Synthesis and Characterization of Aromatic Polyamides Containing Alkylphthalimido Pendent Groups


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ABSTRACT: A series of polyisophthalamides containing pendent phthalimido groups and flexible side spacers were prepared from four novel diacids and three commercial aromatic diamines. These polyamides were prepared in high yields and with high molecular weights by direct polycondensation with triphenyl phosphate and pyridine as condensing agents. The weight-average and number-average molecular weights, measured by gel permeation chromatography, were 70,000–137,000 and 47,000–86,000 g/mol, respectively. The novel polyamides were amorphous and readily soluble and showed glass-transition temperatures of 150–240 °C, as measured by differential scanning calorimetry. Thermogravimetric analysis showed that the 10% weight-loss temperatures in nitrogen were 355–430 °C, a significant improvement in thermal stability having been observed with the increase in the side-chain length. A theoretical quantum mechanical study was successfully carried out to explain these results. Flexible and tough films, cast from polymer solutions, showed tensile strengths of 50–125 MPa. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 3711–3724, 2002

Keywords: polyamides; step-growth polymerization; thermal properties; structure-property relations; quantum mechanical calculations

INTRODUCTION

Aromatic polyamides have received special attention in past years because of their high thermal and chemical resistance and their potential as high-performance materials for several applications, such as high-strength, high-modulus fibers, high-temperature coatings, and high-efficiency semipermeable membranes.1–4 Because of the stiffness of the polymer chains and the strong molecular interactions through hydrogen bonding, wholly aromatic polyamides do not melt and cannot be dissolved in organic solvents; this makes them generally difficult or too expensive to process, restricting their applications. Approaches have been outlined to improve the solubility of polyamides by means of chemical modifications, such as the incorporation of pendent groups5–13 or flexible units14–18 This enhancement of solubility is desirable in some cases, such as the preparation of insulating coatings or semipermeable membranes. Early results have demonstrated that the introduction of phthalimide groups as side substituents is a convenient approach for positively modifying the physical properties of polyisophthalamides.19–23

This article describes the successful synthesis and characterization of four new dicarboxylic acids containing pendent alkylphthalimide groups and their use for the preparation of polyamides by direct polycondensation with various aromatic diamines. The introduction of these side chains should disrupt interchain hydrogen bonding and reduce packing efficiency and crystallinity. More-
over, the presence of heat-resistant phthalimide heterorings as pendant groups may counterbalance any loss of thermal properties that can be caused by the incorporation of aliphatic spacers. Therefore, this methodology should enhance solubility and maintain reasonably high glass-transition temperatures ($T_g$’s) through controlled segmental mobility. The incorporation of phthalimido groups has also been adopted because of the possibility of functionalization by hydrazinolysis, which would provide polymers with free amino groups. The polyamides have been fully characterized, and the effect of the modification has been evaluated by the determination of the most interesting properties, such as solubility in organic solvents, thermal transitions and thermal resistance, and mechanical properties.

**EXPERIMENTAL**

**Materials**

$N$-Methyl-2-pyrrolidinone (NMP) was purified twice by distillation under reduced pressure over calcium hydride and stored over molecular sieves (4 Å). Pyridine was refluxed over KOH for 24 h and then distilled at normal pressure and stored over molecular sieves (4 Å). Triphenyl phosphate (TPP) was distilled twice under low pressure. Reagent-grade lithium chloride was dried at 300 °C before use. $\beta$-Alanine, $\gamma$-aminobutyric acid, 6-aminocaproic acid, 11-aminoundecanoic acid, phthalic anhydride, thionyl chloride, and 5-aminopentanoic acid were used as received.

Commercial bis($4$-aminophenyl) ether (ODA) and $2,2$-bis($4$-aminophenyl) hexafluoropropane (6F) were sublimated before use. Bis(4-aminophenyl) methane (MDA) was recrystallized from water and thoroughly dried under reduced pressure over phosphorus pentoxide.

