Synthesis and Properties of New Aromatic Polyisophthalamides with Adamantyleamide Pendent Groups

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ABSTRACT: A new diacid monomer containing a pendent adamantyl ring was reacted with various aromatic diamines to prepare novel aromatic polyisophthalamides (PIPAs). The polymers were obtained in high yield and high molecular weight by the Yamazaki-Higashi phosphorylation method of polycondensation. Inherent viscosities ranged from 0.40 to 0.82 dL/g, which corresponds to weight-average and number-average molecular weights (GPC) in the range 21,000–63,000 g/mol and 9000–31,000 g/mol, respectively. The polymers were essentially amorphous and soluble in a variety of polar aprotic solvents, and they afforded transparent, creasable films by the solution-casting method. The great size of the polyhedral adamantyl moiety brought about a significant restriction of segmental mobility, which translated into a strong increase of \( T_g \) so that very high glass transition temperatures were observed, in the range 335–370 °C (DSC), which are 70–90 °C above the glass transition temperatures of homologous PIPAs without pendent groups. Thus, it can be stated that these adamantyl containing polyamides are among the soluble aromatic PIPAs with highest \( T_g \) ever described. Conversely, the initial decomposition temperature, as measured by thermogravimetric analysis, was about 400 °C, which is lower by 40–70° than that of unsubstituted counterparts. Polymer films exhibited good mechanical properties, with tensile strengths over 65 MPa and tensile moduli between 2.0 and 2.6 GPa. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 1743–1751, 2010

KEYWORDS: adamantane; mechanical properties; pendent groups; polyamides; thermal properties

INTRODUCTION Aromatic polyamides constitute a special group of engineering organic materials, which are considered among the so-called high performance polymers. Wholly aromatic polyisophthalamides (PIPAs) and polyterephthalamides were the most important families among aromatic polyamides. They are characterized by a very favorable combination of thermal and mechanical properties, which enable them to be used in the fabrication of, for instance, high-strength/high-modulus fibers, high-temperature and fire-resistant fibers, and high-performance films. On the other hand, wholly aromatic polyamides show very poor solubility, and they do not melt below their decomposition temperatures; therefore, they show a remarkable intractability, which limits their utilization in many modern fields of application where good processability is required. Thus, in the last few decades, many studies have been undertaken to chemically modify the primary structure of polyamides to improve their tractability without severely impairing their excellent thermal and mechanical properties. Among the approaches outlined for these purposes, the incorporation of bulky pendant groups has proved to be a reasonably good alternative to enhance the solubility (processability) of aromatic polyamides. In this regard, it is worth stressing that, as a rule, aliphatic pendant groups do lead to an improvement of solubility, but they bring about both a drop of the transition temperature and a lowering of the initial decomposition temperature. On the other hand, aromatic and heterocyclic pendant groups generally improve the solubility and do not substantially impair the thermal properties, and their incorporation into aromatic polyamides can even enhance the thermal resistance and can substantially increase the glass transition temperature. That is the case, for instance, for PIPAs which were modified by introducing phthalimido, benzothiazole, benzoxazole, or benzimidazole pendant groups.

As a contribution to a continuous effort to further improve the properties of modified aromatic PIPAs, the systematic incorporation of bulky pendant groups has now been extended to the preparation of PIPAs with a bulky cycloaliphatic group, viz., the adamantyl group. Aromatic condensation polymers containing adamantane groups in the backbone have repeatedly been reported in the past. Thus, polyamides, polyimid; phenolic resins, polysulfones, and polycarbonates have been synthesized from monomers based on the adamantane ring. As a rule, the incorporation of these moieties into the polymer structure has brought about an increase of both solubility and glass transition temperatures, so that the incorporation of

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adamantyl pendant groups was foreseen as a suitable alternative to improve the properties of traditional PIPAs. The novel polymers reported here were synthesized from a new monomer derived from isophthalic acid, which served as the bearer of the pendant group. Thus, the adamantyl group was joined to the main chain through an amide linkage, which was expected not to bring about any significant loss of thermal resistance of the modified PIPAs, because its dissociation energy should be comparable to that of the main chain amide linkages.

The main purpose of this work was to study the effect of the bulky adamantyl pendant group on the general properties of PIPAs, in comparison with those of homologous unsubstituted PIPAs and other related polyamides containing pendant groups. In particular, the effect of chemical structure on solubility, thermal transitions, thermal resistance, and mechanical strength of films was the main target of this study.

