

# Soluble Aromatic Polyimides and Polyamides Based on 4,4'-Diaminotriphenylmethane

D. LIKHATCHEV,\* L. ALEXANDROVA, M. TLENKOPATCHEV, R. VILAR, and R. VERA-GRAZIANO

IIM, UNAM, Apdo. Postal 70-360, Delga, Coyoacan, 04510, Mexico, DF

## SYNOPSIS

Aromatic polyamides and polyimides were synthesized from 4,4'-diaminotriphenylmethane (DA-TPM) for studying their solubility, thermal, and mechanical properties. The polymers were found to be soluble in amide solvents and pyridine, and this could be attributed to the practically free rotation of the polymer chain segments around the bridging group within the DA-TPM and the effect of its pendant phenyl ring. The polyimides and polyamides exhibited well-distinguished glass transition in the range of temperatures, which is typical for flexible-chain polymers. For the polyimides, significant differences in solubility and mechanical properties were observed between the samples prepared by chemical and thermal imidization of poly(amic acids). Thermal imidization brought about remarkably less soluble brittle films. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Aromatic polyamides and polyimides have a large number of applications in modern industry because of their excellent mechanical properties and high thermal and chemical resistance. However, many of these polymers are difficult to process because of their infusibility and insolubility in organic solvents.

In order to overcome this problem, the derivatives of 4,4' diaminodiphenylmethane, such as 4,4'-diaminotetraphenylmethane<sup>1</sup> or 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane,<sup>2</sup> as well as 4,4'-diaminotriphenylamine,<sup>3-5</sup> have been used as monomers in several previous studies for the synthesis of aromatic polyamides and polyimides.

The resulting polymers were seen to be soluble in polar organic solvents and exhibit a combination of interesting properties. However, the synthesis of the monomers is complicated, which limits the possibility of their practical application.

In this study, we have focused on the synthesis and characterization of most common fully aromatic polyamides and polyimides based on 4,4'-diamino-

