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PII: S0032-3861(96)00836-1

Polymer Vol. 38 No. 11, pp. 2733–2740, 1997

0032-3861/97/\$17.00 + 0.00

Rigid-rod polyamides and polyimides prepared from 4,3′-diamino-3,5-diphenyl-biphenyl and 4-amino-4′-carboxy-3,5-diphenyl-biphenyl

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(Received 14 June 1996; revised 21 August 1996)

4,3′-Diamino-3,5-diphenyl-biphenyl and 4-amino-4′-carboxy-3,5-diphenyl-biphenyl were synthesized from the corresponding pyrylium slats. A novel class of rigid-rod polyamides and polyimides containing phenyl pendent groups were synthesized and characterized by viscosities, elemental analyses, ^{1}H n.m.r., ^{13}C n.m.r., X-ray, t.m.a., t.g.a. and isothermal gravimetric analysis. They were amorphous or semicrystalline and dissolved in polar aprotic solvents and certain other solvents. Some of the polymers showed T_g at 225–256°C. The polymers were stable up to 375–426°C in N_2 and 336–376°C in air and afforded anaerobic char yields of 59–79% at 800°C. © 1997 Elsevier Science Ltd.

(Keywords: polyamides; polyimides; rigid-rod polymers)

INTRODUCTION

Aromatic polyamides and polyimides are known for their high temperature resistance, high mechanical strength and are widely used as fibres for a variety of applications[1]. Incorporation of aromatic rings into the main chain increases the rigidity, which leads to polymers with outstanding thermal stability and mechanical properties[2,3]. These rigid-rod polymers are high anisotropic materials. Fibres obtained from anisotropic solutions of these materials have been used in applications where high thermal stability and mechanical strength are required[4].

In most cases rigid-rod polymers are infusible and insoluble properties which restrict synthesis and applications especially of high molecular weight materials. There are several ways to reduce melting point and increase solubility of these polymers. One involves the incorporation of bulky pendent groups along the main chain. This modification lower the melting temperature and leads to soluble and in some cases amorphous polymers. A literature survey revealed that this approach has been employed many times to modify rigid-rod polymers[5–26].

The present investigation describes the synthesis and characterization of rigid-rod polyamides and polyimides containing biphenyl units in the main chain. The attachment of two side phenyls onto the polymer backbone aimed to lower the melting temperatures and enhance the solubilities. On the other hand, the direction of the main chain in some of the synthesized polymers was *p*–*m*′ which is expected to affect their properties. Since the rigid-rod polymers are anisotropic the physical properties should vary with direction of orientation.

The starting materials were synthesized by a method, involving the formation of pyrylium tetrafluoroborate salts as intermediate, which turn out a facile and inexpensive method.

This work is a continuation of our previous research on rigid-rod polymers containing substituted *p*-terphenyl[27].

EXPERIMENTAL

Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. I.r. spectra were recorded on a Perkin–Elmer 16PC *FT*i.r. spectrometer with KBr pellets. ^{1}H n.m.r. (400 MHz) and ^{13}C n.m.r. (100 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. T.g.a. was performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by t.g.a. and isothermal gravimetric analysis (i.g.a.), and the weight loss comparisons were made between comparable specimens. Dynamic t.g.a. measurements were made at a heating rate of 20°C min^{-1} in atmospheres of N_2 or air at a flow rate of 60 cm^3 min^{-1}. Thermomechanical analysis (t.m.a.) was recorded on a DuPont 943 t.m.a. using a loaded penetration probe at a scan rate of 20°C min^{-1} in N_2 with a flow rate of 60 cm^3 min^{-1}. The t.m.a. experiments were conducted in duplicate. The t.m.a. speciments 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

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temperature. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 ml in DMAc at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyser. 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

3-Nitrobenzaldehyde and 4-carboxybenzaldehyde were recrystallized from ethanol 95%. Terephthalic acid was purified by sublimation. Pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Acetophenone and pyridine were purified by distillation. *N,N*-Dimethylacetamide (DMAc), nitromethane and toluene were distilled over CaH_2. Hydrazine hydrate, triphenyl phosphite (TPP) and boron trifluoride etherate were used as supplied.

Preparation of starting materials

4,3'-Diamino-3,5-diphenyl-biphenyl (**4**) (Scheme 1). A flask equipped with magnetic stirrer was charged with a mixture of 3-nitrobenzaldehyde (3.00 g, 19.9 mmol), acetophenone (7.17 g, 59.7 mmol) and acetic anhydride (10 ml). It was refluxed overnight. 3-Nitrobenzalacetophenone (**1**) precipitated as a whitish solid upon cooling in an ice-bath. It was filtered off, washed thoroughly with water then with cold methanol and dried (3.97 g, 79%). A purified sample was obtained by recrystallization from acetonitrile, M.p. 142–144°C.

I.r. (KBr, cm^{-1}): 1662 (C=O); 1608 (olefinic bond and aromatic); 1528, 1350 (NO_2); 1218 (C–C(O)–C).

