Novel chalcone-based aromatic polyamides: synthesis, characterization, and properties

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ABSTRACT

Two novel diacid-based monomers have been synthesized by anchoring a benzylideneacetophenone (chalcone) moiety through an amide or ester bridge at the fifth position of the isophthalic acid ring. Two series of new polyamides bearing chalcone side chains were prepared by direct polycondensation reaction of the aforementioned dicarboxylic acids and various aromatic diamines in N-methyl-2-pyrrolidinone, using triphenyl phosphite and pyridine as condensing agents. Their molecular structure and the basic properties were investigated by nuclear magnetic resonance, Fourier-transform IR and UV–vis spectroscopy, differential scanning calorimetry, thermogravimetric analysis, and wide-angle X-ray diffraction. The inherent viscosity, molecular weights measurements (by gel permeation chromatography), water uptake, and solubility tests completed the research study. Introduction of the rigid and bulky chalcone units into the polymer side chains improved remarkably the solubility of the aromatic polyamides, endowed them with an amorphous nature, good thermal stability, and photosensitivity. The resulting polymers were obtained in good yields, inherent viscosities varied between 0.49 and 0.86 dL/g, and their relative high molecular weights conferred them film-forming properties. They were soluble in amide-type polar solvents, such as N,N-dimethylformamide, dimethyl sulfoxide, N,N-dimethylacetamide, and N-methyl-2-pyrrolidone. These polyamides had glass transition temperatures between 219 and 264 °C, and 10% weight loss temperatures in the range of 394–436 °C and around 50% residue at 700 °C in nitrogen atmosphere. The polyamides underwent a [2 + 2] photocycloaddition reaction upon UV light irradiation both in solution and film state in the absence of a photoinitiator or photosensitizer. The polymer films became insoluble in solvents as a result of the crosslinking.

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1. Introduction

Aromatic polyamides are well known as high-performance polymers due to their outstanding thermal, mechanical, and chemical properties that make them useful in applications for advanced technologies. At the same time, owing to their strong interchain forces, inherent macromolecular rigidity, or semicrystallinity aromatic polyamides are intractable materials of low solubility and high melting or softening temperatures which decrease their processability and restrict their extended applications. To overcome these drawbacks, substantial efforts have been made to modify their chemical structure in order to improve the solubility and processing conditions with protection of their high thermal stability and make easier their use in a specific field. There are various successful approaches employed to accomplish this purpose, and the most common used is the introduction of new chemical functionalities into the polyamide backbone or lateral structure, usually bulky and packing-disruptive groups into the main chain that generally form non-coplanar structures and, as a consequence, they prevent crystallization. Polymers with functional groups in the side chains are usually synthesized by two alternative methods, the first one based on the polymer reaction with functional reagents, and the second one on the polymerization of monomers with various functional groups as substituents. The main method used and reported in literature is the attachment of side chains onto the rod-like polymer backbone. In this way, the polymerization or copolymerization of monomers bearing pendant groups lead to polymers with enhanced solubility, low melting, and glass transition temperatures and often amorphous. The solubility of polyamides is frequently increased when flexible bonds such as –CH2–, –O–, –SO2–, –C(CF3)2–, or –C(CH3)2– are incorporated into the polymer backbone by decreasing crystallinity and intermolecular interactions.[1–4]

Photosensitive polymers have gained considerable attention in recent times because of their wide variety of applications such as printing plates, photoresists, photolithography, photocurable coatings, photorecorders, energy
exchange materials, microlithography, paints, compact discs, cathode ray tubes, or liquid crystal display panels. [5] Belonging to the large class of photopolymers, those containing photocrosslinkable groups have attracted remarkable interest because of their potential use as negative photoresists in the field of microelectronics. [6] Among various photocrosslinkable groups, α,β-unsaturated carbonyl unit is the best studied system. Polymers containing photosensitive moieties such as chalcone,[7–10] cinnamate,[11–13] coumarine,[14] thymine,[15] dibenzalacetone,[16–18] cinnamylidene,[19] 1,4-phenylenediacrylate,[20] 2-styrylpyridine,[21] and their derivatives both in main chains or side chains undergo crosslinking through [2π + 2π] cycloaddition reaction of the carbon–carbon double bonds upon ultraviolet irradiation. Chalcone is widely investigated because of its high photoactivity and high level of photocrosslinking upon irradiation with UV light even in the absence of photosensitizers, and used in different polymer fields, especially in photoresist technology. There are only few reports in the literature about polymers containing chalcone group in the main chain, mainly because of their poor solubility owing to the planar structure and rigid rod-like nature of chalcone moiety. Therefore, most researches focus on polymers with side-chain chalcone units.[22]