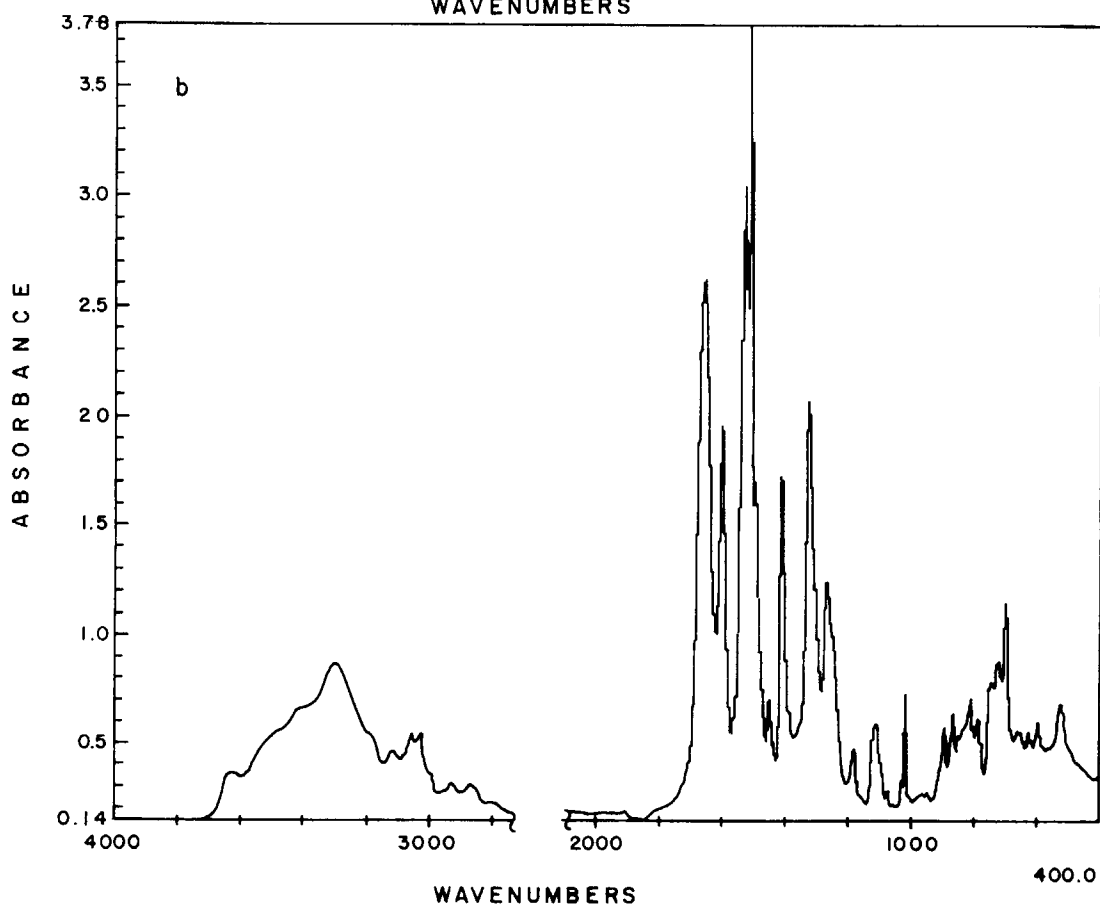
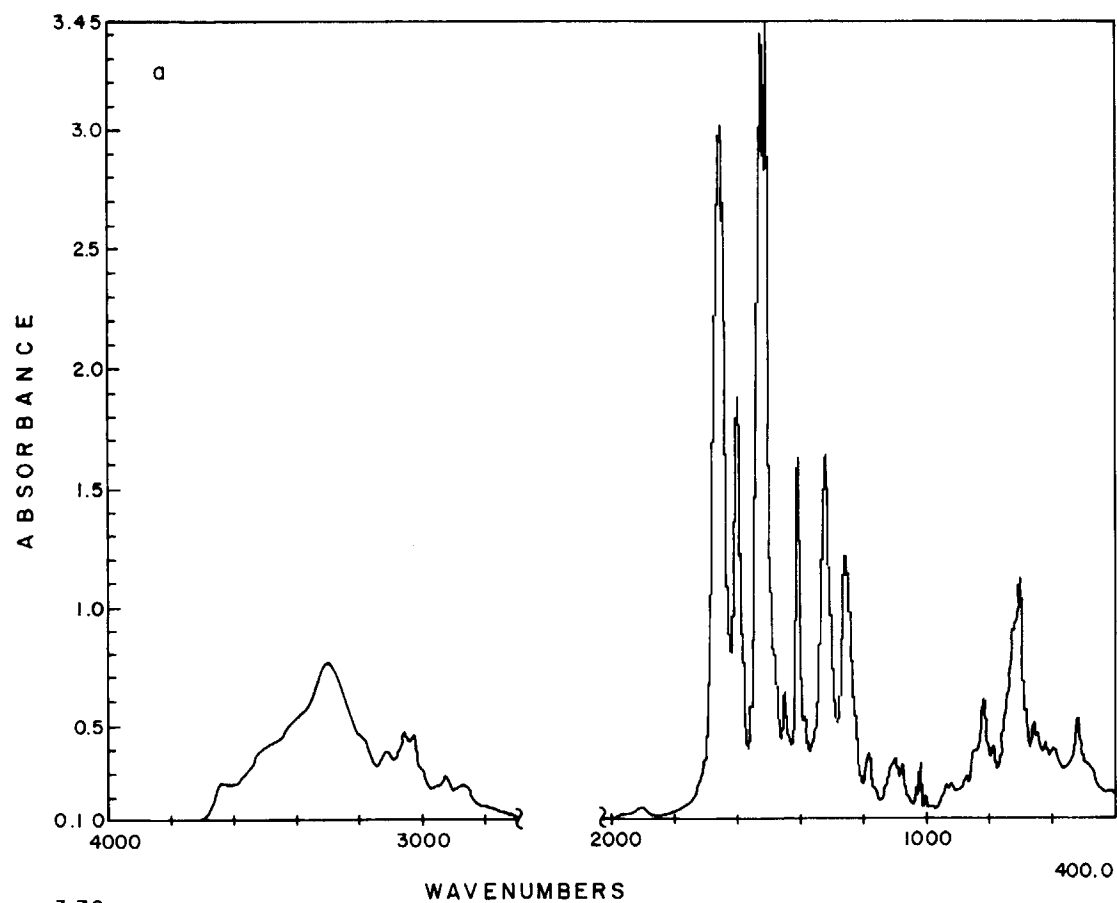
triphenylmethane (DA-TPM). This monomer can be prepared from common starting materials in one stage reaction with very good yield. Despite the fact that its synthesis was reported in detail in 1928,<sup>6</sup> there have been very few articles about its polymerization.<sup>7,8</sup>