^{1}H n.m.r. (DMSO-d_6) ppm: 8.67, 8.22 (*d*, 2H, aromatic ortho to nitro group); 8.12 (*s*, 1H aromatic *meta* to nitro group); 8.00 (*s*, 1H aromatic *para* to nitro group); 7.85–7.42 (*m*, 2H, olefinic and 5H, other aromatic).

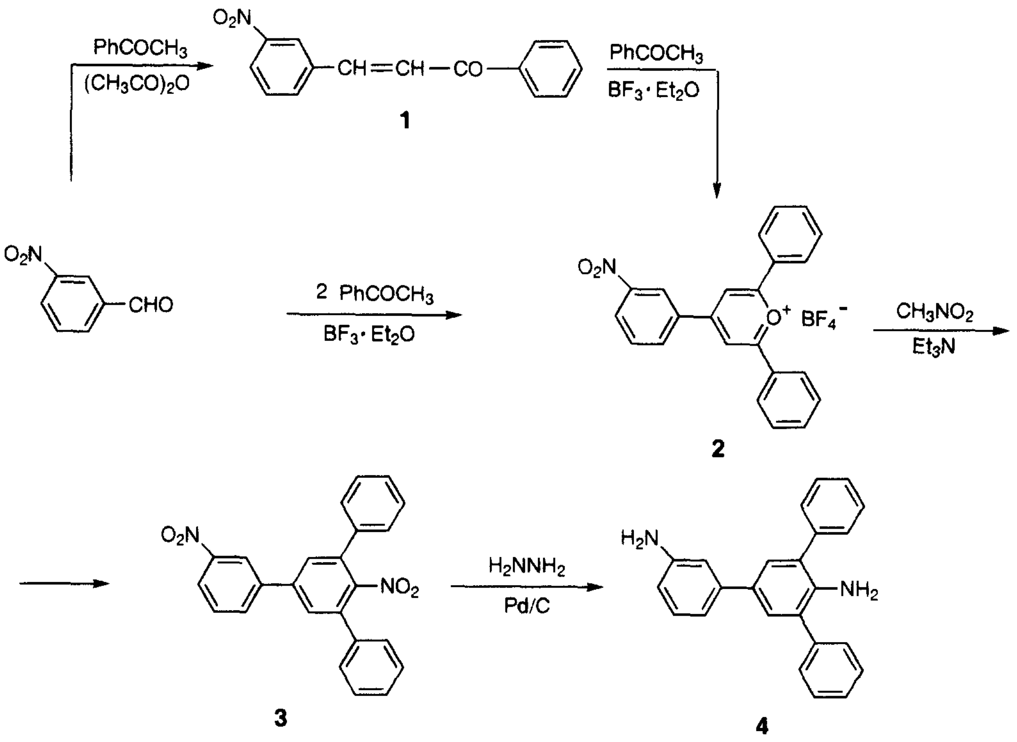
A flask was charged with a mixture of **1** (2.18 g, 8.6 mmol), acetophenone (1.04 g, 8.7 mmol) and toluene (10 ml). Boron trifluoride etherate (4.24 ml, 34.5 mmol) was added dropwise to the stirred mixture at room temperature. The mixture became yellow and it was refluxed for 3 h under N_2. The dark red solution was concentrated under reduced pressure and the residue was stirred with 1,4-dioxane at 0°C. The yellowish solid was filtered off, washed with 1,4-dioxane and dried to afford 4-(3-nitrophenyl)-2,6-diphenylpyrylium tetrafluoroborate (**2**) in 25% yield (0.25 g). It was recrystallized from acetic acid. M.p. 258–261°C.

I.r. (KBr, cm^{-1}): 1624, 1498, 1468, 1444 (pyrylium structure and aromatic); 1530, 1352 (NO_2); 1062 (*br*, BF_4^-).

^{1}H n.m.r. (DMSO d_6) ppm: 9.27 (*m*, 2H, aromatic *meta* to O^+); 8.70–8.53 (*m*, 4H, aromatic *ortho*, *meta* and *para* to nitro group); 7.87–6.40 (*m*, 10H, other aromatic).

Compound **2** was alternatively prepared in 65% yield (15.2 g) by reacting 3-nitrobenzaldehyde (8.00 g, 52.9 mmol) with acetophenone (12.72 g, 105.9 mmol) in the presence of boron trifluoride etherate (15.5 ml, 126.0 mmol) in toluene (45 ml) according to the procedure described above and it was similarly characterized.

A mixture of **2** (13.00 g, 29.5 mmol), nitromethane (20 ml) and triethylamine (5.97 g, 59.0 mmol) was refluxed overnight under N_2. It was concentrated under reduced pressure and the viscous oil obtained was



Scheme 1

dissolved in methanol and poured into ice-water. The pale brown solid precipitate was filtered off, washed with water and dried to afford 4,3′-dinitro-3,5-diphenyl-biphenyl (**3**) in 74% yield (8.51 g). It was recrystallized from toluene. M.p. 148–150°C.

I.r. (KBr, cm^{-1}): 1594, 1494 (aromatic); 1528, 1348 (NO_2).

