

# Synthesis and Characterization of New Soluble Aromatic Polyamides Based on 4-(1-Adamantyl)-1,3-bis(4-aminophenoxy)benzene

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**ABSTRACT:** A set of new aromatic polyamides were synthesized by the direct phosphorylation condensation of 4-(1-adamantyl)-1,3-bis-(4-aminophenoxy)benzene with various diacids. The polymers were produced with high yields and moderate to high inherent viscosities (0.43–1.03 dL/g), and the weight-average molecular weights and number-average molecular weights, determined by gel permeation chromatography, were in the range of 37,000–93,000 and 12,000–59,000, respectively. The polyamides were essentially amorphous and soluble in a variety of solvents such as *N,N*-dimethylacetamide (DMAc), cyclohexanone, and tetrahydrofuran. They showed glass-transition temperatures in the range of 240–300 °C (differential scanning calorimetry) and 10% weight-loss temperatures over 450 °C, as revealed by thermogravimetric analysis in nitrogen. All the polymers gave strong films via casting from DMAc solutions, and these films exhibited good mechanical properties, with tensile strengths in the range of 77–92 MPa and tensile moduli between 1.5 and 2.5 GPa. © 2000 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 38: 1014–1023, 2000

**Keywords:** aromatic polyamides; new monomer; solubility; modeling

## INTRODUCTION

Aromatic polyamides are an important class of engineering polymers that have excellent thermo-oxidative stability, mechanical strength, and electrical and chemical resistance, but in turn they possess limited solubility in organic solvents, which makes them generally difficult or too expensive to process, thus restricting their applications.<sup>1–3</sup>

During recent years, many studies have focused on designing the chemical structure of the rigid aromatic backbone to obtain aromatic polyamides that are processable by conventional techniques.<sup>4</sup> In this respect, the introduction of ether linkages is known to enhance processability of

aromatic polymers without a significant reduction in thermal stability.<sup>5–8</sup> Furthermore, the incorporation of bulky pendent groups can provide a significant increase in both the glass-transition temperature ( $T_g$ ) and the solubility of aromatic polymers.<sup>9–11</sup> Thus, the  $T_g$  is raised by the restriction of molecular mobility brought about by the incorporation of bulky groups, whereas solubility (processability) is improved by the decreasing of packing density and crystallinity. Combining these structural modifications minimizes the trade-off between the processability and properties of wholly aromatic polyamides.

Very recently, aromatic condensation polymers have been reported containing adamantane groups into the backbone. Thus, polyamides,<sup>12</sup> polyimides,<sup>13,14</sup> polycarbonates,<sup>15</sup> and polysulfones<sup>15</sup> have been synthesized from monomers based on the adamantane ring, and, in every case, the incorporation of this bulky moiety has

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brought about an increase of the  $T_g$ . In addition, Mathias et al.<sup>16,17</sup> reported on poly(arylether ketone)s and aromatic polyesters from monomers containing adamantane groups, with the result of substantially increased  $T_g$ 's and enhanced solubility in organic solvents. Just as with other bulky pendent groups, adamantane tends to inhibit packing of chains, which ultimately decreases crystallinity and increases solubility.

In this work, we report the synthesis and characterization of new polyamides with adamantane pendent groups by the polycondensation of 4-(1-adamantyl)-1,3-bis(aminophenoxy)benzene with various aromatic dicarboxylic acids. The set of polyamides was fully characterized, and the effect of the adamantane side groups was evaluated by the determination of the most interesting properties of the polymers, such as solubility in organic solvents, thermal transitions and thermal resistance, and mechanical properties. Emphasis was also placed on explaining, by theoretical means, the influence of the adamantyl rest on molecular mobility and free volume.

## EXPERIMENTAL

### Materials

Resorcinol (Acros; 99%), 1-bromoadamantane (Acros; 99%), and *p*-chloronitrobenzene (Acros), as well as the other reagents and solvents, were used as received unless further purification is reported. Reagent-grade lithium chloride was dried at 300 °C before use. *N*-methyl-2-pyrrolidone (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-(4-carboxyphenoxy)phenyl] hexafluoropropane and 1,4-bis-(4-carboxyphenoxy)-2,5-ditertbutylbenzene were synthesized by methods previously reported.<sup>18,19</sup>

### Monomer Synthesis

#### 4-(1-Adamantyl)-1,3-benzenediol

4-(1-adamantyl)-1,3-benzenediol was synthesized by an improved version of a method previously reported.<sup>20</sup> In a typical reaction, 1-bromoadamantane (26.95 g, 0.125 mol) and 1,3-benzenediol (20.65 g, 0.184 mol) were made to react in benzene (180 mL) at 90 °C for 15 h. The reaction

mixture was cooled to room temperature, and the adamantyl-substituted resorcinol crystallized from the solution. The solid was filtered off and washed several times with hexane and hot water to remove unreacted reagents, and the resulting adamantyl compound was recrystallized from toluene to give 23.7 g (77%) of white crystals.

mp: 253–254 °C (unc.; lit.<sup>20</sup> 249–250 °C). IR (KBr,  $\text{cm}^{-1}$ ): 3488, 3991 (O—H stretch), 2905, 2848 (C—H stretch). <sup>1</sup>H NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 1.69 (s), 1.99 (s), 6.11 (dd), 6.22 (d), 6.79 (d), 8.91 (s), 9.00 (s). <sup>13</sup>C NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 28.50, 35.43, 36.74, 40.40, 103.65, 105.49, 126.48, 126.51, 155.86, 156.75.