**Intermediates and Monomers**

**3-Phthalimidyl-$n$-propanoic Acid (A2)**

A mechanically stirred mixture of $\beta$-alanine (19.6 g, 0.22 mol), phthalic anhydride (33.24 g, 0.22 mol), and acetic acid (50 mL) was heated to reflux for 9 h. The product that crystallized on cooling was isolated by filtration, washed several times with water, and dried in vacuo at 100 °C to obtain 48.2 g (98%) of 3-phthalimidylpropanoic acid.

mp: 158 °C. IR (KBr, cm$^{-1}$): 3600–2800 (O–H stretching), 3030 (aromatic C–H stretching), 2970 (aliphatic C–H stretching), 1775, 1725 (C=O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 2.58 (t), 3.78 (t), 7.79–7.92 (m). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 32.4, 33.6, 123.1, 131.6, 134.4, 167.6, 172.2. ELEM. ANAL. Calcd. for C$_{11}$H$_9$NO$_4$ (219.19): C, 60.28%; H, 4.14%; N, 6.39%. Found: C, 59.99%; H, 4.15%; N, 6.47%.

**4-Phthalimidyl-$n$-butanoic Acid (A3)**

This compound was obtained from phthalic anhydride and $\gamma$-aminobutyric acid by the method described previously for A2. The yield was 97%.

mp: 124 °C. IR (KBr, cm$^{-1}$): 3600–2500 (O–H stretching), 3045 (aromatic C–H stretching), 2945 (aliphatic C–H stretching), 1775, 1725 (C=O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 1.82 (q), 2.28 (t), 3.61 (t), 7.79–7.92 (m). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 23.3, 31.1, 36.9, 122.9, 131.8, 134.3, 168.2, 173.9. ELEM. ANAL. Calcd. for C$_{14}$H$_{15}$NO$_4$ (232.22): C, 61.80%; H, 4.75%; N, 6.01%. Found: C, 61.53%; H, 5.00%; N, 6.09%.

**6-Phthalimidyl-$n$-hexanoic Acid (A5)**

The compound was prepared by the same method, from phthalic anhydride and 6-aminocaproic acid. The yield was 95%.

mp: 116 °C. IR (KBr, cm$^{-1}$): 3600–2500 (O–H stretching), 3035 (aromatic C–H stretching), 2935, 2865 (aliphatic C–H stretching), 1775, 1725 (C=O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 1.10–1.35 (m), 1.35–1.70 (m), 2.18 (t), 3.55 (t), 7.79–7.92 (m). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 24.1, 25.8, 27.6, 33.3, 37.2, 123.0, 131.6, 134.3, 168.1, 174.5. ELEM. ANAL. Calcd. for C$_{13}$H$_{21}$NO$_4$ (261.27): C, 64.36%; H, 5.79%; N, 5.36%. Found: C, 64.18%; H, 6.02%; N, 5.65%.

**11-Phthalimidyl-$n$-undecanoic Acid (A10)**

A10 was obtained by the same general method from phthalic anhydride and 11-aminoundecanoic acid. The yield was 97%.

mp: 99 °C. IR (KBr, cm$^{-1}$): 3600–2500 (O–H stretching), 3035 (aromatic C–H stretching), 2935, 2855 (aliphatic C–H stretching), 1775, 1725 (C=O stretching). $^1$H NMR (DMSO-$d_6$, $\delta$, ppm): 1.10–1.35 (m), 1.35–1.70 (m), 2.18 (t), 3.55 (t), 7.79–7.92 (m). $^{13}$C NMR (DMSO-$d_6$, $\delta$, ppm): 24.5, 26.3, 27.9, 28.5, 28.6, 28.7, 28.8, 28.9, 33.6, 37.3, 122.9, 131.5, 134.3, 167.9, 174.5. ELEM. ANAL. Calcd. for C$_{19}$H$_{25}$NO$_4$ (331.17): C, 68.86%; H, 7.60%; N, 4.23%. Found: C, 68.58%; H, 8.02%; N, 4.43%.
3-Phthalimidyld-n-propanoyl Chloride (B2)

A mixture of A2 (20.0 g, 0.09 mol), thionyl chloride (13 mL, 0.18 mol), dichloromethane (40 mL), and four drops of N,N-dimethylformamide (DMF) was refluxed for 5 h. Dichloromethane and the excess of thionyl chloride was stripped off by distillation to obtain 19.96 g of the acid chloride. The yield was 92%. The crude product was directly used in the next step, without further purification. For the synthesis of all the acid chlorides, the same acylation method was used.

mp: 108 °C. IR (KBr, cm⁻¹): 3045 (aromatic C–H stretching), 2965 (aliphatic C–H stretching), 1805, 1725 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 2.42 (q), 2.83 (t), 3.61 (t), 7.79–7.92 (m). 13C NMR (DMSO-d₆, δ, ppm): 24.2, 36.5, 44.0, 123.1, 132.6, 133.1, 167.8, 171.6.