^1H n.m.r. (DMSO-d_6) ppm: 8.30 (*s*, 1H, aromatic of position 2′ of biphenyl); 8.08 (*s*, 1H, aromatic of position 4′ of biphenyl); 7.70–7.20 (*m*, 14H, other aromatic).

A flask equipped with dropping funnel and magnetic stirrer was charged with a mixture of **3** (6.50 g, 16.4 mmol), ethanol 95% (15 ml) and a catalytic amount of palladium 10% on activated carbon. Hydrazine hydrate (5 ml) was added stepwise to the stirred mixture at reflux temperature. Refluxing of the mixture was continued for 20 h. During this period the solid was gradually dissolved. The catalyst was removed by filtration and the filtrate was poured into ice-water. The brown solid precipitate was filtered off, washed with water and dried to afford **4** in 87% yield (5.23 g). It was recrystallized from a mixture $CHCl_3$/*n*-hexane (3 : 2 v/v). M.p. 96–98°C.

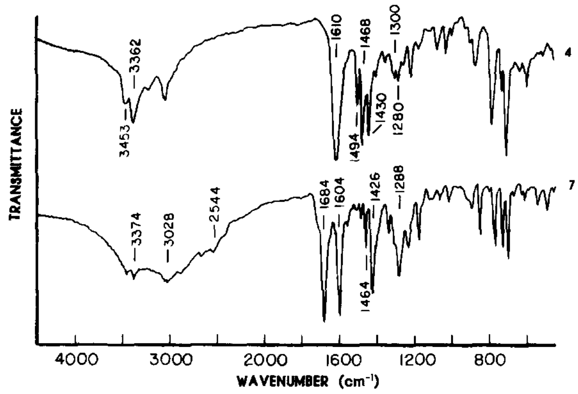


Figure 1 *FT*i.r. spectra of compounds **4** (upper) and **7** (lower)

Anal. calcd. for $C_{24}H_{20}N_2$: C, 85.68%; H, 5.99%; N, 8.33%.

Found: C, 84.93%; H, 6.03%; N, 8.30%.

^1H n.m.r. (DMSO-d_6) ppm: 7.07 (*m*, 10H, aromatic of pendent phenyls); 6.90 (*s*, 2H, aromatic of positions 2 and 6 of biphenyl); 6.53 (*m*, 4H, aromatic of positions 2′, 4′, 5′ and 6′ of biphenyl).

The i.r. spectrum is shown in *Figure 1*.

4-Amino-4′-carboxy-3,5-diphenyl-biphenyl hydrochloric salt (**7**) (Scheme 2). Boron trifluoride etherate (7.82 ml, 63.6 mmol) was added dropwise to a stirred mixture of 4-carboxybenzaldehyde (3.98 g, 26.5 mmol), acetophenone (6.37 g, 53.0 mmol) and toluene (30 ml) at room temperature. The mixture was refluxed for 3 h under N_2. The yellow solid precipitate was filtered off, washed with 1,4-dioxane and dried to afford 4-(4-carboxy)-2,6-diphenylpyrylium tetrafluoroborate (**5**) in 60% yield (7.00 g). It was recrystallized from acetic acid. M.p. >300°C.

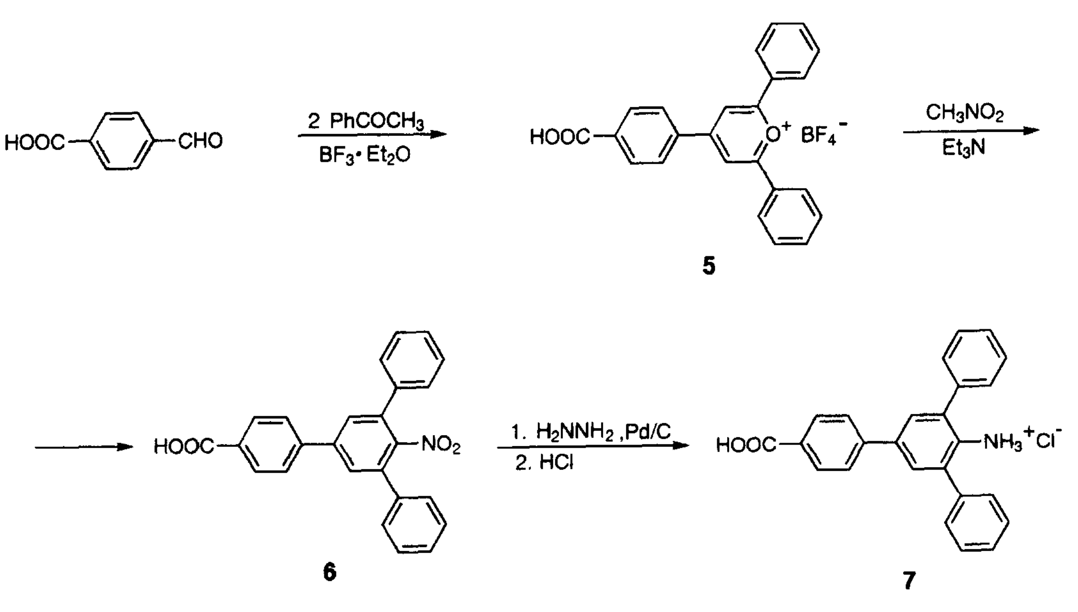
I.r. (KBr, cm^{-1}): 3052–2485 (O–H stretching); 1720 (C=O); 1622, 1578, 1516, 1496 (pyrylium structure and aromatic); 1438, 1254 (C–O stretching and O–H deformation); 1114 (*br*, BF_4^-).

