers

				elemental analyses			
polymer	yield (%)	η_{inh} (dL/g)	empirical formula		C (%)	H (%)	N (%)
PA1	91	1.06[a]	$(C_{38}H_{26}N_2O_2)_n$	calcd	84.11	4.83	5.16
				found	83.05	4.75	5.08
PA2	97	0.97[a]	$(C_{50}H_{34}N_2O_2)_n$	calcd	86.42	4.94	4.03
				found	85.11	4.87	4.09
PA3	96	0.88[a]	$(C_{31}H_{21}NO)_n$	calcd	87.91	5.00	3.31
				found	86.21	5.14	3.21
PIB1	87	1.22[b]	$(C_{47}H_{26}N_2O_5)_n$	calcd	80.79	3.75	4.01
				found	79.86	3.70	4.07
PIB2	99	1.11[a]	$(C_{59}H_{34}N_2O_5)_n$	calcd	83.28	4.03	3.29
				found	81.62	3.89	3.41
PIP1	90	1.52[b]	$(C_{40}H_{22}N_2O_4)_n$	calcd	80.80	3.73	4.71
				found	80.13	3.75	4.68
PIP2	93	1.39[b]	$(C_{52}H_{30}N_2O_4)_n$	calcd	83.63	4.05	3.75
				found	82.87	4.11	3.68

[a] Inherent viscosity in DMAc (0.5 g/dL) at 30 °C. [b] Inherent viscosity in H_2SO_4 (0.5 g/dL) at 30 °C.

Polyamide **PA2** was similarly prepared as a pale brown solid in 97% yield.

Polyamide PA3. A flask was charged with a mixture of **6** (0.25 g, 0.52 mmol), triphenyl phosphite (0.16 g, 0.52 mmol), pyridine (2 mL), and DMAc (10 mL) containing 5 wt % LiCl. It was heated at 120 °C overnight under N_2 and poured into water. The yellowish solid precipitate was filtered off, washed with water and then with hot acetone, and dried to afford **PA3** (0.23 g, 96%).

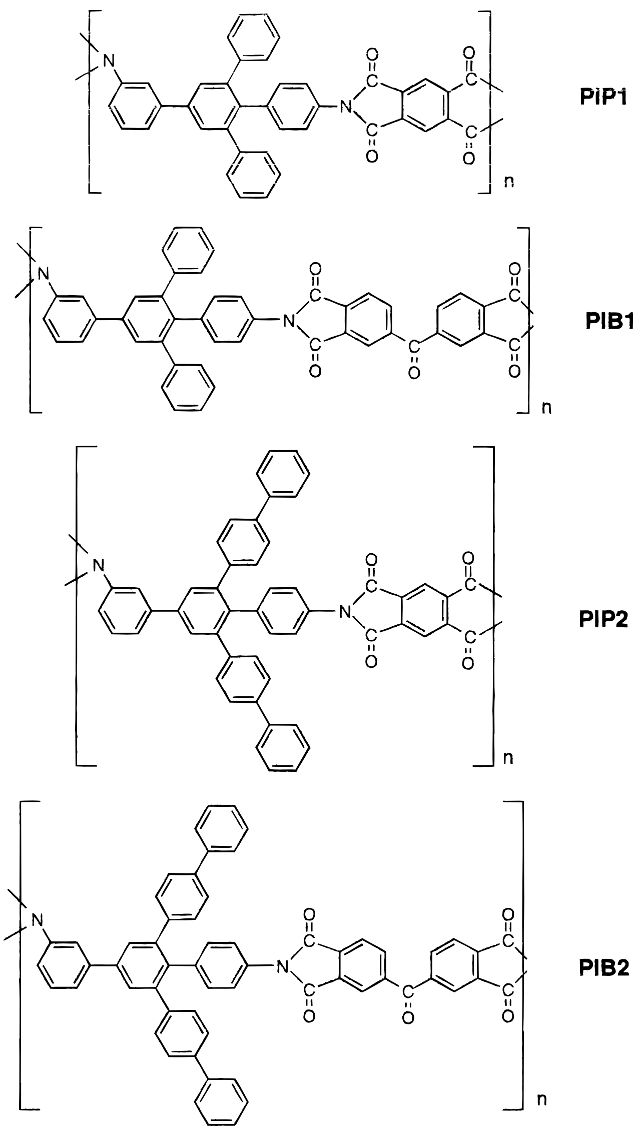
Preparation of Polyimides (Chart 2). As a typical procedure for the preparation of polyimides, the synthesis of **PIP1** is given: PMDA (0.19 g, 0.85 mmol) was added to a stirred solution of **3a** (0.35 g, 0.85 mmol) in DMAc (20 mL) containing 5 wt % LiCl at 0 °C. The solution became viscous, and stirring was continued at room temperature for 3 h. Acetic anhydride (5 mL) and pyridine (2 mL) were added to the solution, and it was heated at 100 °C overnight. It was subsequently poured into water, and the brown solid precipitate was filtered off, washed with water and then with hot acetone, and dried (0.46 g, 90%).

