Synthesis of Soluble, Blue-Light-Emitting Rigid-Rod Polyamides and Polyimides Prepared from 2′,6′,3′′′,5′′′-Tetraphenyl- or Tetra(4-Biphenylyl)-4, 4′′′′-diamino-*p*-quinquephenyl

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ABSTRACT: 2′,6′,3′′′,5′′′-Tetraphenyl- or tetra(4-biphenylyl)-4,4′′′′-diamino-*p*-quinquephenyls were synthesized from the corresponding pyrylium salts. Using them as starting materials, rigid-rod polyamides and polyimides containing phenyl or 4-biphenylyl side groups on the *p*-quinquephenyl segments of the backbone were prepared. They were characterized by inherent viscosity, elemental analysis, ^{1}H-NMR, ^{13}C-NMR, X-ray analysis, differential scanning calorimetry, thermomechanical analysis, thermogravimetric analysis, isothermal gravimetric analysis, and water uptake measurements. The polymers with 4-biphenylyl pendent groups showed an enhanced solubility, lower crystallinity and hydrophilicity, and higher thermal stability in comparison to the corresponding polymers with phenyl pendent groups. Polyamides displayed strong blue fluorescence in the DMF solution. The polyamide containing 4-biphenylyl pendent groups possessed a well-defined chromophore, resulting from steric interactions in the polymer chain.

Introduction

Aromatic polyamides and polyimides constantly attract much interest because of their high-temperature resistance and mechanical strength.[1] In recent years the interest has been focused on the synthesis of rigid-rod polyamides and polyimides by incorporating aromatic rings into the polymer backbone. The increased number of aromatic rings enhanced the rigidity of the polymer backbone, and their polarizable π-electrons lead to strong intermolecular interactions increasing the transition temperatures of these polymers. Rigid-rod polymers also exhibit high thermal stability and exceptional mechanical,[2,3] optical, and morphological properties.[4] They can easily form lyotropic solutions from which high-strength fibers can be spun.[5]

Infusibility and limited solubility are characteristic properties of rigid-rod polymers which restrict their synthesis, characterization, and applications, especially of high molecular weight materials. Particularly, polyamides prepared from 4,4′′-bis(chloroformyl)-*p*-terphenyl and 4,4′′-diamino-*p*-terphenyl, benzidine, or 1,4-phenylenediamine were insoluble in polar aprotic solvents containing LiCl, even in strong acids.[6] Analogous behavior has been observed for poly(amide−imides) prepared from 3,4-dicarboxy-(4′-chloroformyl)biphenyl anhydride.[7] Therefore, much effort has been made to increase the solubility of rigid-rod polymers. The most common method to achieve this goal is the incorporation of bulky pendent groups along the backbone.[8−38] Rod-like polymers which are soluble in organic solvents without the addition of inorganic salts enable not only processing routes such as dry spinning but also open applications in the area of films, coatings, polymer blends, and composites.

Recently, we have prepared soluble rigid-rod polyamide and polyimides derived from an aromatic diamine of *p*-terphenyl containing two phenyls ortho to each

amino group.[39] In addition, we have synthesized soluble rigid-rod polyamides and polyimides starting from an analogous diamine or amino acid of biphenyl.[40] These diamines or amino acids were obtained from intermediate pyrylium tetrafluoroborate salts. The polymers synthesized in this way, displayed a relatively low degree of polymerization due to the deactivation effect caused mainly by steric hindrance of the two phenyls ortho to each amino group.

To overcome this problem, we synthesized rigid-rod polyamides and polyimides derived from two new aromatic diamines of *p*-quinquephenyl having phenyl or 4-biphenylyl pendent groups in such positions so that they do not interact on the amino groups. Specifically, 2′,6′,3′′′,5′′′-tetraphenyl- or tetra(4-biphenylyl)-4,4′′′′-diamino-*p*-quinquephenyls were prepared through pyrylium salts. The method applied for the preparation of diamines consisted of three steps, was simple, and used readily available and inexpensive commercial compounds. The wholly aromatic polyamides and polyimides synthesized are expected to exhibit an outstanding thermal stability, high glass transition temperatures, and an enhanced solubility owing to the presence of the bulky phenyl or 4-biphenylyl pendent groups. Finally, the optical properties and especially the light emission of the synthesized polyamides were investigated and correlated with their structures.

Experimental Section

Characterizatiom 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. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg

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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. Thermomechanical analysis (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 98% H$_2$SO$_4$ or DMAc 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 a 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. 4-Phenylacetophenone and triphenylmethanol were recrystallized from ethanol. 1,4-Benzenedicarboxaldehyde was recrystallized from distilled water. Terephthalic acid was sublimed under vacuum. Terephthaloyl chloride was recrystallized from *n*-hexane. Pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Acetophenone was distilled under vacuum. Dimethylacetamide (DMAc) and toluene were dried by distillation over CaH$_2$. 4-Nitrophenylacetic acid sodium salt was prepared by reacting equimolar amounts of 4-nitrophenylacetic acid with aqueous sodium hydroxide and fusing. Boron trifluoride etherate, 48% tetrafluoroboric acid, propionic anhydride, and hydrazine hydrate were used as supplied.