#### 4-(1-Adamantyl)-1,3-bis(4-nitrophenoxy)benzene (ANPB)

4-(1-adamantyl)-1,3-benzenediol (14.70 g, 0.06 mol) and 4-chloronitrobenzene (18.93 g, 0.12 mol) were dissolved in 120 mL of DMF, and anhydrous  $\text{K}_2\text{CO}_3$  (18.25 g, 0.13 mol) was added to this solution, which was then heated to 160 °C and stirred overnight (10 h) under nitrogen. After cooling to room temperature, the product was precipitated in a mixture (1 : 1) of ethanol and water, and the resulting dinitro compound was recrystallized from acetonitrile to give 28.04 g (96%) of yellow needles.

mp: 190–191 °C (unc.). IR (KBr,  $\text{cm}^{-1}$ ): 3117, 3080 (aromatic C—C—H stretching), 2900, 2847 (aliphatic C—H stretching), 1579, 1345 (symmetric and asymmetric  $\text{NO}_2$  stretching), 1257, 1226 (C—O—C stretching). <sup>1</sup>H NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.73 (q), 2.05 (s), 6.61 (d), 6.91 (dd), 7.00 (m), 7.04 (m), 7.44 (d), 8.19 (m), 8.23 (m). <sup>13</sup>C NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 28.76, 36.67, 36.78, 41.17, 113.65, 116.74, 117.12, 117.60, 125.92, 126.14, 129.30, 139.23, 142.84, 142.87, 153.47, 155.06, 162.67, 162.77.

#### 4-(1-Adamantyl)-1,3-bis(4-aminophenoxy)benzene (AAPB)

The dinitro compound ANPB (14.0 g, 0.03 mol) was heated to reflux in absolute ethanol (500 mL) in the presence of a 10% Pd/C catalyst (0.2 g). Hydrazine monohydrate (100 mL) was added dropwise to this mixture over a period of 1 h at 85 °C, and the reaction was continued at reflux temperature for 24 h. After cooling, the precipitated crystals were isolated by filtration and recrystallized from ethanol to give 9.8 g (77%) of white needles.

mp: 176–177 °C. IR (KBr,  $\text{cm}^{-1}$ ): 3406, 3197 (N—H stretching), 3038, 3013 (aromatic C=C—H

stretching), 2912, 2848 (aliphatic C—H stretching), 1249, 1210 (C—O—C stretching).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 1.74 (s), 2.05 (s), 2.13 (d), 6.42 (d), 6.47 (dd), 6.61 (m), 6.65 (m), 6.80 (m), 6.82 (m), 7.15 (d).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ,  $\delta$ , ppm): 28.76, 36.67, 36.78, 41.17, 113.65, 116.74, 117.12, 117.60, 125.92, 126.14, 129.30, 139.23, 142.84, 142.87, 153.47, 155.06, 162.67, 162.77. ELEM. ANAL. Calcd. for  $\text{C}_{28}\text{H}_{30}\text{N}_2\text{O}_2$  (426.55): C, 78.84%; H, 7.09%; N, 6.57%. Found: C, 78.61%; H, 7.13%; N, 6.44%.

### Polymers Synthesis

The phosphorylation polycondensation method was used to obtain the polymers presented in this article. An illustrative example of this method is the following: 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 until all solids had dissolved. 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, with the reaction proceeding 3 h more. The resulting polymer solution was precipitated in 500 mL of ethanol and washed several times with hot water and ethanol. All of the polymers were dried overnight under vacuum at 100 °C. Yields over 90% were obtained.

### Measurements

Melting points were measured in capillaries on a Büchi 535 apparatus. Elemental analyses were made in a Perkin–Elmer 2400 instrument. Fourier transform infrared (FTIR) spectra were obtained on a Nicolet 520 FTIR spectrometer on KBr cells. Solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian-Unity 500 spectrometer at 499.88- and 125.70-MHz frequencies with standard acquisition parameters and with a mixture of deuterated dimethyl sulfoxide/chloroform as a solvent and tetramethylsilane as an internal reference. Differential scanning calorimetry (DSC) analyses were performed on a Perkin–Elmer DSC-7 analyzer at a heating rate of 20 °C/min under nitrogen. Thermogravimetric analyses (TGAs) were performed in  $\text{N}_2$  with a Perkin–Elmer TGA-7 analyzer at 10 °C/min on 2–3-mg samples. The inherent viscosities were measured on filtered 0.5 g/dL DMAc solutions at  $25 \pm 0.1$  °C in an automated Ubbelohde viscometer. For the measurement of the mechanical properties, strips

5 mm wide, 80 mm long, and 40–60  $\mu\text{m}$  thick were cut from polymer films and tested on an MTS Synergie 200 Universal Testing Machine. An extension rate of 1 mm/min was applied with a gauge length of 10 mm.

