Synthesis and Characterization of New Soluble Aromatic Polyamides Derived from 1,4-Bis(4-carboxyphenoxy)-2,5-di-*tert*-butylbenzene

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ABSTRACT: Aromatic polyamides based on a novel bis(ether-carboxylic acid) were synthesized by the direct phosphorylation condensation method. 1,4-Bis(4-carboxyphenoxy)-2,5-di-*tert*-butylbenzene was combined with various diamines containing flexible linkages and side substituents to render a set of eight novel aromatic polyamides. The polymers were produced with high yields and moderate to high inherent viscosities (0.49–1.32 dL/g) that corresponded to weight-average and number-average molecular weights (by gel permeation chromatography) of 31,000–80,000 and 19,000–50,000, respectively. Except for a single example, the polyamides were essentially amorphous and soluble in a variety of common solvents such as cyclohexanone, dioxane, and tetrahydrofuran. They showed glass-transition temperatures of 250–295 °C (by differential scanning calorimetry) and 10% weight loss temperatures above 460 °C, as revealed by thermogravimetric analysis in nitrogen. Polymer films, obtained by casting from *N,N*-dimethylacetamide solutions, exhibited good mechanical properties, with tensile strengths of 83–111 MPa and tensile moduli of 2.0–2.2 GPa. © 2001 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 39: 475–485, 2001

Keywords: aromatic polyamides; new monomer; synthesis; solubility; thermal properties

INTRODUCTION

Aromatic polyamides are a class of functional polyphenylenes with an excellent balance of mechanical and thermal properties, which qualify them as high-performance polymer materials.[1–3] Despite their outstanding properties, they have limited application because of their intractability. In fact, they do not melt below their decomposition temperatures (T_d's) and can be processed only from solutions in highly polar organic solvents containing inorganic salts.[4]

Therefore, efforts focused on chemically modifying the composition of these materials are being made with the objective of improving their processability and, more specifically, their solubility in organic solvents. Major elements that account for the low solubility of aromatic polyamides are molecular order; high crystallinity; chain stiffness provided by the high density of aromatic rings; and strong interchain attractive forces, mainly hydrogen bonding, that enhance effective molecular packing. In this respect, it is known that the introduction of flexible linkages[5–7] into the main chain of aromatic polymers greatly enhances molecular mobility and provides better solubility, but it decreases thermal transitions and stability. The incorporation of bulky pendent groups[8–13] can provide beneficial effects for solubility be-

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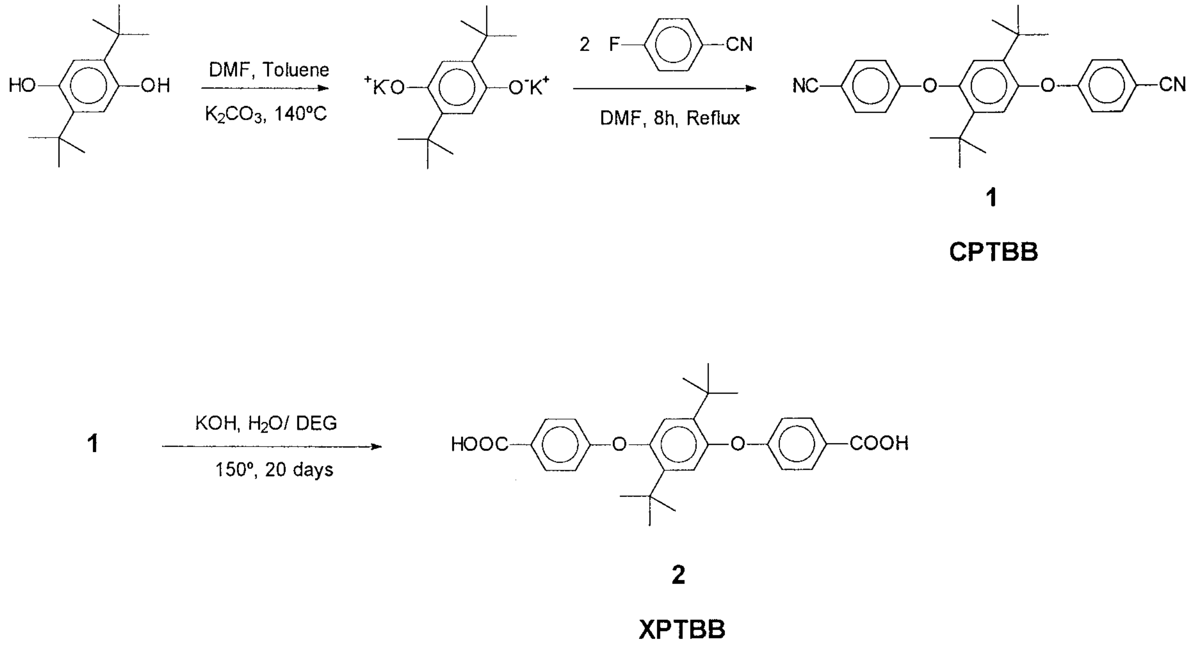


Scheme 1. Synthesis of XPTBB.

cause this approach produces a separation of chains, a weakening of hydrogen bonding, and a lowering of chain packing with a gain of free volume. Bulky side groups also give rise to restricted molecular mobility, so that the overall observable effect is a raising of the glass-transition temperatures (T_g's) and an improvement of solubility (processability) at the same time.