The synthesis of new types of aromatic polyamides containing chalcone pendant groups, which act as photocrosslinking units due to their photosensitive characteristics, and the study on their properties are the main objectives of this communication.

2. Experimental

2.1. Materials

5-Aminoisophthalic acid, 5-hydroxyisophthalic acid, N,N-dimethylformamide (DMF), KOH, HCl, CaCl₂, and MgSO₄ were used as received. Commercial diamines were purified before use as follows: 4,4'-oxydianiline (5a), 4,4'-methylenedianiline (5b), and 4,4'-diaminodiphenyl sulfone (5d) were vacuum sublimed, and 4,4'-hexafluorosopropylidendianiline (5c) was recrystallized from ethanol. Thionyl chloride was distilled under reduced pressure. N-Methyl-2-pyrrolidone (NMP) was vacuum-distilled twice over phosphorous pentoxide under reduced pressure and stored over 4 Å molecular sieves. Pyridine was dried under reflux over sodium hydroxide for 8 h and distilled over molecular sieves (4 Å). Triphenylphosphite (TPP) and benzene was vacuum-distilled twice over calcium hydride and then stored over 4 Å molecular sieves. Tetrahydrofuran was distilled under nitrogen from sodium wire and benzophenone. Reagent grade lithium chloride (LiCl) and calcium chloride (CaCl₂) were dried at 200 °C for 12 h under vacuum. All reagents and solvents were provided by Sigma-Aldrich Chemical Co. (Taufkirchen, Germany).

2.2. Measurements

The FT-IR spectra were recorded using a Bruker Vertex 70 Fourier transform infrared spectrometer within the wavenumber range of 600–4000 cm⁻¹ at 25 °C. ¹H and ¹³C NMR spectra were recorded using a Bruker AC 400 instrument, at 400 and 100 MHz, respectively, at room temperature with deuterated chloroform (CDCl₃) or deuterated methyl sulfoxide (DMSO-d₆) as solvents and tetramethylsilane as internal reference. Electronic absorption spectra were run on a SPECORD M42 spectrophotometer. A 500 W high-pressure mercury lamp was used as source of UV light to irradiate polymer films and solution samples without a filter, at room temperature, at various exposure periods. The polymer films were obtained by spin-casting solutions of polymers (10 mg/mL DMF) onto quartz plates. The films were dried at room temperature for 12 h under vacuum. For FTIR spectral measurements, polymer solutions (20 mg/mL DMF) were cast onto KBr windows (2 mm thick). The solvent was evaporated and the films were stored under vacuum at 100 °C for 5 h to remove the residual solvent completely. Inherent viscosity (ηinh) was measured with an Ubbelohde suspended level viscometer at a concentration of 0.5 g/dL in NMP as solvent at 25 ± 0.1 °C. Elemental analysis was done with a Perkin-Elmer 2400 Series II CHNS/O Elemental Analyzer (Perkin-Elmer, UK). The solubility was tested at a concentration of 10 mg polymer/mL in different solvents. TGA was carried out using a Mettler Toledo TGA/SDTA851e-thermogravimetric analyzer, under nitrogen flow (20 mL/min) at a heating rate of 10 °C/min from room temperature to 700 °C, and at 3–5 mg of sample mass. Water sorption measurements were determined gravimetrically at room temperature. The powdered polymer samples were dried in vacuum at 100 °C for 12 h and weighed. They were placed into a desiccator where 65% relative humidity was provided by an oversaturated aqueous solution of NaN₂ and kept for a few days until constant weight was reached. Differential scanning calorimetry (DSC) analysis was performed on a Mettler DSC 112E instrument, with heating and cooling rate of 10 °C/min in flowing nitrogen. Wide-angle X-ray scattering (WAXS) measurements were done on a Bruker AXS-D8 Avance X-ray diffractometer using CuKa radiation (ʎ = 1.54 Å), at 36 kV and 30 mA, using samples as powders. The measurements were performed at 2θ between 5 and 60°. Weight-average molecular weights (Mw) and number-average molecular weights (Mn) were obtained in DMF/0.01 mol% of LiBr via gel permeation chromatography (GPC) on a PL-EMD 950 evaporative mass detector instrument equipped with two PL gel-mixed columns based on polystyrene calibration.
### 2.3. Synthesis of monomers