4-Phthalimidyld-n-butanoyl Chloride (B3)

B3 was obtained in a 92% yield and was used without further purification.

mp: 71 °C. IR (KBr, cm⁻¹): 2950 (aliphatic C–H stretching), 2965 (aliphatic C–H stretching), 1800, 1722 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 1.61 (s), 2.51 (t), 3.64 (t), 7.79–7.88 (m). 13C NMR (DMSO-d₆, δ, ppm): 23.66, 33.75, 37.12, 123.1, 131.4, 133.2, 168.1, 169.3.

6-Phthalimidyld-n-hexanoyl Chloride (B5)

The product was isolated in a 91% yield and was used without further purification.

mp: 66 °C. IR (KBr, cm⁻¹): 3050 (aromatic C–H stretching), 2965 (aliphatic C–H stretching), 1800, 1722 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 1.06–1.35 (m), 1.40–1.70 (m), 2.80 (t), 3.60 (t), 7.79–7.92 (m). 13C NMR (DMSO-d₆, δ, ppm): 25.5, 26.12, 29.4, 33.3, 42.1, 123.1, 131.4, 133.2, 168.1, 169.3.

11-Phthalimidyld-n-undecanoyl Chloride (B10)

This compound was obtained in a 97% yield and was used without further purification.

mp: 45 °C. IR (KBr, cm⁻¹): 3048 (aromatic C–H stretching), 2935 (aliphatic C–H stretching), 1805, 1725 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 1.06–1.35 (m), 1.40–1.70 (m), 2.80 (t), 3.60 (t), 7.79–7.92 (m). 13C NMR (DMSO-d₆, δ, ppm): 24.7, 26.3, 27.9, 28.5, 28.6, 28.7, 28.8, 28.9, 36.7, 45.7, 122.9, 131.5, 134.3, 167.8, 171.2.

5-(3-Phthalimidyl-d-n-propanoylamino)isophthalic Acid (C2)

B2 (71.3 g, 0.30 mol) was added portionwise to a solution of 5-AIPA (54.3 g, 0.30 mol) in 500 mL of N,N-dimethylacetamide (DMAc) cooled to 0 °C. Next, the temperature was slowly raised to room temperature, and the reaction was maintained for 12 h. The reaction mixture was poured into water, and the precipitate was filtered off, washed with hot water several times, and dried in a vacuum oven at 100 °C. The product was recrystallized twice from H₂O/DMF (2/1). The yield was 85%.

mp: 322 °C. IR (KBr, cm⁻¹): 3600–2400 (O–H stretching), 3290 (N–H stretching), 3085 (aromatic C–H stretching), 2950 (aliphatic C–H stretching), 1775, 1710 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 2.71 (t), 3.90 (t), 7.72–8.00 (m), 8.13 (t), 8.36 (d), 10.40 (s). 13C NMR (DMSO-d₆, δ, ppm): 35.24, 35.28, 123.11, 123.71, 124.74, 131.77, 134.42, 139.72, 166.61, 167.77, 169.32. ELEM. Anal. Calcd. for C₁₅H₁₁N₂O₇ (382.32): C, 59.69%; H, 3.69%; N, 7.33%. Found: C, 59.47%; H, 3.91%; N, 7.47%.