Previous results have validated this approach,[14–17] and work reported in this article was designed to extend heuristic options through the synthesis of a new condensation monomer containing flexible ether linkages and bulky, pendent *t*-butyl groups and its polycondensation with a set of aromatic diamines chosen by their favorable geometry to enhance molecular mobility and prevent molecular order and packing. A major objective was to study the effect of the flexible linkages and the *t*-butyl side groups on key properties of the polymers, that is, solubility in polar and common organic solvents, thermal transitions and thermal resistance, abilities to crystallize, and mechanical properties.

EXPERIMENTAL

Materials

2,5-Di-*tert*-butylhydroquinone (Acros) and 4-fluorobenzonitrile (Acros) were used as received, as well as the other reagents and solvents, unless further purification is reported. Reagent-grade LiCl was dried at 300 °C before use. *N*-Methyl-2-pyrrolidinone (NMP) was purified by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Pyridine was purified by distillation and stored over molecular sieves (4 Å). Triphenyl phosphite (TPP) was distilled twice at low pressure.

2,2-Bis(4-aminophenyl)hexafluoropropane was supplied by Chriskev, and it was purified by sublimation just before use. Bis(4-amino-3-isopropyl-5-methylphenyl)methane was supplied from ACROS and recrystallized from hexane three times, the last time just before use. 2,2-Bis(4-aminophenyl)propane,[18] 2,2-bis(4-amino-3-methylphenyl)propane,[18] 2,2-bis(4-amino-3,5-dimethylphenyl)propane,[18] 3,3′,5,5′-tetramethyl-bis[4-(4-aminophenoxy)phenyl]sulfone,[19] 4-(1-adamantyl)-1,3-bis(4-aminophenoxy)benzene,[14] and 1,4-bis(4-aminophenoxy)-2,5-di-*tert*-butylbenzene[20] were synthesized in our laboratory and purified according to the method reported.

Monomer Synthesis

1,4-Bis(4-cyanophenoxy)-2,5-di-tert-butylbenzene (CPTBB)

2,5-Di-*tert*-butylhydroquinone (22.23 g, 0.10 mol) and anhydrous K_2CO_3 (29.02 g, 0.21 mol) were

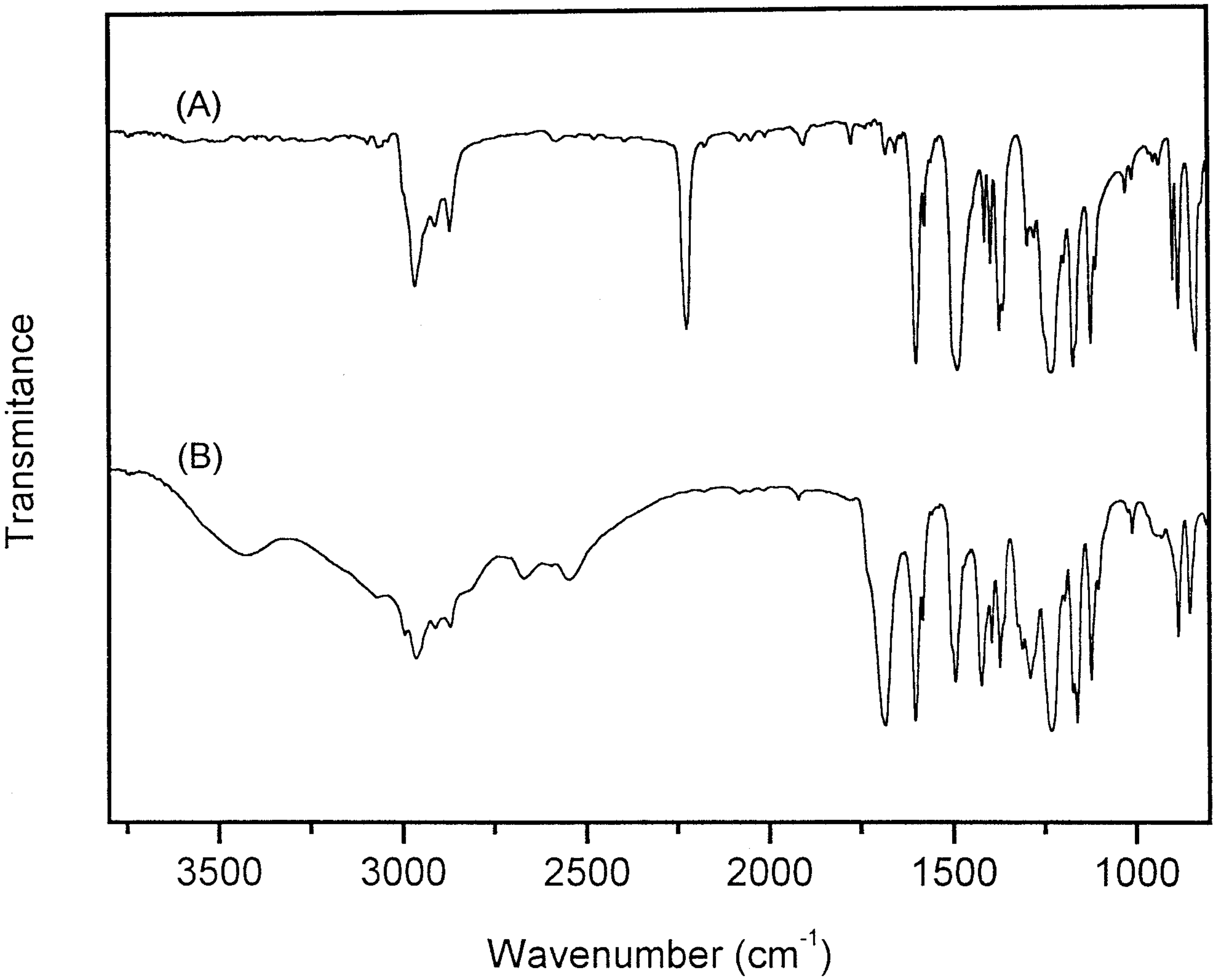


Figure 1. IR spectra of (A) the cyano precursor and (B) the diacid XPTBB.

