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Soluble, Rigid-Rod Polyamide, Polyimides, and Polyazomethine with Phenyl Pendent Groups Derived from 4,4″-Diamino-3,5,3″,5″-tetraphenyl-*p*-terphenyl

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ABSTRACT: The reaction of 4,4′-(1,4-phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) with nitromethane afforded 4,4″-dinitro-3,5,3″,5″-tetraphenyl-*p*-terphenyl, which was catalytically hydrogenated to the corresponding diamine. The latter was used as starting material for the preparation of new rigid-rod polyamide, polyimides, and polyazomethine bearing phenyl pendent groups as well as the respective model compounds. Characterization of polymers was accomplished by inherent viscosity measurements, elemental analysis, ^{1}H-NMR, ^{13}C-NMR, X-ray, DTA, TMA, TGA, and isothermal gravimetric analysis. The polymers were amorphous and soluble in polar aprotic solvents. Polyamide showed an outstanding solubility, being soluble even in *o*-dichlorobenzene and chloroform. Polyamide displayed T_g and softening temperature at 135 and 155 °C, respectively, whereas other polymers showed only T_g above 265 °C. The polymers were stable up to 397−441 °C in N_2 and 344−363 °C in air and afforded anaerobic char yields of 68−77% at 800 °C. In addition, the thermal stability of polyazomethine was investigated as a function of the curing time.

Introduction

Aromatic polyamides and polyimides have already reported for their high temperature resistance and excellent mechanical properties.[1] The last decade wholly aromatic rigid-rod polyamides and polyimides attracted much interest because of their exceptional technological importance. They are known for their enhanced thermal stability as well as outstanding mechanical,[2,3] optical, and morphological properties.[4] Fibers obtained from nematic solution of these polymers have been used in applications where high mechanical strength and thermal stability are required.[5]

Recently, much effort has made to develop rigid-rod polyamides[6−11] and polyimides[6,12−23] by introducing aromatic rings into the polymer backbone. However, these polymers present usually limited solubility and high melting temperatures, which decrease their processability and restrict further applications. The main method employed to overcome these important problems is the attachment of substituents onto the rodlike polymer backbone.[24−27] In this way, the polymerization or copolymerization of monomers bearing pendent groups lead to polymers with enhanced solubility, low melting and glass transition temperature, and in some cases amorphous polymers.

The present investigation deals with the synthesis and characterization of new rigid-rod polyamide, polyimides, and polyazomethine prepared from an aromatic diamine of *p*-terphenyl bearing two phenyls ortho to each amino group. Note that this diamine was prepared by a facile method utilizing inexpensive and widely used starting materials. The polymers synthesized are expected to exhibit an outstanding thermal stability due to their wholly aromatic structure. In addition, the incorporation of phenyls as pendent groups along the polymer backbone is expected to enhance their solubility. Other properties such as glass transition and softening temperatures were also investigated.

Experimental Section

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 AMX spectrometer. Chemical shifts (δ values) are given in parts per million with tetramethylsilane as an internal standard. DTA 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. DTA measurements were made using a high temperature (1200 °C) cell at a heating rate of 20 °C/min in N_2 atmosphere at a flow rate of 60 cm^3/min and with a ΔT sensitivity of 0.5 °C/in. 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 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-184O 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% rh (relative humidity) was maintained by means of an oversaturated aqueous solution of $NaNO_2$ at 20 °C, and they were periodically weighed.

Reagents and Solvents. 1,4-Benzenedicarboxaldehyde and benzoic acid were recrystallized from distilled water. Terephthalic acid was recrystallized from ethanol (30%). Pyromellitic dianhydride (PMDA) and benzophenonetetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Phthalic anhydride was purified by sublimation. Acetophenone, benzaldehyde, nitromethane, and pyridine were distilled under vacuum. Triethylamine and dimethylaceta-

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mide (DMAc) were dried by distillation over KOH and CaH_2, respectively.

Preparation of Starting Materials (Scheme 1). 3,3′-(1,4-Phenylene)bis(1,5-diphenyl-1,5-pentadione) (1). It was prepared in 95% yield by a reported method[28–30] and characterized as follows: mp 204–206 °C (lit.[28] 205–206 °C, lit.[29] 204–206 °C, lit.[30] 205 °C). IR (KBr, cm^{-1}): 1682 (C=O); 1596 (aromatic); 1270 (C–C(=O)–C stretching). ^{1}H-NMR (DMSO-d_6, δ, ppm): 8.17–7.27 (m, 24H, aromatic); 2.90 (d, 8H, CH_2); 2.80 (m, 2H, CH). Anal. Calcd for $C_{40}H_{34}O_4$: C, 83.02%; H, 5.92%. Found: C, 81.95%; H, 5.85%.

4,4′-(1,4-Phenylene)bis(2,6-diphenylpyrylium tetrafluoroborate) (2). It was prepared in 90% yield according to a reported method[28–30] and characterized as follows: mp > 300 °C (lit.[28] > 350 °C dec, lit.[29,30] > 350 °C). IR (KBr, cm^{-1}): 1616 (s), 1578 (m), 1502 (s), 1466 (s), 1258 (m), 1052 (br), 782 (m), 684 (m). ^{1}H-NMR (DMSO-d_6, δ, ppm): 9.29 (s, 4H, aromatic meta to oxygen); 9.05–7.53 (m, 24H, other aromatic). Anal. Calcd for $C_{40}H_{28}O_2B_2F_8$: C, 67.26%, H, 3.93%. Found: C, 66.92%; H, 4.07%.