#### 2.3.1. 3-(4-Carboxyphenyl)-1-phenyl-2-propen-1-one (1)

A mixture of acetophenone (7 mL, 0.06 mol) and terephthaldehydeic acid (9.0 g, 0.06 mol) was stirred in 98% ethanol (60 mL), and then an aqueous solution of KOH (40%, 12.5 mL) was added dropwise to the above mixture with constant stirring at 10–15 °C temperature. The mixture was left at room temperature overnight and then was poured into crushed ice and acidified with 2 M HCl to pH 3, and extracted with ethyl acetate. The organic layer was dried over MgSO4 and concentrated in vacuo. The residual solid was purified by recrystallization from ethanol and dried under vacuum at 60 °C. The 4-carboxychalcone (1) was obtained in a 72% yield (10.90 g) as pale yellow crystals. Elemental analysis: Calcd. for C16H11ClO2: C, 76.11; H, 4.72; O, 18.96%. UV–vis (1,4-dioxane) \( \lambda_{\text{max}} = 356 \) nm. IR (KBr disk) \( \nu = 305 \) cm\(^{-1}\). Cl, 13.06; O, 11.90%. UV–vis (1,4-dioxane) \( \lambda_{\text{max}} = 305 \) nm. IR (KBr disk) \( \nu = 356 \) nm. Cl, 13.06; O, 11.90%. UV–vis (1,4-dioxane) \( \lambda_{\text{max}} = 305 \) nm. IR (KBr disk) \( \nu = 305 \) cm\(^{-1}\).

#### 2.3.2. 4-(3-Oxo-3-phenyl-prop-1-enyl)benzoyl chloride (2)

To a mixture of chalcone 1 (10 g, 0.06 mol) and a few drops of anhydrous DMF in dry benzene (50 mL), freshly distilled thionyl chloride (11.5 mL, 0.16 mol) was added for about 20–30 min at –10 to –5 °C under nitrogen atmosphere. The mixture was raised to 0 °C and the reaction mixture was kept at this temperature for 30–60 min and then refluxed for 3 h. The solvent and excess of thionyl chloride was evaporated under reduced pressure. The crude product was dissolved in cold ethylacetate, filtered, and the solvent was removed by distillation under reduced pressure to obtain 6.3 g of acid chloride 2 (75% yield). Elemental analysis: Calcd. for C16H11ClO2: C, 76.18; H, 4.79; O, 19.03; Found: C, 76.11; H, 4.72; O, 18.96%.

#### 2.3.3. 5-[4-(3-Oxo-3-phenyl-prop-1-enyl)benzoyl]oxybenzene-1,3-dicarboxylic acid (3)

Under argon atmosphere, to a solution of 2.73 g of 5-hydroxisophthalic acid (0.015 mol) and 2.5 mL of triethylamine (0.018 mol) in 20 mL of anhydrous THF, a solution of 4.87 g of acid chloride 2 (0.018 mol) in 25 mL of THF was gradually added at 0 °C. The reaction mixture was stirred at room temperature for 24 h, and then it was poured into an excess amount of distilled water. The mixture was extracted with chloroform, and the organic layer was dried over sodium sulfate. After the solvent was removed under reduced pressure, the product was purified by recrystallization from hexane/ethyl acetate (1/2 by vol.) to give 3 as a yellow powder; yield: 4.80 g (77%). Elemental analysis (%): Calcd. for C24H16O7: C, 69.23; H, 3.87; O, 26.90; Found: C, 69.48; H, 3.99; O, 27.06. UV–vis (1,4-dioxane) \( \lambda_{\text{max}} = 299 \) nm. IR (KBr disk) \( \nu = 3449 \) (acid O–H stretching). 3087 (acidic C–H stretching), 2653 (OH, carboxylic acid), 1724 (C=O stretching, ester), 1669 (C=O stretching, ketone), 1601 (C=O stretching, chalcone and aromatic), 1569 and 1508 (C=O stretching, aromatic), 1480 (aryl stretching), 1269 (C=O bending, ketone), 1238 (C=O bending, ketone), 1228 (CH=, a).
2.4. Synthesis of polymers