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

### Theoretical Calculations and Molecular Simulation Study

The simulation of the amorphous structures of the polymers was done with the program Cerius2, version 3.8,<sup>21</sup> running on a Silicon Graphics Indigo 2 R-10000 workstation. A combination of molecular mechanics and molecular dynamics was used to obtain low-energy structures.

The building of the polymer structure was generated as follows:

1. A hydrogen end-capped monomer was built. Thereafter, the end-capped hydrogens were removed and substituted by ghost head and tail atoms.
2. An isolated chain of polyamide, with a polymerization degree of 10, was created by the connection of monomers via the polymer builder incorporated into the Cerius2 package.
3. Ten bulk amorphous polymer chains were built from the initial polymer chain via the amorphous builder incorporated into Cerius2, imposing an initial density of 1.3  $\text{g}/\text{cm}^3$ . The amorphous polymer chains were generated with a random method without any rotational restriction, except for the amide groups, which were forced to be trans.
4. Each bulk polymer chain was minimized by use of the following parameters: The PCFF 300, force-field version 2.21,<sup>22</sup> was used. An external stress of 0.0001 GPa (1 atm) was applied to the cell. Convergence criteria of less than 0.001 (kcal/mol)/Å for the root-mean-square residual (RMS) force and less than 0.001 GPa for the stress of the cell were used. The Ewald<sup>23,24</sup> summation was

used for the determination of van der Waals and Coulomb energy terms by use of a non-bond list with a 2.0Å buffer in both cases. A dielectric constant of 3.5 was employed for the Coulomb terms.

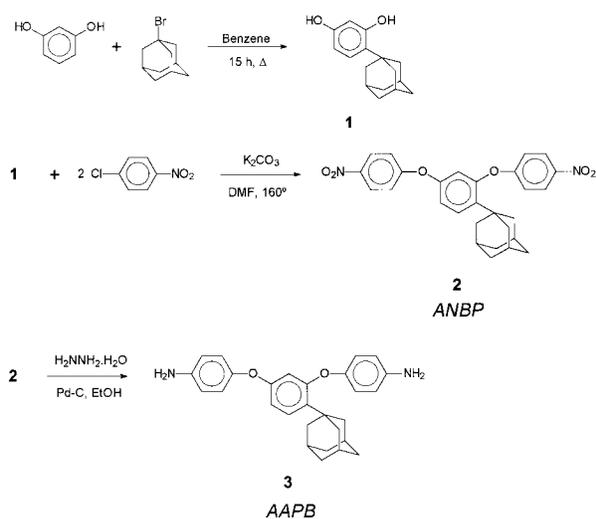
- The aforementioned molecular mechanics minimization is likely to trap the simulated systems in metastable local high-energy minima. To avoid this situation, molecular dynamic simulations were carried out to provide thermal energy to the system to cross energy barriers between local minima. The Verlet algorithm was used to integrate Newton's law of motion with a timestep of 1 fs. The conditions were as follows: a canonical NPT at 1 atm with five annealing cycles starting and ending at 300 K, a midcycle temperature of 1000 K, a temperature increment of 25 K, and 50 steps by increment. The structures obtained after each cycle were minimized again as described in Step 4.

Calculations 4 and 5 were repeated several times until a convergence of energy and density was reached.

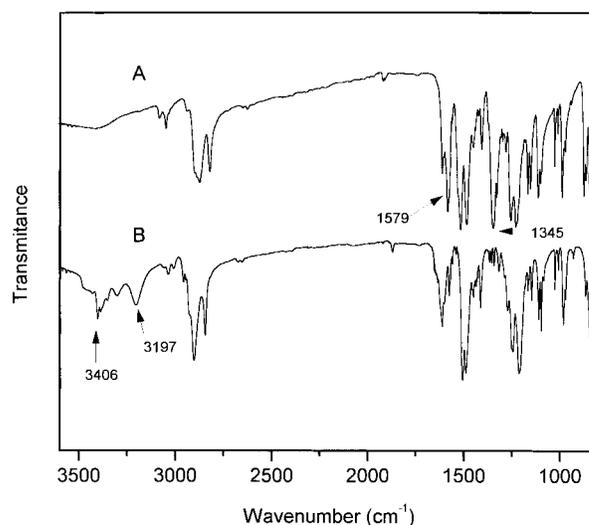
## RESULTS AND DISCUSSION

### Monomer and Polymer Synthesis

The adamantane diamine AAPB was prepared from *p*-chloronitrobenzene and 4-(1-adamantyl)-1,3-benzenediol **1** according to a two-step syn-