## EXPERIMENTAL AND THEORETICAL METHODS

### Materials

All reagents were supplied by Aldrich Chemical Co. Aniline was distilled in vacuum (87°C and 20 mmHg) just before use. Benzaldehyde was used without purification. Iso- and tere-phthaloylchlorides were distilled at 170°C and 57 mmHg, and 165°C and 50 mmHg, respectively. The 1,2,4,5-benzenetetracarboxylic dianhydride [pyromellitic dianhydride (PM)] was sublimated twice at 245°C and 10<sup>-4</sup> mmHg. The 3,3',4,4'-benzophenonetetracarboxylic dianhydride [BZPH (Aldrich Chem. Corp., sublimated, purity 98%)] was used without purification. *N*-Methyl-2-pyrrolidone (NMP) was distilled over barium oxide at 96°C and 20 mmHg and then stored over calcium hydride.

\* To whom correspondence should be addressed.



**Figure 1** IR-spectra of the DA-TPM-based polymers: (a) *i*-PH-TPM; (b) *t*-PH-TPM; (c) BZPH-TPM; (d) PM-TPM.

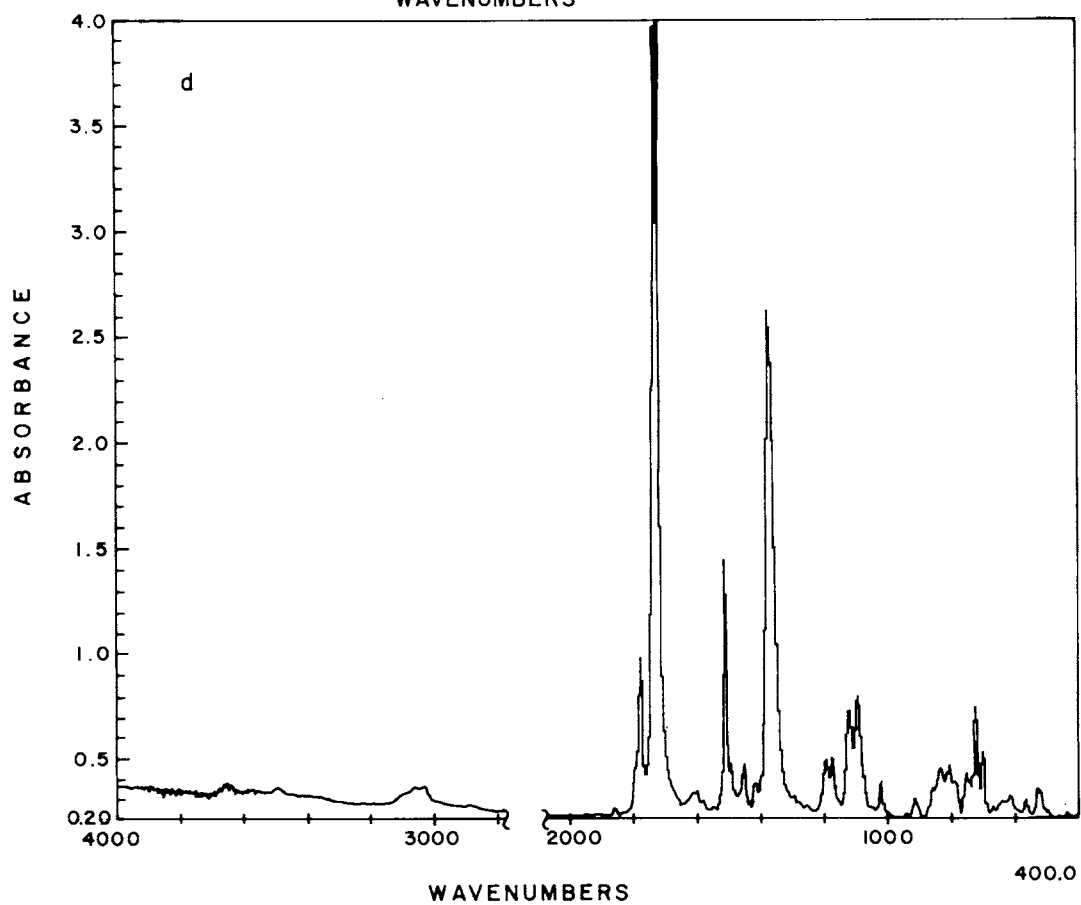
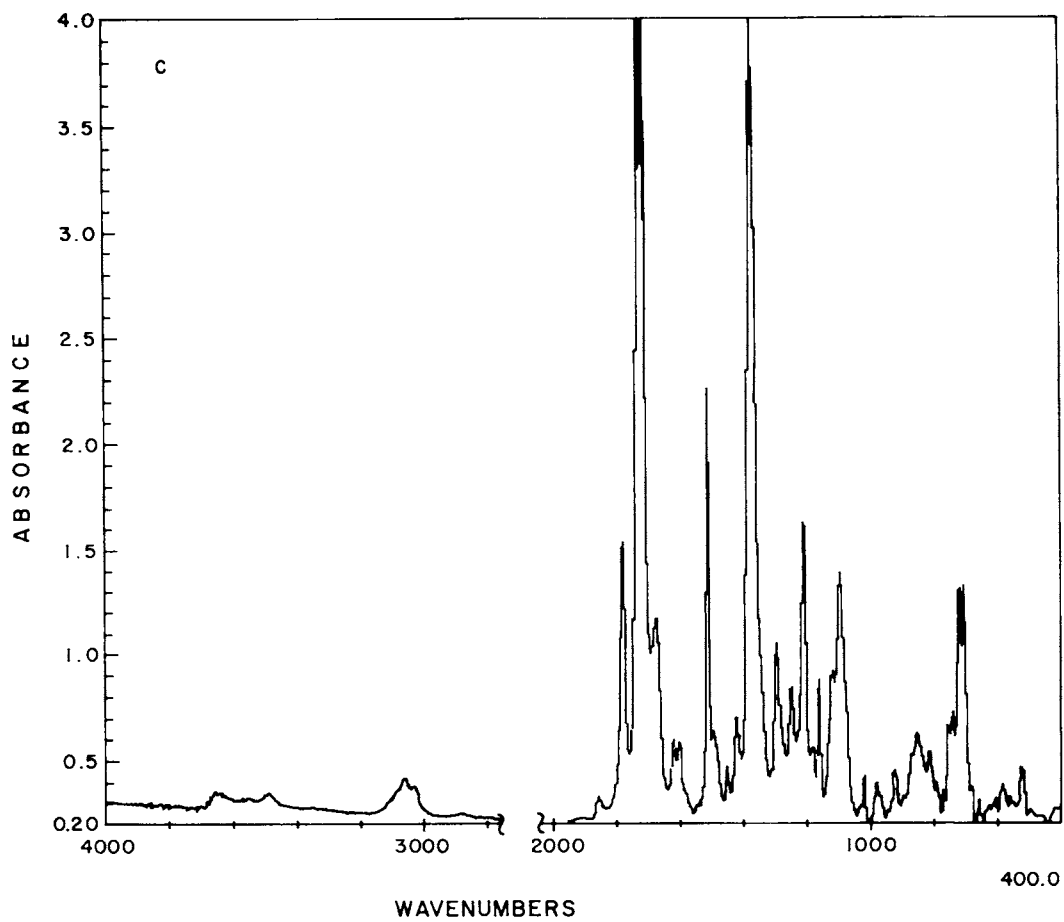


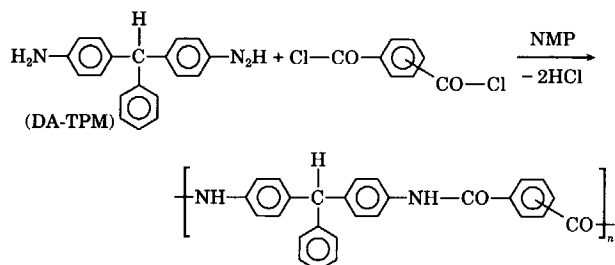
Figure 1 (Continued from the previous page)