In a typical experiment, polyamide PA6a was prepared as follows: under inert atmosphere, 0.41 g (0.001 mol) of dicarboxylic acid monomer 4, 0.2 g (0.001 mol) of diamine 5a, 1.80 g (0.016 mol) of anhydrous CaCl₂, and 0.6 g (0.014 mol) of anhydrous LiCl were dissolved in a mixture of anhydrous NMP (25 mL) and pyridine (5 mL) by heating with stirring at 80 °C. The temperature was then raised to 110 ± 5 °C and a solution of TPP (0.57 mL, 0.0024 mol) in 1 mL anhydrous pyridine was added dropwise. The solution was refluxed for 5 h. After cooling, the viscous solution was poured into a large amount of stirring methanol. The precipitated polymer was washed successively with methanol and hot water to remove the unreacted monomers and solvent. The polymer sample was filtered and dried under vacuum at 80 °C for 12 h and then kept in a vacuum desiccator. The yield was 88% (0.51 g of polymer). The inherent viscosity of the polymer PA6a in NMP was 0.79 dL/g, measured at a concentration of 0.5 g/dL at 25 °C.

3. Results and discussion

3.1. Synthesis of monomers

The dicarboxylic acid monomers 3 and 4 were prepared by a sequence of three reactions. Chalcone derivative 1 was synthesized by a Claisen–Schmidt reaction from acetophenone and 4-carboxybenzaldehyde in the presence of ethanolic KOH with the exclusive formation of the trans-isomer, which by further treatment with thionyl chloride gave 4-(chlorocarbonyl)chalcone 2; the latter reacted with 5-hydroxyisophthalic acid or 5-aminoisophthalic acid in the presence of TeA as HCl scavenger to produce the dicarboxylic acid monomers 3 and 4, respectively (Scheme 1). The chemical structure and purity of compounds 1–4 were confirmed by elemental analysis, FTIR, 1H, and 13C-NMR spectroscopy. The results found in elemental analysis of these compounds corresponded closely to the calculated ones, demonstrating that the expected structures were obtained. The FT-IR spectra of all compounds showed a medium band at 1665 (1), 1666 (2), 1669 (3), and 1663 (4) cm⁻¹ attributed to ν(C=O) of chalcone and a strong band at around 1601–1604 cm⁻¹ corresponding to ν(C=C) of chalcone and benzene ring. The sharp and medium bands observed in 1569–1502 cm⁻¹ region were ascribed to aromatic ν(C=C) stretching vibration. The 1H-NMR spectra of the synthesized chalcone derivatives
3.2. Synthesis and characterization of polymers

Two series of novel chalcone-based aromatic polyamides, PA6(a–d) and PA7(a–d), were prepared according to the phosphorylation technique introduced by Yamazaki and co-workers.[23] This direct polycondensation reaction is a one-step pathway used to produce soluble aromatic polyamides from equimolar amounts of dicarboxylic acid 3 or 4 and aromatic diamines 5(a–d) in NMP solution containing dissolved CaCl₂ and LiCl in the presence of TPP and pyridine as condensing agents (Scheme 1). All polymerization reactions proceeded homogeneously throughout the reaction and gave clear and viscous polymer solutions. The resulted polymers were slightly colored in yellow, orange, or red.