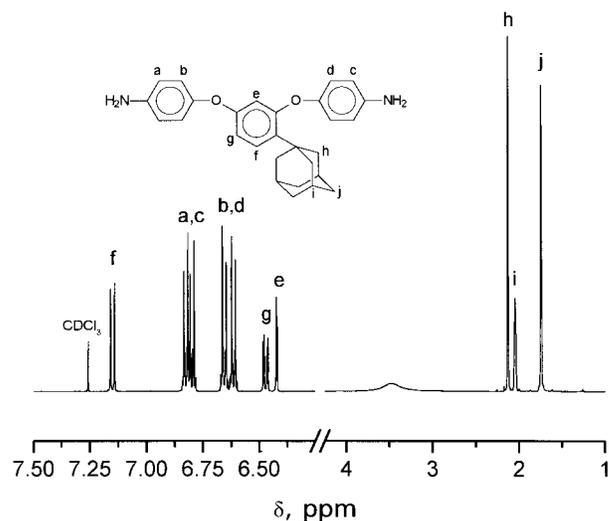


**Scheme 1.** Synthesis of AAPB.

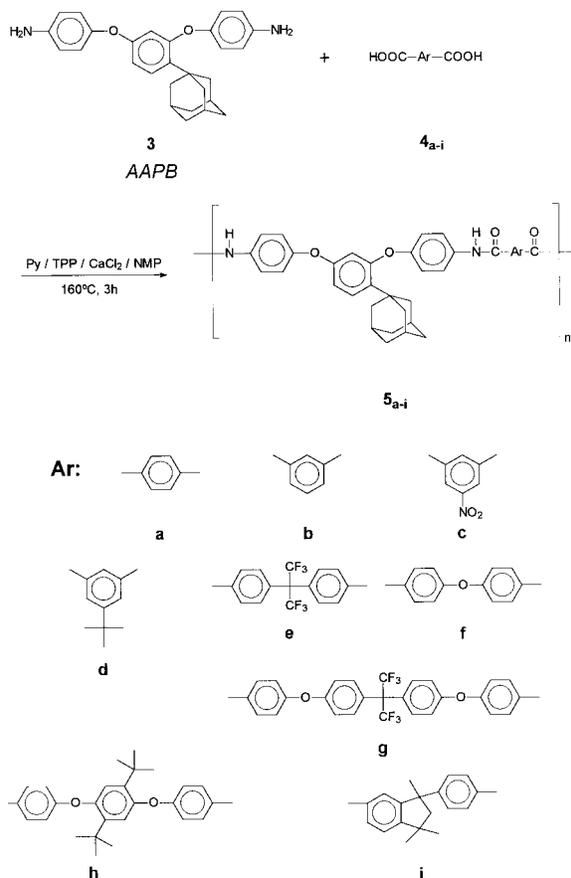


**Figure 1.** IR spectra of (A) the nitro precursor and (B) the diamine AAPB.

thetic route outlined in Scheme 1. In the first step, the adamantane-resorcinol **1** and *p*-chloronitrobenzene were condensed in the presence of potassium carbonate in DMF, giving rise to the bis-(4-nitrophenoxy)compound **2**. This intermediate compound was then catalytically reduced to the adamantane-diether-diamine with hydrazine as the reducing agent and palladium as the catalyst. The monomer was characterized by elemental analysis and spectroscopic means and was purified by recrystallization in alcohol until the purity was enough for the preparation of high molecular weight condensation polymers. Figure



**Figure 2.**  $^1\text{H}$  NMR spectrum of the diamine AAPB.



**Scheme 2.** Synthesis of the polyamides from AAPB and the diacids.

1 shows the IR spectra of the dinitro intermediate and the diamine, and Figure 2 shows the  $^1\text{H}$  spectrum of the diamine, all of them being consistent with the proposed structures.

The direct amidation reaction promoted by the pyridine–TPP–salt system was used to obtain the polyamides from nine aromatic diacids and the diamine AAPB (see Scheme 2). Because a major objective of this work was the attainment of soluble materials, diacid monomers were chosen with a very diversified structure, including short wholly aromatic diacids and enlarged diacids, with flexible connecting linkages and side substituents like methyl and *t*-butyl. The use of a rather wide number of structures should allow the evaluation of their influence on solubility and other general properties. Monomer **4h** is a new diacid, never used as a condensation monomer before.

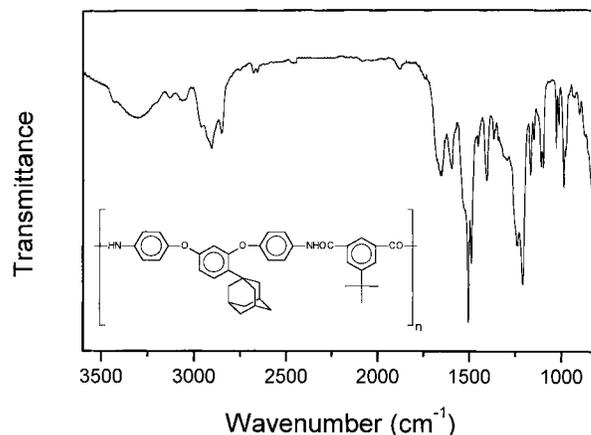
The yields were high in all cases, and the viscosities were high enough (0.42–1 dL/g) to assure that medium to high molecular weights had been

