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# Polycondensates of 2'-(Chalcone-4-Oxy)-Ethyl-3,5-Diaminobenzoate with Some Aromatic Dicarboxylic Acids

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*A new set of polycondensates with –CO–NH– groups was synthesized by the direct reaction of 2'-(chalcone-4-oxy)ethyl 3,5-diaminobenzoate with various aromatic dicarboxylic acids using phosphorylation protocol. The polymers were produced in high yields and with moderate inherent viscosities (0.62–0.76 dL/g). The obtained polyamides were essentially amorphous as revealed by differential scanning calorimetry (DSC) and X-ray diffraction (XRD) measurements and are readily soluble in a variety of aprotic polar solvents affording films from their solutions. They showed glass-transition temperatures ranging from 216 to 254°C and were thermally stable with 10% weight loss temperatures over 380°C, in nitrogen atmosphere. UV spectroscopy was used in order to confirm the presence of oxyethylchalconyl pendant group in the polymer structures.*

**Keywords** polycondensates, polyamides, Yamazaki-Higashi reaction, chalcone, oxyethyl segment

## Introduction

Aromatic polyamides belong to a polycondensates class and have generated tremendous interest as high-performance polymers having excellent mechanical properties and good thermal stability. In their continuing investigations, the researchers have reported design and synthesis of novel polyamides in order to improve the processability of these polymers. The incorporation of voluminous pendant substituents along the polymer main chain of polyamides either on the amidic nitrogen or on the aromatic rings is one of the various attempts tested. Such a modification brings enhancement in the solubility of the polyamides in organic solvents while trying not to modify their thermal properties significantly (1–6).

Direct polycondensation of *in situ* activated dicarboxylic acids with diamines is a useful approach developed by Yamazaki and Higashi for synthesis of polyamides under mild conditions (7–9).

Different combinations of monomers containing various substituents are used for the design of new polyamide structures with pendant groups by a polycondensation reaction. Moreover, the obtained polymers can exhibit new properties tailored for

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specific applications. Numerous investigations have been focused on the polymers with  $\alpha,\beta$ -unsaturated carbonyl pendant groups of chalcone and cinnamate type (10–16).

In this paper, we present the synthesis of a new set of polyamides bearing pendant extended chalcone groups using triphenyl phosphite (TPP)-mediated polycondensation. The characterization of compounds was also accomplished.

## Experimental

### Materials

Acetophenone, 4-hydroxybenzaldehyde, 1,3-dioxolan-2-one (ethylene carbonate), 3,5-dinitrobenzoyl chloride, ammonium formate, zinc, terephthalic acid, isophthalic acid, 4,4'-biphenyldicarboxylic acid and 2,6-naphthalenedicarboxylic acid were obtained from Fluka and used as purchased. Triphenyl phosphite (Fluka) was purified by distillation at reduced pressure and stored over  $\text{CaH}_2$ . Calcium chloride (Fluka) was dried in vacuum at 200°C overnight. The solvents were dried and distilled just before use.

### Measurements

Infrared and  $^1\text{H-NMR}$  spectra were acquired on a Bomem-MB-104 Type FT-IR spectrophotometer and a Bruker AC 250 instrument, respectively. UV-VIS absorption spectra were recorded on a SPECORD M 42 Carl Zeiss Jena spectrophotometer. The samples were irradiated with a 500 W high-pressure mercury lamp. The inherent viscosities of polyamides were carried out on an Ubbelohde suspended level viscometer for solutions of 0.5 g/100 mL in N-methyl-2-pyrrolidinone (NMP), at  $25 \pm 0.1^\circ\text{C}$ . The glass transition temperatures were determined with a METTLER DSC 112E differential scanning calorimeter at a heating rate of  $10^\circ\text{C}/\text{min}$ . Thermogravimetric analysis (TGA) was performed on a F. Paulik Derivatograph in air/nitrogen atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$ . Water absorption values of the polyamide films were calculated from the weight differences between the films dried and soaked in water. The films were obtained by dissolving about 0.75 g of the polyamide sample in 7.5 mL DMSO and casting the polymer solution on glass plates followed by drying in an oven at  $120^\circ\text{C}$  overnight. Test samples were previously conditioned for 24 h at  $50^\circ\text{C}$  before immersing them into deionized water at  $23 \pm 1^\circ\text{C}$  for 24 h in accordance to ASTM D 570. The X-ray diffraction data were performed on a PW 1830 Philips diffractometer (Ni-filtered  $\text{Cu-K}_\alpha$  radiation of wavelength 0.1542 nm) in the reflection mode over the range of diffraction angles ( $2\theta$ ) from 5 to  $35^\circ$ , at room temperature. The voltage and tube current were 40 kV and 30 mA, respectively.