### Synthesis of 4,4'-Diaminotriphenylmethane (DA-TPM)

DA-TPM was prepared by the reaction of aniline with benzaldehyde at 140°C under a nitrogen flow. The details of this synthesis are described elsewhere.<sup>6,7</sup> Polymer grade DA-TPM (m.p. 126°C) was produced by recrystallization of the crude product from benzene followed by sublimation at 110°C and 10<sup>-4</sup> mmHg. Its elemental analysis showed C 83.15%, H 6.47%, and N 10.17%, while the calculated values are C 83.17%, H 6.61%, and N 10.21%.

### Synthesis of Polyamides Based on DA-TPM

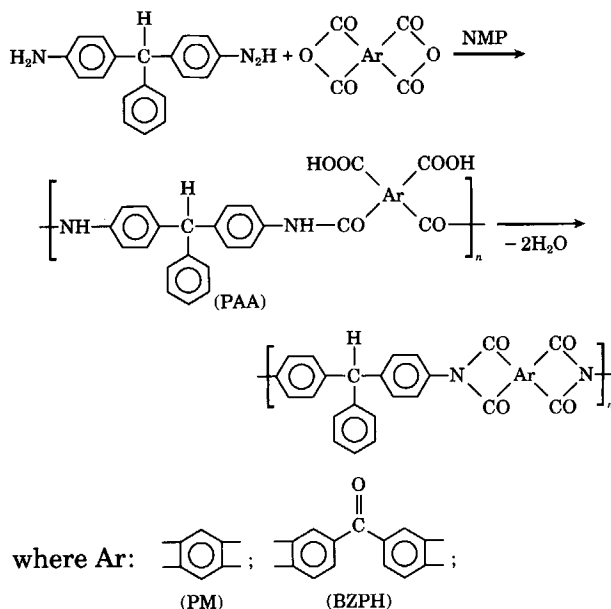
The poly(triphenylmethaneisophthalamide) —*i*-PH-TPM—and poly(triphenylmethaneterephthalamide) —*t*-PH-TPM—were prepared by a polycondensation of DA-TPM with iso- and terephthaloylchlorides, respectively:



DA-TPM was dissolved in dry NMP and cooled to 0°C, then stoichiometric amounts of iso- or terephthaloylchloride were added as solids to the solutions and the mixture was heated to room temperature with continuous stirring. After the monomers were dissolved completely, the reacting solutions, with a concentration of 15% by weight, were stirred for 4–5 h. The resulting polyamides were precipitated into water and purified by reprecipitation from NMP. Then they were dissolved again in NMP and the solutions (20% by weight) were cast onto glass plates and dried at 150°C and 50 mmHg for 10 h to produce thin films of about 25 μm thickness.

### Synthesis of Polyimides Based on DA-TPM

The polyimides were prepared by a two-stage polycondensation of DA-TPM with PM or BZPH:



and the polyimides, PM-TPM and BZPH-TPM, correspondingly.

The prepolymers PAAs were converted to the desired polyimides using thermal imidization at 270°C during 30 min or chemical imidization with acetic anhydride and various tertiary amines. Both synthesis of the PAAs and imidization techniques, as well as the film-casting procedure, have been described in detail elsewhere.<sup>3,9,10</sup> The imidization degree, *i*, was monitored by IR-spectroscopy.<sup>9</sup> For all samples *i* was very close to 100%.

### Measurements

Inherent viscosity ( $\eta_{inh}$ ) was determined in 0.5 g/dL *N,N*-dimethylformamide (DMF) solutions in a Ubbelohde viscometer at 25°C. IR-spectra were recorded using a FT-IR spectrometer NICOLET 510P; the spectra of the four DA-TPM polymers are shown in Figure 1. Wide-angle x-ray diffractometry (WAXD) was performed on a Siemen's D-500 diffractometer, with CuK<sub>α1</sub> radiation of 1.5406 Å. A Du Pont, high-resolution Thermogravimetric Analyzer, TGA 2950, was used for the thermal analysis at a heating rate of 5°C/min. The glass transition temperature,  $T_g$ , was determined by a film-elongation technique<sup>11</sup> using a Du Pont Thermomechanical Analyzer, Model TA 2940 (nitrogen atmosphere and 5°C/min). Mechanical tests of polymer films (about 25 μm thickness) were performed by using an INSTRON Tester, Model 111, at a drawing rate 50 mm/min, on samples of 5 × 20 mm.