suspended in a mixture of 200 mL of *N,N*-dimethylformamide (DMF) and 120 mL of toluene. The mixture was heated with stirring at 140 °C for 4h with a Dean–Stark trap to remove small amounts of water azeotropically. After the toluene was completely removed, 4-fluorobenzonitrile (24.82 g, 0.20 mol) was added to the mixture, and heating was continued at reflux for 8 h. Once the reaction mixture was at room temperature, it was poured into water, and the precipitate was thoroughly washed with water and dried. The resulting dicyano compound was recrystallized from DMF to give 35 g (83%) of white needles [mp = 274 °C by differential scanning calorimetry (DSC)].

IR (KBr, cm^{-1}): 2969, 2912, 2872 (aliphatic C—H stretching), 2226 (C≡N stretching), 1238 (C—O—C stretching). ^{1}H NMR (CDCl$_3$, δ, ppm): 1.27 (s), 6.94 (s), 7.03 (d), 7.56 (d). ^{13}C NMR (CDCl$_3$, δ, ppm): 30.57, 34.99, 106.07, 118.13, 119.34, 121.65, 134.77, 141.90, 150.16, 162.31. Elem. Anal. Calcd. for $C_{28}H_{28}N_2O_2$ (424.54): C, 79.22%; H, 6.65%; N, 6.60%. Found: C, 78.95%; H, 6.87%; N, 6.58%.

*1,4-Bis(4-carboxyphenoxy)-2,5-di-*tert-butylbenzene (XPTBB)

The dicyano compound CPTBB (30.0 g, 0.071 mol) was heated to reflux in the presence of KOH (73 g, 1.3 mol) in 1500 mL of a mixture (1/1) of H_2O and diethylenglycol (DEG) over a period of 21 days until ammonia evolution ceased. The resulting hot mixture was filtered to remove the suspended solid, cooled, and acidified with concentrated HCl to pH 2–3 when a white solid precipitated. The solid was filtered off and washed several times