4,4′′-Dinitro-3,5,3′′,5′′-tetraphenyl-*p*-terphenyl (3). A flask was charged with a mixture of **2** (5.50 g, 7.70 mmol), nitromethane (1.41 g, 23.11 mmol), and absolute ethanol (50 mL). Triethylamine (2.49 g, 24.65 mmol) was added to the vigorously stirred mixture. It was refluxed for 3 h. The hot mixture was filtered to afford **3** as a brown solid which was washed with methanol (3.60 g, 75%). It was recrystallized from a mixture of 1,4-dioxane/CH_3CN (1:1 v/v) to give a pale yellow solid: mp > 300 °C. IR (KBr, cm^{-1}): 1592, 1494 (aromatic); 1530, 1368 (NO_2). The ^{1}H-NMR spectrum could not be recorded due to the limited solubility of **3** in DMSO. Anal. Calcd for $C_{42}H_{28}N_2O_4$: C, 80.75%; H, 4.52%; N, 4.48%. Found: C, 79.11%, H, 4.47%; N, 4.55%.

4,4′′-Diamino-3,5,3′′,5′′-tetraphenyl-*p*-terpheyl (4). A flask equipped with a dropping funnel and condenser was charged with a mixture of **3** (4.89 g, 7.48 mmol), 1,4-dioxane (60 mL), ethanol 95% (30 mL), and a catalytic amount of 10% palladium on activated carbon. Hydrazine hydrate (10 mL) was added dropwise over 5 h to the stirred mixture at reflux temperature. The solid was gradually dissolved during this period. The mixture was refluxed for additional 20 h. The hydrogenation product precipitated was dissolved by adding 1,4-dioxane. The catalyst was filtered off, and the filtrate was poured into water. Compound **4** obtained as a whitish solid was filtered off, washed with methanol, and dried (4.20 g, 95%). It was recrystallized from 1,2-dichlorobenzene to afford a brownish solid: mp 309–310 °C. IR (KBr, cm^{-1}): 3450, 3364 (N–H stretching); 1610 (N–H deformation); 1460, 1426 (aromatic); 1244 (C–N stretching). The ^{1}H-NMR and ^{13}C-NMR spectra are shown in Figure 2. Anal. Calcd for $C_{42}H_{32}N_2$: C, 89.33%; H, 5.71%; N, 4.96%. Found: C, 88.17%; H, 5.65%; N, 4.89%.

Preparation of Model Compound (Scheme 2). Model Diamide (MDA). A flask was charged with a mixture of **4** (0.20 g, 0.35 mmol), benzoic acid (0.09 g, 0.70 mmol), triphenyl phosphite (0.33 g, 1.05 mmol), pyridine (1 mL), and DMAc (15 mL). It was refluxed under N_2 overnight and poured into water. **MDA** was obtained by filtration as a whitish solid, washed with methanol, and dried (0.19 g, 70%). It was recrystallized from a mixture of 1,4-dioxane/water (1:1 v/v): mp > 300 °C. IR (KBr, cm^{-1}): 3255 (N–H stretching); 1668 (C=O); 1598 (N–H deformation); 1494, 1462, 1430 (aromatic); 1252 (C–N stretching). ^{1}H-NMR ($CDCl_3$, δ, ppm): 7.62–7.55 (m, 10H, aromatic of benzoic acid moieties); 7.38–7.18 (m, 28H, aromatic of diamine moieties). ^{13}C-NMR (DMSO-d_6, δ, ppm): 169.53, 141.93, 139.78, 132.01, 129.37, 129.21, 128.97, 128.94, 128.81, 128.54, 128.43, 128.30, 128.18, 127.64, 127.48. Anal. Calcd for $C_{56}H_{40}N_2O_2$: C, 87.02%; H, 5.22%; N, 3.62%. Found: C, 86.70%; H, 5.17%; N, 3.74%.

Model Diimide (MDI). A mixture of **4** (0.25 g, 0.44 mmol), phthalic anhydride (0.13 g, 0.88 mmol), and DMAc (20 mL) was stirred and heated at 100 °C under N_2 for about 4 h. Acetic anhydride (5 mL) and pyridine (2 mL) were added to the solution, and it was heated at 140 °C overnight. It was subsequently poured into water. The brown solid was filtered off, washed with water and then with hot acetone, and dried to afford **MDI** (0.31 g, 85%). A purified sample was obtained by recrystallization from a mixture DMF/water (1:1 v.v): mp 290–292 °C. IR (KBr, cm^{-1}): 1763, 1704, 1366, 1018, 758 (imide structure); 1596, 1494, 1460, 1430 (aromatic). ^{1}H-NMR (DMSO-d_6, δ, ppm): 8.07–7.89 (m, 8H, aromatic of phthalic anhydride moieties); 7.74–7.30 (m, 28H, aromatic of diamine moieties). ^{13}C-NMR (DMSO-d_6, δ, ppm): 173.69, 141.81, 141.31, 139.17, 138.69, 134.61, 129.19, 128.58, 128.31, 128.12, 127.92, 127.77, 123.35. Anal. Calcd for $C_{58}H_{36}N_2O_4$: C, 84.45%; H, 4.40%; N, 3.40%. Found: C, 83.27%; H, 4.35%; N, 3.31%.