### Diamine Monomer Synthesis

*Synthesis of 4-Hydroxychalcone (3-(4-Hydroxyphenyl)-1-phenyl-2-propen-1-one).* 6.10 g (50 mmol) of 4-hydroxybenzaldehyde was added under stirring to a 50 mL pyridine cold solution, which contains 7.2 g (60 mmol) of acetophenone. The mixture was allowed to heat at  $40^\circ\text{C}$  and then piperidine (5 mmol) was added to it dropwise with constant stirring. Stirring was continued for a further 6 h. The synthesized compound formed a cream white precipitate on pouring of the reaction mixture into 250 mL of ice water acidified with concentrated HCl under vigorous stirring. The product was filtered off, washed with water several times, and recrystallized from methanol to give 80% yield.

m. p. 182°C.  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 6.76–8.18 (m, 9H, aromatic), 7.38 (d, 1H,  $-\text{CH}=\text{CH}-\text{C}(\text{O})-$ ), 7.72 (d, 1H,  $\text{Ph}-\text{CH}=\text{CH}-$ ).

*Synthesis of 4-( $\beta$ -Hydroxyethoxy)chalcone.* A mixture of 6.72 g (30 mmol) 4-hydroxychalcone, 2.64 g (30 mmol) ethylene carbonate and 0.05 g KI, as catalyst, was heated to 165–170°C under nitrogen for about 4 h until  $\text{CO}_2$  evolution ceases. The unreacted ethylene carbonate and catalyst were removed by washing the reaction mixture with water ( $3 \times 100$  mL). The product was recrystallized from chloroform. Yield 84%, m.p. 54°C.  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 6.74–8.14 (m, 9H, aromatic), 7.35 (d, 1H,  $-\text{CH}=\text{CH}-\text{C}(\text{O})-$ ), 7.70 (d, 1H,  $\text{Ph}-\text{CH}=\text{CH}-$ ), 4.15, 4.05 (2t, 4H,  $\text{Ar}-\text{O}-\text{CH}_2-$  and  $-\text{CH}_2-\text{OH}$ ).

*Synthesis of 4'-( $\beta$ -Hydroxyethoxy)chalconyl-3,5-dinitrobenzoate.* 4-( $\beta$ -Hydroxyethoxy)chalcone (5.36 g, 20 mmol) and triethylamine (4.2 mL, 30 mmol) were dissolved in 30 mL of dichloromethane. A solution of 3,5-dinitrobenzoyl chloride (5.52 g, 24 mmol) in 30 mL  $\text{CH}_2\text{Cl}_2$  at 0°C was slowly added to the stirred solution. The whole mixture was stirred for 4 h at 30°C, and then washed with 50 mL of 0.5 N HCl solution, 50 mL of 0.5 N  $\text{NaHCO}_3$  and 100 mL NaCl solution (10%). The organic layer was dried over anhydrous  $\text{MgSO}_4$  and then evaporated to dryness. The residue was purified using ethyl acetate as a crystallization solvent. Yield 86%, m.p. 136–138°C. N analysis  $\text{C}_{24}\text{H}_{18}\text{N}_2\text{O}_8$  (462.418): Calcd% (Found%) N, 6.05 (6.09).  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 7.05–8.50 (m, 12 H, Ar), 7.75 (d, 1H,  $-\text{CH}=\text{CH}-\text{Ph}$ ), 7.40 (d,  $J = 16.1$  Hz, 1H,  $-\text{CH}=\text{CH}-\text{CO}$ ), 4.12 (t, 2H,  $\text{Ar}-\text{O}-\text{CH}_2-$ ), 3.9 (t, 2H,  $-\text{CH}_2-\text{OOC}-$ ).