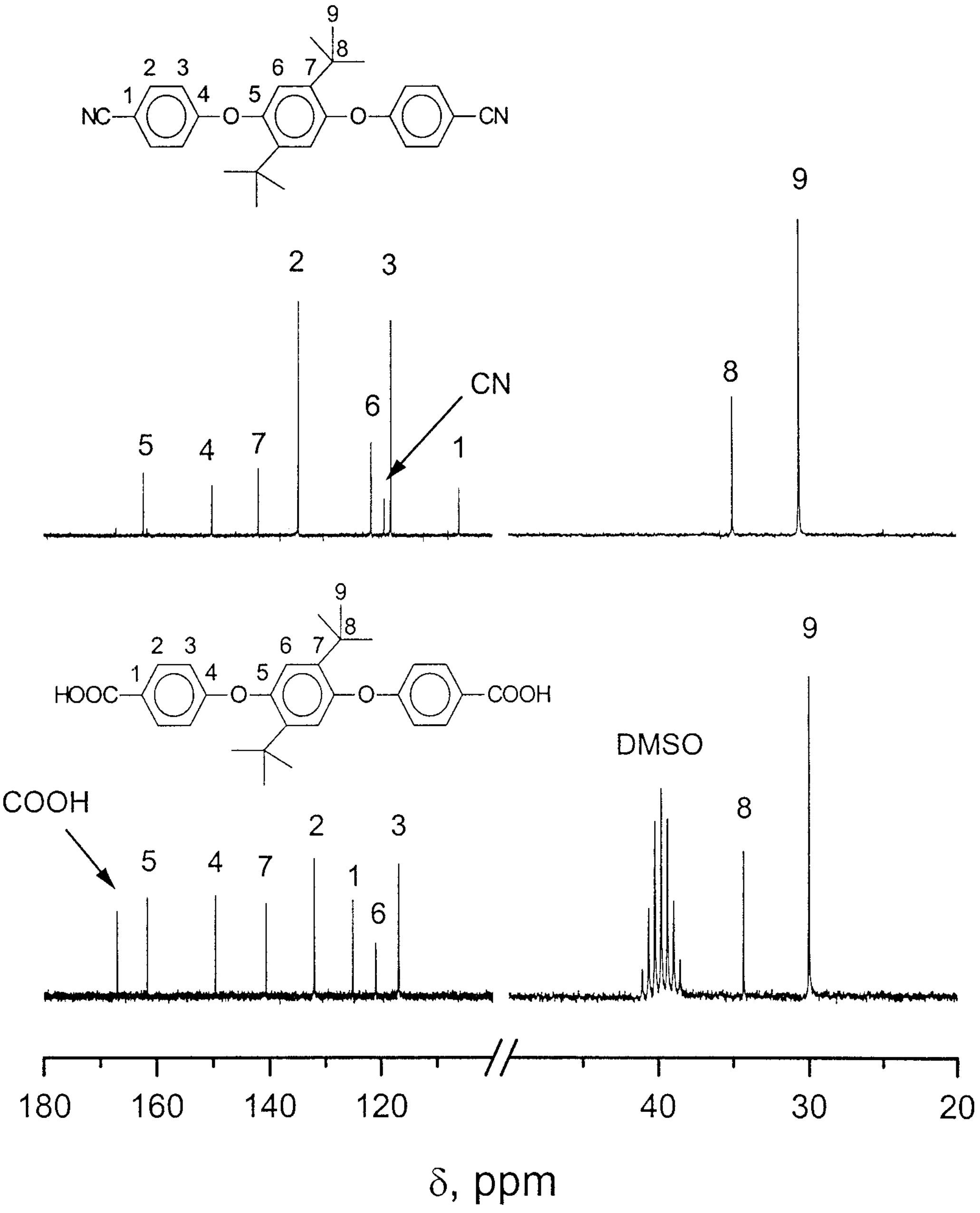


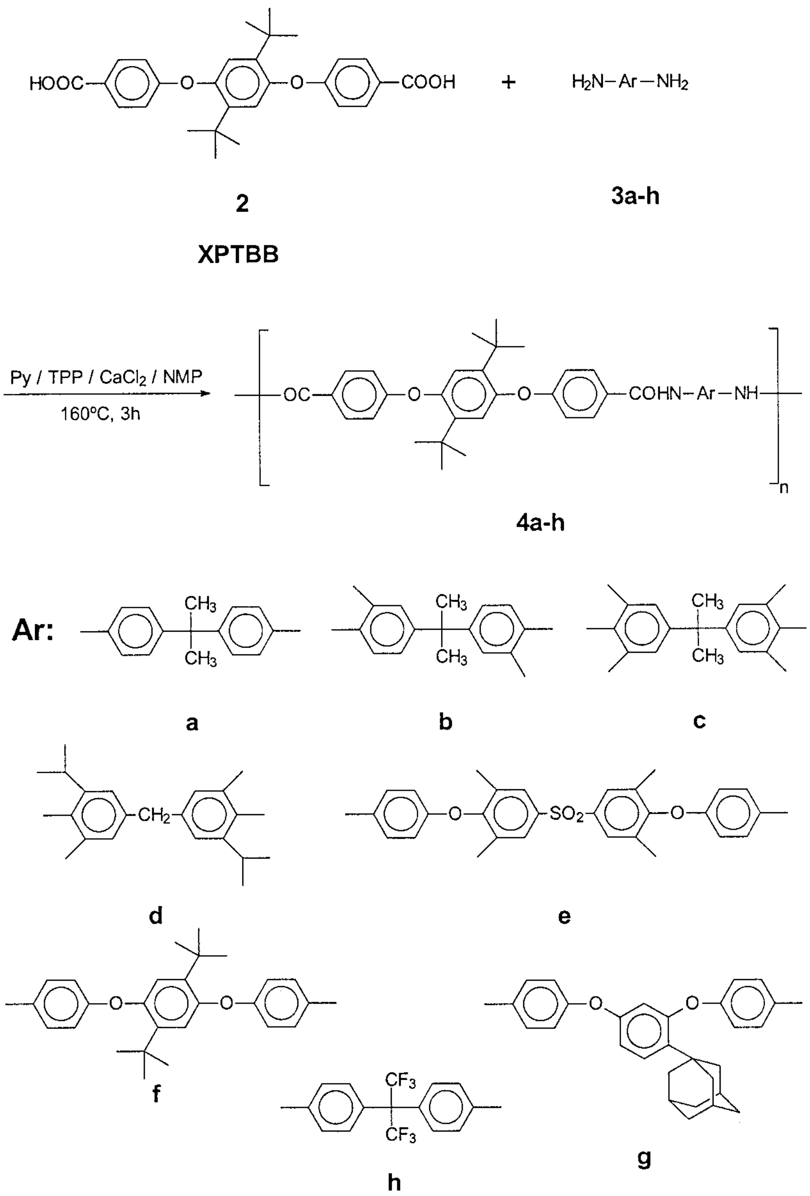
Figure 2. ^{13}C NMR spectra of (A) the cyano precursor CPTBB and (B) the diacid XPTBB.

with hot water to remove the residual HCl, and the crude product was recrystallized from DMF to obtain 23.9 g (73%) of pure product (mp = 371 °C by DSC).

IR (KBr, cm^{-1}): 3315–2200 (O—H stretching), 1689 (C═O stretching), 1232 (C—O—C stretching). ^{1}H NMR (DMSO-d_6, δ, ppm): 1.22 (s), 6.92 (s), 7.04 (d), 7.98 (d). ^{13}C NMR (DMSO-d_6, δ, ppm): 30.00, 34.34, 116.88, 120.94, 125.06, 132.01, 140.60, 149.74, 161.77, 167.15. ELEM. ANAL. Calcd. for $C_{28}H_{30}O_6$ (462.54): C, 72.71%; H, 6.54%. Found: C, 72.57%; H, 6.69%.

Polymers Syntheses

The phosphorylation polycondensation method was used to prepare the polymers presented in this article. One example of the method is given next.



Scheme 2. Synthesis of the polyamides from the XPTBB and diamines.

A flask equipped with a mechanical stirrer was flame-dried and charged under a nitrogen atmosphere with NMP (10 mL), diacid (0.01 mol), LiCl (1.4 g), and pyridine (6 mL). The mixture was stirred at room temperature (the diacid XPTBB did not dissolve in any case). Then, the diamine (0.01 mol) and TPP (0.022 mol) were rapidly added with the rest of the NMP (10 mL), and the solution was heated to 105 °C and maintained at this temperature for 3 h. The resulting polymer solution was poured into 500 mL of ethanol, and the precipitate was washed several times with hot water and ethanol and dried overnight under vacuum at 100 °C. Yields over 90% were attained in every case.