Preparation of Starting Materials (Scheme 1). 3,3′-(1,4-Phenylene)bis(1,5-diphenyl-1,5-pentadione) (**1**) and 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (**2a**) were prepared by a reported method[41−43] and characterized previously.[39]

4,4′-(1,4-Phenylene)bis[2,6-di(4-biphenylyl)pyrylium tetrafluoroborate] (2b). A flask was charged with a mixture of 1,4-benzenedicarboxaldehyde (1.23 g, 9.16 mmol), 4-phenylacetophenone (7.11 g, 36.64 mmol), and toluene (10 mL). Boron trifluoride etherate (5.75 mL, 45.8 mmol) diluted with toluene (3 mL) was added portionwise to the stirred mixture at room temperature, and it was refluxed for 3 h. The dark red solution was concentrated under reduced pressure, and the residue was stirred and refluxed with ether. The red solid obtained was filtered off, washed with ether, and dried to afford **2b** in 60% yield (5.60 g). It was recrystallized from acetic acid. Mp: 182−185 °C. IR (KBr, cm^{-1}): 1622, 1596, 1486, 1460 (pyrylium structure and aromatic); 1056 (br, BF$_4^-$). ^{1}H-NMR (DMSO-d_6): δ 9.18 (s, 4H, aromatic meta to oxygen); 8.18−7.20 (m, 40H, other aromatic).

2′,6′,3‴,5‴-Tetraphenyl-4,4⁗-dinitro-*p*-quinquephenyl (3a). A mixture of **2a** (5.74 g, 8.04 mmol), 4-nitrophenylacetic acid sodium salt (6.53 g, 32.16 mmol), and propionic anhydride (18 mL) was stirred and refluxed for about 3 h. It was cooled at ca. −10 °C overnight, and the yellow solid precipitate was filtered off, washed with acetone, and dried to afford **3a** (3.50 g, 56%). A purified sample was obtained by recrystallization from nitrobenzene. Mp: >300 °C. IR (KBr, cm^{-1}): 1596, 1518 (aromatic); 1518, 1346 (NO$_2$). ^{1}H-NMR (DMSO-d_6): δ 8.23−8.21 (d, 4H, aromatic ortho to NO$_2$ groups); 7.86−7.84 (d, 4H, aromatic meta to NO$_2$ groups); 7.77−7.66 (m, 8H, aromatic of positions 3′, 5′, 2″, 3″, 5″, 6″, 2‴, 6‴); 7.22−7.15 (m, 20H, aromatic of side phenyls).

2′,6′,3‴,5‴-Tetra(4-biphenylyl)-4,4⁗-dinitro-*p*-quinquephenyl (3b). A mixture of **2b** (5.18 g, 5.09 mmol), 4-nitrophenylacetic acid sodium salt (4.13 g, 20.34 mmol), and propionic anhydride (12 mL) was refluxed for 3 h. Methanol
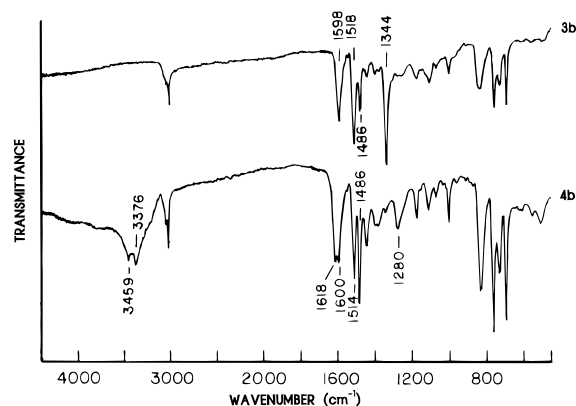
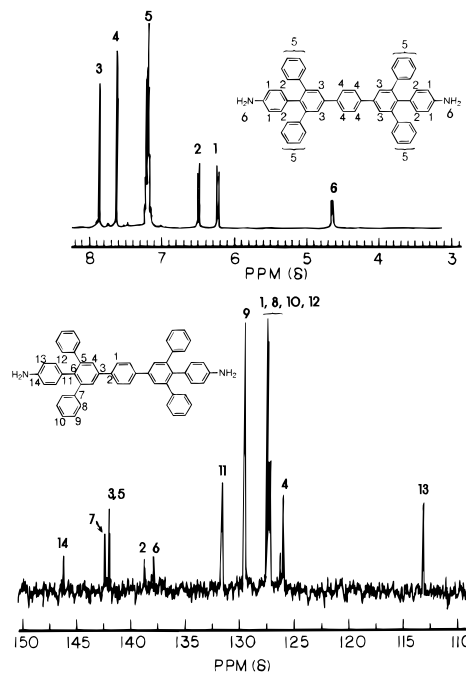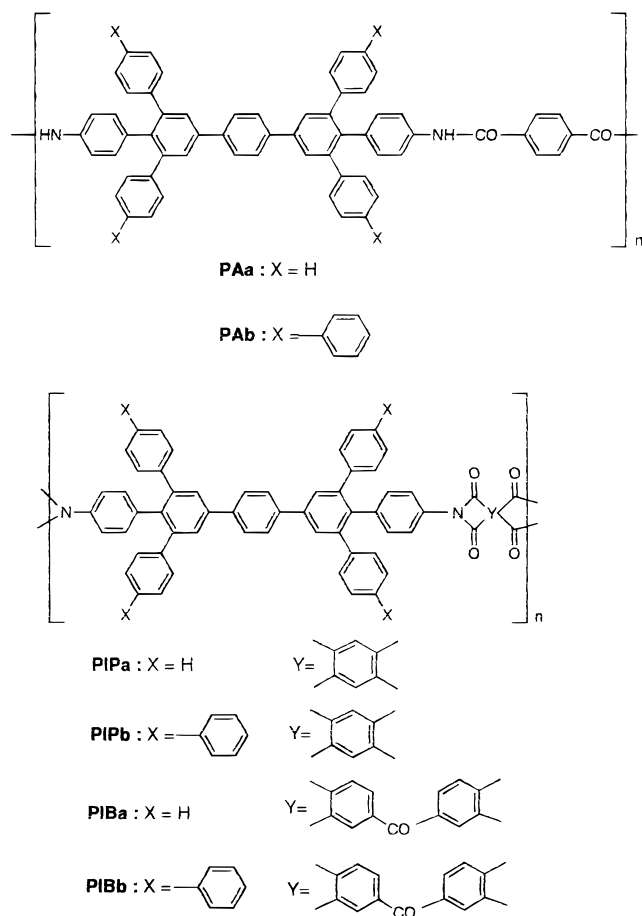**Figure 1.** FT-IR spectra of compounds **3b** and **4b**.