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

polymer	yield (%)	η_{inh}[a] (dL/g)	empirical formula		elemental analyses C (%)	H (%)	N (%)
PA	96	0.57	$(C_{50}H_{34}N_2O_2)_n$	calcd	86.43	4.93	4.03
				found	85.34	4.86	4.15
PIP	96	0.68	$(C_{52}H_{30}N_2O_4)_n$	calcd	83.63	4.05	3.75
				found	81.64	4.16	3.62
PIB	93	0.62	$(C_{59}H_{34}N_2O_5)_n$	calcd	83.28	4.03	3.29
				found	82.31	4.12	3.18
PAM	90	0.47	$(C_{50}H_{34}N_2)_n$	calcd	90.60	5.17	4.23
				found	89.43	5.04	4.08

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

Model Diazomethine (MDZ). A mixture of **4** (0.18 g, 0.32 mmol), benzaldehyde (0.07 g, 0.64 mmol), and DMAc (20 mL) was refluxed under N_2 overnight. It was poured into water. The brown-yellow solid was filtered off, washed with methanol, and dried to afford **MDZ** (0.22 g, 93%). It was recrystallized from acetonitrile: mp 245–247 °C. IR (KBr, cm^{-1}): 1632 (CH=N); 1578, 1492, 1456, 1422 (aromatic). ^{1}H-NMR (DMSO-d_6, δ, ppm): 8.40 (s, 2H, CH=N); 7.78 (s, 4H, aromatic ortho to CH=N); 7.65–7.30 (m, 34H other aromatic). Anal. Calcd for $C_{56}H_{40}N_2$: C, 90.78%; H, 5.44%; N, 3.78%. Found: C, 89.14%; H, 5.32%; N, 3.69%.

Preparation of Polymers (Scheme 3). Polyamide PA. PA was prepared as a whitish solid by reacting **4** with terephthalic acid in DMAc in the presence of triphenyl phosphite, pyridine, and lithium chloride according to the procedure described for **DMA**.

Polyimides PIP and PIB. PIP and **PIB** were prepared as brown solids from the reactions of **4** with PMDA or BDTA, respectively, according to the procedure described for **MDI**.

Polyazomethine PAM. PAM was prepared as a yellow solid from the reaction of **4** with 1,4-benzenedicarboxyaldehyde according to the procedure described for **MDZ**.

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

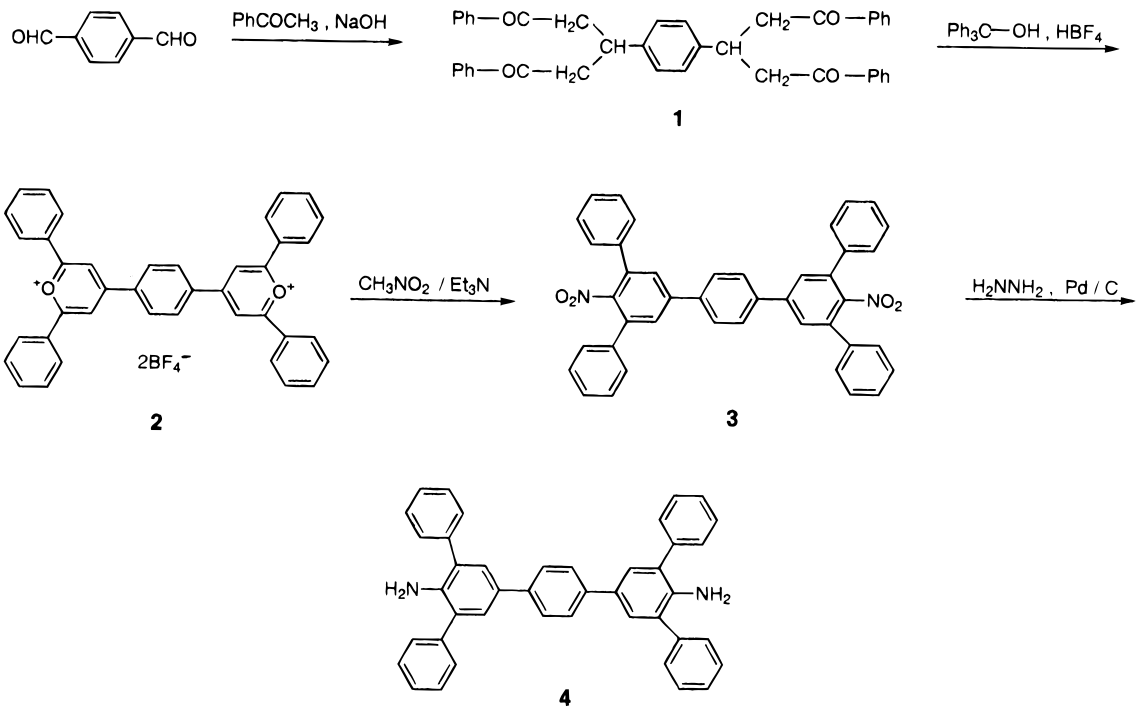
Results and Discussion

Diamine **4** was synthesized according to the reaction sequence of Scheme 1. Compounds **1** and **2** were prepared by a reported method.[28–30] The reaction of **2** with nitromethane[31] in absolute ethanol in the presence of triethylamine afforded compound **3**. This reaction took place by a nucleophilic addition of nitromethane to C2 of pyrylium ring, followed by an intramolecular aldol condensation.[32]