^1H n.m.r. (DMSO-d_6) ppm: 9.15 (*s*, 2H, aromatic *meta* to O^+); 8.45 (*m*, 4H, aromatic *ortho* and *meta* to COOH); 7.78 (*m*, 10H, other aromatic). The carboxylic proton was unobserved.

4-Nitro-4′-carboxy-3,5-diphenyl-biphenyl (**6**) was prepared as a whitish solid in 72% yield (3.87 g) by refluxing a mixture of **5** (6.00 g, 13.6 mmol), nitromethane (15 ml) and triethylamine (4.14 g, 40.9 mmol) according to the procedure described for **3**. It was recrystallized from acetic acid. M.p. 250–253°C.

I.r. (KBr, cm^{-1}): 3034–2548 (O–H stretching); 1696 (C=O); 1530, 1370 (NO_2); 1416, 1294 (C–O stretching and O–H deformation).

^1H n.m.r. (DMSO-d_6) ppm: 8.67 (*m*, 4H, aromatic *ortho* and *meta* to COOH); 8.33–7.07 (*m*, 12H, other aromatic). The carboxylic proton was unobserved.



Scheme 2

Compound **6** (3.00 g, 7.6 mmol) was hydrogenated by means of hydrazine hydrate (3 ml) in ethanol 95% (10 ml) utilizing palladium 10% on activated carbon as catalyst according to the procedure described for **4**. The catalyst was removed by filtration and the filtrate was concentrated under reduced pressure. Dilute hydrochloric acid was added to the residue and the whitish solid precipitate was filtered off, washed with water and dried to afford **7** (2.32 g, 76%). It was purified by sublimation. M.p. 291–292°C.

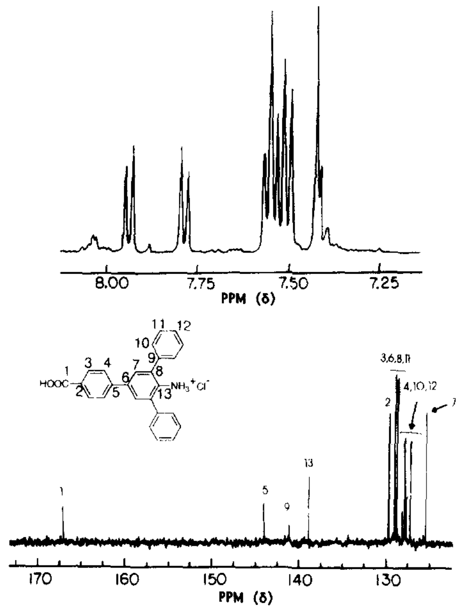


Figure 2 ^1H n.m.r. (upper) and ^{13}C n.m.r. (lower) spectra of compound 7 in DMSO-d_6 solution

Anal. calcd for $C_{25}H_{20}NO_2Cl$: C, 74.72%, H, 5.02%; N, 3.49%.

Found: C, 73.97%; H, 4.96%; N, 3.45%.