5-(4-Phthalimidyl-d-n-butanoylamino)isophthalic Acid (C3)

This compound was obtained from B3 and 5-AIPA as described previously for C2. It was recrystallized twice from H₂O/DMF (2/1). The yield was 82%.

mp: 336 °C. IR (KBr, cm⁻¹): 3600–2400 (O–H stretching), 3335 (N–H stretching), 3075 (aromatic C–H stretching), 2975, 2935 (aliphatic C–H stretching), 1775, 1715 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 1.96 (q), 2.40 (t), 3.65 (t), 7.63–7.86 (m), 8.12 (t), 8.39 (d), 10.24 (s). 13C NMR (DMSO-d₆, δ, ppm): 23.66, 33.75, 37.12, 122.95, 123.45, 124.42, 131.66, 134.25, 139.83, 166.57, 168.02, 170.99. ELEM. Anal. Calcd. for C₁₉H₁₆N₂O₇ (396.35): C, 60.61%; H, 4.07%; N, 7.07%. Found: C, 60.37%; H, 4.36%; N, 7.28%.

5-(6-Phthalimidyl-d-n-hexanoylamino)isophthalic Acid (C5)

C5 was obtained from B5 and 5-AIPA by the same method and recrystallized from H₂O/DMF (2/1). The yield was 86%.

mp: 324 °C. IR (KBr, cm⁻¹): 3650–2400 (O–H stretching), 3360 (N–H stretching), 3070 (aromatic C–H stretching), 2935, 2860 (aliphatic C–H stretching), 1775, 1710 (C=O stretching). 1H NMR (DMSO-d₆, δ, ppm): 1.19–1.40 (m), 1.48–1.72 (m), 2.30 (t), 3.53 (t), 7.70–7.84 (m), 8.11 (t), 8.39 (d), 10.20 (s). 13C NMR (DMSO-d₆, δ, ppm): 24.60, 25.93, 27.83, 36.25, 37.32, 122.95, 123.48, 124.43, 131.59, 131.70, 134.30, 139.92, 166.60, 167.94, 171.72. ELEM. Anal. Calcd. for
C_{22}H_{20}N_{2}O_{7} (424.41): C, 62.26%; H, 4.75%; N, 6.60%. Found: C, 61.97%; H, 5.06%; N, 6.72%.

5-(11-Thalimidyl-n-undecanoylamino)isophthalic Acid (C10)

This monomer was obtained from B10 and 5-AIPA by the described general method. It was purified by recrystallization from H_{2}O/DMF (2/1). The yield was 80%.

mp: 285 °C. IR (KBr, cm⁻¹): 3600–2450 (O—H stretching), 3455 (N—H stretching), 3080 (aromatic C—H stretching), 2930, 2850 (aliphatic C—H stretching), 1765, 1715 (C=O stretching).


{1H NMR (DMSO-d_6, δ, ppm): 1.14–1.40 (m), 1.45–1.71 (m), 2.30 (t), 3.52 (t), 7.74–7.93 (m), 8.11 (t), 8.42 (d), 10.23(s). 13C NMR (DMSO-d_6, δ, ppm): 25.09, 26.33, 27.97, 28.63, 28.73, 28.88, 28.97, 36.52, 37.40, 122.99, 123.50, 124.45, 131.62, 131.71, 134.31, 139.99, 166.64, 167.90, 171.87. ELEM. ANAL. Calcd. for C_{27}H_{30}N_{2}O_{7} (494.54): C, 65.57%; H, 6.11%; N, 5.66%. Found: C, 65.28%; H, 6.39%; N, 5.58%.

Polymor Synthesis

The general procedure is illustrated by the synthesis of polymer 2-MDA. A flask equipped with a mechanical stirrer and a condenser was charged with a mixture of diacid C2 (3.82 g, 10.0 mmol), diamine MDA (1.98 g, 10.0 mmol), pyridine (6 mL), lithium chloride (1.4 g), and NMP (20 mL). The mixture, blanketed by nitrogen, was stirred and heated to 105 °C. TPP (22.0 mmol) was then added to the solution, and the reaction proceeded for 4 h. The viscous final solution was poured into methanol, and the collected polymer was washed thoroughly with water and methanol. The polymer was dried in a vacuum oven at 110 °C overnight. A 96% yield was obtained. All other polymides were prepared with a similar procedure. The elemental analysis showed values within ±0.3% of the calculated ones.

Measurements

Differential scanning calorimetry (DSC) analyses were performed on a 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.

Uncorrected melting points were measured by DSC at a heating rate of 10 °C/min.