**EXPERIMENTAL**

**Materials**
1-Chlorocarbonyladamantane (Aldrich), 5-aminoisophthalic acid (Aldrich), and N,N-dimethylacetamide (DMA, Scharlau) were used as received. Reagent grade lithium chloride was dried at 300 °C before use. N-Methyl-2-pyrrolidinone (NMP, Aldrich) was purified by distillation twice under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Pyridine (Py, Aldrich) was refluxed over potassium hydroxide overnight, distilled at atmospheric pressure, and stored over molecular sieves (4 Å). Triphenyl phosphite (TPP, Aldrich) was distilled twice at low pressure.

The diamines, m-phenylenediamine (Aldrich), bis(4-amino-phenyl)ether (Aldrich), 4,4’-diaminobenzanilide (Aldrich), 9,9-bis(4-aminophenyl)fluorene (Chriskev), and 2,2-bis(4-aminophenyl)hexafluoropropane (Chriskev) were purified by sublimation just before use. 4(5)-(1-Adamantyl)-1,3-bis(4-aminophenoxy)benzene was synthesized and purified in our laboratory, according to the previously reported method.

**Monomer Synthesis**

5-(1-Adamantylcarbamoyl) Isophthalic Acid

To a three-necked glass flask equipped with magnetic stirrer was added 45.3 g (0.25 mol) of 5-aminoisophthalic in 125 mL of dry DMA. The mixture was warmed to 80 °C under a gentle nitrogen stream, until a clear solution was obtained. The solution was cooled to 10 °C and a solution of 53.6 g (0.27 mol) of 1-chlorocarbonyladamantane in 100 mL of DMA was added dropwise during 1 h. The reaction mixture was maintained at room temperature for 3 h, and then it was poured into water. The white precipitate was filtered, washed three times with warm water, and finally dried in a vacuum oven. The crude product was recrystallized from a mixture of DMA: H2O (50:50) to afford 81 g (92%) of white needles, (mp: 304 °C, by DSC).

**FIGURE 1** IR and 1H NMR spectra of 4(5)-(1-adamantylcarbonyl) amino)isophthalic acid.

IR (KBr; cm⁻¹): 3390 (N—H stretching), 3240 (O—H stretching), 2965–2832 (aliphatic C—H stretching), 1720 (C=O carboxylic stretching), 1670 (C=O amide stretching, amide band I), 1575 (combination of C—N stretching and N—H bending, amide band II) (Fig. 1).

1H NMR (300 MHz, DMSO-d₆, δ, ppm) 1.69 (s, 6H), 1.92 (s, 6H), 2.01 (s, 3H), 8.14 (t, J = 1.55 Hz, 1H), 8.56 (d, J = 1.55 Hz, 2H), 9.55 (s, 1H), 13.21 (br s, 2H);13C NMR (300 MHz, DMSO-d₆, δ, ppm): 27.72, 36.04, 38.18, 41.13, 124.54, 131.50, 140.14, 145.35, 166.70, 176.51 (Fig. 2).

**ELEM. ANAL.** Calcd. for C19H21NO5 (343.38 g/mol): C, 66.46%; H, 6.16%; N, 4.08%. Found: C, 66.26%; H, 6.34%; N, 4.12%.

**Polymers Syntheses**

All of the polymers were synthesized by the Yamazaki-Higa-shi phosphorylation polyamidation method, which is described in detail for the case of polymer 2c (Scheme 2).

A three-necked flask equipped with a mechanical stirrer, was flame dried and charged under a blanket of nitrogen with NMP (10 mL), diacid 5-ADIP (3.434 g, 0.01 mol), lithium chloride (1.4 g), and pyridine (6 mL). The mixture was stirred at room temperature until the diacid was completely
dissolved. After that, the diamine 2,2-bis[4-aminophenyl]hexafluoropropane (3.343 g, 0.01 mol) and TPP (6.826 g, 0.022 mol) were rapidly added with additional NMP (10 mL), and the solution was heated to 105 °C and held at this temperature for 3 h. The resulting viscous solution was poured into 500 mL of ethanol and the polymer precipitate was washed several times with hot water; extracted with ethanol for 24 h in a Soxhlet apparatus, and dried overnight in a vacuum dryer.