## Theoretical Calculations

The structural parameters and rotational barriers of the phenyl rings around the central carbon atom were calculated for the DA-TPM molecule and for its monoamide with terephthalic acid, as a model compound simulating a part of the polyamide chain (see Fig. 2), on a CRAY super-computer and associated software. After full minimization with the Molecular Mechanics Method MMX-89 software,<sup>12</sup> the structures were optimized with the Molecular Orbitals Semiempirical Method AM1<sup>13</sup> using the UniChem software package developed by CRAY Research Inc., using the standard parameters throughout.

## RESULTS AND DISCUSSION

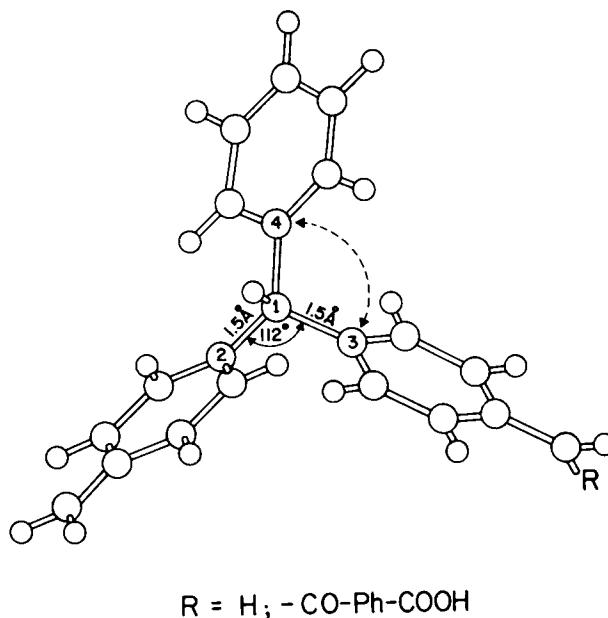
### Internal Rotation

The structural parameters and energetic rotational barriers of the central carbon atom were calculated for both the DA-TPM and its monoamide with terephthalic acid (the model compound) in order to estimate the possible hindrance to internal rotation of fragments of the polymer chain on the bridging group of this monomer.

The obtained data show that  $sp^3$  hybridization of the central carbon atom leads to a pyramidal structure of the DA-TPM molecule. The calculated value of  $C_2C_1C_3$  angle (see Fig. 2) within the DA-TPM is  $112.07^\circ$  and appears to be very similar to that of the 4,4'-diaminodiphenylmethane.<sup>14</sup>

The rotational barrier around the central carbon atom was found to be of 5.89 kcal/mol. This value increases up to 6.39 kcal/mol for the model compound, but is still only slightly higher than the rotational barriers on the bridging groups of the flexible chain aromatic polyamides and polyimides based on conventional diamines such as 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenyl ether, etc.<sup>15</sup>

The obtained theoretical results are in good agreement with experimental data concerning the flexibility of the polyimide chains based on  $N,N'$ -diaminotriphenylamine,<sup>4</sup> whose structure and geometry are very similar to those of the DA-TPM. In ref. 4, the equilibrium flexibility was characterized by the quantity  $\sigma = A^{1/2}/A_f^{1/2}$ , where  $A$  is the experimental Kuhn segment and  $A_f$  is the Kuhn segment calculated for the case of free rotation around the virtual bonds. The values of  $\sigma$ , obtained for the  $N,N'$ -diaminotriphenylamine-based polyimides, were lower than 1.1, indicating the very insignificant hindrance to the free internal rotation of the macro-



**Figure 2** Structure of DA-TPM and the model compound.

chains. Several of those polyimides were found to have good solubility in 1,1,2,2-tetrachloroethane and amide solvents.