Measurements

Melting points were measured by DSC. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 520 FTIR spectrometer on KBr pellets and thin films. Solution ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 spectrometer at 199.97 and 50.28 MHz frequencies, respectively, with standard acquisition parameters. DSC analyses were performed on a

Table I. Inherent Viscosities, Elemental Analyses, and GPC Data of the Polyamides

						Elemental Analyses				
Polymer	η_{inh} (dL/g)	M_n	M_w	M_w/M_n	Molecular Formula		C	H	N	S
4a	1.25	34500	62000	1.8	$C_{43}H_{44}N_2O_4$	Calcd.	79.11	6.79	4.29	
						Found	78.94	6.88	3.90	
4b	0.71	23000	38000	1.6	$C_{45}H_{48}N_2O_4$	Calcd.	79.38	7.11	4.11	
						Found	78.74	7.32	3.79	
4c	1.29	49500	79500	1.6	$C_{47}H_{52}N_2O_4$	Calcd.	79.63	7.39	3.95	
						Found	78.28	7.51	3.51	
4d	1.32	41000	74000	1.8	$C_{49}H_{56}N_2O_4$	Calcd.	79.86	7.66	3.80	
						Found	78.65	7.97	3.47	
4e	1.24	38000	63500	1.7	$C_{56}H_{54}N_2O_8S$	Calcd.	73.50	5.95	3.06	3.50
						Found	72.52	6.16	2.95	3.08
4f	—	—	—	—	$C_{54}H_{58}N_2O_6$	Calcd.	78.04	7.03	3.37	
						Found	77.18	7.35	3.57	
4g	0.49	23500	37000	1.5	$C_{56}H_{56}N_2O_6$	Calcd.	78.85	6.62	3.28	
						Found	78.60	6.74	3.50	
4h	0.51	19000	31000	1.6	$C_{34}H_{38}F_6N_2O_4$	Calcd.	67.89	5.03	3.68	
						Found	65.56	5.03	3.32	

PerkinElmer DSC-7 analyzer at a heating rate of 20 °C/min under nitrogen. Thermogravimetric analyses (TGAs) were performed in N_2 with a PerkinElmer TGA-7 analyzer at 10 °C/min on 2–3-mg samples. Inherent viscosities were measured on filtered 0.5 g/dL *N,N*-dimethylacetamide (DMA) solutions at 25 ± 0.1 °C in an Ubbelohde viscometer. Elemental analyses were made with a Carlo Erba EA1108 elemental analyzer. For the measurement of mechanical properties, strips 5 mm wide, 30 mm long, and 40–60 μm thick were cut from polymer films and tested on a MTS Synergie 200 universal testing machine. An extension rate of 1 mm/min was applied with a gauge length of 10 mm. Wide-angle X-ray diffraction (WAXD) patterns were obtained with a Philips X-ray diffractometer with Cu Kα radiation.

Gel permeation chromatography (GPC) analyses were carried out with PL gel columns (Polymer Laboratories) of the nominal pore sizes 500, 10^4, and 10^5 Å. DMF with 0.1% LiBr was used as a solvent, and the measurements were done at 70 °C with a flow rate of 1.0 mL/min with a UV detector. The columns were calibrated with narrow standards of a suitable aromatic polyamide [poly(*m*-phenylene-isophthalamide)].

Water sorption was measured on milled samples in a humidity-controlled atmosphere prepared with a saturated solution of $NaNO_2$ to achieve a medium of 67% relative humidity. Weight gain was measured at 1, 2, 3, 4, 8, 24, 48, and 120 h.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomer XPTBB was synthesized with a two-step route outlined in Scheme 1. In the first step, the dicyano compound was obtained from the aromatic nucleophilic substitution displacement of 4-fluorobenzonitrile with potassium phenolate of 2,5-di-*tert*-butylhydroquinone. The second step was the more stringent because of the difficulty of achieving a complete alkaline hydrolysis of the cyano groups. Nevertheless, the overall yield was over 60% based on 2,5-di-*tert*-butylhydroquinone. Figure 1 shows the IR spectra of the dicyano intermediate and the monomer. The most relevant change on passing from the dicyano compound to the dicarboxylic acid monomer was the disappearance of the sharp absorption band due to $\mathrm{—C{\equiv}N}$ stretching at 2226 cm^{-1} and the appearance of strong absorption bands of —COOH at 2200–3300 (OH stretching) and 1690 cm^{-1} ($\mathrm{C{=}O}$ stretching).

Other important evidence of this change is the shifts of the carbon resonance signals of the cyano and carboxylic groups. The original signal at 119.34 ppm assigned to cyano carbon disappeared, and the resonance of carbonyl carbon appeared downfield at 167.15 ppm, as can be observed in Figure 2. All the data obtained were in good agreement with the expected structures.