1H NMR results for all polymers were the following:

Polymer NMR results: 2a: 1H NMR (300 MHz, DMSO-d6, δ, ppm) 1.70 (s, 6H), 1.95 (s, 6H), 2.02 (s, 3H), 3.75 (t, J = 8.0 Hz, 1H), 7.52 (d, J = 7.8 Hz, 2H), 8.20 (s, 1H), 8.34 (s, 1H), 8.43 (s, 2H), 9.58 (s, 1H), 10.49 (s, 2H).

2b: 1H NMR (300 MHz, DMSO-d6, δ, ppm) 1.72 (s, 6H), 1.93 (m, 6H), 2.04 (s, 3H), 7.05 (d, J = 8.9 Hz, 4H), 7.81 (d, J = 8.9 Hz, 4H), 8.19 (s, 1H), 8.43 (s, 2H), 9.60 (s, 1H) 10.46 (s, 2H).

2c: 1H NMR (300 MHz, DMSO-d6, δ, ppm) 1.70 (s, 6H), 1.94 (s, 6H), 2.02 (s, 3H), 7.37 (d, J = 7.7 Hz, 4H), 7.91 (d, J = 8.9 Hz, 4H), 8.19 (s, 1H), 8.45 (s, 2H), 9.60 (s, 1H), 10.67 (s, 2H).

2d: 1H NMR (400 MHz, DMSO-d6, δ, ppm, T = 80 °C) 1.73 (s, 6H), 1.97 (s, 6H), 2.04 (s, 3H), 7.72 (d, J = 20.5 Hz, 4H), 7.96 (d, J = 19.9 Hz, 4H), 8.21 (s, 1H), 8.42 (s, 2H), 9.36 (s, 1H), 9.98 (s, 1H), 10.19 (s, 1H), 10.48 (s, 1H).

2e: 1H NMR (300 MHz, DMSO-d6, δ, ppm) 1.68 (s, 6H), 1.92 (s, 6H), 2.00 (s, 3H), 7.11 (d, J = 8.5 Hz, 4H), 7.35 (d, J = 14.2, 7.3 Hz, 4H), 7.48 (d, J = 7.3 Hz, 2H), 7.65 (d, J = 8.6 Hz, 4H), 7.92 (d, J = 7.2 Hz, 2H), 8.10 (s, 1H), 8.37 (s, 2H), 9.54 (s, 1H), 10.40 (s, 2H).

2f: 1H NMR (400 MHz, DMSO-d6, δ, ppm, T = 80 °C) 1.68 (m, 12H), 1.92 (m, 18H), 6.42 (s, 1H), 6.66 (d, J = 7.6 Hz, 1H), 6.97 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.3 Hz, 1H), 7.74 (m, 4H), 8.13 (s, 1H), 8.36 (s, 2H), 9.34 (s, 1H), 10.20 (s, 2H).

Measurements
Elemental analyses were made in a Carlo Erba EA11108 Elemental Analyzer. FT-IR spectra were obtained on a Perkin-Elmer Spectrum One FT-IR spectrometer on pressed powder samples and thin films. 1H and 13C NMR spectra were recorded on a Varian Inova-300 spectrometer at 299.95 and 75.43 MHz, respectively, with standard acquisition parameters. 1H NMR spectra at 80 °C of 2d and 2f were recorded on a Varian Inova-400 spectrometer at 399.95 MHz. Solubilities were determined by mixing 10 mg of polymer with 1 mL of solvent for 24 h at room temperature. Samples that did not dissolve were heated to the solvent boiling temperature. Differential scanning calorimetry (DSC) analyses were performed on a TA instruments TA-Q-2000 calorimeter at a heating rate of 20 °C/min under nitrogen. Thermogravimetric analyses (TGA) were performed under nitrogen, with a TA Q-500 analyzer at 10 °C/min, on 2–3 mg samples. Additional high-resolution TGA analyses were carried out by using the standard TA Hi-Res method implemented in the TA Q-500 device. Inherent viscosities were measured on filtered 0.5 g/dL polymer solutions in DMA at 25.0 ± 0.1 °C, in an automated Ubbelohde viscometer. The mechanical properties were tested on a MTS Synergie 200 Universal Testing Machine, using strips 5 mm wide, 50 mm long, and 40–60 μm thick, that were cut from polymer films. An extension rate of 1 mm/min was applied with a gauge length of 10 mm. Wide angle X-ray diffraction patterns were obtained by means of a Philips X-ray diffractometer using Cu Kα radiation over polymer films.