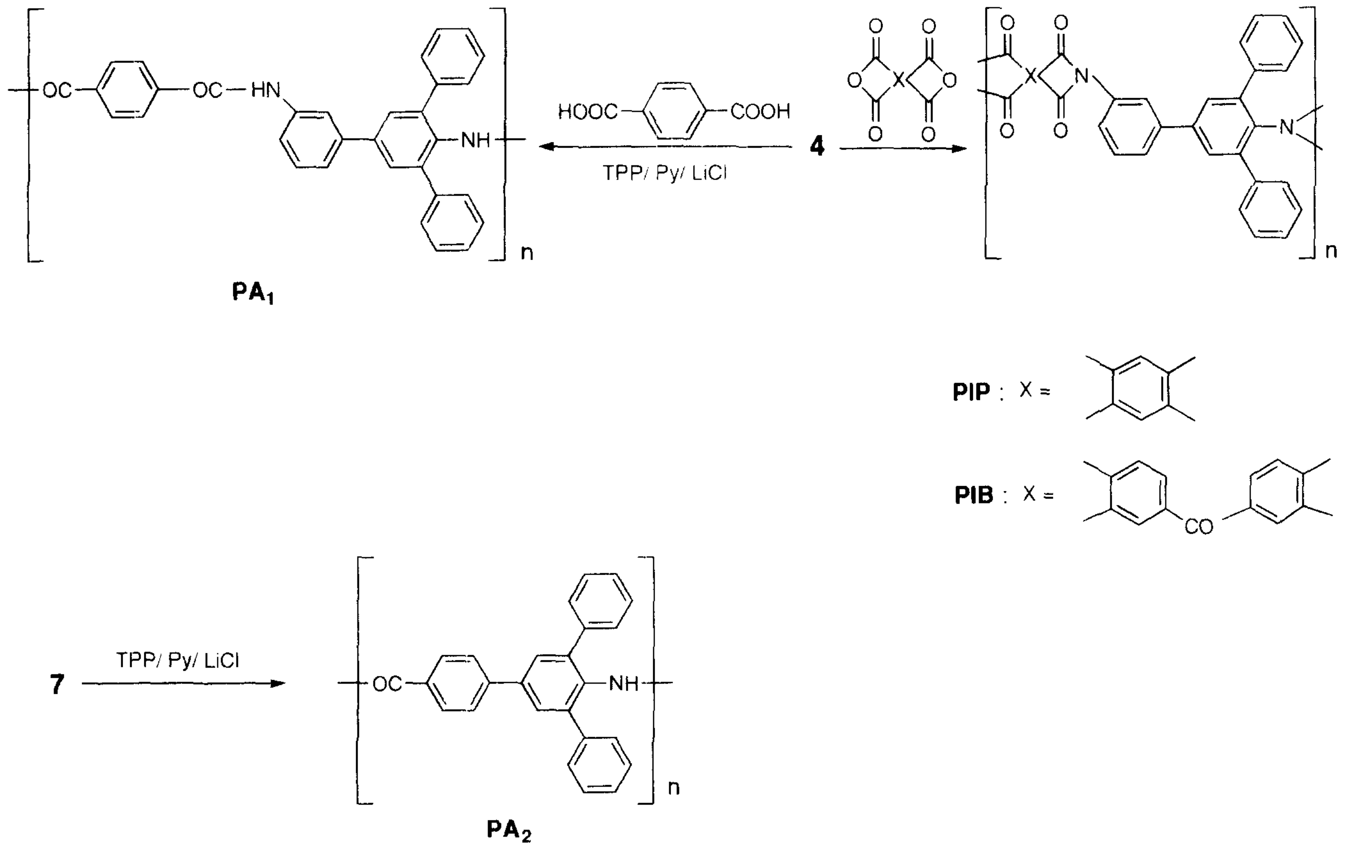
The i.r. and ^1H, ^{13}C n.m.r. spectra are shown in *Figures 1* and *2*, respectively.

Preparation of polymers (Scheme 3)

Polyamides **PA$_1$** *and* **PA$_2$**. A flask was charged with a mixture of **4** (0.41 g, 1.2 mmol), terephthalic acid (0.20 g, 1.2 mmol), triphenyl phosphite (0.76 g, 2.4 mmol), pyridine (2 ml), lithium chloride and DMAc (10 ml). It was refluxed under N_2 overnight and poured into water. The light brown precipitate was filtered off, washed with water, then with hot acetone and dried to afford **PA$_1$** (0.48 g).

A solution of **7** (0.60 g, 1.5 mmol) in DMAc (8 ml) was refluxed for 2 h. Then triphenyl phosphite (0.46 g, 1.5 mmol), pyridine (2 ml) and lithium chloride were added to the solution and polycondensation was accomplished as described for **PA$_1$** to afford **PA$_2$** (0.46 g).

Polyimides **PIP** *and* **PIB**. A mixture of **4** (0.37 g, 1.1 mmol), PMDA (0.24 g, 1.1 mmol) and DMAc (10 ml) was stirred and heated at 100°C under N_2 for 4 h. Acetic anhydride (3 ml) and pyridine (1 ml) were added to the solution and it was heated at 100°C overnight. It was subsequently poured into water. The dark brown solid was filtered off, washed with water, then with hot acetone and dried to afford **PIP** (0.52 g).



Scheme 3

Table 1 Yields, inherent viscosities and elemental analyses of polymers

Polymer	Yield (%)	η_{inh} [a] (dl g^{-1})	Empirical formula		Elemental analyses		
					C(%)	H (%)	N (%)
PA$_1$	92	0.47	$(C_{32}H_{22}N_2O_2)_n$	Calcd	82.38	4.75	6.00
				Found	80.94	4.79	6.08
PA$_2$	94	0.55	$(C_{25}H_{17}NO)_n$	Calcd	86.43	4.93	4.03
				Found	85.56	4.88	4.07
PIB	91	0.52	$(C_{41}H_{22}N_2O_5)_n$	Calcd	79.09	3.56	4.50
				Found	78.07	3.52	4.43
PIP	88	0.57	$(C_{34}H_{18}N_2O_4)_n$	Calcd	78.76	3.50	5.40
				Found	77.84	3.47	5.45

[a] Inherent viscosity in DMAc (0.5 g dl^{-1}) at 30°C

Polyimide **PIB** was similarly prepared by reacting **4** (0.31 g, 0.9 mmol) with BTDA (0.30 g, 0.9 mmol) as a dark brown solid (0.51 g).