The reaction yields, the inherent viscosities, and the elemental analyses of all polymers are given in Table 1.

Results and Discussion

New aromatic diamines of *p*-terphenyl bearing phenyl or 4-biphenylyl pendent groups on the middle ring were synthesized according to the reaction sequence of Scheme 1. Specifically, 3-nitrobenzaldehyde reacted with acetophenone or 4-phenylacetophenone in the presence of $BF_3{\cdot}Et_2O$ to yield the substituted pyrylium salts **1**. The latter reacted with 4-nitrophenylacetic acid sodium salt in acetic anhydride to afford the substituted dinitro-*p*-terphenyls **2**. In this reaction, 4-nitrophenylacetic acid anhydride was formed *in situ* from 4-nitrophenylacetic acid sodium salt and excess of acetic anhydride.[40,41] Finally, the hydrogenation of dinitro compounds **2** to the corresponding diamines **3** was accomplished using hydrazine hydrate. An analogous synthetic route was

Chart 2



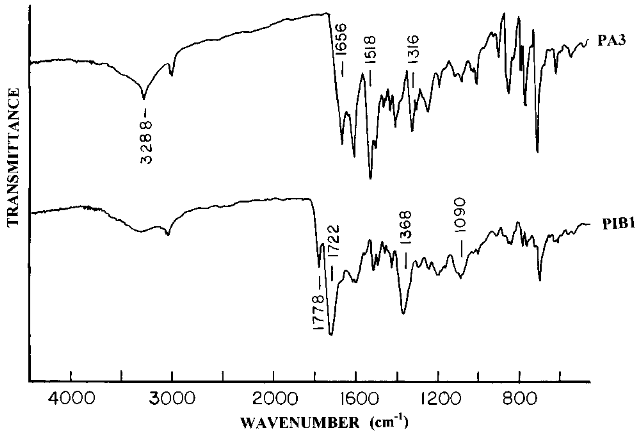


Figure 3. FT-IR spectra of polyamide **PA3** and polyimide **PIB1**.

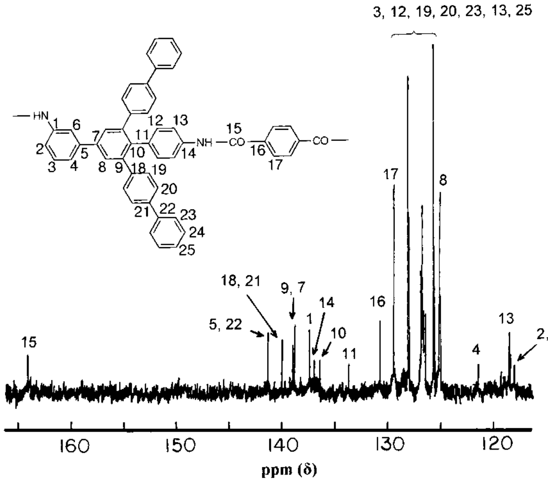


Figure 4. ^{13}C-NMR spectrum of polyamide **PA2** in DMSO-d_6 solution.

applied for the synthesis of amino acid **6** starting from 4-carboxybenzaldehyde (Scheme 2).

The monomers were characterized by elemental analyses as well as IR and NMR spectroscopy (see the Experimental Section). Figure 1 presents the ^{13}C-NMR spectra of compounds **2a** and **3a** as well as assignments of peaks. Figure 2 shows the ^{13}C-NMR spectrum of compound **6**. The carboxyl carbon displayed a characteristic peak at δ 167. This spectrum confirmed the structure of amino acid, since the carboxyl proton as well as the amine protons were unobserved in the ^{1}H-NMR spectrum of **6**.

Certain structural characteristics of the synthesized diamines **3** and amino acid **6** were estimated using a modeling system. The optimized geometry of **6**, as calculated by means of CS Chem3D Pro version 3.2 modeling system, showed that the phenyl ring bearing the amino group as well as the two pendent phenyl rings was almost vertical to the plane of the other two phenyl rings of *p*-terphenyl. An analogous structure was observed for diamines **3**.