Figure 2. ^{1}H-NMR (upper) and ^{13}C-NMR (lower) spectra of compound **4a** in a DMSO-d_6 solution.

(10 mL) was added to the mixture, and it was cooled at −10 °C overnight. The light brown solid precipitate was filtered off, washed with methanol, and dried to afford **3b** (4.02 g, 73%). It was recrystallized from acetic acid. Mp: 191−193 °C. The IR spectrum is shown in Figure 1. ^{1}H-NMR (DMSO-d_6): δ 8.20−8.16 (d, 4H, aromatic ortho to NO$_2$ groups); 7.90−7.86 (d, 4H, aromatic meta to NO$_2$ groups); 7.80−7.25 (m, 44H, other aromatic).

2′,6′,3‴,5‴-Tetraphenyl-4,4⁗-diamino-*p*-quinquephenyl (4a). Hydrazine hydrate (5 mL) was added dropwise to a mixture of **3a** (3.37 g, 4.34 mmol), 1,4-dioxane (15 mL), and a catalytic amount of 10% palladium on activated carbon at the boiling temperature. The mixture was refluxed overnight, and **3a** was dissolved during this period. It was subsequently filtered, and water was added to the filtrate. The whitish solid precipitate was filtered off, washed with methanol, and dried to afford **4a** (2.44 g, 78%). It was recrystallized from 1,2-dichlorobenzene. Mp: >300 °C. IR (KBr, cm^{-1}): 3455−3376 (N−H stretching); 1618 (N−H deformation); 1514, 1486, 1450 (aromatic); 1280 (C−N stretching). ^{1}H-NMR and ^{13}C-NMR are shown in Figure 2. Anal. Calcd for C$_{54}$H$_{40}$N$_2$: C, 90.47; H, 5.62; N, 3.91. Found : C, 89.16; H, 5.60; N, 3.94.

2′,6′,3‴,5‴-Tetra(4-biphenylyl)-4,4⁗-diamino-*p*-quinquephenyl (4b). This was prepared as a light brown solid in 79% (2.83 g) by hydrogenating **3b** (3.80 g, 3.51 mmol) according to the procedure described for **4a**. A purified sample was obtained by recrystallization from a mixture of 1,4-

Chart 1

PAa : X = H

PAb : X = (phenyl)

PIPa : X = H   Y=

PIPb : X = (phenyl)   Y=

PIBa : X = H   Y=

PIBb : X = (phenyl)   Y=

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

polymer	yield (%)	$\eta_{inh}{}^a$ (dL/g)	empirical formula	elemental analyses		
					C (%)	H (%)	N (%)
PAa	95	1.02^b	$(C_{62}H_{42}N_2O_2)_n$	calcd	87.92	5.00	3.31
				found	86.55	4.89	3.28
PAb	86	0.94^b	$(C_{86}H_{58}N_2O_2)_n$	calcd	89.71	5.08	2.43
				found	88.89	4.98	2.47
PIBa	95	1.26^a	$(C_{71}H_{42}N_2O_5)_n$	calcd	80.89	5.38	3.56
				found	79.71	5.35	3.58
PIBb	92	1.07^b	$(C_{95}H_{58}N_2O_5)_n$	calcd	87.27	4.47	2.14
				found	85.98	4.38	2.10
PIPa	98	1.21^a	$(C_{66}H_{38}N_2O_4)_n$	calcd	80.89	5.38	3.56
				found	79.71	5.35	3.58
PIPb	88	1.34^b	$(C_{88}H_{54}N_2O_4)_n$	calcd	87.83	4.52	2.33
				found	87.06	4.50	2.35

^{a} Inherent viscosity in H_2SO_4 (0.5 dL/g)) at 30 °C. ^{b} Inherent viscosity in DMAc (0.5 dL/g)) at 30 °C.

Acetic anhydride (5 mL) and pyridine (1 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 dried to afford **PIPa** (0.48 g, 98%). It was extracted with acetone in a Soxhlet apparatus for 3 h.