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

RESULTS AND DISCUSSION

The reaction sequence of *Scheme 1* outlines the synthesis of diamine **4**. The intermediate compound **2** was prepared utilizing two synthetic routes. More particularly, the condensation of 3-nitrobenzaldehyde with an equimolar amount of acetophenone in boiling acetic anhydride afforded **1** in 80% yield. The latter reacted with acetophenone in the presence of $BF_3{\cdot}Et_2O$ to afford **2** in 25% yield (overall yield 20%). Compound **2** was alternatively prepared in 65% yield from the reaction of 3-nitrobenzaldehyde with a double molar amount of acetophenone in the presence of $BF_3{\cdot}Et_2O$. The last synthetic route is more short and affords **2** in significantly higher yield. The reaction of **2** with nitromethane afforded **3**. Nitromethane was used as reagent and reaction medium as well. When this reaction took place in absolute ethanol[27], compound **3** was prepared in remarkably lower yield. The catalytic hydrogenation of **3** to the corresponding diamine **4** was accomplished by means of hydrazine hydrate. Note that this hydrogenation method is simple, if we take into consideration that 4-amino-3,5-diphenyl-biphenyl has been hydrogenated under high pressure (*ca.* 70 atm) utilizing Raney nickel catalyst[28].

Compound **7** was similarly prepared starting from 4-carboxybenzaldehyde (*Scheme 2*). It was prepared as hydrochloric salt, because the corresponding amino acid was obtained as a gel due the formation of a salt judging from the i.r. spectrum.

The starting materials **4** and **7** were characterized by elemental analyses as well as i.r. and n.m.r. spectroscopy. *Figure 1* presents their *FT*i.r. spectra. Diamine **4** showed characteristic absorption bands at 3453, 3362 (N–H stretching); 1610 (N–H deformation and aromatic); 1494, 1468, 1430 (aromatic); 1300, 1280 cm^{-1} (C–N stretching). Amino acid **7** displayed absorptions at 3374, 3028–2544 (N–H and O–H stretching); 1684 (C=O); 1604 (N–H deformation); 1464 (aromatic); 1426, 1288 cm^{-1} (C–O stretching and O–H deformation).

Figure 2 presents the ^1H n.m.r. and ^{13}C n.m.r. spectra of amino acid **7**. Assignments of peaks for both spectra are given in the figure. The carboxylic proton was unobserved in the ^1H n.m.r. spectrum. The amino protons, exchangeable with D_2O, appeared upfield at 7.50 δ due to the existence of the hydrochloric salt. The presence of the carboxyl was confirmed from the peak at 167 δ in the ^{13}C n.m.r. spectrum.

Certain structural characteristics of compounds **4** and **7** were estimated by means of the CSC ChemDraw 3D plusΣ Molecular Modeling System. The two pendent phenyls *ortho* to amino group cause a significant steric hindrance. In addition, the amino group is deactivated by the electron-withdrawing phenyls. For these reasons the reactivity of the amino group between the two phenyls is expected to be low.

Rigid-rod polymers bearing phenyl pendent groups were synthesized (*Scheme 3*). Specifically, the reactions of diamine **4** with terephthalic acid, PMDA or BTDA afforded polyamide **PA$_1$** and polyimides **PIP** and **PIB**, respectively. In addition, the polycondensation of amino acid **7** yielded polyamide **PA$_2$**. Due to the low reactivity of the amino group between the two pendent phenyls, polyamides **PA$_1$** and **PA$_2$** were prepared by the phosphorylation method in boiling DMAc utilizing triphenyl phosphite and pyridine as condensing agents. The polycondensation of **7** was more difficult because of the hydrochloric salt, and the polymerization proceeds after the removal of hydrochloric acid. Polyimides **PIP** and **PIB** were synthesized by the two steps process in DMAc at 100°C and their intermediate poly(amic acids) were cyclodehydrated by means of acetic anhydride and pyridine.

The polymers were obtained in high yields (88–94%) and their inherent viscosities ranged from 0.47 to 0.57 dl g^{-1} (*Table 1*). The relatively low degree of polymerization was attributed to the steric hindrance of the two side phenyls on the amino group as well as to the low nucleophilicity of this amino group.

Structural characterization of polymers was accomplished by i.r., ^1H n.m.r. and ^{13}C n.m.r. spectroscopy as well as X-ray. The *FT*i.r. spectrum for a typical polyamide **PA$_2$** showed characteristic absorptions at 3386, 3202 (N–H stretching); 1644 (C=O); 1610, 1492 (aromatic); 1524 (N–H deformation) and 1268 cm^{-1} (C–N stretching). On the other hand, the *FT*i.r. spectrum for a representative polyimide **PIB** exhibited absorptions associated with the imide structure at 1782, 1724, 1368, 1102 and 758 cm^{-1}. The absorption at 1672 cm^{-1} was assigned to the benzophenone carbonyl.

Figure 3 presents the ^1H n.m.r. and ^{13}C n.m.r. spectra of polyamide **PA$_1$**. The ^1H n.m.r. spectrum showed singlets at 9.33 (NHCO), 8.13 (aromatic of terephthalic acid segments) and multiplets at 7.94 (aromatic of diamine segments *ortho* to NHCO) and 7.59–7.33 δ

(other aromatic of diamine segments). Assignments of peaks for the ^{13}C n.m.r. spectrum of **PA$_1$** are given in the figure.