**Table I.** Inherent Viscosities and GPC Data of the Polyamides

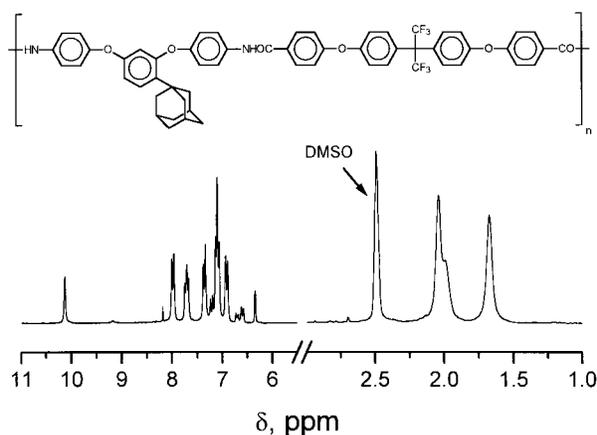
Polymer Code	$\eta_{\text{inh}}$ (dL/g)	$M_n$	$M_w$	$M_w/M_n$
<b>5a</b>	0.75	38,000	59,500	1.6
<b>5b</b>	0.43	34,500	51,000	1.5
<b>5c</b>	0.61	12,000	70,000	5.8
<b>5d</b>	0.44	33,500	54,000	1.6
<b>5e</b>	0.84	56,500	82,000	1.4
<b>5f</b>	0.86	45,000	66,000	1.5
<b>5g</b>	1.03	59,000	93,000	1.6
<b>5h</b>	0.51	23,500	37,000	1.6
<b>5i</b>	0.42	27,000	42,000	1.5

obtained (see Table I). Figure 3 shows the IR spectrum of polymer **5d**, where amide absorption bands can be recognized at 3300 (N–H stretching), 1660 (C=O stretching), 1520 (amide band II, combination of N–H bending and C–N stretching), and 1220  $\text{cm}^{-1}$  (C–O–C aromatic). The absorption bands of the aliphatic C–H stretching due to the cycloaliphatic adamantane ring appeared as a complex wide band at 2800–2950  $\text{cm}^{-1}$ . Figure 4 shows the  $^1\text{H}$  NMR spectrum of the polymers **5d** that was run under the conditions necessary to accomplish quantitative determinations of the peaks areas. All the peaks could be readily assigned to the protons of the repeating unit, and the absence of nonassignable peaks indicated that a sufficient degree of polymerization was achieved in the synthesis step.

To get information about the real molecular weights achieved in the synthesis of these polyamides, measurements of the molecular size were



**Figure 3.** IR spectrum of the polyamide **5d**.



**Figure 4.**  $^1\text{H}$  NMR spectrum of the polyamide **5g**.

performed by size exclusion chromatography. Fractionated poly(*m*-phenyleneisophthalamide) standards were used as a reference because it was previously observed that they provide more reliable values in the determination of molecular weights of aromatic polyamides than those attainable by the use of the more available polystyrene standards.<sup>8</sup> Number-average molecular weights ( $M_n$ ) between 12,000 and 59,000 and weight-average molecular weights ( $M_w$ ) in the range of 37,000–93,000 were measured, the values showing a consistent relationship between inherent viscosity and molecular weight, with the highest values of the  $M_n$  and  $M_w$  reasonably corresponding to the highest values of viscosity. Polymer **5c**, derived from AAPB and 5-nitroisophthalic acid, showed abnormal behavior, having an unexpectedly low  $M_n$ , and a polydispersity index (5.7) almost four times higher than the other polymers (ca. 1.5). The explanation could be a strong association of the polymer, either with the solvent or with other polymer chains, due to the highly polar nature of the nitro groups. However, only a slight increase in viscosity (from 0.61 to 0.70 dL/g) was observed on measuring this polymer in DMAc with 3% LiCl to try to avoid the possible associations. Thus, the wide distribution observed for

this polymer must be related to the nature of the nitro-containing monomer and its behavior as a condensation monomer against the diamine AAPB.