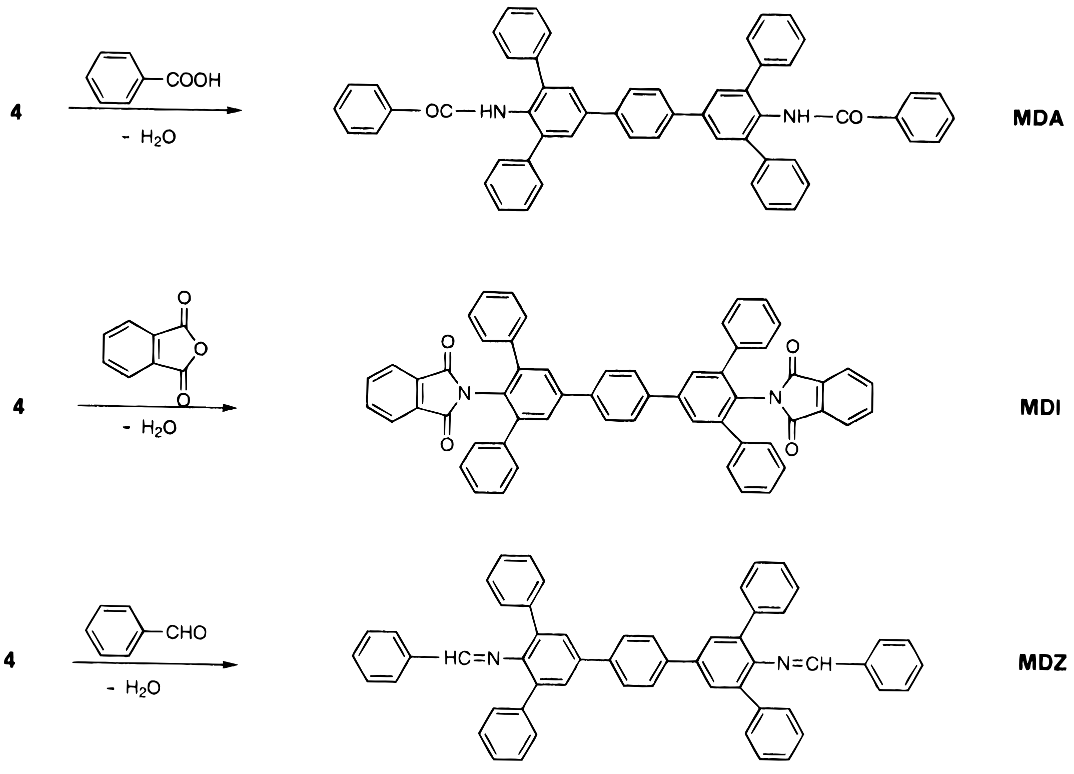
Compound **3** was catalytically hydrogenated to the corresponding diamine **4** by means of hydrazine hydrate. The reaction was carried out in a mixture of 1,4-dioxane/ethanol (3:1 v/v) at boiling temperature for a prolonged time (24 h). When only 1,4-dioxane was used as reaction medium, the hydrogenation was completed after 48 h.

To obtain fundamental information about the structure of polymers model compounds were synthesized (Scheme 2). Specifically, model diamide (**MDA**), diimide