The ^1H n.m.r. spectrum of polyimide **PIP** showed a singlet at 8.41 (aromatic of pyromellitic segments) and multiples at 8.29–7.49 δ (aromatic of diamine segments). On the other, the ^{13}C n.m.r. spectrum of this polymer exhibited a characteristic peak at 165 δ ascribable to the C=O carbon.

The structural characterization of polymers included X-ray studies. *Figure 4* presents the wide angle X-ray diffractograms for polymers. It is seen that the polymers **PA$_1$**, **PIP** and **PIB** derived from diamine **4** were amorphous. Polyimides **PIP** and **PIB** had the same pattern. Polyamide **PA$_2$** showed a degree of crystallinity and displayed peaks at 21.0 and 28.9°. This feature was attributed to the *para* substitution of the backbone benzene rings which can lead to a better packing of the chains. The higher crystallinity of **PA$_2$** in comparison to **PA$_1$** reflected in the lower solubility of the former in certain solvents (see below).

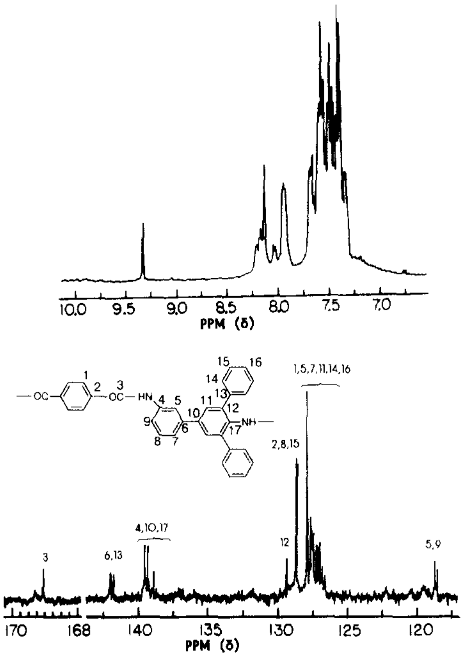


Figure 3 ^1H n.m.r. (upper) and ^{13}C n.m.r. (lower) spectra of polyamide **PA$_1$** in DMSO-d_6 solution

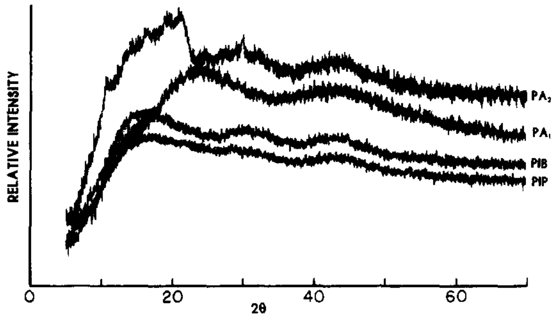


Figure 4 X-ray diffraction patterns of polymers

One of the objectives of the present investigation was the preparation of soluble polymers by introducing phenyl side groups. *Table 2* summarizes the solubility behaviour of polymers. All polymers dissolved at room temperature in polar aprotic solvents (DMF, DMSO, NMP) and in H_2SO_4 upon heating. Polyamides and polyimides dissolved also in CCl_3COOH at room or medium temperature, respectively. In addition, all polymers dissolved readily or upon heating in *m*-cresol. Polyamide **PA$_2$** displayed somewhat lower solubility than **PA$_1$** in 1,4-dioxane and cyclohexanone because of its crystallinity.

The hydrophilicity of polyamides was estimated by measuring the isothermal water absorption (*Figure 5*). A saturation in water absorption was observed for both polyamides after a time exposure of about 50 h, which is dependent on the sample particle size. The water uptake for **PA$_1$** and **PA$_2$** was 2.24 and 1.35%, respectively, after 50 h. The corresponding number of moles of absorbed water per amide equivalent weight was 0.29 and 0.26. The higher hydrophilicity of **PA$_1$** was attributed to the less dense packing of the chains due to the *p,m′*-substitution of biphenyl that increased the water accessibility. Note that the two phenyls *ortho* to –NH– linkages decreased their electron density and therefore the hydrogen bonding ability. A polyamide analogous to **PA$_2$** prepared from 4,4″-diamino-3,5,3″,5″-tetraphenyl-*p*-terphenyl absorbed also 0.26 mol water per amide equivalent weight[27].

The thermal characterization of polymers was carried out by t.m.a., t.g.a. and isothermal gravimetric analysis (i.g.a.). The t.m.a. method was used to determine the glass transition (T_g) and softening (T_s) temperatures of polymers (*Figure 6*). The T_g and T_s values were obtained from the onset temperatures of these transitions. Among the synthesized polymers only polyamide **PA$_1$** showed both T_g and T_s at 225 and 263°C, respectively. Polyamide **PA$_2$** displayed higher T_g at 240°C owing to its stiffer structure. Polyimide **PIB** showed T_g at 256°C whereas no transition was detected for polyimide **PIP** upon heating up to 300°C.