Structural features of these polyamides were supported by FT-IR and ¹H NMR spectroscopy. The FT-IR spectra exhibited a broad band in the range of 3300–3450 cm⁻¹ ascribed to \( \nu_{\text{NH}} \) (amide A), and two strong bands in the range of 1650–1670 cm⁻¹ and 1710–1730 cm⁻¹, attributed to \( \delta_{\text{NH}} \) and \( \nu_{\text{CO}} \) (amide I) respectively. The presence of other strong bands at 1550–1595 cm⁻¹, characteristic to combined N–H bending and C–N stretching (amide II), and at 1350 cm⁻¹ (amide III) assigned to N–H deformation.

The compounds synthesized in the present work were slightly colored, and therefore electronic spectra recorded in 1,4-dioxane solutions revealed that a \( \pi \rightarrow \pi^* \) transition having a high intensity took place. All compounds showed an absorption maximum (\( \lambda_{\text{max}} = 299–356 \) nm) which is attributed to the transition through the chalcone system for the trans-isomer.
confirmed the amic structure. The presence of chalcone pendant group in polyamide structures was evidenced by the relevant bands located around 1665 cm$^{-1}$, ascribed to the carbonyl stretching, around 1600 cm$^{-1}$ attributed to $\nu(-C=\equiv-C-)$ vinyl group and around 980 cm$^{-1}$ (out-of-plane bending vibration of C–H in the vinylene linkage).

The $^1$H NMR spectra of all the polymers presented a singlet in the downfield (around 10.5–11.0 ppm) attributed to amide proton from the NH–CO linkage in the main chain. The appearance of the two signals assigned to N–H protons of amide groups in the spectra of the polymers belonging to the series PA7(a–d) indicated the presence of two different amide groups in the polymer backbone and side chain. Besides the peaks particular to chalcone side chain and isophthalic ring, in the aromatic region appeared new signals ascribed to the protons from diamine structure (Figure 3). Similar observations were valid by the examination of the $^{13}$C NMR spectra (Figure 4). In addition, the resonance signals at 166.8 and 166.4 ppm proper to the carbonyl carbons of the carboxyl group in monomers 3 and 4, respectively, disappeared and new resonance signals ascribed to the carbonyl carbons from new generated amide groups appeared at around 164.5 ppm.

These results further supported that the polyamides had the expected chemical structures.

As shown in Table 1, the resulting PA6 and PA7 had reasonably good values of inherent viscosity placed in the range of 0.49–0.79 and 0.53–0.86 dL/g, respectively. In the series PA6, the lower value corresponded to the polymer PA6d derived from diamine 5d with a low reactivity due to the presence of the sulfone electron-withdrawing group, and the higher one belonged to the polymer PA6a derived from the more reactive diamine 5a. Polyamides in the series PA7(a–d) had slightly higher values probably due to the supplementary intermolecular hydrogen bonds formed between amide groups in the side chains, and the values did not rank similarly to those of the series PA6.

The solubility was determined by stirring 10 mg of polymer with 1 mL of solvent for 24 h at room temperature. All the polymers are soluble in aprotic polar solvents such as NMP, DMF, DMSO, DMAc, and in protic $p$-cresol and have moderate solubility in less polar THF, pyridine, chloroform, and 1,4-dioxane. They are insoluble in common organic solvents, such as benzene, toluene, xylene, methanol, ethanol, and methylene chloride, even on heating at 50 °C for the same time (Table 2). The presence of chalcone as
Figure 3. $^1$H NMR spectrum of polyamide PA6c.

Figure 4. $^{13}$C NMR spectrum of polyamide PA6c; the peaks corresponding to tetrasubstituted C and trifluoromethyl CF3 were not observed.
The isothermal water absorption of polyamides PA6(a–c) and PA7(a–c) was measured to evaluate their hydrophilicity. Generally, the ability of polymers to absorb water is due to the presence of hydrophilic groups. One of them, the polar amide group, is able to act as hydrogen-bond donors for water, while carbonyl group from the ester moiety is known as the primary hydrogen-bond acceptor. Consequently, both of them display similar interactions with water. The presence of bulky side groups increases the free volume of the structural unit, which facilitates the accessibility of water among polymer chains. The experimental results evidenced that water was more tightly bound to the amide carbonyl group than to the ester carbonyl group in the pendant chains. After exposure for 80 h, the water uptake of the aromatic polyamides PA6(a–c) and PA7(a–c) ranged between 3.42 and 4.57%, and between 5.01 and 6.38%, respectively (Table 1). The lowest water absorption values of samples PA6c and PA7c were attributed to the presence of –CF3 groups having hydrophobic properties.