Scheme 1



Scheme 2

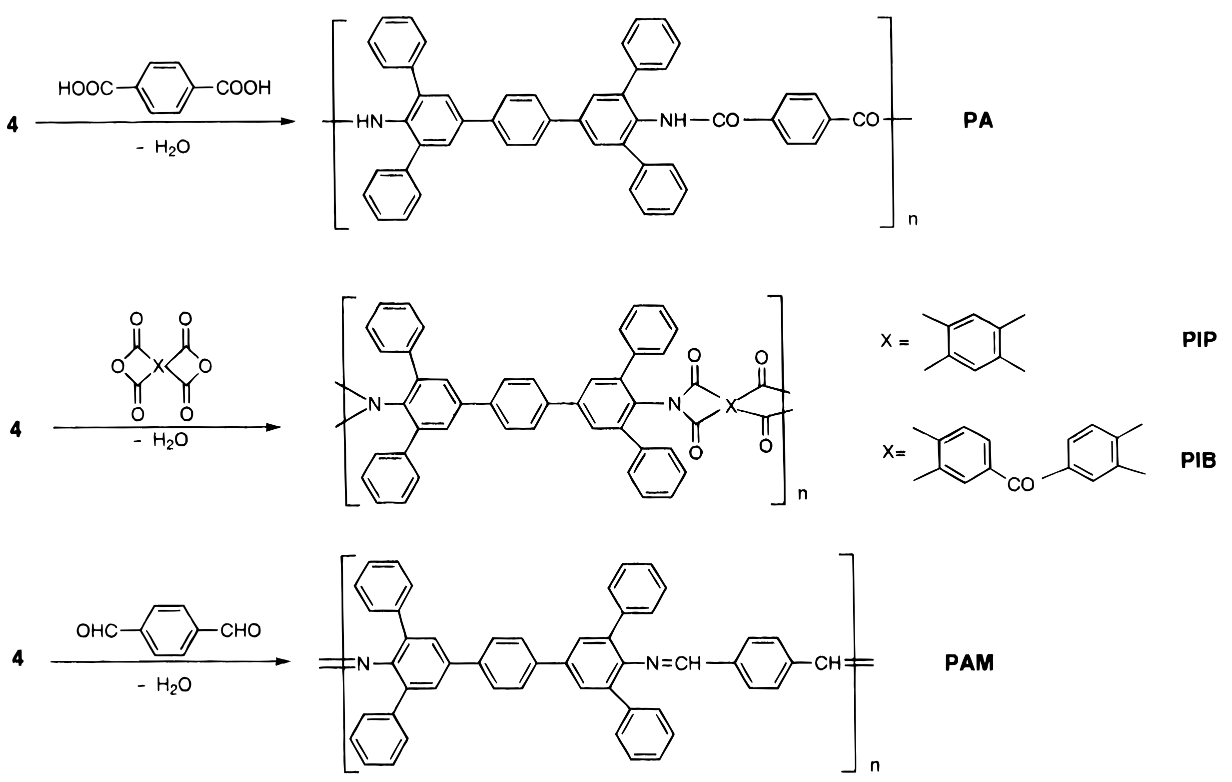


(**MDI**), and diazomethine (**MDZ**) were prepared by reacting **4** with benzoic acid, phthalic anhydride, and benzaldehyde, respectively.

Rigid-rod polymers bearing phenyl pendent groups were synthesized (Scheme 3). More particularly, the reactions of diamine **4** with terephthalic acid, PMDA, BTDA, or 1,4-benzenedicarboxyaldehyde yielded polyamide **PA**, polyimides **PIP** and **PIB**, and polyazomethine **PAM**, respectively. **PA** was prepared by the phosphorylation method in boiling DMAc utilizing triphenyl phosphite and pyridine as condensing agents. No reaction took place when the mixture was heated at lower temperature (100 °C), due to the deactivation effect which was caused mainly by steric hindrance of the two bulky phenyls ortho to amino group. In addition, the electron-withdrawing phenyls reduced the nucleophilicity of the amino groups. For these reasons, polyimides **PIP** and **PIB** were prepared at high temperature, and their intermediate polyamic acids were cyclodehydrated by means of acetic anhydride and pyridine.

The optimized geometry of diamine **4** was calculated by means of CSC ChemDraw 3D PlusΣ Molecular Modeling System (Figure 1). It revealed that all aro-

Scheme 3



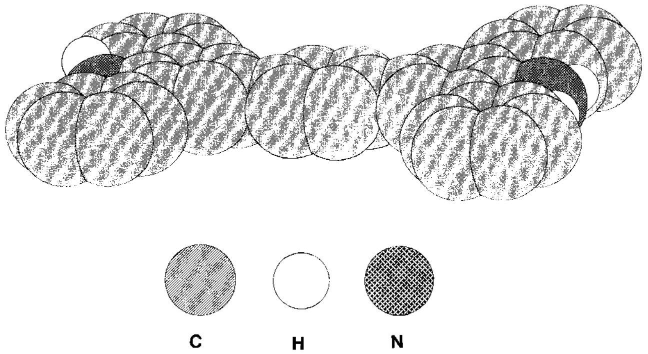
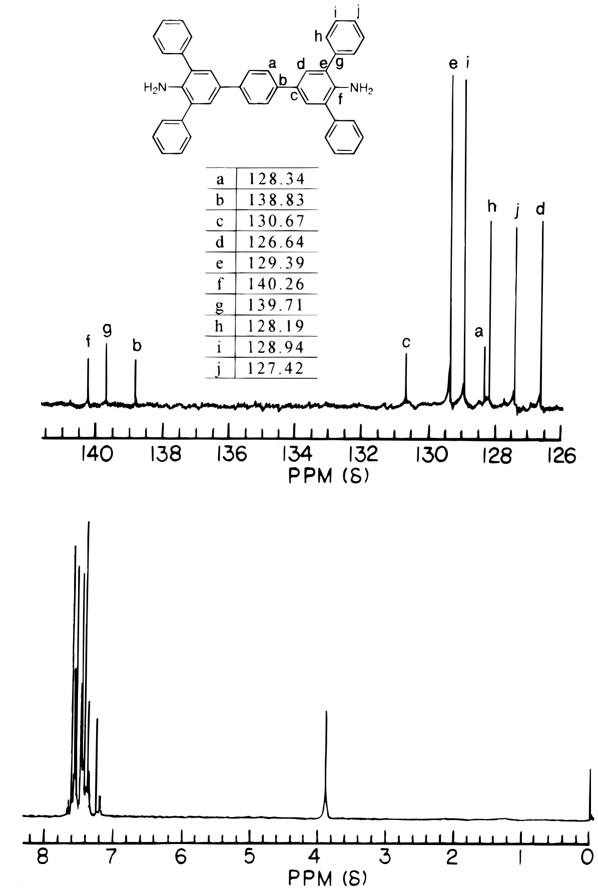


Figure 1. Optimized geometry of diamine **4**. (ChemDraw 3D PlusΣ Molecular Modeling System, Version 3.11, 1993; Cambridge Scientific Computing, Inc.).



a	128.34
b	138.83
c	130.67
d	126.64
e	129.39
f	140.26
g	139.71
h	128.19
i	128.94
j	127.42

Figure 2. ^{1}H-NMR and ^{13}C-NMR spectra of compound **4** in a $CDCl_3$ solution.

matic rings are almost coplanar and the side phenyls cause a significant steric hindrance on the amino groups.