Size exclusion chromatography (SEC) measurements were carried out using PL gel columns (Polymer Laboratories) of nominal pore sizes 500, 10, and 105 Å. N,N-Dimethylformamide (DMF) with 0.1% LiBr was used as solvent, and the measurements were done at 70 °C with a flow rate of 1.0 mL/min using an UV detector. The columns were calibrated with narrow standards of a suitable aromatic polyamide, poly(m-phenyleneisophthalamide), and polystyrene.

RESULTS AND DISCUSSION
Monomer Synthesis
The monomer 5-(1-adamantylcarbonylamino) isophthalic acid (5-ADIP) was prepared by a synthetic route depicted in Scheme 1, using as starting material 1-adamantanecarbonyl chloride in a classical, high yield amidation synthesis. Attempts to synthesize the diacid chloride of 5-ADIP, to use it in a conventional polyamidation with diamines at low temperature, were unsuccessful. This was due to the presence of the amide groups in 5-ADIP, which leads to secondary reactions when chlorinating agents such as thionyl chloride are used.24

Figure 1 shows the IR spectra of the dicarboxylic acid monomer, with a narrow absorption band at approximately 3390 cm⁻¹ (amide N—H stretching); the characteristic wide band of aromatic carboxylic acid with a maximum at 3240 cm⁻¹ (O—H stretching) and the carbonyl absorption band at 1720 cm⁻¹ (C=O stretching); two intense, sharp bands at 2832 and 2965 cm⁻¹ (aliphatic C—H stretching); and the bands of
secondary amide groups at 1670 cm\(^{-1}\) (C=O stretching) and 1575 cm\(^{-1}\) (combination of C–N stretching and N–H bending). Figure 1 also shows the \(^1\)H NMR spectrum of the monomer, where it can be seen that all of the signals are in good agreement with the expected chemical structure.

**Synthesis of Polymers**

Polyamides were prepared from the monomer 5-ADIP and a series of technical and experimental aromatic diamines by the synthetic route depicted in Scheme 2. The phosphorylation method first described by Yamazaki et al.\(^{25}\) was used as the general preparation method for all of the polymers, using the system triphenylphosphite-pyridine as a condensing promoter and LiCl as solubility enhancer. All of the polycondensation reactions proceeded readily in homogeneous solutions and high yields and relatively high-molecular weights were obtained. FTIR and NMR spectroscopies were used to confirm the chemical structure of all of the polymers. As an example, the \(^1\)H NMR spectrum of polymer 2c has been reproduced in Figure 2.

Tables 1 and 2 list the results of polycondensation, along with the elemental analyses of the polymers. Inherent viscosities up to 0.92 dL/g were achieved, which correspond to an estimated number average molecular weight, \(M_n\), of 31,000 g/mol, and weight average molecular weight, \(M_w\), of 63,000 g/mol (based on SEC measurements) for polymer 2f using standards of poly(m-phenyleneisophthalamide, MPD-I). \(M_n\) of 62,000 and \(M_w\) of 158,000 g/mol were obtained using polystyrene standards as reference. It can be presumed that the values obtained from the MPD-I references are more reliable than those measured taking polystyrene as reference, because of the structural similarity of samples and references in the first case. The polydispersity (\(M_w/M_n\)) values, between 1.7 and 2.6, suggested that a suitable polycondensation method and a careful purification of the final materials were implemented. Furthermore, the molecular weights achieved for the set of polyamides can be considered, as a whole, as reasonably high but not very high, particularly in comparison to those achieved for aromatic polyamides prepared by the solution polycondensation method using diacid chlorides at low temperature.

**Polymers Properties**

The presence of the pendent bulky groups greatly affected the properties of these polymers compared with those of unsubstituted PIPAs. The chain separation caused by the adamantyl side groups contributed to enhance the solubility of the current PIPAs in organic aprotic polar solvents related to unmodified PIPAs. For instance, they all were soluble in aprotic polar solvents and, in particular polymer 2a with \(m\)-phenylene moieties, readily dissolved in NMP, DMA, or DMF at room temperature, whereas the corresponding unsubstituted aromatic polyamide [poly(\(m\)-phenylene isophthalamide), MPD-I], does not dissolve in organic solvents without adding a significant amount of inorganic salts.\(^{26}\) On the other hand, the current PIPAs were insoluble in common organic solvents, that is, ketones, chlorinated hydrocarbons, alcohols, and cyclic ethers such as tetrahydrofuran or dioxane.