The molecular weights of all the polyamides were sufficiently high to permit the formation of transparent and flexible films by casting from their DMF solutions. The GPC curves indicated that \( M_w \) values of the polyamides were in the range of 52,200–68,700, and the polydispersity index \( M_w/M_n \) varied from 1.8 to 2.5 (Table 1). The \( M_w \) values in the PA6(a–d) series were slightly smaller than those of the PA7(a–d) series probably because the steric hindrance between the two phenyl rings through ester linkage is greater (compared with the amide bridge) and electronic interactions between side chains and backbone are minimal. The same arguments could explain the difference between the values of glass transition temperature \( T_g \) of the two series of polymers (Table 3). The \( T_g \) values were obtained from DSC curves of the polyamides, which evidenced the thermal behavior of typical amorphous polymers.
Table 1. Values of inherent viscosity, water uptake, and molecular weights of the polyamides PA6(a–d) and PA7(a–d).

| Polyamide | η_{inh} | Water uptake (%) | M_a<sup>a</sup> (g/mol) | M_w<sup>b</sup> (g/mol) | M_w/M_n |
|-----------|---------|------------------|---------------------------|--------------------------|---------|
| PA6a      | 0.77    | 4.57             | 28,200                    | 64,800                   | 2.3     |
| PA6b      | 0.64    | 4.36             | 26,900                    | 59,100                   | 2.2     |
| PA6c      | 0.58    | 3.42             | 27,800                    | 55,600                   | 2.0     |
| PA6d      | 0.49    | 4.44             | 29,000                    | 52,200                   | 1.8     |
| PA7a      | 0.81    | 5.93             | 28,600                    | 68,700                   | 2.4     |
| PA7b      | 0.86    | 5.65             | 26,100                    | 65,300                   | 2.5     |
| PA7c      | 0.63    | 5.01             | 29,100                    | 61,100                   | 2.1     |
| PA7d      | 0.54    | 6.38             | 26,500                    | 58,300                   | 2.2     |

<sup>a</sup>Inherent viscosity measured in NMP (0.5 g/dl concentration) at 25 °C.
<sup>b</sup>By GPC measurements, polystyrene standards, DMF as eluent.

Table 2. Solubility of the aromatic polyamides<sup>a</sup>.

| PA       | DMF, DMSO, NMP, DMAc, <em>p</em>-cresol | THF | Py | Dioxane | CHCl_3 |
|----------|----------------------------------------|-----|----|---------|--------|
| PA6a     | +                                      | ±   | +  | ±       | ±      |
| PA6b     | +                                      | ±   | +  | ±       | ±      |
| PA6c     | +                                      | h   | ±  | ±       | ±      |
| PA6d     | +                                      | h   | ±  | ±       | ±      |
| PA7a     | +                                      | h   | h  | ±       | ±      |
| PA7b     | +                                      | h   | h  | ±       | ±      |
| PA7c     | +                                      | h   | h  | ±       | ±      |
| PA7d     | +                                      | h   | h  | ±       | ±      |

<sup>a</sup>Solubility: +soluble at room temperature; +h soluble on heating; ±partially soluble or swelling on heating.

Table 3. Thermal properties and spectroscopic data of polyamides PA6(a–d) and PA7(a–d).

| Polyamide | T<sub>g</sub> (°C) | IDT (°C) | PDT (°C) | Char yield<sup>d</sup> (%) | λ<sub>max</sub> (nm) |
|-----------|--------------------|----------|----------|-----------------------------|-------------------|
|           |                    |          |          |                             | Solution | Film  |
| PA6a      | 219                | 338      | 409      | 48                          | 305      | 307   |
| PA6b      | 227                | 331      | 398      | 50                          | 302      | 304   |
| PA6c      | 230                | 339      | 408      | 51                          | 295      | 297   |
| PA6d      | 242                | 342      | 436      | 53                          | 298      | 301   |
| PA7a      | 226                | 336      | 402      | 47                          | 317      | 319   |
| PA7b      | 241                | 338      | 394      | 49                          | 315      | 318   |
| PA7c      | 253                | 341      | 403      | 52                          | 308      | 310   |
| PA7d      | 264                | 343      | 429      | 49                          | 310      | 312   |