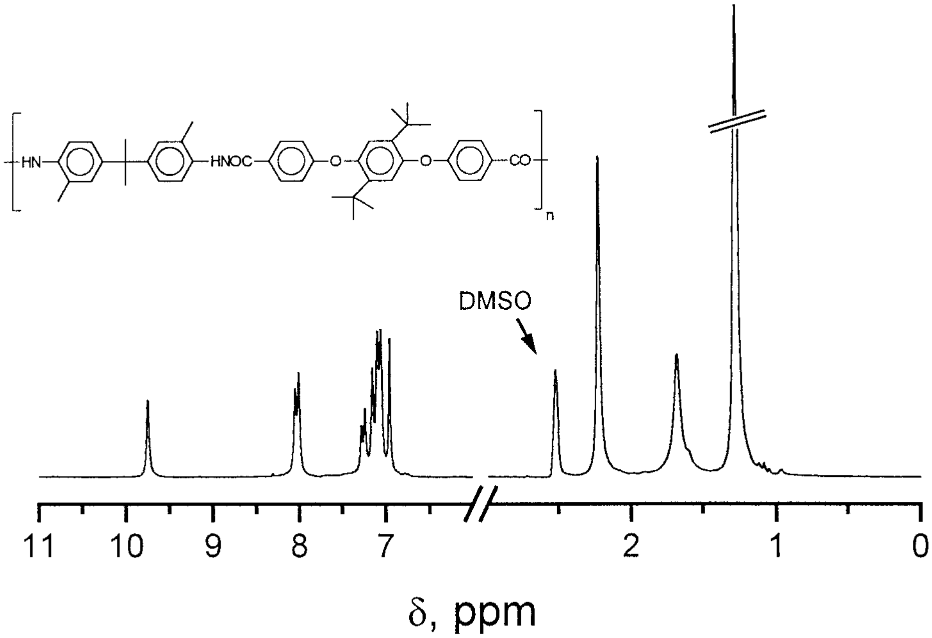


Figure 3. ^{1}H NMR spectrum of polyamide **4b**.

Polymers Syntheses

Aromatic polyamides were prepared by the synthetic route depicted in Scheme 2. The phosphorylation method first described by Yamazaki et al.[21] was used as a general approach for all the polymers with the triphenylphosphite–pyridine system as a condensing promoter and LiCl as a solubility enhancer. High yields and acceptable molecular weights were obtained. All the polycondensations proceeded readily in homogeneous solutions, except for polyamide **4f**, which precipitated from the reaction medium when the system became viscous. Table I shows the results of polycondensation, along with the elemental analyses of the polymers. Inherent viscosities up to 1.32 dL/g were achieved, which corresponds to an estimated number-average molecular weight (M_n) of 41,000 g/mol and a weight-average molecular weight (M_w), of 74,000 g/mol for polymer **4d** on the basis of GPC results. Polymer **4c**, with a very close value of η_{inh}, showed even higher M_n and M_w values, 49,500 and 79,500 g/mol, respectively. The molecular weights were determined by GPC with DMF as a solvent and fractionated samples of poly(m-phenylene-isophthalamide) as standards for calibration. Moreover, a comparatively low value of M_w/M_n, not greater than 2, for the set of polymers accounts for a suitable polycondensation method and a careful purification of the final materials.

Table II. Solubility of the Polyamides[a]

	Solvents					
Polymer	DMF	DMA	NMP	CH	THF	DX
4a	+	+	+	+	+−	−
4b	+	+	+	+	+−	−
4c	+	+	+	+−	−	−
4d	+	+	+	+−	+−	+−
4e	+	+	+	+−	+	+−
4f	−	−	−	−	−	−
4g	+	+	+	+	+	+
4h	+	+	+	+	+	+

[a] + = soluble at room temperature; +− = swollen; − = insoluble even on heating.

Polyamide formation was also confirmed by IR and NMR spectroscopy. Amide absorption bands could be observed by IR spectroscopy for all the polyamides around 3300 (NH stretching), 1600 (C═O stretching), and 1550 cm^{-1} (combination of NH bending and C—N stretching), along with characteristic absorption bands of aromatic compounds at 3050 and 1600 cm^{-1}. Figure 3 reproduces the ^{1}H NMR spectrum of polymer **4b**, where all the peaks have been readily assigned to the protons of the repeating unit.