Characterization of monomers was accomplished by elemental analyses as well as IR and NMR spectroscopy. The reduction of **3** to **4** was monitored by IR spectroscopy. Compound **3** showed strong absorption bands at 1530 and 1368 cm^{-1} assigned to nitro groups whereas **4** lacked these absorptions. In addition, the latter displayed new absorptions at 3450, 3364 (N–H stretching), 1610 (N–H deformation), and 1244 cm^{-1} (C–N stretching).

Figure 2 shows the ^{1}H-NMR and ^{13}C-NMR spectra of diamine **4** in a $CDCl_3$ solution. The aromatic protons appeared in the ^{1}H-NMR spectrum as a multiplet at 7.62–7.26 δ and the amino protons, exchangeable with D_2O, gave a singlet at 3.90 δ. Assignments of peaks for the ^{13}C-NMR spectrum are given on Figure 2.

The polymers were obtained in 90–96% yields, and their inherent viscosities ranged from 0.47 to 0.68 dL/g (Table 1). Although they are rigid-rod polymers, they had a moderate degree of polymerization, which was attributed to the relatively low nucleophilicity of diamine **4** as well as to a considerable steric hindrance caused by the two phenyls ortho to each amino group.[11,27] When a solution 10% wt/wt of polyamide **PA** in DMF was examined under polarization microscope, it displayed lyotropic behavior.

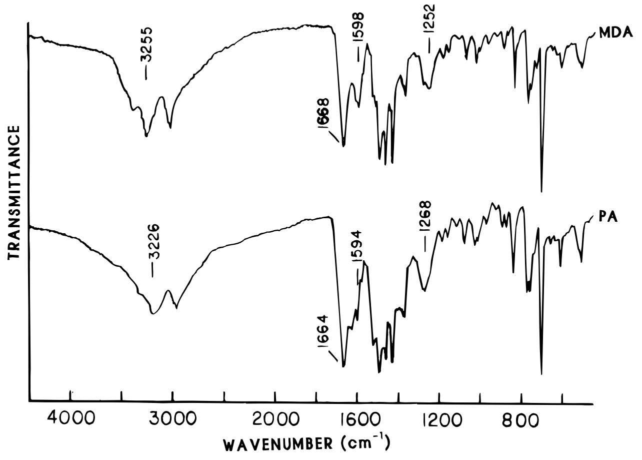


Figure 3. FT-IR spectra of model diamide **MDA** and polyamide **PA**.

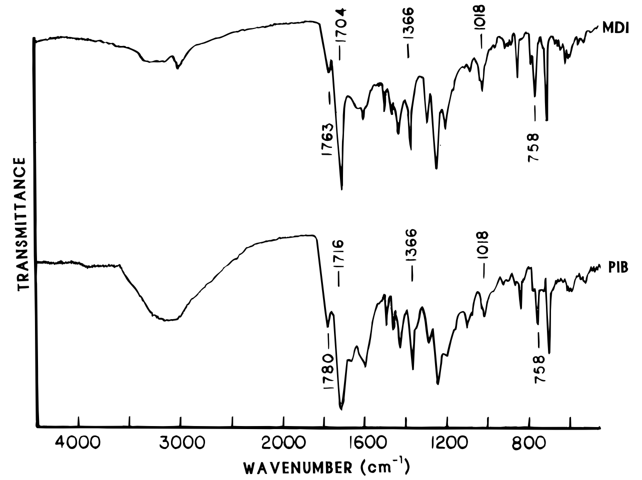


Figure 4. FT-IR spectra of model diimide **MDI** and polyimide **PIB**.

The polymers were characterized by elemental analysis (Table 1) as well as IR, ^{1}H-NMR, and ^{13}C-NMR spectroscopy. Their IR spectra were in agreement with those of the corresponding model compounds. Figures 3 and 4 present the FT-IR spectra of **MDA**, **PA** and **MDI**, **PIB**, respectively. Polyamide **PA** showed characteristic absorption bands at 3226 (N—H stretching), 1664 (C═O), 1594 (N—H deformation) and 1268 (C—N stretching and N—H bending). Polyimide **PIB** displayed absorptions associated with the imide structure at 1780, 1716, 1366, 1018, and 758 cm^{-1}. On the other hand, polyazomethine **PAM** exhibited a strong absorption at 1628 cm^{-1} assigned to C═N bond.

Figure 5 presents the ^{1}H-NMR and ^{13}C-NMR spectra of polyamide **PA**. The ^{1}H-NMR spectrum showed singlets at 9.33 (NHCO), 7.88 (aromatic of terephthalic acid segment), and multiplets at 7.65−7.37 δ (aromatic of diamine segment). Assignments of peaks for the ^{13}C-NMR spectrum of **PA** (Figure 5) as well as for that of polyimide **PIP** (Figure 6) are given on Figures.