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

Results and Discussion

Synthesis of Monomers and Polymers. Scheme 1 outlines the synthetic route applied for the preparation of two new aromatic diamines **4a** and **4b** of *p*-quinquephenyl with phenyl or 4-biphenylyl pendent groups. The key stages of this method were the preparation of pyrylium tetrafluoroborate salts as intermediates and their reaction with substituted sodium acetate. More particularly, compound **2a** was prepared by a reported method.[41–43] Compound **2b** was synthesized from the reaction of 1,4-benzenedicarboxaldehyde with 4-phenylacetophenone in the presence of $BF_3 \cdot Et_2O$. The preparation of **2b** was accomplished by this method, because it is more convenient since it involves only one step. Compounds **2** reacted with 4-nitrophenylacetic acid sodium salt in propionic anhydride and afforded compounds **3**. It has been reported that the reaction of 2,4,6-triarylpyrylium salts with phenylacetic acid anhydrides, generated in situ from phenylacetic acid sodium salt and an excess of acetic or propionic anhydride, yields 1,2,3,5-tetraarylbenzenes.[44] 2-(Acyloxy)-benzophenones are formed as byproducts from the reaction, which are easily separated from the desired compound.[44] The obtained dinitro compounds **3** were hydrogenated to the corresponding diamines **4** by means of hydrazine hydrate in 1,4-dioxane. In the case of **4b**, the hydrogenation time was significantly shortened, when a mixture of 1,4-dioxane/ethanol (4:1, v/v) was used as the reaction medium.

The structure of the monomers was confirmed by elemental analyses as well as IR and NMR spectroscopies. The hydrogenation of dinitro compounds **3** to the corresponding diamines **4** was monitored by IR spectroscopy (Figure 1). Specifically, **3b** showed characteristic absorptions at 1518 and 1344 cm^{-1} associated with the nitro groups, whereas **4b** lacked these absorption bands. The latter displayed new absorptions at 3459–3376 (N–H stretching), 1618 (N–H deformation), and 1280 cm^{-1} (C–N stretching). Both compounds exhibited absorptions around 1600, 1514, and 1486 cm^{-1} assigned to the aromatic rings.
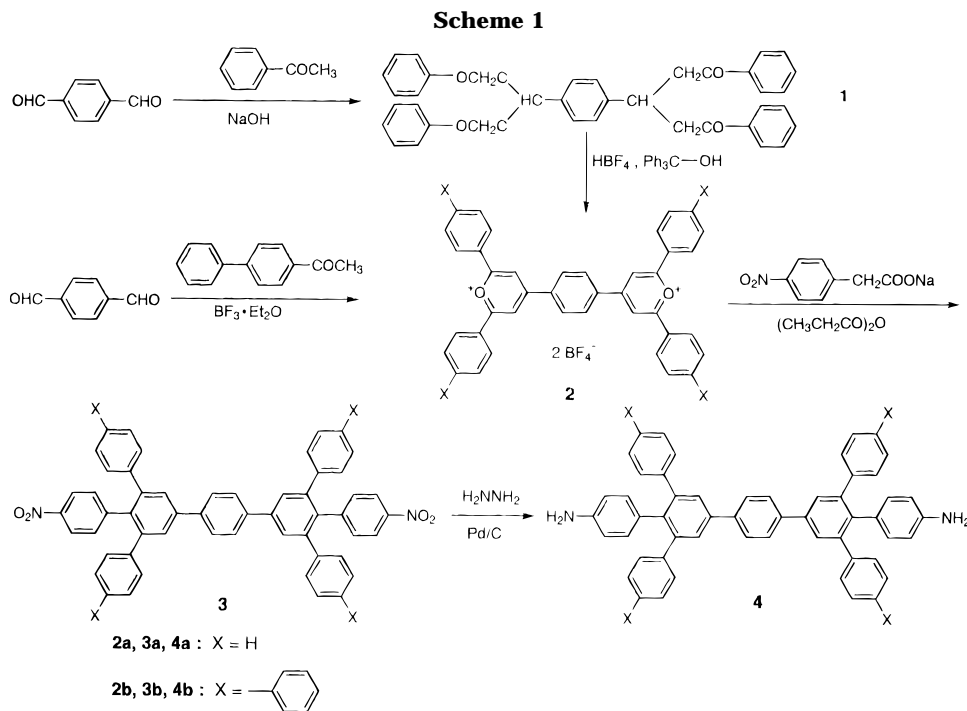
dioxane/ethanol (1:1, v/v). Mp: 174–176 °C. The IR spectrum is shown in Figure 1. ^{1}H-NMR (DMSO-d_6 at 80 °C): δ 7.78–7.73 (d, 4H, aromatic of positions 3′, 5′, 2‴, and 6‴); 7.65–7.63 (m, 4H, aromatic of positions 2″, 3″, 5″, and 6″); 7.51–7.17 (m, 36H, aromatic of side biphenyls); 7.11–7.06 (d, 4H, aromatic of positions 2, 6, 2‴, and 6‴); 6.30–6.28 (d, 4H, of positions 3, 5, 3‴′, and 5‴′); 4.62 (br, 4H, NH$_2$). ^{13}C-NMR (DMSO-d_6 at 80 °C): δ 146.44, 141.95, 139.73, 137.80, 131.75, 130.15, 128.83, 128.74, 127.39, 127.16, 126.55, 126.35, 125.63, 125.53, 113.34. Anal. Calcd for $C_{78}H_{56}N_2$: C, 91.73; H, 5.53; N, 2.74. Found: C, 91.12; H, 5.54; N, 2.76.