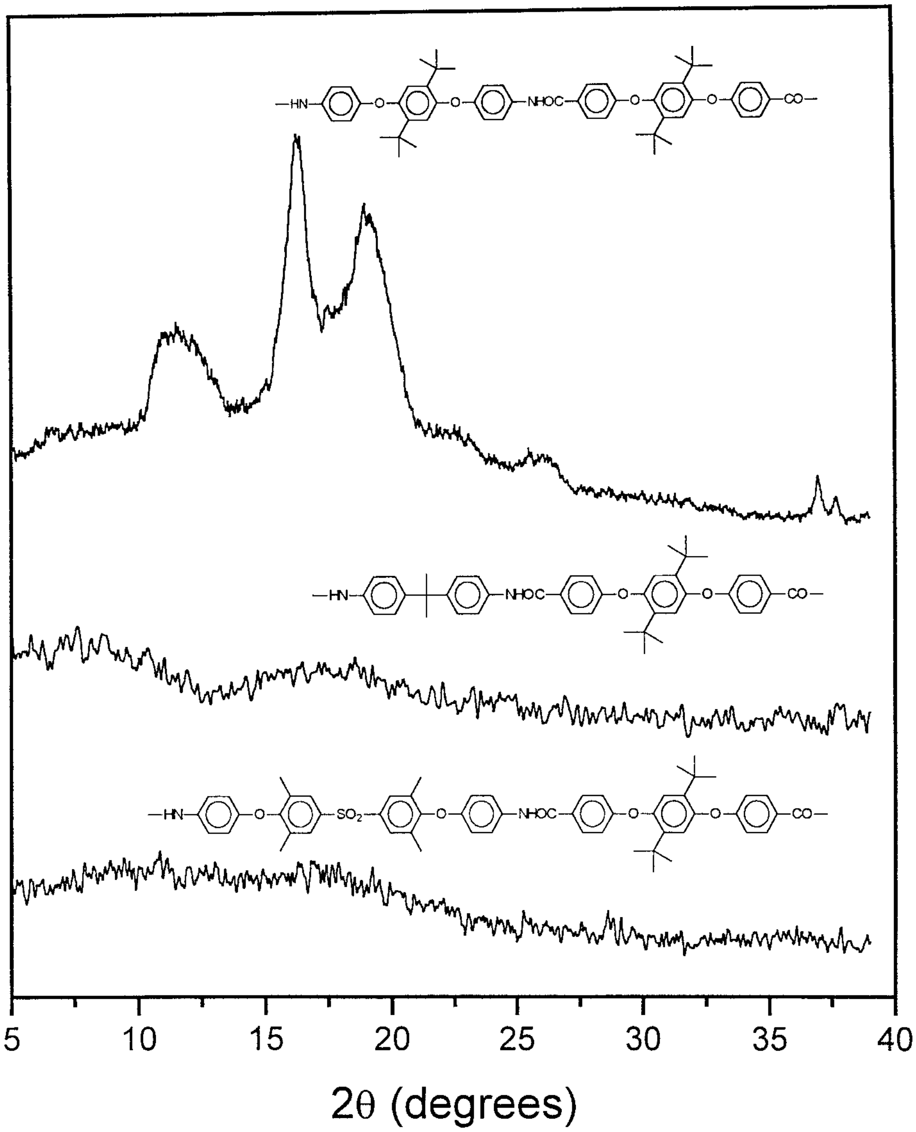


Figure 4. Wide-angle X-ray diffractograms of some polyamides.

Properties of Polymers

As mentioned, improving polymer solubility was a major aim of this work, so solubility was investigated for a number of solvents, as summarized in Table II. All of the polymers were soluble in DMF, DMA, and NMP at room temperature, with the exception of polymer **4f**. Polymers **4a**, **4b**, **4g**, and **4h** were also soluble in cyclohexanone (CH), and polymers **4g** and **4h** were soluble even in tetrahydrofuran (THF) and dioxane (DX). These results are interesting because very few aromatic polyamides have been reported that are soluble in common organic solvents. As a matter of fact, novel aromatic polyamides described in the last few years have been claimed to be soluble in polar aprotic solvents such as DMF, DMA, NMP, and dimethylsulfoxide, but only aromatic polyamides derived from fluorinated diamines and other novel especial monomers have shown solubility in THF or DX.[14,22]

The only exception to this observation was polymer **4f**, which could not be dissolved in any of the solvents tested. Even polar aprotic solvents with added salt could not dissolve it. Polymer **4f** is the combination of monomer XPTBB and its homologous diamine, which resulted in high symmetry and molecular order. Thus, despite the bulky *tert*-butyl groups that should cause an ef-

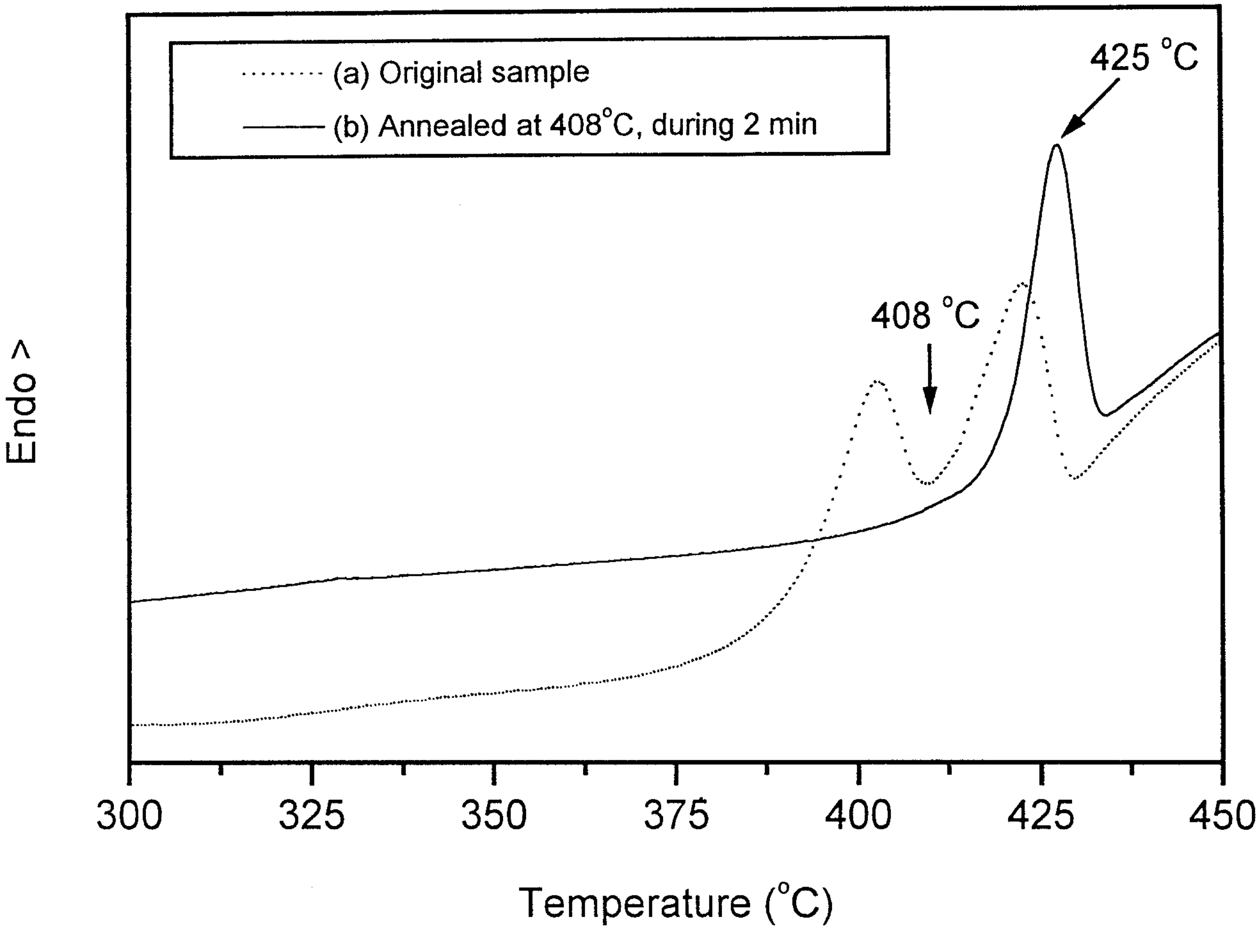


Figure 5. DSC curves for polyamide **4f**.