Fourier transform infrared (FTIR) spectra of intermediates and monomers were recorded on a Nicolet 520 FTIR spectrometer on KBr disks. An attenuated total reflectance device (Spectra Tech model 300 with a Ge crystal) was used for polymer films.

1H and 13C NMR spectra were recorded on a Varian Gemini 200 spectrometer at 199.97 and 50.28 MHz, respectively, with deuterated dimethylsulfoxide (DMSO-d_6) as a solvent and internal reference.

The qualitative solubility was determined with 20 mg of polymer in 1 mL of solvent.

Elemental analyses were obtained with a Carlo Erba EA1108 elemental analyzer.

Inherent viscosities were measured on filtered 0.5 g/dL DMAc solutions at 25 ± 0.1 °C in an automated Ubbelohde viscosimeter.

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 performed at 70 °C at a flow rate of 1.0 mL/min with a UV detector operating at 273 nm. The columns were calibrated with narrow standards (fractionated in our laboratory according to a method described previously) of a suitable aromatic polyamide [poly(m-phenyleneisophthalamide)]. The molecular weight of the fractions was estimated from the viscosimetric equation, with the molecular weight in the peak assigned to the weight-average molecular weight (M_w).

For the measurement of the mechanical properties, strips 5 mm wide, 50 mm long, and 40–100 μm 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.

Semiempirical quantum mechanical calculations were performed with the original parameters of the program PM3 based on the restricted Hartree–Fock methodology. This method is included in MOPAC version 6.0. The Cerius² program was used as a graphics interface and for data analysis. The MOPAC program ran on a Silicon Graphics Octane R12000 workstation. Geometries were optimized in internal coordinates, and the optimization was stopped when Herbert or Peter tests were satisfied in the Broyden–Fletcher–Goldfarb–Shanno method. The PRECISE option was applied during the optimization process, with the gradient norm set to 0.01. The calculations were carried out with full geometry optimization (bond lengths, bond
angles, and dihedral angles) without any assumption of symmetry. PM3 semiempirical calculations were also used to study the homolytic breakdown of the aliphatic pendant groups. In this case, the unrestricted Hartree–Fock methodology\textsuperscript{27,28} was used. Finally, the PM3 structures determined by the MOPAC program were refined to obtain lower enthalpy values by means of the HyperChem program (version 6.03)\textsuperscript{33} with the Polak–Ribiere optimization methodology, with a root-mean-square gradient of 0.01 kcal/mol Å.

RESULTS AND DISCUSSION

Monomer and Polymer Syntheses

The monomers, 5-(ω-phthalimidyl-n-alkanoylaminoo)isophthalic acids, were prepared by the general, three-step route depicted in Scheme 1 from the corresponding acid chlorides and 5-AIPA. In the first step, the intermediate ω-phthalimidyl-n-alkylcarboxylic acid was obtained from the reaction of the ω-amino acid and phthalic anhydride in acetic acid with a practically quantitative yield. The reaction of the acid compound with thionyl chloride was used to obtain the intermediate acid chlorides, which were subsequently reacted with 5-AIPA in a typical low-temperature condensation reaction with high yields (>85%). The new derivatives of isophthalic acid containing alkylphthalimido pendant groups were thoroughly purified by recrystallization from H₂O/DMF mixtures. The structures of the intermediates and dicarboxylic monomers were confirmed by elemental analysis, IR, and \(^1\)H and \(^{13}\)C NMR spectroscopy.

The direct polycondensation of diacids and aromatic diamines in a typical Yamazaki–Higashi reaction was adopted for the preparation of the polymers\textsuperscript{34–36} (Scheme 2). The traditional method at low temperatures, from diacid chlorides, was
not adequate because the presence of an amide function in the diacid monomers made the synthesis of the acid chlorides problematic.\textsuperscript{37} By the Yamazaki–Higashi method (phosphorylation method), it is possible to obtain high molecular weight polymers from aromatic or aliphatic diacids and aromatic diamines; however, a drawback of this procedure is the strong dependence between the reactivity and electronic properties of the diamine monomers. Therefore, the use of aromatic diamines bearing electron-withdrawing groups generally leads to polyamides with low or, at most, medium molecular weights.\textsuperscript{38,39}