Rigid-rod polyamides and polyimides containing phenyl or 4-biphenylyl pendent groups were prepared, and their structures are presented in Charts 1 and 2. Polyamides **PA1** and **PA2** were prepared from diamines **3** while polyamide **PA3** was prepared from amino acid **6**. Polyimides were synthesized from the reaction of diamines **3** with PMDA or BTDA. All polymers remained soluble in the reaction medium, thus permitting an increase of their molecular weight and giving viscous solutions. The yields of the preparation reactions for all polymers were almost quantitative (87–99%), and their inherent viscosities ranged from 0.88 to 1.52 dL/g (Table 1).

The structures of the polymers were verified by elemental analyses as well as IR and NMR spectroscopies. Figure 3 presents typical FT-IR spectra of polyamide **PA3** and polyimide **PIB1**. Each class of the synthesized polymers displayed IR spectra with the same pattern. **PA3** showed characteristic absorptions for the amide structure at 3288 (N–H stretching), 1656 (C=O), 1518 (N–H deformation), and 1316 cm^{-1} (C–N stretching and N–H bending). **PIB1** showed absorption bands associated with the imide structure at 1778, 1722, 1368, and 1090 cm^{-1}. Figure 4 present the ^{13}C-NMR spectrum of polyamide **PA2**. Assignments of peaks are given in the figure.

All polymers presented amorphous X-ray diffraction patterns (Figure 5). This is reasonable because the side phenyl or 4-biphenylyl groups increased significantly the disorder in chains. In addition, the phenyl rings both of *p*-terphenyl segments and the pendent groups deviate considerably from the coplanar conformation (see above) and therefore should cause less chain

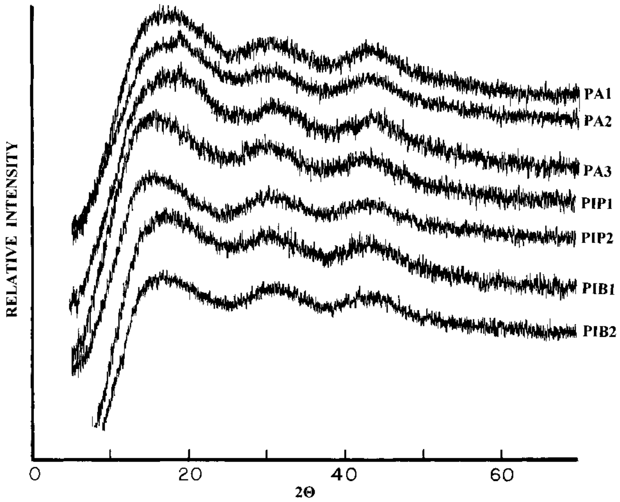


Figure 5. X-ray diffraction patterns of polymers.

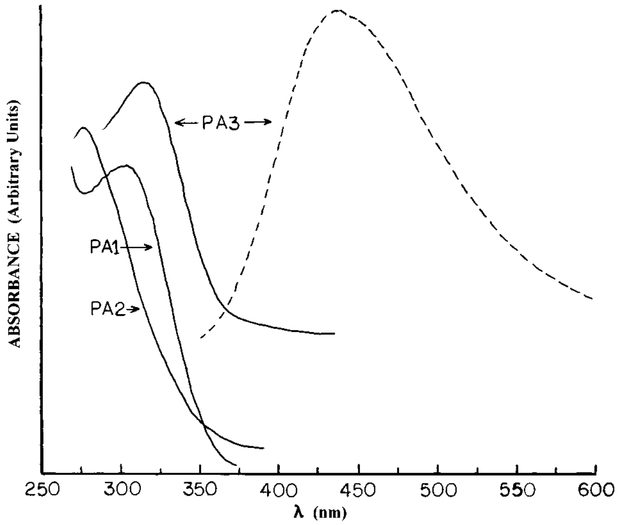


Figure 6. Absorption (—) spectra of polyamides **PA1**, **PA2**, and **PA3** as well as an emission (- - -) spectrum of polyamide **PA3** in DMF solution. The intensities were arbitrarily chosen in order to optimally fit the graphs.

packing. The amorphous character of polymers is in agreement with their enhanced solubility.