*Synthesis of 4'-( $\beta$ -Hydroxyethoxy)chalconyl-3,5-diaminobenzoate.* The reduction reaction was performed at room temperature for a period of 30 min as follows: to a solution containing 4'-( $\beta$ -hydroxyethoxy)chalconyl-3,5-dinitrobenzoate (3.62 g, 10 mmol), 50 mL ethanol and 1.0 g of ammonium formate zinc dust (0.76 g, 12 mmol) was added portionwise under vigorous stirring. The reaction mixture was filtered off and the filtrate was evaporated to obtain the product. It was extracted with dichloromethane ( $3 \times 50$  mL), washed thoroughly with 10% NaCl solution ( $2 \times 50$  mL) and water ( $3 \times 50$  mL) to remove ammonium formate and subsequently dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The solvent was removed under reduced pressure and the product was recrystallized from methanol. Yield 90%. m.p. 143–145°C. N analysis  $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4$  (402.456): Calcd. % (Found%) N, 6.96 (7.03).  $^1\text{H}$  NMR (DMSO- $d_6$ ),  $\delta$  (ppm): 6.80–8.30 (m, 12 H, Ar), 7.75 (d, 1H,  $-\text{CH}=\text{CH}-\text{Ph}$ ), 7.40 (d,  $J = 16.1$  Hz, 1H,  $-\text{CH}=\text{CH}-\text{CO}$ ), 4.0 (t, 2H,  $\text{Ar}-\text{O}-\text{CH}_2-$ ), 4.45 (t, 2H,  $-\text{CH}_2-\text{OOC}-$ ), 3.72 (s, 4H,  $-\text{NH}_2$ ).

### Polyamide Synthesis

The synthesis of polyamide PT is presented as a typical phosphorylation procedure for the preparation of all polyamides and was as follows:

A mixture of terephthalic acid (1.66 g, 10 mmol), NMP (20 mL), pyridine (8 mL) and calcium chloride (4 g) was stirred at room temperature until all solids dissolved. Then 4'-( $\beta$ -hydroxyethoxy)chalconyl-3,5-diaminobenzoate (3.72 g, 10 mmol), triphenyl phosphite (8 mL) and 20 mL NMP were quickly added and the solution was heated with stirring at 120°C for 4 h under a nitrogen atmosphere. The resulting viscous solution was poured slowly into 300 mL of stirring methanol and a fibrous precipitate polymer was obtained. The product was isolated by filtration, washed with a large amount of methanol and hot water and dried. The yield was almost quantitative.

## Results and Discussion

### Polymer Synthesis

Synthesis of polyamides (PI, PT, PD, PN) was performed in five steps starting with a condensation reaction between an active methylene compound (acetophenone) and 4-hydroxybenzaldehyde (Scheme 1).