Preparation of Polymers (Chart 1). Polyamide PAa. A flask was charged with a mixture of **4a** (0.80 g, 1.12 mmol), terephthalic acid (0.18 g, 1.12 mmol), triphenyl phosphite (0.70 g, 2.24 mmol), pyridine (1 mL), DMAc (5 mL), and 5 wt % LiCl. It was refluxed under N$_2$ overnight and poured into water. The yellowish solid precipitate was filtered off, washed with water, and dried to afford **PAa** (0.89 g, 95%). It was extracted with acetone in a Soxhled apparatus for 3 h.

Polyamide PAb. A flask was charged with a solution of **4b** (1.00 g, 0.98 mmol) in DMAc (12 mL). Triethylamine (0.20 g, 1.96 mmol) was added to the solution. Terephthaloyl chloride (0.20 g, 0.98 mmol), dissolved in DMAc (5 mL), was added dropwise to the stirred solution at −10 °C. Stirring of the mixture was continued at this temperature for 5 h and then at room temperature overnight in a stream of N$_2$. It was poured into water, and the yellow–brown solid precipitate was filtered off, washed with hot acetone, and dried to afford **PAb** (0.97 g, 86%). It was extracted with acetone in a Soxhlet apparatus for 3 h.

Polyimides PIPa, PIPb, PIBa, and PIBb. A typical procedure for the preparation of **PIPa** is as follows: Granual PMDA (0.12 g, 0.54 mmol) was added to a stirred solution of **4a** (0.39 g, 0.54 mmol) in DMAc (10 mL) at room temperature. The solution became viscous, and stirring was continued at this temperature for 3 h and then at 100 °C for 2 h under N$_2$.

Scheme 1

2a, 3a, 4a : X = H

2b, 3b, 4b : X = —⟨phenyl⟩

Figure 2 presents the ^{1}H-NMR and ^{13}C-NMR spectra of diamine **4a**. Assignments of peaks for both spectra are given in the figure. In the ^{1}H-NMR spectrum the amino protons were exchangeable with D_2O.

Rigid-rod polymers bearing phenyl or 4-biphenylyl pendent groups were synthesized (Chart 1). Polyamide **PAa** was prepared from terephthalic acid by the phosphorylation method due to the limited solubility of diamine **4a** in DMAc at low temperature. Since diamine **4b** showed remarkably higher solubility in DMAc, polyamide **PAb** was prepared from terephthaloyl chloride utilizing the solution polycondensation method. In addition, polyimides **PIP** and **PIB** were synthesized by reacting diamines **4** with PMDA and BTDA, respectively.

The yields of the preparation reactions were almost quantitative (86–98%) for all polymers (Table 1). Their inherent viscosities ranged from 0.94 to 1.34 dL/g and were considerably higher than those of other phenyl-substituted rigid-rod polymers derived from less reactive diamines or amino acids.[39,40]

Structural Characterization of Polymers. The structural characterization of polymers was accomplished by FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy as well as X-ray analysis. Figure 3 presents typical FT-IR spectra of polymers **PAa** and **PIBa**. Polyamide **PAa** showed absorptions at 3265 (N–H stretching), 1667 (C=O), 1596 (aromatic), 1518 (N–H deformation and aromatic), and 1314 cm^{-1} (C–N stretching). Polyimide **PIBa** displayed absorptions at 1780, 1720, 1366, and 1094 cm^{-1} assigned to the imide structure. The ^{1}H-NMR spectrum of polyamide **PAb** in a DMSO solution showed peaks at δ 9.95 (NHCO), 7.98 (aromatic of terephthalic acid segments), and 7.62–6.97 (other aromatic). Figure 4 presents the ^{13}C-NMR spectrum of polyamide **PAb** as well as the assignments of peaks. The carbonyl displayed an upfield peak at δ 164.59.

The crystallinity of polymers was estimated by means of X-ray diffractograms (Figure 5). All polymers were microcrystalline, while **PIPb** was amorphous. Upon comparing polyamides **PAa** and **PAb**, the first polymer
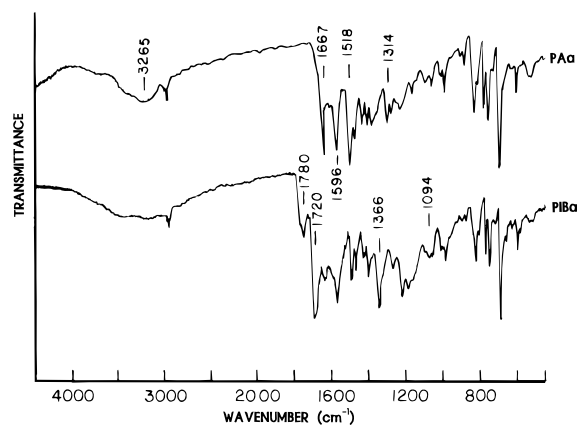

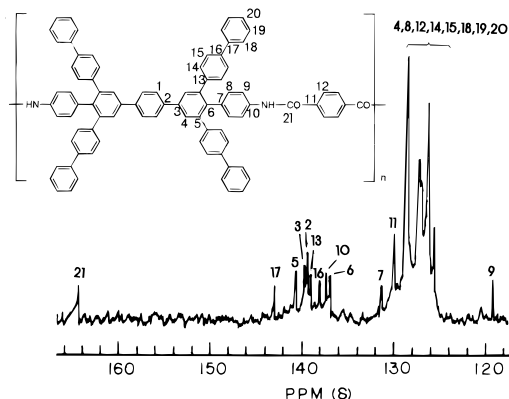**Figure 3.** FT-IR spectra of polymers **PAa** and **PIBa**.