### Solubility

The solubility data for aromatic polyimides and polyamides based on DA-TPM are summarized in the Table I. Taking into consideration that the polymers of similar chemical structure based on conventional diamines, such as 4,4'-diaminodiphenylmethane or 4,4'-diaminodiphenyl ether are not soluble in organic solvents, the solubility of DA-TPM based polymers can be attributed to the effect of the pendant phenyl rings in the triphenylmethane moieties. This monomer can be considered as the initial case of the so called "cardoidal diamines,"<sup>16</sup> which are known to result in soluble polyamides and polyimides.

As expected, the DA-TPM-based polyamides were found to be more soluble than the corresponding polyimides. It was possible to prepare solutions of these polymers in NMP or DMF with concentrations up to 30–35% by weight. To a lesser extent, they are soluble in THF and pyridine like it was previously reported for the polytere- and polyisophthalamides based on 4,4'-diaminotriphenylamine.<sup>5</sup>

Acetone has not any apparent effect on size, shape, and transparency of the polyamide films. However, these films become extremely fragile when

**Table I Solubility of DA-TPM-Based Polyamides and Polyimides<sup>a</sup>**

Polymer	Solvent														
	DMF			NMP			Py			THF			C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>		
	3h	1d	7d	3h	1d	7d	3h	1d	7d	3h	1d	7d	3h	1d	7d
<b>Polyamides</b>															
<i>i</i> -PH-TPM	s	s	s	s	s	s	s	s	s	i	ps	s	i	i	i
<i>t</i> -PH-TPM	s	s	s	s	s	s	s	s	s	i	ps	s	i	i	i
<b>Polyimides<sup>b</sup></b>															
BZPH-TPM	s	s	s	s	s	s	s	s	s	i	i	ps	i	ps	ps
PM-TPM	s	s	s	s	s	s	s	s	s	i	i	i	i	ps	ps

<sup>a</sup> Solubility was tested after 3 h (3h), 1 day (1d), and 7 days (7d) at room temperature: s = totally soluble; ps = partially soluble or swollen; i = insoluble. DMF = *N,N*-dimethylformamide; NMP = *N*-methyl-2-pyrrolidone; Py = pyridine; THF = tetrahydrofuran.

<sup>b</sup> Obtained by chemical imidisation.

they come into contact with even a small amount of this solvent. The samples recover the initial flexibility completely after the acetone evaporates. This reversible change in the flexibility of the polyamide films may be a consequence of the antiplasticizing effect of acetone.<sup>17</sup> The latter can result from both the reduction of free volume of the polymer and/or the distortion in the intermolecular hydrogen-bonded network of the polyamides caused by the polar acetone molecules, which diffuse inside the sample.

In the case of the polyimides, remarkable differences in solubility were observed between the samples prepared by chemical and thermal imidization of PAAs. Chemical imidisation yielded polymers (*i* = 100%) readily soluble in NMP and DMF (maximum concentration up to 15–20% by weight) and pyridine (up to 10–15% by weight). These polyimides, BZPH-TPM and PM-TPM, swelled considerably in 1,1,2,2-dichloroethane. It should be noted that no solubility data has been reported for poly(triphenylaminepyromellitimide).<sup>4</sup> So, PM-TPM seems to be one of the very few poly(pyromellitimides) that are soluble in organic solvents.

On the other hand, BZPH-TPM and PM-TPM, prepared by thermal imidization of PAAs at 270°C for 30 min, to ensure practically 100% imidization degree, were only partially soluble in DMF or NMP and insoluble in all other solvents listed in Table I. The insoluble fraction increased with the temperature of the imidization process and/or time of thermal treatment. A similar effect was observed for the initially soluble polyimides, prepared by chemical imidisation at room temperature, when they were annealed at temperatures higher than 270°C.

It is known that thermal imidization or postimidization aging at high temperatures may cause

crosslinking of aromatic polyimides.<sup>18,19</sup> We believe that significant crosslinking can be the main reason for the lower solubility of the DA-TPM-based polyimides produced by thermal imidization.

### Thermal and Mechanical Analysis

The glass transition temperature,  $T_g$ , and the temperatures for 5 and 10% weight loss of both the polyamides and the polyimides obtained by chemical imidisation are listed in the Table II. Before thermomechanical and mechanical testing, the polyamide and polyimide samples were dried at 230°C and 10<sup>-4</sup> mmHg until complete evaporation of residual solvents was achieved, as monitored by TGA, in order to exclude its plasticizing effect.