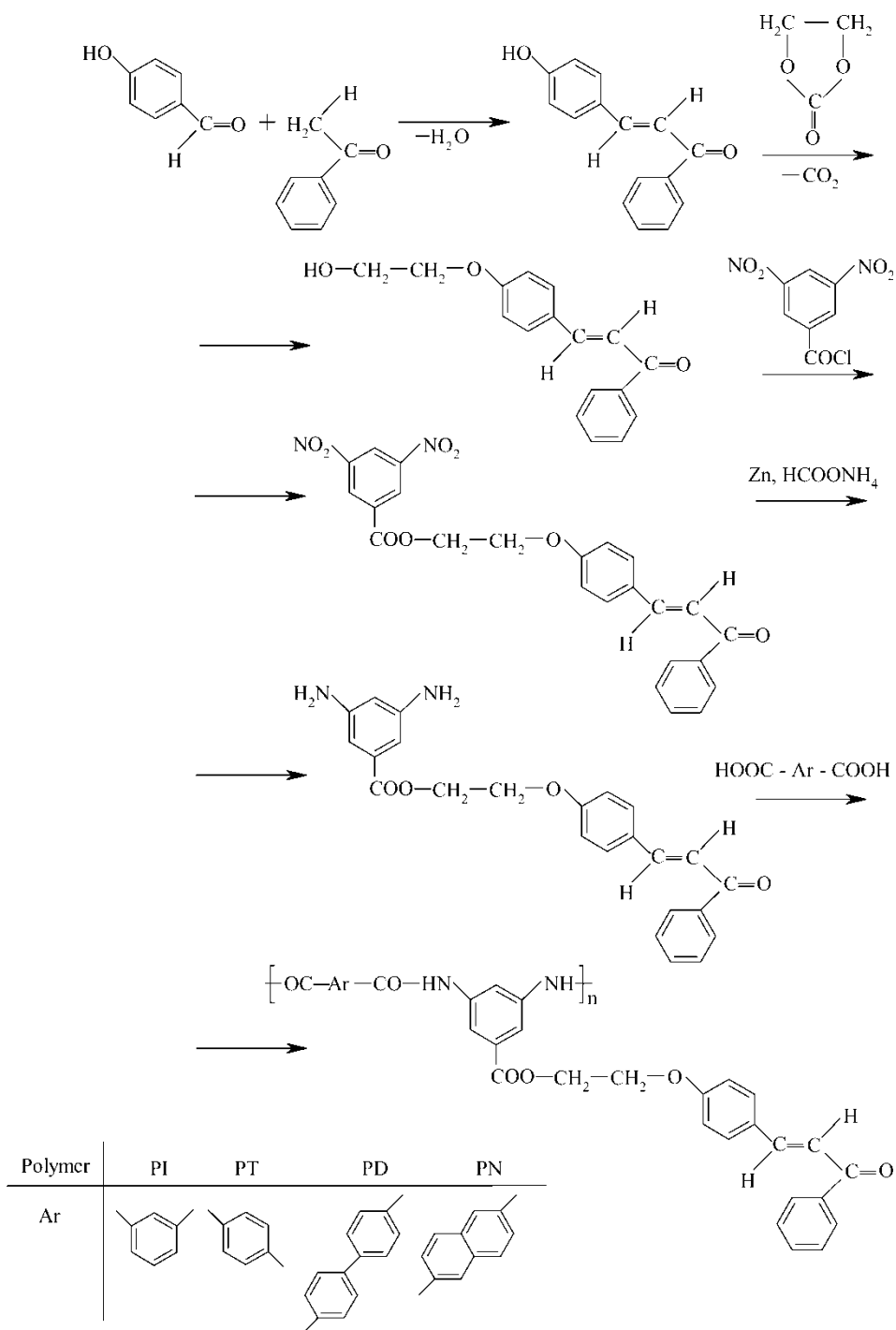
This C–C bond-forming reaction took place in the presence of an amine catalyst, namely piperidine and pyridine as solvents to afford 4-hydroxychalcone. Due to good solubility of piperidine in organic and aqueous media, the use of this compound as catalyst is more suitable for purification and analysis of product than an inorganic basic catalyst. 4-Hydroxychalcone reacted subsequently with ethylene carbonate and an alkoxylation reaction occurred leading to 4-( $\beta$ -hydroxyethoxy)chalcone. It is known that alkylene carbonates are quite versatile and undergo reaction with aliphatic and aromatic hydroxyl, amine, thiol functional groups *via* an alkoxylation mechanism, yielding the corresponding hydroxyalkyl derivative and carbon dioxide byproduct. Most notably is that alkylation employing alkylene carbonates does not require the use of solvent (17, 18). Subsequent treatment with 3,5-dinitrobenzoyl chloride gave 4'-( $\beta$ -hydroxyethoxy) chalconyl-3,5-dinitrobenzoate. It is preferable to use acid chlorides because they frequently react quantitatively and often rapidly. The esterification was performed in dichloromethane as a solvent and in the presence of triethylamine, which is usually added to neutralize the hydrogen chloride. Dinitro compound was catalytically hydrogenated at room temperature to the corresponding diamine by means of zinc/ammonium formate system. The zinc powder was activated, prior to use, by treating with HCl, washing with water and ether according to the literature (19, 20).

The direct amidation reaction was promoted as a route to synthesize the polyamides with chalcone pendant groups extended with oxyethylene spacer segments from 4'-( $\beta$ -hydroxyethoxy)chalconyl-3,5-diaminobenzoate and four aromatic dicarboxylic acids. Metal salts, such as  $\text{CaCl}_2$  as a solubility enhancer and triphenyl phosphite/pyridine system as a condensing promoter have been chosen to facilitate polyamides generation. All polycondensations proceeded homogeneously throughout the reaction, under nitrogen atmosphere at 120°C and fiber-like polyamides with moderate inherent viscosities were quantitatively obtained.