fective separation of chains, the regular alternation of amide, ether, and *p*-phenylene groups along the backbone apparently led to efficient packing and poor solubility. Because of its molecular regularity, polymer **4f** was also the only one that developed a three-dimensional crystalline order as observed by X-ray diffractometry. Figure 4 shows the WAXD diagram of polymer **4f** along with those of polymers **4a** and **4e**; although the latter showed amorphous diffraction patterns, the diagram of polymer **4f** showed several diffraction signals of high intensity assignable to a semicrystalline polymer, with strong reflections at $2\theta = 17$ and 20°.

Conclusive evidence of these features was attained in the study of the thermal properties of the polymers. DSC showed only one inflection of the specific-heat–temperature curve in every case, which was attributed to the T_g. The T_g values ranged from 250 to 295 °C, with the lowest value corresponding to polymer **4b** and the highest to polymers **4c** and **4e**. This indicates that the presence of four methyl substituents on the diamine greatly enhanced the T_g's of polymers **4c** and **4e**. Polymer **4f** did not follow this trend, and it showed two endothermal melting peaks beyond the T_g inflection (Fig. 5). Curve a corresponds to the first run, where the sample was heated well above the melting temperature, and curve b corresponds to a second run, registered after annealing at 408 °C for 2 min and cooling to room temperature. The presence of two peaks within the melting interval in the first case probably indicates a range of crystallite sizes or perfection that disappears after annealing.

Thermal stability was investigated by TGA. Initial T_d's of over 400 °C were measured for these polymers in nitrogen, with individual values for the T_d depending on the nature of the diamine used as a starting material. The following trend was observed for T_d values: **4g** > **4e** > **4f** > **4h** = **4a** > **4c** > **4d** > **4b**. There was an apparent

Table III. Mechanical and Thermal Properties of the Polyamides Based on XPTBB

Polymer	Tensile Strength (MPa)	Young's Modulus (GPa)	T_g (°C)	T_d (°C)[a]	T_{d10} (°C)[b]	Y_{800} (%)[c]
4a	101	2.0	277	440	475	36
4b	98	2.1	251	405	440	38
4c	99	2.1	295	425	460	25
4d	111	2.2	260	410	475	24
4e	96	2.0	290	460	480	46
4f	—	—	280	445	480	30
4g	93	2.0	260	465	490	39
4h	83	2.2	268	440	505	48

[a] Temperature of first onset in the TGA curve measured by TGA at a heating rate of 10 °C/min.
[b] 10% weight loss temperature.
[c] Residual weight percentage at 800 °C in nitrogen by TGA.

higher stability for polymers containing phenylene oxide linkages in the backbone compared with those containing aliphatic linkages such as methylene, isopropylidene, or hexafluoroisopropylidene. However, slower decomposition kinetics were seen for polymers **4h** and **4e** with hexafluoroisopropylidene and sulfonyl groups, respectively, as they showed a much greater residue (ca. 50%) on heating to 800 °C, whereas polymers with a high density of aliphatic substituents such as **4c**, **4d**, and **4f** showed the smallest residues (25–30%) at high temperatures.

All the soluble polyamides could be processed to flexible, tough films by casting from solutions in DMA. The tensile properties of the films are given in Table III. Tensile strengths of 83–111 MPa and tensile moduli of 2.0–2.2 GPa qualify them as strong and rigid materials that compare fairly well with conventional aromatic amorphous polyamides.

Water absorption values were measured for all the polymers. They presented very low absorption values, ranging from 0.9 to 1.6% (Table IV), that could be attributed to the presence of hydrophobic groups in their structure. The small differences found between the polymers did not permit a clear relationship to be established between the chemical structure and the absorption values, except for polymer **4f**, which showed the lowest value because of the highest crystallinity.

Table IV. Water Absorption Data of the Polyamides

Polymer	Water Absorption (% w/w)	Moles of H_2O per Equivalent of Amide
4a	1.44	0.52
4b	1.26	0.47
4c	1.62	0.63
4d	1.03	0.42
4e	1.5	0.76
4f	0.86	0.4
4g	1.16	0.55
4h	1.34	0.56

CONCLUSIONS

The results reported here confirm that aromatic dicarboxylic acids, such as XPTBB, containing phenylene oxide units and pendent *tert*-butyl groups are suitable reactants for polycondensation with diamines by the phosphorylation method in solution at high temperature to yield polyamides in high yields and high molecular weights. Polymers of this class are essentially amorphous and generally show an outstanding solubility in common organic solvents compared with conventional aromatic polyamides. Additionally, the enhancement of solubility does not impair the thermal properties of these polymers that exhibit high T_g's (250–290 °C) and display onset T_d's of 405–465 °C as revealed by TGA. Despite their amorphous character, these polymers show excellent mechanical properties, with tensile strengths and moduli that compare well with those of commercial engineering thermoplastics.

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