The thermal behavior was evaluated by means of DSC and TGA. The data presented in Table 3 and Figure 3 demonstrate that the incorporation of adamantly amide groups as pendent substituents of PIPAs caused a significant increase in the glass transition temperature (\(T_g\)) related to PIPAs previously reported. \(T_g\)'s ranged from 335 °C for polymer 2b to 370 °C for polymer 2e (Table 2), whereas the \(T_g\) of a wholly aromatic, commercial PIPA such as MPD-I is about 275 °C. For instance, the \(T_g\) of poly(\(m\)-phenylene-5-benzoylaminoisophthalamide), a related polyamide with a pendent benzyllamino group, is 298 °C,\(^{27}\) which is 67 °C lower than the \(T_g\) of 2a. They have also much higher \(T_g\) than the PIPA prepared from isophthalic acid and an adamantane-based cardo diamine, for which a \(T_g\) of 231 °C has been reported.\(^{18}\)

The strong increase of \(T_g\) observed upon incorporating the polyhedral, voluminous adamantane ring as a pendent group deserves a more in depth discussion. On comparing the glass transition temperature found for polymer 2a with that of other PIPAs from \(m\)-phenylene diamine and 5-substituted isophthaloyl units, a good correlation between \(T_g\) and volume of the pendent group could be found. It can be seen in Figure 4, where the \(T_g\) of different poly(\(m\)-phenylene isophthalamides) were plotted versus the van der Waals
volume of the monomeric unit, calculated using the Compass force field using the program Materials Studio 4.4.27 The correlation is quite good in spite of the different structures and functional groups depicted in Figure 4. This clearly suggests that the bulky adamantyl side groups brought about a decrease of molecular mobility, leading to a dramatic enhancement of the \(T_g\) and, what is more important, without any loss in solubility (processability). Furthermore, pendent adamantane rings yielded PIPAs with higher \(T_g\) than those containing pendent polar aromatic heterocycles such as phthalimide, benzoxazole, and benzothiazole, which are the moieties of condensation polymers with highest thermal resistance. The explanation of this behavior is very probably due to the much higher effective volume of adamantane relative to the volume of the heterocycles, which are essentially planar. The biggest difference corresponds to the related PIPA with phenoxy pendent groups, for which a \(T_g\) of 245 °C has been reported. 28 In this regard, the presence of the \(-\text{COHN}\) linkage that connects the adamantyl group with the polymer chain, surely plays a significant role on preserving a high value for \(T_g\), thanks to an increase of the cohesive energy density through interchain hydrogen bonding.

The polyamides 2a, 2c, 2d, and 2e exhibited the highest \(T_g\)s, as was to be expected on considering the chemical structure of the corresponding diamines. Diamine a (MPD) is a short, wholly aromatic diamine, which imparts high density of hydrogen bonds, diamine c (diamine 6F) is a fluorinated symmetric diamine which provides high \(T_g\) thanks to its voluminous hexafluoroisopropylidene group and by the polar character of the C-F bonds, diamine d (4,4′-diamino-benzanilide) is a para-oriented diamine with an amide linkage, which provides efficient molecular packing and additional hydrogen bonds through its amide linkage, and diamine e is a cardo diamine which is recognized to provide good solubility, high free volume and high \(T_g\) at the same time. On the other hand, amines b and f contain ether linkages, which impart chain flexibility and segmental rotational freedom, and these characteristics make for a decrease of \(T_g\)s.

No endothermic peak was detected on the DSC traces in any case, which, in principle, indicated that the novel PIPAs did not develop crystallinity. This was confirmed by wide angle X-ray scattering, where an amorphous pattern was recorded in all cases (Fig. 5). Hence, the family of PIPAs reported here