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

containing phenyl pendent groups was more crystalline. The longer 4-biphenylyl pendent groups of **PAb** caused higher disorder in chains and therefore less chain packing. This feature conforms with the significantly higher solubility of **PAb** in comparison to **PAa**.

Hydrophilicity and Solubility of Polymers. The hydrophilicity of polyamides **PAa** and **PAb** was evalu-

Table 2. Solubilities of Polymers[a]

polymer	DMF	NMP	DMSO	CCl₃COOH	H₂SO₄	1,4-dioxane	CH	DCB
PAa	+[c]	+[c]	+[c]	++	++	+−	+	+−
PAb	++	++	+	++	++	+	++	+
PIBa	+[c]	+[c]	+[c]	+	+	+−	+−	+−
PIBb	++	++	++	++	+	+−	+	+
PIPa	+[c]	+[c]	+[c]	+	+	+−	+−	+−
PIPb	++	++	+[c]	+	+	+−	+	+

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +−, partially soluble. [b] DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethyl sulfoxide; CH, cyclohexanone; DCB, 1,2-dichlorobenzene. [c] Solvent containing 5% w/w LiCl.
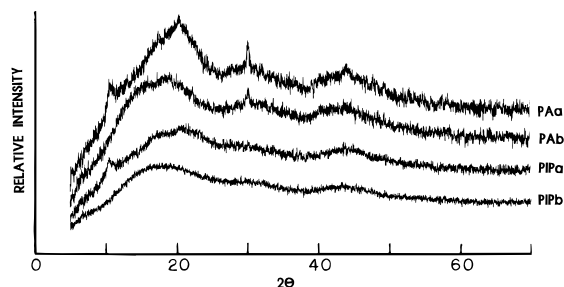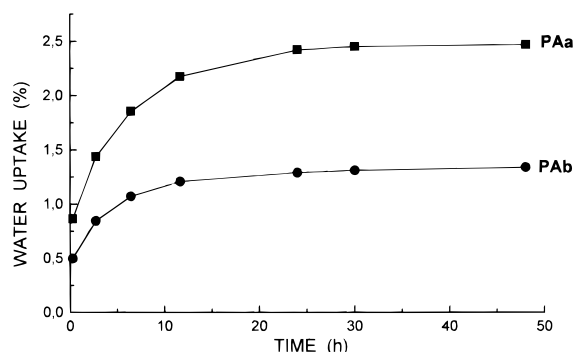

Figure 5. X-ray diffraction patterns of typical polymers.

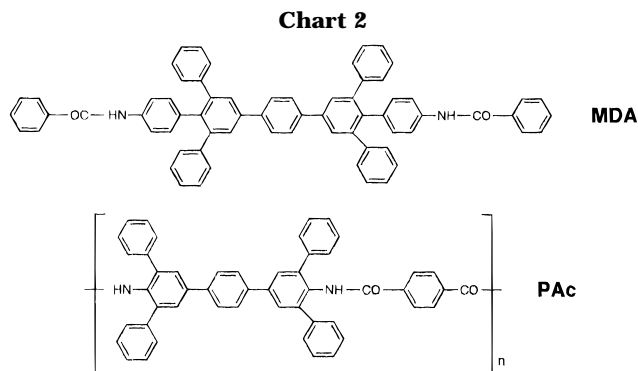**Figure 6.** Water absorption versus time for polyamides **PAa** and **PAb**.

ated by determination of their isothermal water absorption (Figure 6). Following exposure for 50 h, the water uptake was 2.47 and 1.34%, respectively, and the corresponding numbers of moles of absorbed water per amide equivalent weight (NMAW) were 0.57 and 0.43. Interestingly, the polyamide **PAb** with 4-biphenylyl pendent groups displayed lower hydrophilicity than that of polyamide **PAa** with phenyl pendent groups. The present polyamides showed higher hydrophilicity than our previously synthesized analogous rigid-rod polyamides, the NMAW values of which were 0.26−0.29. Such a behavior was expected, since the latter polyamides exhibited lower hydrogen-bonding ability.[39,40]