Molecular weight determinations were carried out by GPC. In general, high molecular weights were achieved, with number-average molecular weight ($M_n$) values ranging from 47,000 to 86,000 g/mol; GPC results also displayed low polydispersity values ranging from 1.4 to 1.7. As can be seen in Table 1, the inherent viscosities and molecular weights depended mainly on the reactivity of the diamine moiety. Therefore, the polymers from the very reactive ODA diamine showed the highest molecular weight, with inherent viscosities ranging from 1.12 to 1.70 dL/g, whereas the less reactive 6F diamine gave polymers of a much lower

### Table 1. Inherent Viscosity ($\eta_{inh}$) and GPC Values

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<tr>
<th>Polymer Code</th>
<th>$\eta_{inh}$ (dL/g)$^a$</th>
<th>$M_n$$^b$</th>
<th>$M_w$$^b$</th>
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<td>0.75</td>
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<td>0.62</td>
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<td>75,000</td>
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<tr>
<td>10-ODA</td>
<td>1.70</td>
<td>86,000</td>
<td>137,000</td>
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</table>

$^a$Measured in DMAc at a concentration of 0.5 g dL$^{-1}$ at 25 °C.

$^b$Determined by GPC with DMF containing 0.1 wt % dissolved LiBr and fractionated poly(m-phenyleneisophthalamide) as a reference.
viscosity. The polymers from MDA showed intermediate inherent viscosity values.

Polymers were also studied by spectroscopic methods: FTIR, $^1$H NMR, and $^{13}$C NMR. As an example, the FTIR spectrum of polymer 10-MDA is shown in Figure 1. A weak, fine absorption band at 1782 cm$^{-1}$ can be seen, as well as a much stronger band at 1728 cm$^{-1}$, and these bands correspond to symmetric and asymmetric C=O stretching of the imide ring, respectively. A strong band corresponding to C=N stretching can also be observed at 1340 cm$^{-1}$. $^1$H and $^{13}$C NMR spectra were also used to identify the polymers and to quantify the presence of terminal groups. As can be seen in Figure 2, no peaks attributable to final groups could be observed for...
Table 2. Mechanical and Thermal properties

<table>
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<th>Polymer Code</th>
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<th>Young’s Modulus (GPa)</th>
<th>Elongation at Break (%)</th>
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<th>$T_d$ (°C)$^a$</th>
<th>$T_{d10}$ (°C)$^b$</th>
<th>$Y_{800}$ (%)$^c$</th>
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<td>420</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Temperature of the first onset in the TGA curve. In parentheses are given $T_d$s of the corresponding unsubstituted polyamides.

$^b$ Ten percent weight-loss temperature measured by TGA at a heating rate of 10 °C/min.

$^c$ Residual weight percentage at 800 °C in nitrogen by TGA.

Figure 3. Correlation of the number of methylenic groups of the substituent to $1/T_g$ for the polymers of the ODA series.
ODA polymers, and this result can extend to polymers from MDA. However, terminal group peaks were seen in $^1$H NMR spectra of polymers from 6F, and this agrees with comparatively low molecular weights.

**Mechanical Properties**

Polymers films were tested to evaluate their tensile strength, tensile modulus, and elongation. All of them showed good mechanical properties, with tensile strengths above 100 MPa, except for the polymers prepared from 6F, which showed values around 50 MPa. The reason for this low mechanical resistance should again be the low inherent viscosity (low molecular weight) found for these polymers. As commented previously, this is because of the low reactivity of diamine 6F under the conditions of the phosphorylation reaction. The elastic moduli were 2–3 GPa, and this range can be considered acceptable for this class of polymers. The elongation values were not very high, as expected for semistiff polymers, with elongations ranging from 7 to 12%, except for the polymers containing 6F moieties, which again showed poorer resistance than the other members of the
series, with elongations at break of only 2–3%. On the basis of these results, it can be stated that these polymers have good mechanical properties, with tensile strengths and elastic moduli comparable to those of other aromatic polyamides and engineering thermoplastics.