| TABLE 1 Preparation of Polyisophthalamides Containing Adamantyl Pendent Groups |
|---|---|---|---|---|
| Polymer | Yield (%) | Repeat Unit Mol. Formula | Elemental Analyses |
| 2a | 95 | C\(_{25}\)H\(_{25}\)N\(_3\)O\(_3\) | calcd. C 66.55, N 6.06, H 10.11 |
| 2b | 97 | C\(_{31}\)H\(_{29}\)N\(_3\)O\(_4\) | calcd. C 73.35, N 5.76, H 8.28 |
| 2c | 98 | C\(_{25}\)H\(_{25}\)F\(_2\)N\(_3\)O\(_3\) | calcd. C 63.65, N 4.56, H 6.55 |
| 2d | 98 | C\(_{32}\)H\(_{30}\)N\(_4\)O\(_4\) | calcd. C 71.89, N 5.66, H 10.48 |
| 2e | 97 | C\(_{44}\)H\(_{37}\)N\(_3\)O\(_3\) | calcd. C 80.59, N 5.69, H 6.41 |
| 2f | 99 | C\(_{47}\)H\(_{47}\)N\(_3\)O\(_5\) | calcd. C 76.92, N 6.45, H 5.73 |

| TABLE 2 Inherent Viscosities and SEC Data of Polyisophthalamides Containing Adamantyl Pendent Groups |
|---|---|---|---|---|---|---|
| Polymer | \(\eta_{inh}\) (dL/g) | Polystyrene Standards | Poly(m-phenyleneisophthalamide) Standards |
| 2a | 0.41 | 19,000 | 42,000 | 2.2 | 9,000 | 19,000 | 2.1 |
| 2b | 0.52 | 26,000 | 48,000 | 1.9 | 11,000 | 21,000 | 1.9 |
| 2c | 0.61 | 32,000 | 73,000 | 2.3 | 14,000 | 32,000 | 2.3 |
| 2d | 0.66 | 34,000 | 51,000 | 1.5 | 15,000 | 25,500 | 1.7 |
| 2e | 0.69 | 37,000 | 91,000 | 2.5 | 17,000 | 40,000 | 2.4 |
| 2f | 0.92 | 62,000 | 158,000 | 2.5 | 31,000 | 63,000 | 2.0 |
should be considered as glassy materials, essentially amor-
phous and with very high $T_g$s.

The thermal resistance, in terms of initial decomposition
temperature ($T_{\text{d onset}}$), was evaluated by TGA. All of the
polymers showed relatively high $T_{\text{d}}$s in N$_2$, around 400 °C. The
small differences observed in $T_{\text{d}}$, regardless the diamine
moiety, could be attributed to the fact that decomposition
always started with the thermal breakdown of the amide
linkage that connects the main chain with the adamantyl
pendent group. As an example, Figure 6 shows the TGA trace
of one of the current PIPAs, which was recorded by using
the TA Hi-Res method. It can be observed how a first
weight loss occurred from around 400 °C to about 480 °C,
which should be associated with the loss of the pendent
group. An accurate determination of this first loss amount
could not be done because a second strong loss, correspond-
ing to the extensive decomposition of the polymers, over-
lapped in every case. Yet, the two-step decomposition pro-
cess could be confirmed as two distinguishable peaks were
registered on the differential weight loss curve.

A similar behavior had been previously observed for PIPAs
containing benzyolamino pendent groups, which also showed
a first weight loss onset at about 410 °C. Thus, it was con-

To figure out how the thermal breakdown of these polymers
proceeds, and in particular the side amide breakdown, a

![TABLE 3](image)

**TABLE 3** Mechanical and Thermal Properties of Polyisophthalamides Containing Adamantyl Pendent Groups

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Tensile Strength (MPa)</th>
<th>Young Moduli (GPa)</th>
<th>$T_g$ (°C)</th>
<th>$T_{d10}$ (°C)</th>
<th>$T_{d10}^a$ (°C)</th>
<th>$Y_{800}^c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>–</td>
<td>–</td>
<td>365</td>
<td>400</td>
<td>420</td>
<td>49</td>
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<tr>
<td>2b</td>
<td>83</td>
<td>2.4</td>
<td>335</td>
<td>390</td>
<td>425</td>
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</tr>
<tr>
<td>2c</td>
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<td>410</td>
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<td>51</td>
</tr>
<tr>
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</tr>
<tr>
<td>2f</td>
<td>70</td>
<td>2.3</td>
<td>345</td>
<td>410</td>
<td>430</td>
<td>43</td>
</tr>
</tbody>
</table>

$^a$ Temperature of first onset in the TGA curve at a heating rate of 10 °C/min.

$^b$ Temperature of 10% weight loss.

$^c$ Residual wt % at 800 °C.