### Polymer Characterization

Table 1 shows some characteristics of polyamides. The polymers exhibited moderate inherent viscosities ranging from 0.62 to 0.76 dL/g. The elemental analysis of the nitrogen content in the polyamides was in good agreement with the theoretical amount.

The molecular structure of the polyamides was verified by FT IR and  $^1\text{H}$  NMR spectroscopy. The typical IR bands at 3400–3300  $\text{cm}^{-1}$  (amide A,  $>\text{N}-\text{H}$ ) and signals at 1665–1640  $\text{cm}^{-1}$  (amide I,  $>\text{C}=\text{O}$  stretching), 1545–1535  $\text{cm}^{-1}$  (amide II,  $>\text{N}-\text{H}$  bending) and at 1360–1345  $\text{cm}^{-1}$  (C–N stretching) showed that polymers belong to the group of amides. These bands are characteristic of the amide groups existing in the *trans* planar conformation. The bands corresponding to the aromatic parts of polyamides associated to  $-\text{CH}-$  and  $>\text{C}=\text{C}<$  stretch vibration appear in the IR spectra in the range of 3080–3060  $\text{cm}^{-1}$  and 1560–1450  $\text{cm}^{-1}$ , respectively. All polymers display absorption associated with *p*-disubstituted aromatic ring around 820  $\text{cm}^{-1}$  and ester linkage in the range 1260–1100  $\text{cm}^{-1}$ . The carbonyl stretching associated to ester group is resolved



Scheme 1. Synthesis of polyamides.

**Table 1**  
Characteristics of polyamides under study

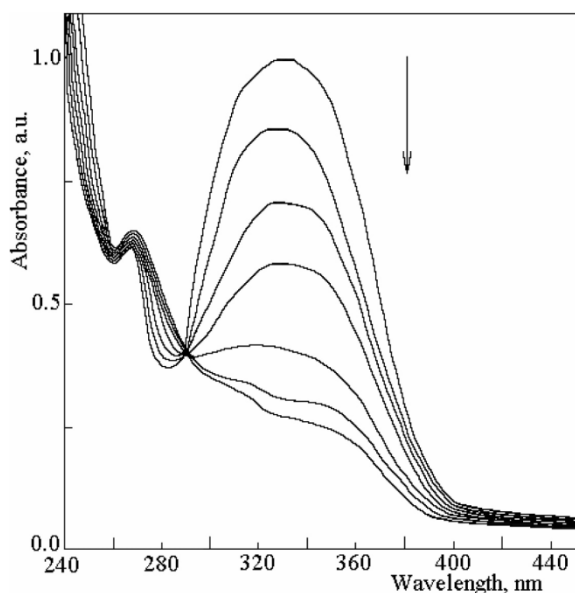
Polymer	Nitrogen calcd/found (wt%)	$\eta_{inh}^a$ (dL/g)	Water absorption (wt%)	Amide group (wt%)
PI	5.27/5.30	0.62	5.85	16.177
PT	5.27/5.32	0.76	5.42	16.177
PD	4.60/4.67	0.71	4.89	14.112
PN	4.80/4.88	0.68	5.16	14.757

<sup>a</sup>Measured at a concentration of 0.5 g/dL in NMP, at 25 ± 0.1°C.

into an intensive band at about 1740 cm<sup>-1</sup>. The polymers show C=O unsaturated ketone carbonyl stretching bands at about 1665 cm<sup>-1</sup> (strong) and 1630 cm<sup>-1</sup> (weak). The absorption band around 1600 cm<sup>-1</sup> is due to the >C=C< group flanked by a ketone and a phenyl group. The IR spectra of the samples also clearly indicated the presence of a *trans*-vinyl group (975 cm<sup>-1</sup>). No absorption attributed to the *cis*-vinyl group was detected around 730–680 cm<sup>-1</sup>, implying the absence of the *cis*-vinyl group. The IR spectra show also absorptions corresponding to the ether group at about 1238 cm<sup>-1</sup> and 1040 cm<sup>-1</sup>. The representative bands corresponding to the aliphatic parts of side chain associated to –CH<sub>2</sub>– stretch vibration appear in the IR spectra around 2940 cm<sup>-1</sup>, 2860 cm<sup>-1</sup> and 730 cm<sup>-1</sup>.