Thermal Characterization of the Polymers

The thermal properties were investigated by DSC and dynamic TGA. The data listed in Table 2 reveal that $T_g$’s of these polymers are not very high, with values ranging from 150 to 240 °C, yet they are still high in comparison with those of conventional aliphatic polyamides and aliphatic poly(amide imide)s. The results presented in Figure 3, for the polymers from ODA, permitted us to confirm that $T_g$ of these polyamides is greatly influenced by the number of flexible units in the side substituent.

As for the diamine moiety, $T_g$ values for the polymers from MDA were the lowest in any series, whereas those of polymers from 6F were, on average, 20 °C higher. $T_g$ values for the polyamides from ODA were slightly higher, 5–10 °C, than those from MDA. This correlation is consistent with previous results$^{40,41}$ and also with the results for polymers of relatively low molecular weights prepared from diamine 6F.

The thermal stability of these polymers, as defined by the initial decomposition temperature ($T_d$) observed by dynamic TGA, is higher than 350 °C, and it is dependent on the length of the polymethylene chain. Therefore, the longer the aliphatic chain is, the higher the observed $T_d$ is. This result appears abnormal because the thermal sta-
bility of methylene chains is lower than that of aromatic moieties, as can be seen in Table 2, in which the decomposition temperatures of the corresponding unsubstituted polyamides are given. Furthermore, because there is no electronic difference for $C_3$, $C_5$, and $C_{10}$, as proved by NMR spectroscopy, it seems reasonable to presume that the thermal stability for the polymers derived from these three monomers should be very similar, in contrast to the results of TGA. Therefore, to elucidate the mechanism of the thermal degradation process, two models were prepared from aniline and the acid monomers $C_3$ and $C_{10}$ ($M_3$ and $M_{10}$), with reaction conditions similar to those applied for the synthesis of the polymers. Both models were heated in a thermobalance at 10 °C/min under an inert atmosphere, and quite similar $T_d$ values were observed, 278 and 282 °C, for $M_3$ and $M_{10}$, respectively. This difference, about 5 °C, is much lower than that found for the thermal degradation of the analogous polymers (40–50 °C). Therefore, it seems reasonable to think that the difference between the models and polymers is due to the different physical states of the samples at the degradation temperature (liquids for the models and solids or very viscous liquids for the polymers), which determines the diffusive behavior of the degradation fragments.

It can then be postulated that the initial thermal breakdown occurs just on the linkages joining the side groups to the main chain and that the temperature for the subsequent loss of the fragments (what the thermobalance actually detects) is higher for the fragments of bigger size, in our case for polymers with longer spacers.

To confirm this assumption, we carried out a PM3 semiempirical theoretical study of the homolytic breakdown for the entities shown in Scheme 3. Two of these compounds have the same structure as models $M_3$ and $M_{10}$, and the other two

### Table 3. Enthalpy of Formation of the Models and Radicals as Determined by PM3

<table>
<thead>
<tr>
<th>Radical</th>
<th>Ph0</th>
<th>Ph1</th>
<th>Ph2</th>
<th>Ph3</th>
<th>Ph4</th>
<th>Ph5</th>
<th>Ph9</th>
<th>Ph10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kcal/mol)</td>
<td>0.35</td>
<td>-18.86</td>
<td>-19.12</td>
<td>-24.37</td>
<td>-29.87</td>
<td>-35.36</td>
<td>-57.23</td>
<td>-62.69</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Radical</th>
<th>Ip0</th>
<th>Ip1</th>
<th>Ip2</th>
<th>Ip3</th>
<th>Ip4</th>
<th>Ip5</th>
<th>Ip7</th>
<th>Ip9</th>
<th>Ip10</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Model</th>
<th>M2</th>
<th>M3</th>
<th>M5</th>
<th>M10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H$ (kcal/mol)</td>
<td>-57.79</td>
<td>-62.77</td>
<td>-74.66</td>
<td>-101.98</td>
</tr>
</tbody>
</table>
correspond to the other members of the homologous series with two and five methylenic units; these have been called **M2** and **M5**.