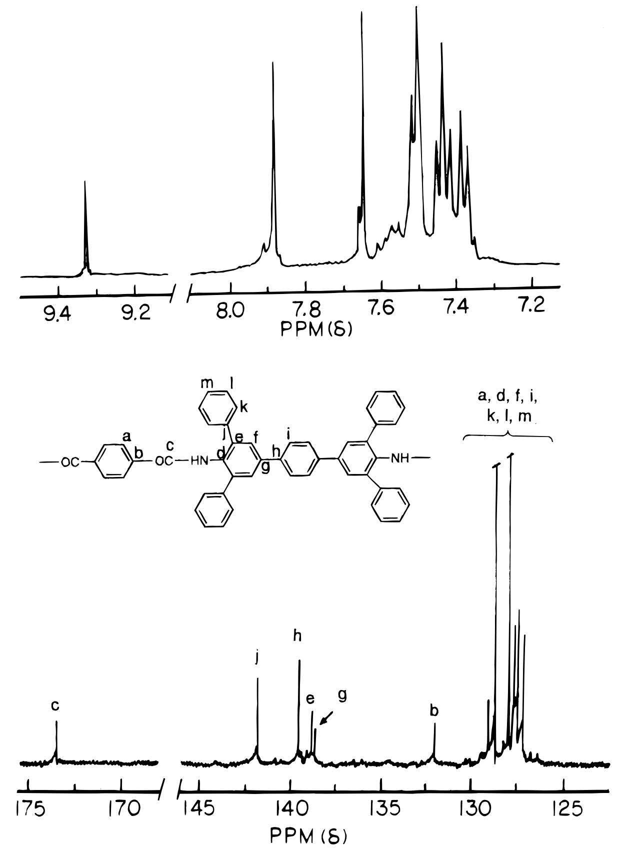


Figure 5. ^{1}H-NMR and ^{13}C-NMR spectra of polyamide **PA** in a DMSO-d_6 solution.

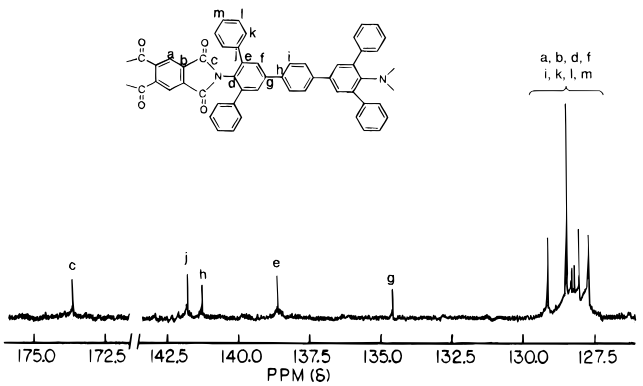


Figure 6. ^{13}C-NMR spectrum of polyimide **PIP** in a DMSO-d_6 solution.

The polymers are expected to exhibit an enhanced solubility in common organic solvents due to the presence of the pendent phenyls. Table 2 shows the solubility behavior of polymers. Polyamide **PA** displayed an outstanding solubility being soluble in all tested solvents at room temperature or upon heating. It dissolved even in less efficient solvents such as *o*-dichlorobenzene and chloroform. The pendent phenyls influenced the ability of polyamide to form intermolecular hydrogen bonds.

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	++	++	++	++	+	+	+	+	+	+
PIB	++	++	++	+	+−	+−	+	+−	+−	+−
PIP	++	++	++	+	+−	+−	+	+−	+−	+−
PAM	+	+	+	++	+	+	+	+	−	−

[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, *o*-dichlorobenzene.

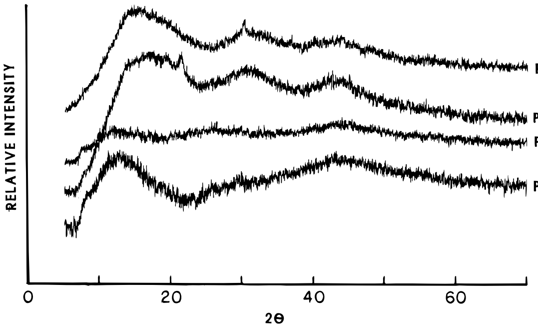


Figure 7. Wide-angle X-ray diffractograms of polymers.

Polyimides **PIP** and **PIB** were readily soluble in polar aprotic solvents (DMF, DMSO, NMP). They dissolved also in hot CCl_3COOH, *m*-cresol and were partially soluble in other solvents. Polyazomethine **PAM** dissolved upon heating in polar aprotic solvents as well as in H_2SO_4, 1,4-dioxane, *m*-cresol, and cyclohexanone. In addition, it dissolved in CCl_3COOH at ambient temperature. However, it is well known[33,34] that polyazomethines undergo remarkable degradation in strong acids due to hydrolysis of the CH=N linkage. The relatively lower solubility of polyimides and polyazomethine in comparison to that of polyamide was attributed to the more rigid structure of the former.

An attempt was made for structural characterization of polymers by X-ray method with as prepared powders (Figure 7). The X-ray diffractograms revealed that they were generally amorphous. However, **PA** and **PAM** showed weak diffraction peaks at 29.8 and 21.0°, respectively, which indicate a small crystalline nature. The amorphous character of polymers was in line with their enhanced solubility.

The isothermal water absorption of polyamide **PA** was measured to estimate its hydrophilicity. After exposure for 100 h, the water uptake was 1.34% and the corresponding number of moles of absorbed water per amide equivalent weight was 0.26. This value is significantly lower than that (0.76−0.83) of aromatic polyamides containing benzoxazole or benzothiazole pendent groups.[35] Such a behavior could be attributed to the almost coplanar conformation of diamine segment which did not increase considerably the disorder in the chain and consequently the water accessibility. In addition, the two phenyls ortho to −NH− linkages decreased their electron density and therefore the hydrogen bonding ability.