The solubility of polymers was correlated with the structure of the pendent groups. Table 2 presents the solubility behavior of polymers. It is seen that the polymers with 4-biphenylyl pendent groups were remarkably more soluble than the corresponding ones with phenyl pendent groups. Note that polyamide **PAb** and in most cases polyimides **PIPb** and **PIBb** dissolved readily at ambient temperature in polar aprotic solvents (DMF, DMSO, NMP) and trichloroacetic acid. In addition, they dissolved in cyclohexanone and 1,2-dichlorobenzene. The polymers **PAa** and **PIBa** dissolved only in hot polar aprotic solvents containing LiCl, and the maximum attainable concentration of their solutions was 1 wt %. In contrast, solutions of **PAb** in DMF with concentration up to 40 wt % could be obtained.
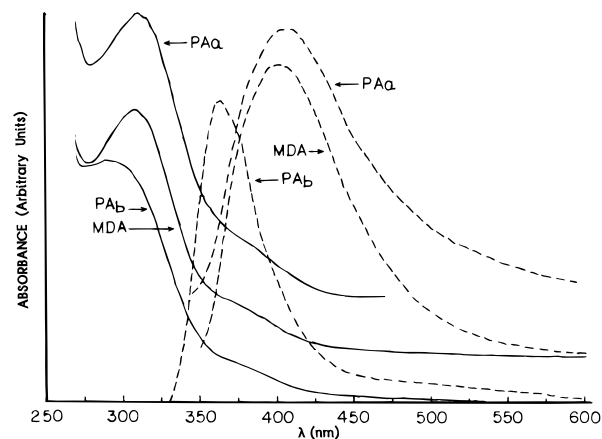
Figure 7. Absorption (—) and emission (- - -) spectra of polyamides **PAa** and **PAb** as well as of model diamide **MDA** in DMF solutions. Note that intensities were arbitrarily, chosen in order to optimally fit the graphs.
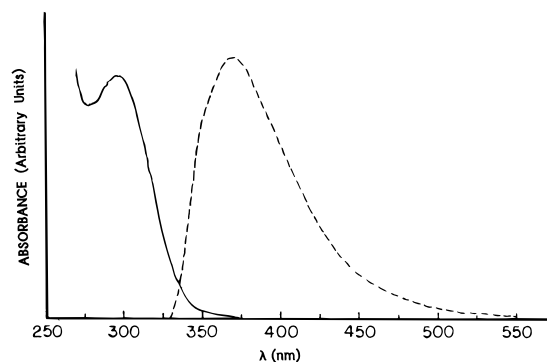
Figure 8. Absorption (—) and emission (- - -) spectra of polyamide **PAc** in a DMF solution.

Optical Properties of Polymers. The photophysical characterization of polyamides included the study of their absorption and emission spectra in solution. Figure 7 presents the absorption and emission spectra of polyamide **PAa** and its model diamide **MDA** as well as of polyamide **PAb** in a DMF solution. In addition, Figure 8 shows for comparative purposes the absorption and emission spectra obtained from a DMF solution of polyamide **PAc**, which has been previously synthesized.[39] The structures of **MDA** and **PAc** are presented in Chart 2. Compound **MDA** was prepared from the condensation of diamine **4a** with terephthalic acid using the same experimental conditions as with those of **PAa**.

All compounds were strong blue fluorescent in a DMF solution. Comparison of the UV/vis absorption and emission spectra of polyamide **PAa** with those of the corresponding model compound **MDA** shows that they are almost identical. Specifically, the UV spectrum of **PAa** displayed an absorption maximum at 310 nm and its fluorescence spectrum showed an emission maximum

Chart 2

MDA

PAc

Figure 9. TMA thermograms of polymers. Conditions: N_2 flow, 60 cm³/min; heating rate, 20 °C/min.

Table 3. Thermal Stabilities of Polymers[a]

	in N_2				in Air			
polymer	TD_1 (°C)	TD_5 (°C)	TD_{50} (°C)	Y_c (%)	TD_1 (°C)	TD_5 (°C)	TD_{50} (°C)	wt loss (%)
PAa	389	449		64	361	431	531	4.18
PAb	395	474		69	368	456	556	3.77
PIBa	411	532		71	389	498	608	2.28
PIBb	421	549		65	397	503	619	3.35
PIPa	403	521		74	400	512	591	2.74
PIPb	426	555		72	406	533	611	3.60

[a] TD_1, TD_5, and TD_{50}: temperatures at which weight losses of 1, 5, and 50% were observed, respectively. Y_c: char yield at 800 °C. wt loss: weight loss after 20 h of isothermal aging at 300 °C in static air.

at 404 nm when excited at 310 nm. The absorption and an emission spectra of **MDA** displayed a very small blue shift (2 nm) compared with those of **PAa**. This supports that both **PAa** and **MDA** have the same effective conjugation length and there is essentially no conjugation between the adjacent repeat units in polyamide.

The absorption and emission spectra of polyamide **PAb** showed maxima at 289 and 364 nm, respectively. These values compared with those of **PAa** are strongly blue-shifted by 21 nm for absorption and 40 nm for emission. Furthermore, the emission spectrum of **PAb** was significantly sharper than that for **PAa**, indicating that the conjugation length is more precisely controlled in **PAb**. Since *p*-terphenyl displayed absorption from a DMF solution with a maximum at 283 nm, it is concluded that the active chromophore in **PAb** converged to that of *p*-terphenyl.