The isothermal water absorption of polyamides was determined to estimate their hydrophilicity. Polyamides **PA1**, **PA2**, and **PA3** showed water uptake 1.19, 0.76, and 1.24%, respectively, after 50 h exposure time. The corresponding numbers of moles of absorbed water per amide equivalent weight were 0.18, 0.15, and 0.29. The relatively lower hydrophilicity of polyamides bearing 4-biphenylyl pendent groups has also been observed in our previous publication.[40]

The solubility behavior of all polymers is summarized in Table 2. Polyamides dissolved in polar aprotic solvents (DMF, DMSO, NMP) and concentrated sulfuric acid at room temperature or upon heating. It seems that polyamides containing phenyl or 4-biphenylyl side groups exhibited comparable solubilities. An analogous behavior has been observed for substituted poly(*p*-phenyleneterephthalamide).[31] Polyamide **PA3** showed lower solubility due to the para orientation of all aromatic rings of backbone.

In the case of polyimides derived from BTDA, the incorporation of 4-biphenylyl as pendent groups along the polymer backbone increased remarkably their solubility. Thus, polyimide **PIB2** was readily soluble at room temperature in polar aprotic solvents as well as in warm H_2SO_4 and CCl_3COOH while the other polyimides were dissolved partially in these solvents.

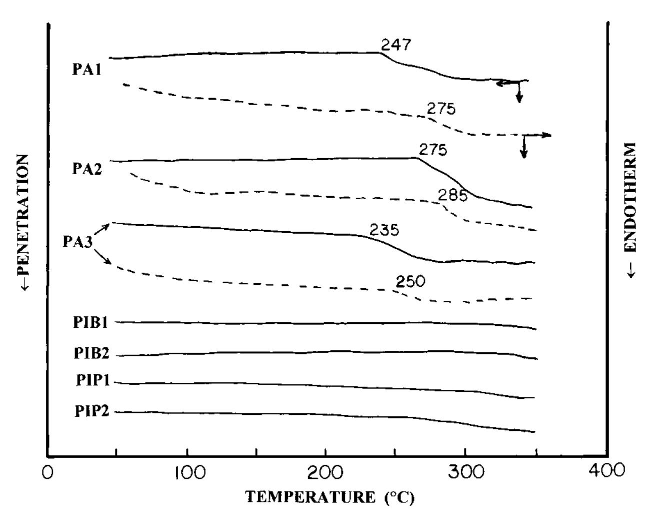


Figure 7. DCS thermograms (second heating) (- - -) of polyamides **PA1**, **PA2**, and **PA3** as well as TMA thermograms (—) of all polymers. Conditions: N_2 flow, 60 cm^3/min; heating rate, 20 °C/min.

The optical properties of polyamides and particularly their UV–vis absorption and emission spectra in DMF solution were investigated. When solutions of polyamide **PA3** in DMF were exposed to a UV lamp, they emitted strong blue light. Figure 6 presents the absorption and emission spectra of **PA3** in DMF solution. The absorption spectrum showed a maximum at 317 nm and had a short tail into the visible region. On the other hand, the emission spectrum was broad and displayed a maximum at 437 nm (excitation at 317 nm). It seems that most of the emission took place in the visible region. It has been reported[38] that the polyamide prepared from the reaction of 4,4″-diamino-3,5,3″,5″-tetraphenyl-*p*-terphenyl with terephthalic acid showed absorption and emission maxima at 298 and 317 nm, respectively. Upon comparing these spectra, the absorption and emission maxima of **PA3** are red shifted by 19 and 66 nm, respectively. This supports that **PA3** possesses a longer effective chromophore. In addition, the broadness of the emission spectrum of **PA3** suggested that the conjugation length was not precisely controlled.

The UV–vis spectra of *p*-terphenyl and 2′,6′-diphenyl-*p*-terphenyl (DTP) in DMF solution were obtained to study the influence of the two side phenyls on the chromophore length of *p*-terphenyl. They displayed absorption maxima at 283 and 266 nm, respectively. The lower value of DTP indicated shorter conjugation length. In the case of DTP, the side phenyls caused a much larger twist of the adjacent phenyl ring and hence an interruption of conjugation. Consequently, the chromophore length of polyamide **PA3** should be controlled by the side phenyls.