Figure 7 presents typical t.g.a. traces of polymers. The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}) in both N_2

Table 2 Solubilities of polymers[a]

	Solvents[b]									
Polymer	DMF	NMP	DMSO	CCl_3COOH	H_2SO_4	1,4-Dioxane	*m*-Cresol	CH	$CHCl_3$	DCB
PA$_1$	++	++	++	++	+	+	++	++	+−	+−
PA$_2$	++	++	++	++	+	+−	++	+−	+−	+−
PIB	++	++	++	−	+	+	++	+	−	+−
PIP	++	++	++	+	+	−	+	+	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +−, partially soluble; −, insoluble

[b] DMF, *N,N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMSO, dimethylsulfoxide; CH, cyclohexanone; DCB, *o*-dichlorobenzene

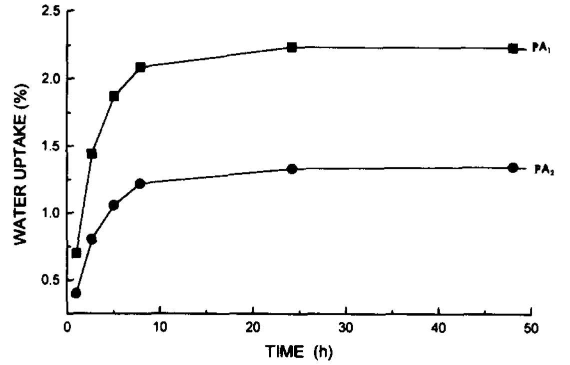


Figure 5 Water absorption vs time for polyamides **PA**$_1$ and **PA**$_2$

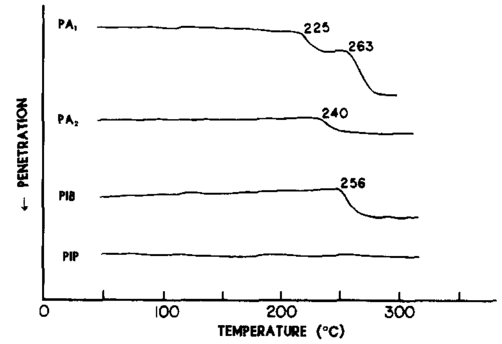


Figure 6 T.m.a. thermograms of polymers. Conditions: N_2 flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

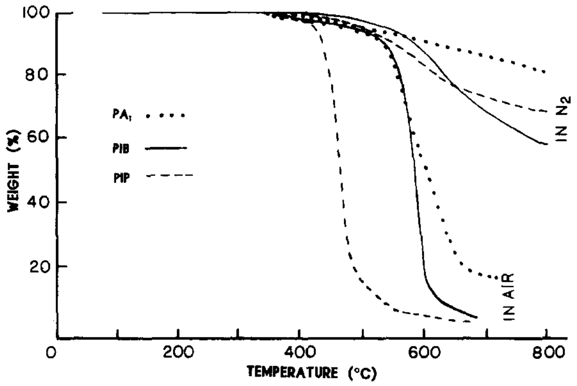


Figure 7 T.g.a. thermograms in N_2 and air of polyamide **PA**$_1$ as well as polyimides **PIP** and **PIB**. Conditions: gas flow 60 cm^3 min^{-1}; heating rate 20°C min^{-1}

and air as well as the anaerobic char yield (Y_c) at 800°C for all polymers are summarized in *Table 3*. The IDT and PDT were determined for the temperature at which 0.5 and 10% weight loss were observed, respectively. PDT$_{max}$ corresponds to the temperature at which the maximum rate of weight loss occurred. The polymers were stable up to 375–426°C in N_2 and 336–376°C in air and afforded anaerobic Y_c of 59–79% at 800°C.

The relative thermal stability of polymers could be assessed from the i.g.a. results. The weight losses obtained after 20 h isothermal ageing at 300°C in static air are listed in *Table 3*. The remaining weights determined from the i.g.a. traces and consequently the relative thermal stability of polymers were of the order **PIB** > **PIP** > **PA**$_1$ > **PA**$_2$.

CONCLUSIONS

An aromatic diamine of biphenyl bearing two pendent phenyls was synthesized and used as starting material for the preparation of rigid-rod amorphous polyamide and polyimides. In addition, an analogous amino acid was synthesized and polymerized to afford a rod-like semicrystalline polyamide. The polymers were readily soluble in polar aprotic solvents and certain other solvents. The polyamide derived from diamine softened at 263°C but no softening was detected for other polymers. Some of the polymers showed T_g at 225–256°C. The polymers were stable up to 375–426°C in N_2 and afforded anaerobic char yields of 59–79% at 800°C.

ACKNOWLEDGEMENTS

A grant from the Greek Ministry of Industry, Energy and Technology (General Secretariat of Research and Technology) in partial support of this work is gratefully acknowledged. The authors wish to thank the Nuclear Magnetic Resonance Center of University of Ioannina, Chemistry Department, for recording the n.m.r. spectra.

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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[e] (%)
PA$_1$	381	611	608	79	342	545	589	14.8
PA$_2$	375	561	605	79	336	530	571	15.5
PIB	426	589	646	59	376	558	623	4.1
PIP	411	560	627	68	364	467	493	7.6

[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 isothermal ageing at 300°C in static air

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