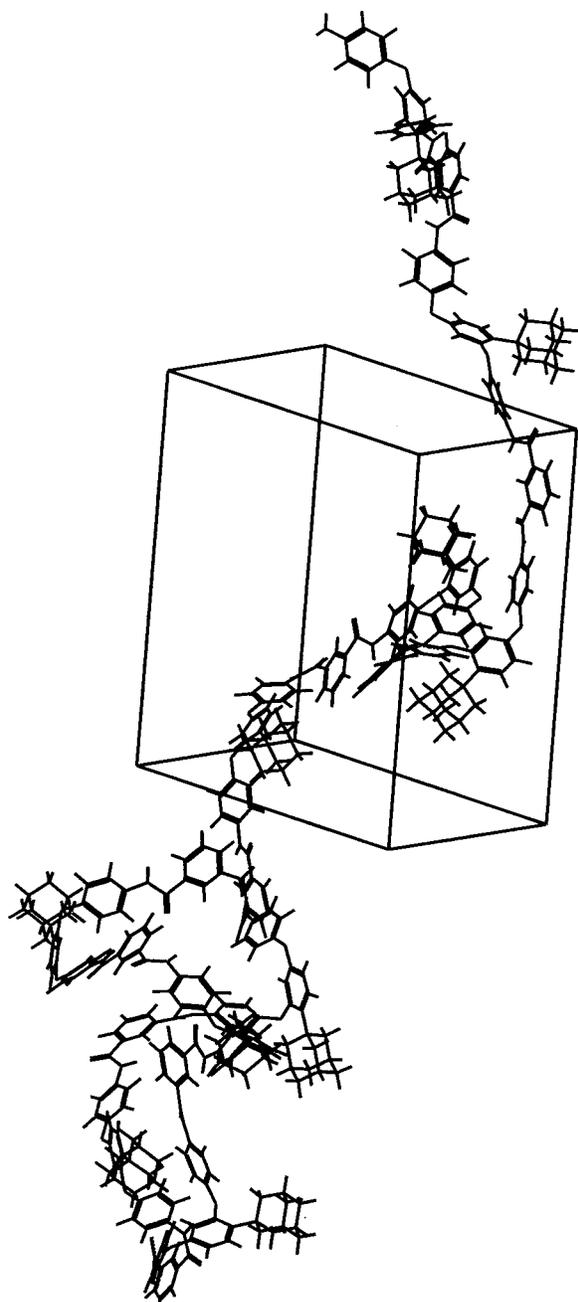
### Molecular Modeling

To exemplify the influence of the bulky substituents on the behavior of the polymers, a molecular modeling study was made with computational chemistry methods. For this study, the polymer **5b** and a theoretical structure without pendent adamantane groups were chosen as models. To do that, 10 amorphous chains of each polymer, with 10 repeat units, were created. To avoid the influence of the amino hydrogen chosen as head atom on the configuration of the final chains, all polymer chains were generated with a random method without any rotational restriction, except for the amide groups, which were forced to be trans. Molecular mechanics and molecular dynamics techniques were used to relax the different structures, from which the density was determined in each case. The average density calculated for each polymer is shown in Table II, where it can be seen that the value is significantly lower (about 10%) for the polymer with adamantane pendent groups.

The average volume of the cell (the volume of a box containing the polymer chain at the equilibrium; see Fig. 5) and the average free volume also were calculated and are shown in the same table. As expected, the calculated volume of the cell was higher for the polymer with adamantane because of the much higher number of atoms in this polymer, and the free volume followed the same tendency. From these data, the ratio between free volume and total volume, which gives information about the fractional free volume (FFV) for each polymer, was calculated and is also shown in Table II. As can be seen, the FFV was about 10% higher for the adamantane polymer, agreeing with the density results and indicating that the presence of adamantane brought about chain sep-

**Table II.** Calculated Parameters (Average of 10 Different Amorphous Chains) for the Polyamide **5b** and the Same Polymer Without Pendent Adamantane Groups (**5b-npg**)

Polymer	Density (g/mL)	$V_{\text{TOTAL}}$ ( $\text{\AA}^3/\text{unit cell}$ )	$V_{\text{FREE}}$ ( $\text{\AA}^3/\text{unit cell}$ )	$V_{\text{FREE}}/V_{\text{TOTAL}}$
<b>5b</b>	1.239	7464	2194	0.294
<b>5b-npg</b>	1.327	5291	1434	0.271



**Figure 5.** Simulation model of the amorphous polymer **5b**. The box corresponds to the volume occupied by the polymer at the equilibrium.

aration, thus decreasing the intrachain and interchain interactions between amide groups and increasing the free volume. Therefore, the presence of adamantane should have an important effect on polymer properties, such as density, solubility and gas diffusivity, that will be substantially different for species with and without pendent groups.

## Polymer Properties

The lowering of intermolecular association forces by the presence of bulky adamantane groups was reflected in terms of enhanced solubility. Table III shows the behavior of the polymers versus some organic solvents. As can be seen, the combination of the new diamine with different diacids led to aromatic polyamides that dissolved in common organic solvents, such as cyclohexanone or tetrahydrofuran, even with fully aromatic diacids such as isophthalic or terephthalic acid (polymers **5a** and **5b**). This result is very interesting because aromatic polyamides, including most of the nonrigid aromatic polyamides reported so far, are generally soluble only in very polar amide solvents. The solubility of these polymers is comparable to that reported for polyamides containing hexafluoroisopropylidene units in the main chain that are synthesized from very expensive fluorinated monomers. In agreement with this, polymers **5e** and **5g** showed the best solubility, but polymer **5h**, with side *t*-butyl substituents on the diacid unit, showed a similar solubility as well. The diacid 1,4-bis(4-carboxyphenoxy)-2,5-di-*t*-butylbenzene is a reagent never before used as a condensation monomer.

As for the thermal properties, they were investigated by DSC and TGA. The results are collected in Table IV, along with data on mechanical properties. Two runs were needed to obtain clean DSC traces because the water absorbed by the samples generally gave rise to a wide endothermal distortion of the curve in the range of 80–150 °C. Heating up to 200 °C, cooling, and heating again produced neat thermograms in a second run from 50 to 400 °C. Within this interval, only the inflection attributable to the  $T_g$  could be observed in every case. Neither crystallization exotherms nor melting endotherms were detected, which was interpreted as an indication of the amorphous nature of these polymers.