![FIGURE 4](image)

**FIGURE 4** Glass transition temperature of polyisophtha-
amides prepared from $m$-phenylenediamine and isophthalic
acid derivatives containing pendent groups versus the van der
Waals volume of the isophthaloyl unit. $T_g$ values taken from
ref. 13.
A theoretical study was carried out on two models with amide linkage (Fig. 7), one of them aromatic and the other one corresponding to the model with the pendant group studied in this work. Theoretical calculations were carried out using the Density Functional Theory (DFT) with the UB3LYP functional and the 6-31+G(d) basis set. The base superposition error was corrected using the Counterpoise Method. All calculations were performed using the GAUSSIAN 03 program. Models 7a and 7b correspond to amide units within the main chain (N-phenylbenzamide or benzanilide) and on the pendant units [N-(1-adamantanyl) benzamide], respectively. Models were optimized at UB3LYP/6-31+G(d) level and their homolytic bond dissociation energies were calculated for the C=O (B1), CO=N (B2), and N=C (B3) bonds marked in the figure at the same computational level (energies calculated as the difference between the molecule and its dissociated parts). The weakest bond in both cases was B2, with dissociation energies of -84.49 kcal/mol for 7a (OCar-N) and -82.06 kcal/mol for 7b (OCad-N). It confirmed that the amide breakdown is more probable for adamantanyl pendant groups than for amide groups inside the main chain, in agreement with that observed by TGA. A more detailed study of these systems should be carried out for a better and quantitative comprehension, as the difference in dissociation energies for B2 and B1 bonds does not unquestionably support the hypothesis. It must be borne in mind that at the high temperature of initial decomposition, bonds B2 and B1 can become almost equally labile, particularly in the case of model 7b, which means that the first thermal breakdown can occur in any of the two linkages. Nonetheless, the decomposition process in two steps observed by TGA would be the same because B2 dissociation energy is also higher for 7a (OCar-N) than for 7b (OCad-N).

In agreement with these observations, temperatures of 10% weight loss measured by TGA lie for all the polymers in a narrow range, viz., between 420 and 445 °C. Small differences were observed for the carbonaceous residue among the current PIPAs and in comparison with classical ones, with weight retention around 60% at 800 °C in N2.

The tensile strength and the Young modulus of polyamide films (Table 3), ranging between 65 and 85 MPa and 2.0–2.6 GPa, respectively, can be considered as acceptable for unoriented samples, made by casting on a laboratory scale and without any post-treatment. Polymer 2a, because of its low-
molecular weight, did give brittle films with insufficient mechanical strength to be tested under standard conditions. However, polymer 2b, which showed only slightly higher molecular weight did give creaseable films that could be properly tested. The less rigid oxydiphenylene moiety of polymer 2b with respect to the short-rigid 1,3-phenylene moiety of polymer 2a should be considered as responsible of this behavior. In general, the mechanical properties compared fairly well with values reported earlier for experimental aromatic polyamides and other engineering thermoplastic polymers. The less rigid oxydiphenylene moiety of polymer 2a with values reported earlier for experimental aromatic polyamides and other engineering thermoplastic polymers.

CONCLUSIONS

By a facile, high yield route, it was possible to prepare the new condensation monomer 5-[(1-adamantylcarbonyl)amino] isophthalic acid (5-ADIP), which was readily purified to polycondensation grade. High yields and high-molecular weights were achieved for the synthesis of adamantyl pendant PIPAs by the direct polyamidation method of Yamazaki-Higashi using 5-ADIP and a series of technical aromatic diamines. The results confirmed that the bulky pendant group did not much effect the reactivity of the carboxylic functions of the isophthalic acid. The presence of the pendant bulky groups greatly affected the general properties of these polymers compared with those of unmodified PIPAs. Better solubility and much higher $T_g$ values were measured for the modified polymers; $T_g$s in the range 335–370 °C qualify the current polymers among the PIPAs with highest $T_g$s ever reported. Furthermore, the current polymers showed higher $T_g$s than homologous PIPAs containing benzamido or heterocyclic moieties as pendant groups. On the other hand, the incorporation of an adamantane pendant group linked to the isophthaloyl moiety by an amide group caused a decrease in thermal resistance, as initial decomposition temperatures around 400 °C were something lower than those observed for classical PIPAs. Mechanical resistance and moduli of films, from 2.0 to 2.6 GPa, were reasonably high and comparable to those of other PIPAs previously reported.

REFERENCES AND NOTES


SYNTHESIS AND PROPERTIES OF NEW AROMATIC PIPAs, ESPESO ET AL. 1751