It is well established that, even in nonsubstituted polyphenylenes, two adjacent phenyl rings are not coplanar but form a twist of about 23°, which however permits yet a reasonable overlap of the π orbitals. It is reasonable to accept that the bulky 4-biphenylyl pendent groups in polyamide **PAb** caused a much larger twist of the two terminal phenyl rings of *p*-quinquephenyl and disabled the possibility of conjugation through them. Thus, a well-defined polyphenylene chromophore resulted, the limits of which were connected with a noncoplanar aromatic structure. An analogous behavior has been observed for a soluble, blue-light-emitting copolymer composed of regularly alternating *p*-phenylene and *p*-phenylenevinylene blocks.[45]

Polyamide **PAc** showed absorption and emission spectra with maxima at 298 and 371 nm, respectively (Figure 8). These values are lower than the corresponding ones of **PAa** and higher than those of **PAb**. Polyamides **PAa** and **PAc** contain phenyl pendent groups, which do not cause a significant rotation of the adjacent phenyl or amide moiety and therefore the conjugation can be extended through them. Consequently, the length of the chromophore is not well-defined for **PAa** and **PAc**, in opposition to **PAb** bearing 4-biphenylyl pendent groups.

Thermal Properties of Polymers. Thermal characterization of the polymers was accomplished by DSC, TMA, TGA, and isothermal gravimetric analysis (IGA). The DSC thermograms obtained from the second heating of polyamide **PAa** and most polyimides did not show any transition up to 350 °C. In contrast, polyamide **PAb** and polyimide **PIBb** displayed a broad endotherm between 180 and 230 °C due to a transition which also was observed in their TMA traces (see below).

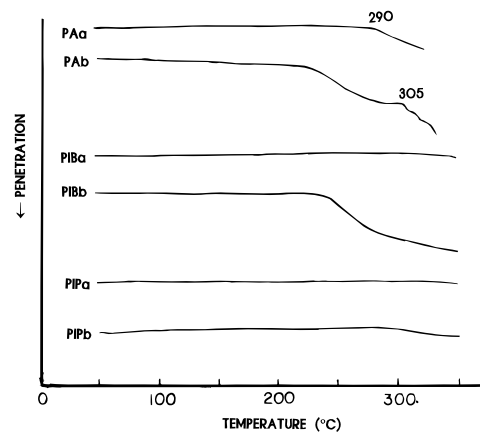The glass transition (T_g) temperatures of polymers were determined from the TMA method using a loaded penetration probe and obtained from the onset temperatures of these transitions (Figure 9). Polyamides **PAa** and **PAb** showed T_gs at 290 and 305 °C, respectively, while all polyimides did not display T_g up to 350 °C. Polyamide **PAb** showed a reproducible, gradual relaxation which began at approximately 230 °C. This feature can be attributed to a gradual weakening of intermolecular forces as the temperature increased,[31] and this has been observed previously for other rigid-rod polyamides.[32] An analogous behavior was also observed for polyimide **PIBb**, which exhibited a relaxation starting at 250 °C.

Owing to their longer rodlike segment, the present polymers showed significantly higher T_g values than our phenyl-substituted rigid-rod polymers containing biphenyl or terphenyl moieties in their backbone.[39,40]

The thermal and thermo-oxidative stability of polymers was ascertained by TGA and IGA. The temperatures at which weight losses of 1, 5, and 50% were observed 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. Figure 10 presents typical TGA traces of **PAb**, **PIPb**, and **PIBb** in N_2 and air. All polymers showed an outstanding thermal stability, being stable up to 380−422 °C in N_2 and 358−397 °C in air and affording anaerobic Y_c of 61−80% at 800 °C. The polymers with 4-biphenylyl pendent groups were more thermally stable than the corresponding ones with phenyl pendent groups, since they showed higher TD in both N_2 and air.

The polymers displayed weight losses of 2.28−4.18%, after 20 h of isothermal aging at 300 °C in static air (Table 3). It is seen that the remaining weight followed the trend of Y_c.
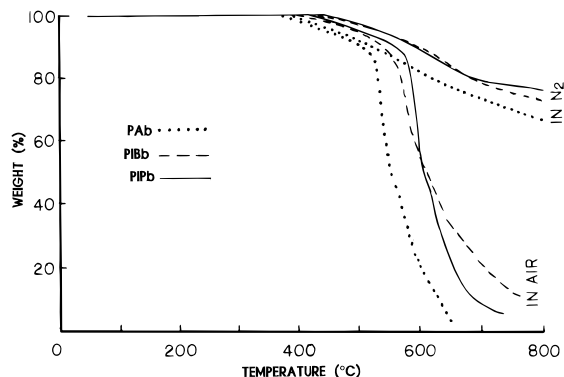
Figure 10. TGA thermograms in N_2 and air of polyamide **PAb** as well as of polyimides **PIPb** and **PIBb**. Conditions: Gas flow, 60 cm^3/min; heating rate, 20 °C/min.

Conclusions

Starting from pyrylium salts, two new aromatic diamines of *p*-quinquephenyl were synthesized and used for the preparation of rigid-rod polyamides and polyimides carrying phenyl or 4-biphenylyl pendent groups. It was shown that the polymers with 4-biphenylyl pendent groups in comparison to the corresponding ones with phenyl pendent groups displayed lower crystallinity, remarkably higher solubility, lower hydrophilicity, and enhanced thermal stability. The polyamides exhibited blue fluorescence in a DMF solution. The absorption and emission spectra of **PAa** and its model diamide revealed that there was not essentially conjugation between the adjacent repeat units in polyamide. The 4-biphenylyl pendent groups of **PAb** caused significant steric hindrance which gave rise to a controlled regular interruption of the conjugation in the *p*-quinquephenyl of backbone.

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