From the values given in Table IV, it could be stated that all the polymers had  $T_g$ 's from about 240 to 300 °C. Apparently, the combination of a bulky pendent group, such as adamantane, with the introduction of oxydiphenylene units in the main chain did not cause any substantial lowering of the  $T_g$  related to fully aromatic, nonrigid polyamides such as polyisophthalamides. In fact, polymer **5b**, from isophthalic acid and AAPB, showed a  $T_g$  of 272 °C, whereas the  $T_g$  of poly(*m*-phenyleneisophthalamide) is about 275 °C; the same is true for the rest of the diacids used. The

**Table III.** Solubility of the Polyamides

Polymer Code	Solvents <sup>a</sup>					
	DMF	DMAc	CH	THF	MEEK	DX
<b>5a</b>	+	+	+-	+-	-	-
<b>5b</b>	+	+	+	+	-	-
<b>5c</b>	+	+	+	+	-	-
<b>5d</b>	+	+	+	+	-	-
<b>5e</b>	+	+	+	+	+-	+
<b>5f</b>	+	+	+	+	-	-
<b>5g</b>	+	+	+	+	+-	+
<b>5h</b>	+	+	+	+	-	+
<b>5i</b>	+	+	+	+	-	-

<sup>a</sup> DMF = *N,N*-dimethylformamide; DMAc = *N,N*-dimethylacetamide; CH = cyclohexanone; THF = tetrahydrofuran; MEEK = methyl-ethyl-ketone; DX = 1,4-dioxane; + = soluble at room temperature; +- = swollen; - = insoluble even on heating.

lowest  $T_g$  corresponded to polymer **5g**, with an hexafluoroisopropylidene linkage and four ether linkages in the repeating unit, and the highest corresponded to polymer **5i**, with a bulky, rigid rest of phenylindane.

The thermal resistance, as measured by TGA, was influenced by the presence of the adamantane side group and by the nature of the diacid moiety as well. Data reported in Table IV confirmed that these polymers had a good thermal resistance, with decomposition temperatures ( $T_d$ ) in the range of 460–490 °C in the conditions of the TGA, the only exception being polymer **5c**, which contained a side nitro group in the repeating unit. For the latter, a  $T_d$  was found of only 345 °C, as is illustrated in Figure 6, where some TGA

curves are shown. Unlike the other polymers of this study, polymer **5c** showed a two-step decomposition path, the first one corresponding to a weight loss that could quantitatively be assigned to the loss of one nitro group per repeating unit (ca. 8%) in the form of nitroic acid; this has also been reported for other nitro-containing aromatic polyamides and polyimides.<sup>25</sup> However, the weight residue of polymer **5c** at 800 °C was the highest for any polymer of this series, which could indicate crosslinking just after the splitting off of the nitro groups. It must be taken into consideration that for each nitro group that separates in the form of nitroic acid, a hydrogen atom should be abstracted from the aromatic matrix of the polymers, with the formation of an active radical,

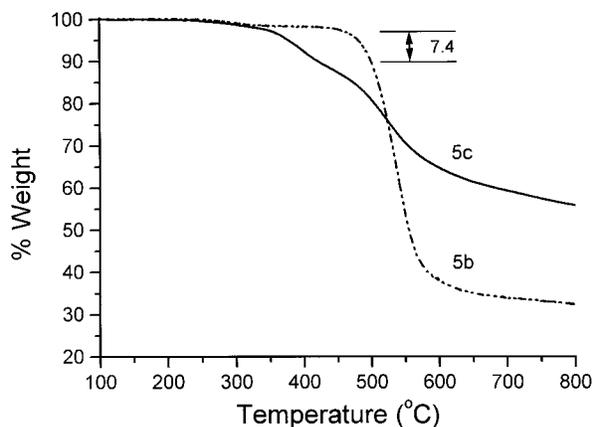
**Table IV.** Mechanical and Thermal Properties of the Polyamides Based on 1-(4-Adamantyl)-1,3-bis(4-aminophenoxy)benzene

Polymer Code	Tensile Strength (MPa)	Young's Moduli (GPa)	$T_g$ (°C)	$T_d$ (°C) <sup>a</sup>	$T_{d10}$ (°C) <sup>b</sup>	$Y_{800}$ (%) <sup>c</sup>
<b>5a</b>	78	2.18	268	490	510	35
<b>5b</b>	80	2.08	272	480	500	32
<b>5c</b>	83	2.51	289	345	440	54
<b>5d</b>	84	2.32	262	475	495	28
<b>5e</b>	85	1.62	290	490	515	40
<b>5f</b>	83	1.55	272	490	510	37
<b>5g</b>	85	1.75	239	480	520	53
<b>5h</b>	93	2.04	260	465	490	39
<b>5i</b>	79	1.97	300	460	500	49

<sup>a</sup> Temperature of the first onset in the TGA curve.

<sup>b</sup> 10% weight-loss temperature measured by TGA at a heating rate of 10°C/min.

<sup>c</sup> Residual weight percentage at 800°C in nitrogen by TGA.