The theoretical study has been carried out under the following assumptions. First, the pendant chain scissions take place exclusively with the formation of two radicals and with no charged species involved. Second, the recombination of the two radicals has zero activation energy, and so the enthalpy difference between the products (radicals produced from the homolytic scission) and reagent (model) should give the global reactivity for the degradation process. (A confirmation of this assumption is shown in Figure 4, in which the reaction path between both radicals to give way to model **M2** is shown). Evidently, a smaller value of $\Delta H_{\text{radicals}} - \Delta H_{\text{models}}$ indicates an easier homolytic breakdown. Third, for simplicity, no reaction between aromatic moieties and radicals is considered, and so the primary scission will denote the initial thermal degradation, without any subsequent or secondary process taken into account. This approximation is classical in this kind of theoretical study, and it was applied previously by Klein et al.\textsuperscript{42} to study the thermal degradation of aromatic polyamides by semiempirical quantum mechanics.

The enthalpies of formation of the different radicals are shown in Table 3, whereas the reaction enthalpies are shown in Table 4. The lowest reaction enthalpies, $\Delta H$, obtained for the four models always corresponded to the C(CO)O bond (the formation of Phn–Ip0), and so this bond will be a priori the most thermolabile one and the point at which the degradation process should begin. There is no meaningful difference from one model to another, and this means that the initial thermal degradation should initiate at the same temperature, as experimentally confirmed with **M3** and **M10**. When the energy is enough to break C(CO)—C\textsubscript{1} bonds, around 300 °C, the alkylphthalimido radicals are formed;

### Table 4. Enthalpy of Reaction of the Different Radicals as Determined by PM3

<table>
<thead>
<tr>
<th>Model</th>
<th>$\Delta H$ (kcal/mol)$^a$</th>
<th>Ph0 + Ip2 − M2</th>
<th>Ph1 + Ip1 − M2</th>
<th>Ph2 + Ip0 − M2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>16.11</td>
<td>2.69</td>
<td>0 (50.09)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>15.67</td>
<td>2.15</td>
<td>7.68</td>
<td>0 (49.82)</td>
</tr>
<tr>
<td>5</td>
<td>15.8</td>
<td>2.14</td>
<td>7.17</td>
<td>7.92</td>
</tr>
<tr>
<td>10</td>
<td>15.84</td>
<td>2.08</td>
<td>7.50</td>
<td>7.42</td>
</tr>
</tbody>
</table>

$a$ Normalized enthalpy of formation ($\Delta H = \Delta H_{\text{radicals}} + \Delta H_{\text{ip}} - \Delta H_{\text{model}}$). The lowest enthalpy of formation is given the value of 0 kcal/mol in each model. The real value of $\Delta H$ is given in parentheses.
having different sizes, they are trapped inside the polymer bulk, undergoing side reactions (hydrogen abstraction, radical recombination, and double-bond formation) and further decomposition. Therefore, the bigger the trapped radicals are, the slower their diffusion rate is through the polymer matrix and the greater $T_d$ is as observed by TGA.

**CONCLUSIONS**

New derivatives of isophthalic acid bearing alkylphthalimido groups as pendent substituents were prepared and successfully used as condensation monomers in combination with aromatic diamines for the synthesis of novel aromatic polyamides.

Of all the polymers prepared from the family of isophthalic acid derivatives, differing from one another only in the length of the alkylene spacer, those synthesized from diamines with electron-donor bridging groups had higher molecular weights than those prepared from diamines with electron-withdrawing bridging groups. Moreover, diamine 6F, bearing the strongly electron-withdrawing hexafluoroisopropylidene group, yielded polyamides of rather low molecular weights.

The solubility and thermal properties were greatly affected by the chemical nature of the monomers, particularly by the length of the alkylene spacers. Unlike fully aromatic polyamides, all the novel polyamides were soluble in organic polar solvents, and a linear dependence was found between the number of flexible groups in the pendent substituents and $T_g$. An unexpected trend was found for the thermal decomposition, as polyamides bearing longer alkylene spacers showed more resistance (a higher decomposition temperature) than those bearing shorter spaces.

The use of computational chemistry methods allowed us to obtain theoretical values of parameters related to monomer reactivity, bond energy, or electronic charge distribution. It provided a useful tool for corroborating the structure–property relationships experimentally observed for the monomers and polymers studied in this work.

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**REFERENCES AND NOTES**

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