The TMA analysis shows that the DA-TPM polymers exhibit well-distinguished glass transitions. The particular values of  $T_g$  increase in the following order: *i*-PH-TPA → *t*-PH-TPA → BZPH-TPM → PM-TPM. For BZPH-TPM and PM-

**Table II Thermal Properties of DA-TPM-Based Polyamides and Polyimides**

Polymer	Glass Transition Temperature, °C	Weight Loss Temperature by TGA, °C			
		Air		Nitrogen	
		5%	10%	5%	10%
<b>Polyamides</b>					
<i>i</i> -PH-TPM	177	408	427	443	470
<i>t</i> -PH-TPM	231	416	434	456	478
<b>Polyimides<sup>a</sup></b>					
BZPH-TPM	288	457	482	506	531
PM-TPM	365	505	529	538	564

<sup>a</sup> Obtained by chemical imidization.

**Table III Mechanical Properties of DA-TPM-Based Polyamides and Polyimides**

Polymer	$\eta_{inh}$ , dL/g	Young's Modulus, GPa	Tensile Strength, MPa	Elongation at Break, %
Polyamides:				
<i>i</i> -PH-TPM	1.2	1.1	125	65
<i>t</i> -PH-TPM	0.9	1.3	147	39
Polyimides <sup>a</sup>				
BZPH-TPM	1.4	1.5	135	75
PM-TPM	1.1	1.8	158	28

<sup>a</sup> Obtained by chemical imidisation.

TPM, the obtained  $T_g$ s are close to those reported in the literature for flexible chain polymers based on 4,4'-diaminodiphenylmethane<sup>20</sup> and 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane.<sup>2</sup>

According to TGA data, thermal decomposition of DA-TPM polymers started above 400°C. The highest thermal and thermo-oxidative resistance, among the studied polymers, was registered for the PM-TPM, and this exhibited a 5 and 10% weight loss under an inert atmosphere at 538°C and 564°C, respectively. For comparison, similar parameters of an industrial polyimide film KAPTON HN are 543°C and 573°C, respectively.<sup>21</sup>

The Young's modulus ( $E_0$ ), tensile strength ( $\sigma_b$ ) and elongation at break ( $\epsilon_b$ ) for the DA-TPM-based polymers are shown in Table III. The polyimides were found to have higher  $E_0$  and  $\sigma_b$  than the polyamides. Tensile strength and elongation at break values for the PM-TPM and BZPH-TPM films, prepared by chemical imidisation (see Table III), are very similar to those previously reported for the polyimides based on 4,4'-diaminotriphenylamine.<sup>4</sup> Thermal imidization of the same polymers resulted in brittle films with  $\epsilon_b$  lower than 6%.

The lower  $\epsilon_b$  of the DA-TPM polyimides, obtained by thermal imidization, can be explained by a decrease of molecular weight<sup>22</sup> and crosslinking of the polymers<sup>18,19</sup> under the severe conditions of the thermal treatment. Another important factor that can affect the mechanical properties of polyimide films is their super-molecular structure. It has been shown that thermal and chemical imidization processes lead to remarkably different packing of the polyimide molecules.<sup>23</sup>

Preliminary WAXD analysis of the DA-TPM-based polyamides and polyimides indicated that all of them had an amorphous structure. Nevertheless, significant differences in the position and shape of amorphous halo were observed for PM-TPM sam-

ples prepared by thermal and chemical imidization. A detailed study on the effect of the imidization technique on molecular characteristics and super-molecular structure of DA-TPM-based polyimides is under way.

## CONCLUDING REMARKS

A series of fully aromatic polyamides and polyimides based on 4,4'-diaminotriphenylmethane were synthesized and characterized. The solubility of DA-TPM-based polymers in organic solvents was attributed to the practically free internal rotation on the triphenylmethane bridging group and to the effect of pendant phenyl ring in the monomer.

The solubility and mechanical properties of DA-TPM-based polyimides depends remarkably on the imidization technique. In contrast to the chemical route, thermal imidization leads to formation of brittle films that are only partially soluble in amide solvents. The remarkable reduction of the solubility of the DA-TPM-based polyimides obtained by thermal imidization could be explained by their crosslinking under the severe conditions of this process.

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