**Figure 6.** TGA traces of the polymers **5b** and **5c**.

that can provide crosslinking to a dense, thermally stable network.

Mechanical properties were investigated on films obtained by the evaporation of cast solutions in suitable solvents, mainly tetrahydrofuran and DMAc. The films were transparent, creasable, and showed good mechanical strength, with an ultimate tensile resistance of about 80–90 MPa and tensile moduli of 1.5–2.5 GPa, which compare fairly well to other aromatic amorphous polyamides previously reported.<sup>26,27</sup> The presence of flexible ether linkages in the main chain and bulky side substituents did not much impair the strength of the films, which indicates a correct combination of structural elements for improved solubility without the loss of the other general properties of aromatic polyamides.

## CONCLUSIONS

The synthetic route reported in this article for the preparation of the diamine AAPB is a convenient method that renders the monomer in good yield and high purity. AAPB can work as a suitable condensation monomer, in combination with aromatic diacids of very varied natures, to render high molecular weight polyamides by the direct polyamidation method in a solution of NMP at a high temperature with the pyridine–TPP–salt system.

The presence of the voluminous adamantane rings greatly affected the general properties of these polymers, particularly the solubility in organic solvents, which was substantially improved. Theoretical calculations have proven that some polymer characteristics that directly influ-

ence properties such as density, solubility, and thermal behavior are changed by the presence of pendent adamantane rings. As a confirmation of this, the data of the solubility, thermal resistance, and mechanical strength measured on these polymers are consistent with the statement that the incorporation of adamantane pendent groups does not greatly impair the thermal resistance or the mechanical strength of aromatic polyamides but still greatly improves their solubility.

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## REFERENCES AND NOTES

- Preston, J. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley Interscience: New York, 1988; Vol. 11, p 381.
- Yang, H. H. *Aromatic High-Strength Fibers*; Wiley Interscience: New York, 1989, p 202.
- Vollbracht, L. In *Comprehensive Polymer Science*; Allen, G.; Bevington, J., Eds.; Pergamon: Exeter, England, 1989; Vol. 5, p 375.
- Lin, J.; Sherrington, D. C. *Adv Polym Sci* 1994, 111, 177.
- Abraham, T.; Solosky, E. J.; Evers, R. C. *J Polym Sci Part A: Polym Chem* 1988, 26, 959.
- Ozawa, S. *Polym J* 1987, 19, 119.
- de Abajo, J.; de la Campa, J. G.; Lozano, A. E.; Alvarez, J. C. *Adv Mater* 1995, 7, 148.
- García, J. M.; Alvarez, J. C.; de la Campa, J. G.; de Abajo, J. *Macromol Chem Phys* 1997, 198, 727.
- Kakimoto, M.-A.; Yoneyama, M.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1988, 26, 149.
- Lozano, A. E.; de la Campa, J. G.; de Abajo, J.; Preston, J. *Polymer* 1994, 35, 872.
- Lozano, A. E.; de Abajo, J.; de la Campa, J. G.; Preston, J. *J Polym Sci Part A: Polym Chem* 1995, 33, 1987.
- Chern, Y. T.; Shiue, H. C.; Kao, S. C. *J Polym Sci Part A: Polym Chem* 1998, 36, 785.
- Hsiao, S. H.; Li, C. T. *Macromolecules* 1988, 21, 7213.
- Hsiao, S. H.; Lee, C. T.; Chern, Y. T. *J Polym Sci Part A: Polym Chem* 1999, 37, 1619.
- Pixton, M. R.; Paul, D. R. *Polymer* 1995, 36, 3165.
- Jensen, J. J.; Grimsley, M.; Mathias, L. J. *J Polym Sci Part A: Polym Chem* 1996, 34, 397.
- Lewis, C. M.; Mathias, L. J. *Polym Bull* 1997, 39, 15.
- Avella, N.; Maglio, G.; Palumbo, R.; Russo, F.; Vignola, M. C. *Macromol Chem Rapid Commun* 1993, 14, 545.

19. Espeso, J. F. Ph.D. Dissertation, University of Valladolid, Spain, 1999.
20. Mathias, L. J.; Lewis, C. M.; Wiegel, K. N. *Macromolecules* 1996, 30, 5970.
21. Cerius2; Molecular Simulations Inc.: San Diego, 1998.
22. Sun, H.; Mumby, S. J.; Maple, J. R.; Hagler, A. T. *J Am Chem Soc* 1994, 116, 2978.
23. Ewald, P. P. *Ann D Phys* 1921, 64, 253.
24. Karasawa, N.; Goddard, W. A., III. *J Phys Chem* 1989, 93, 7320.
25. Ayala, D.; Lozano, A. E.; de Abajo, J.; de la Campa, J. G. *J Polym Sci Part A: Polym Chem* 1999, 37, 3377.
26. Meléndez, A.; de la Campa, J. G.; de Abajo, J. *Polymer* 1988, 29, 1142.
27. Yamashita, M.; Kakimoto, M. A.; Imai, Y. *J Polym Sci Part A: Polym Chem* 1993, 31, 1513.