In addition, Figure 6 presents the UV–vis spectra of polyamides **PA1** and **PA2** in DMF solution, which exhibited maxima at 305 and 276 nm, respectively. It is obvious that the absorption curves of both polyamides were not extended into the visible region. Interestingly, these polyamides were not fluorescent probably because excitation causes other electronic transitions which compete successfully with fluorescence. Relating to the fluorescent structures described in this as well as in our

Table 2. Solubilities of Polymers[a]

polymer	solvents[b]							
	DMF	NMP	DMSO	CCl_3COOH	H_2SO_4	1,4-dioxane	CH	DCB
PA1	++	+	++	++	++	+−	++	+−
PA2	++	++	+	+	+	+	++	+−
PA3	+	+	+	+−	+	−	+−	+−
PIB1	+−	+−	+−	+−	+−	−	+−	+−
PIB2	++	++	++	+	+	−	+−	+−
PIP1	+−	+−	+−	+−	+	−	−	+−
PIP2	+−	+−	+−	+−	+	−	+−	+−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +−, partially soluble, −, insoluble. [b] DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide; CH, cyclohexanone; DCB, 1,2-dichlorobenzene.

Table 3. Thermal Stabilities of Polymers

		in N_2			in air			
polymer	IDT[a] (°C)	PDT[b] (°C)	PDT$_{max}$[c] (°C)	Y_c[d] (%)	IDT (°C)	PDT (°C)	PDT$_{max}$ (°C)	wt loss (%)
PA1	400	500	510	66	390	440	486	2.50
PA2	392	467	493	66	379	441	418	3.73
PA3	397	533	554	69	385	463	489	4.15
PIB1	421	585	575	71	417	472	462	0.93
PIB2	408	571	568	67	398	564	536	1.28
PIP1	411	590	631	70	404	552	617	1.77
PIP2	417	596	645	69	414	573	600	1.48

[a] Initial decomposition temperature. [b] Polymer decomposition temperature. [c] Maximum polymer decomposition temperature. [d] Char yield at 800 °C. [e] Weight loss after 20 h of isothermal aging at 300 °C in static air.

previous publication,[40] substitution in the meta instead of the para position is one main difference. Ion separation during the excitation procedure is a possible mechanism for this nonfluorescence behavior. This quenching mechanism is well-known in some aromatic systems containing amino groups.[42−45]

The thermal behavior of polymers was investigated by DSC and TMA. Figure 7 depicts the TMA traces of all polymers as well as the DSC traces (second heating) of polyamides. The T_g values were obtained from the onset temperatures of these transitions for DSC and TMA. The first heating on the DSC trace did not show a distinct T_g. The DSC thermograms of polyamides **PA1**, **PA2**, and **PA3** showed T_g transitions at 275, 285, and 250 °C, respectively. Their TMA traces displayed relatively lower T_gs at 247, 275, and 235 °C, respectively. The T_gs of polyamides followed the same trend both in DSC and TMA. Polyamide **PA2** bearing 4-biphenylyl pendent groups showed higher T_g than **PA1** with phenyl pendent groups. This feature conforms with literature data.[31,40] Polyamide **PA3** exhibited lower T_g than **PA1** although the reverse order was expected due to the more compact structure and the para orientation of the former. Such a behavior could be attributed to the lower degree of polymerization of **PA3**. No melting of polyamides was detected by both DSC and TMA. The DSC and TMA traces of polyimides did not exhibit any transition up to 350 °C.

The thermal stability of polymers was evaluated by TGA and isothermal gravimetric analysis (IGA). The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), and the maximum polymer decomposition temperature (PDT$_{max}$) in both N_2 and air as well as the anaerobic char yield (Y_c) at 800 °C for all polymers are summarized in Table 3. IDT and PDT were determined for the temperature at which 0.5 and 10% weight losses were observed, respectively. PDT$_{max}$ corresponds to the temperature at which the maximum rate of weight loss occurred. The polymers showed an excellent thermooxidative stability, being stable up to 379−417 °C in air. They displayed weight losses of 0.93−4.15%, after 20 h of isothermal aging at 300 °C in static air (Table 3). It can be seen that the polymers containing phenyl or 4-biphenylyl pendent groups displayed comparable thermal stabilities.

Conclusions

A convenient method using intermediate pyrylium salts was applied for the synthesis of diamines **3** and amino acid **6**, which were derivatives of *p*-terphenyl. They were utilized for the preparation of rigid-rod polyamides and polyimides containing phenyl or 4-biphenylyl pendent groups. The polymers were amorphous. All polyamides and polyimide **PIB2** dissolved in polar aprotic solvents and 98% H_2SO_4 at room temperature or on heating. Polyamide **PA3** was blue fluorescent in DMF solution. Polyamides showed only T_gs at 250−285 or 235−275 °C by DSC or TMA, respectively, whereas polyimides lacked any transition up to 350 °C. The polymers were stable up to 379−417 °C in air.

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