<sup>a</sup>Glass transition temperature determined from DSC measurements at a heating rate of 10 °C/min in N_2 atmosphere.
<sup>b</sup>Onset decomposition temperature in TGA at a heating rate of 20°C/min in nitrogen.
<sup>c</sup>Polymer decomposition temperature at 10% weight loss (T<sub>10</sub>) in nitrogen at a heating rate of 20 °C/min.
<sup>d</sup>Residual weight at 700 °C in nitrogen.
<sup>e</sup>λ<sub>max</sub>: maximum wavelength of UV absorption.

Polymers. Generally, the presence of the bulky side chains influences T<sub>g</sub> of the substituted polyamides by the asymmetry and irregularity which disrupt the chain interactions and by the rigidity characteristic to the polymer which restricts the free rotation of the polymer backbone. The T<sub>g</sub> values of the polymers under study were controlled by the planar and rigid structures of the chalcone unit which restricted the mobility of the polymer chain, and led to a higher T<sub>g</sub> and, on the other hand, the lack of linearity of the meta-linked dicarboxylic acid segments generated an increased flexibility because of the two possible conformations of this group in the chain, resulting in a lower T<sub>g</sub>. Polyamides PA6(a–d) and PA7(a–d) had the T<sub>g</sub> values positioned in the range of 219–242 and 226–264 °C, respectively, and they follow the decreasing order of the chain flexibility and steric hindrance of the polymer backbone. Polyamides derived from diamine 5d had the highest T<sub>g</sub> values due to the high polarity and rigidity of the –SO<sub>2</sub>– group, which gave rise to highly efficient chain packing. Similarly could be explained the higher T<sub>g</sub> values of the polymers derived from diamine 5c in comparison with those containing diamine 5b, and so on. In the series PA6(a–d), the T<sub>g</sub> values are lower because the absence of the amide linkage in the side chain diminishes the density of hydrogen bonds, although the intermolecular hydrogen bonding between ester and amide groups cannot be excluded. As no endothermic peak attributable to melting temperature was observable on DSC curves, the polyisophthalamides reported herein could be considered as amorphous materials with high T<sub>g</sub> values.
The thermal stability of the polymers was further evaluated by thermogravimetric analysis (TGA) in nitrogen atmosphere in the range 25 °C–700 °C. The temperature at 5 and 10% weight loss ($T_5$ and $T_{10}$) were read on the original thermograms (Figure 5) and summarized in Table 3. These polymers exhibited good thermal stability with insignificant weight loss up to 400 °C, although they began to decompose at about 330 °C and showed distinct one-stage degradation pattern. The initial decomposition temperature ($T_{\text{onset}}$) can be associated with the thermal degradation of ketoethylenic group from chalcone side chain, while the major decomposition peaks appeared around 525 °C–600 °C and they may be attributed to the cleavage of the amide bonds. All the polyamides left around 50 wt % char residue at 700 °C in nitrogen.

Wide-angle X-ray diffractograms of polyamides are illustrated in Figure 6. The curves had wide peaks that are characteristic of amorphous polymers. The polymers did not show any characteristic peaks of well-defined long-range order structure or crystallinity.