Thermal characterization of polymers was accomplished by DTA. The DTA thermogram of polyamide **PA** showed a broad endotherm around 155 °C associated with softening. In contrast, polyimides **PIP**, **PIB**, and polyazomethine **PAM** did not soften up to 300 °C. In addition, **PAM** showed a broad exotherm above 300 °C due to the crosslinking through the azomethine bonds.

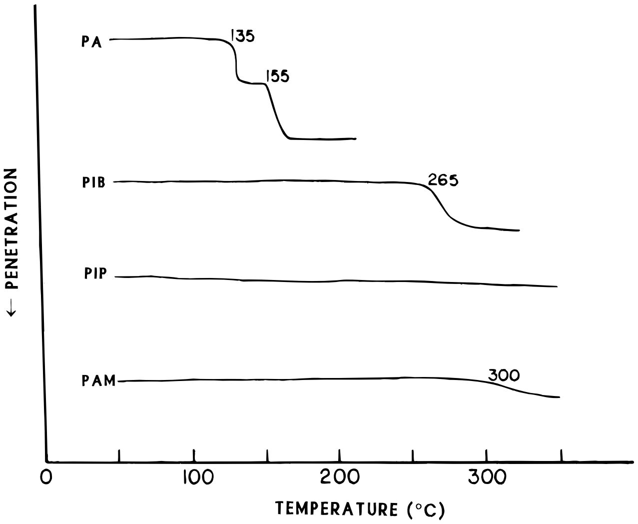


Figure 8. TMA thermograms for polymers. Conditions: N_2 flow 60 cm^3/min; heating rate 20 °C/min.

The glass transition (T_g) and softening (T_s) temperatures of polymers were determined by the TMA method (Figure 8). The T_g and T_s values were obtained from the onset temperatures of these transitions. Polyamide **PA** showed T_g and T_s at 135 and 155 °C, respectively. Polyimide **PIB** displayed only T_g at 265 °C, whereas polyimide **PIP** did not show any transition up to 350 °C. Finally, polyazomethine **PAM** exhibited T_g at 300 °C.

The thermal stability of polymers was evaluated by TGA in N_2 and air as well as isothermal gravimetric analysis (IGA). The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), 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. 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 397−441 °C in N_2 and 344−363 °C in air and afforded anaerobic Y_c of 68−77% at 800 °C. Taking the IDT as criterion of thermal stability, the relative thermal stability of polymers was of the order: **PIB** > **PIP** > **PAM** > **PA**.

The IGA results were in agreement with the TGA data. Specifically, following 20 h isothermal aging at 300 °C in static air the polymers showed weight losses of 3.2−19.4% (Table 3).

The present investigation was extended to include a study of thermal stability of polyazomethine **PAM** as a function of the curing time. More particularly, **PAM** was cured at 300 °C in static air for various periods to obtain a crosslinked resin through the −CH=N− bonds. IGA was used for evaluating thermal stability of the resulting resins. Figure 9 shows the remaining weight of resins after 20 h isothermal aging at 320 °C in static air versus the time of heat-curing at 300 °C. It is seen

Table 3. Thermal Stabilities of Polymers

	in N_2				in air			
polymer	IDT[a] (°C)	PDT[b] (°C)	PDT_{max}[c] (°C)	Yc[d] (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)	wt loss[e] (%)
PA	397	517	489	68	344	385	438	19.4
PIB	441	600	590	77	363	426	444	3.2
PIP	426	600	646	75	355	437	448	10.4
PAM	419	527	616	68	352	416	441	13.8

[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 aging at 300 °C in static air.

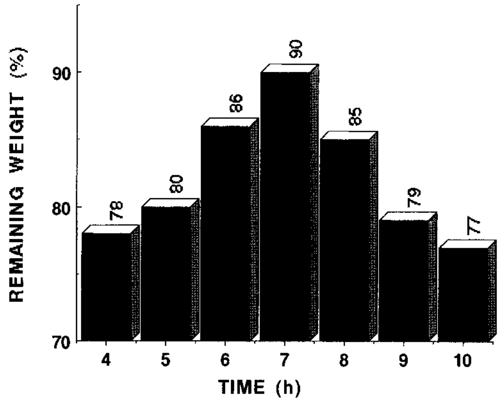


Figure 9. Remaining weight after 20 h isothermal aging at 320 °C in static air versus the time of curing at 300 °C for polyazomethine **PAM**.

that the remaining weight increased with increasing the curing time up to 7 h, and it was reduced beyond this time. Therefore, the optimum time for curing under these conditions was 7 h. The resin thus obtained showed IDT 456 and 385 °C in N_2 and air, respectively. The broadening of the IR absorption band for the cured samples of polyazomethine in the range of 1620−1650 cm^{-1} indicated crosslinking.

Conclusions

A new aromatic diamine of *p*-terphenyl containing two phenyls ortho to each amino group was successfully synthesized and used as starting material for the preparation of rigid-rod polyamide, polyimides, and polyazomethine. Polyamide was soluble even in less efficient solvents such as cyclohexanone, 1,4-dioxane, *o*-dichlorobenzene, and chloroform whereas polyimides and polyazomethine dissolved in polar aprotic solvents. Polyamide softened at 155 °C, but no softening was observed for other polymers. The polymers showed high thermal stability being stable up to 397−441 °C in N_2 and affording anaerobic char yields of 68−77% at 800 °C.

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