3.2.1. Optical properties

The photoreaction of chalcone group occurs under irradiation with relatively longer wavelength UV light than that of the cinnamoyl group because of the closer match between the absorption spectrum of the chalcone group and the emission spectrum of a mercury arc UV light source (365 nm). The photocrosslinking properties of the polymer samples were examined in 1,4-dioxane solutions and in film state (in the absence of photoinitiators), and the values of $\lambda_{\text{max}}$ are given in Table 3. UV–vis absorption peaks of the polyamides in dilute 1,4-dioxane solutions (1.8 mg/mL) showed absorption maxima slightly blue-shifted (2–3 nm) relative to the corresponding polymer films, suggesting that no relevant $\pi$–$\pi$ interaction aggregations between the polymer chains took place. The UV absorption spectra of the polymer PA6a before and after irradiation are shown in Figure 7. Similarly to cinnamoyl chromophore, both trans-cis isomerization and dimerization of chalcone are expected by UV irradiation. The isomerization takes place through a rotation mechanism from the trans to the cis conformation when the $\pi$-electron of the C=C double bonds are excited by UV light. The dimerization is a bimolecular reaction which results in the crosslinking of the polymer chains due to the generation of cyclobutane rings through a [2 + 2] cycloaddition of the C=C double bonds.[24] The polymer PA6a showed an absorption maximum at 305 nm which is attributed to the transition through the chalcone system for the trans-isomer. The intensity of this absorption decreased fast upon exposure to UV light which indicated the destruction of conjugation in the entire $\pi$-electron system, either due to dimerization or trans-cis isomerization. At the same time, an increase in the absorption at 241 nm was attributed to the photochemical product. The isosbestic point located at 271 nm indicated equilibrium between two species demonstrating that only one process occurred exclusively and only one photochemical product is formed. Further photoinitiation was accompanied by deviations from the isosbestic point, meaning that another photochemical process started and more products were generated, and the speed of conversion slowed down. The peaks of both photochemical products, the cis-isomer and the dimer, overlapped each other. After 25-min exposure, there were no changes in the spectra which indicated that the resulted photoproducts (cyclobutane-type dimers) were stable.

Closely related to polymer solutions, polymer films exhibited shape-similar absorption bands. As expected, the rate of photodimerization was much faster in the solution than that occurring in film state. Figure 8 evidences the disappearance of C=C double bond in terms of $A_0$ and $A_T$ which were absorption intensities after irradiation at time $t = 0$ and $t = T$, respectively, for polymer PA6b both in solution and film state. It must be mentioned that the UV-exposed polymer films became insoluble in organic solvents and this was a further evidence for the occurrence of photocrosslinking reaction of the chalcone group. From the above results, one can remark that the copolymers with chalcone as a pendant moiety have a high photosensitivity and it is expected that they might be useful for negative photoresists applications.

The photoreaction of the olefinic –C=C– double bonds of the chalcone group was further substantiated by FTIR spectroscopy. Some changes in the infrared spectra occurred upon UV irradiation. The spectral band from the ethylenic double bond is normally overlapped with the absorption band of the –C=C– double bond in benzene ring (1600 cm$^{-1}$). Consequently, the –C=C– stretching vibration mode at 1600 cm$^{-1}$ decreased significantly for a long time UV exposure (120 min). In addition, the intensity of the C=O unsaturated ketone carbonyl stretching band at 1665 cm$^{-1}$ decreased with the UV exposure time, and a new band shifted to longer wavenumbers (1685 cm$^{-1}$) ascribed to a saturated ketone carbonyl stretching vibration that appeared in the FTIR spectra of the polymer films on prolonged UV irradiation, although the change was not clearly observed for all polymers for the same time of illumination.

4. Conclusion

Two new condensation monomers derived from isophthalic acid bearing chalcone as substituent were prepared and successfully used in reaction with various aromatic diamines to synthesize novel aromatic polyamides. The presence of the side chains rendered the polyamides
soluble in polar aprotic solvents and, on the other hand, decreased their thermal stability as all the polymers showed an initial decomposition temperature in N₂ of about 340 °C. These polyamides had glass transition temperatures between 219–264 °C, and 10% weight loss temperatures in the range of 394–436 °C and around 50% residue at 700 °C in nitrogen atmosphere. The nature of the aromatic diamine influenced the value of Tg, the higher ones belonging to polyamides derived from 4,4′-diaminodiphenyl sulfone. All the polymers were essentially amorphous because they did not show diffraction peaks of crystalline order when investigated by wide-angle X-ray diffraction, and no melting endotherm was observed by DSC. The chalcone chromophore into the polymers structure explained their photosensitivity and, as a result, UV irradiation induced trans-cis isomerization and dimerization reactions in polymer solutions and films.

Disclosure statement

No potential conflict of interest was reported by the author.

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