The <sup>1</sup>H NMR spectra of the polyamides showed two doublet signals present up around 7.52 and 7.78 ppm with a coupling constant  $J_{H\alpha-H\beta} \approx 16$  Hz, characteristic for the *trans*-configurations assigned to the olefinic protons of the cinnamoyl moiety in the chalconyl part. The appearance of the –O–CH<sub>2</sub>– and –CH<sub>2</sub>–OC(O)– resonances as triplets at 4.0 and 4.45 ppm, respectively is associated with the aliphatic segments from pendant chains. The peak at about 7.92 ppm is attributed to the aromatic proton between –NH– groups of the substituted *m*-phenylenediamine unit and the multiplet observed in the range 6.8–8.25 ppm is due to aromatic protons of all polyamides.

The attachment of the chalcone unit on the polymer chains was also supported by the presence of a major absorption band with a maximum at about 335 nm in the UV spectra, attributed to the  $\pi$ - $\pi^*$  transition originated from the chromophore (–CH=CH–C(=O)–) of the pendant chalcone moieties. The chalcones contain  $\alpha,\beta$ -unsaturated carbonyl groups and an extended conjugation may be favored along with the delocalization of  $\pi$  electrons and the transference of electronic deficiency from the C carbonylic atom to the C <sub>$\beta$</sub>  atom. Polyamides with pendant chalcone side groups were tested to UV irradiation in order to confirm the attachment of the chalconyl moieties to the polymer chains. The photodimerization is known as possible photoreaction of the compounds that contain such units (10–12). The prepared polymers as films were irradiated with a mercury lamp (500 W) at a distance of 16 cm from the light source for different intervals of time. The behavior of the polymers under irradiation was monitored by UV-VIS and FT-IR spectroscopy and the spectra of the samples were recorded immediately after each exposure time. Thin films of the polymers were prepared from their solutions in DMSO (25.0 mg in 1 cm<sup>3</sup> of DMSO) by casting on a quartz plate followed by slow drying. Representative spectral changes in UV absorption spectrum for film of the polymer PT exposed to the UV light are presented in Figure 1.

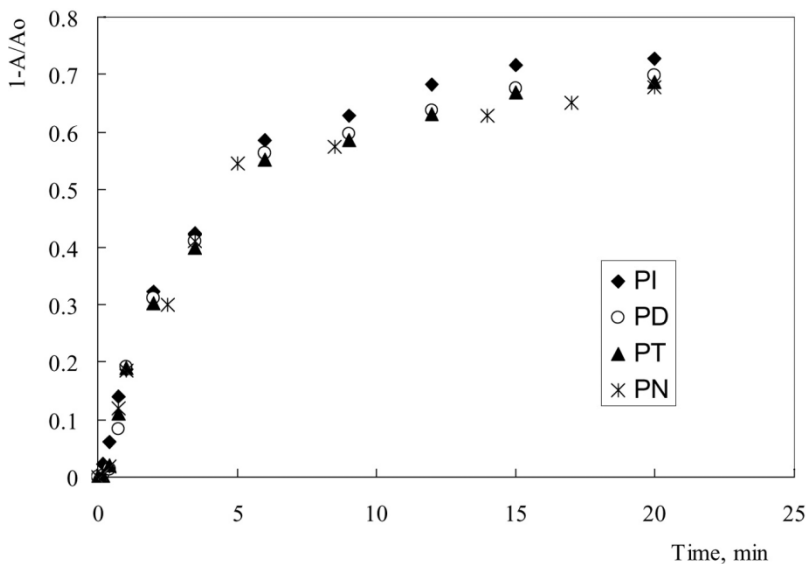


**Figure 1.** Changes in the UV spectra of polymer PT during irradiation.

As can be seen from Figure 1 the intensity of the absorption maximum at 334 nm in the UV spectrum of the polymer PT film diminished rapidly with the irradiation time. At the same time, an increase of the band intensity at about 260 nm occurs and an isosbestic point appears at about 290 nm due to the decrease in the conjugated system upon irradiation. This behavior reveals that the chalcone moieties can be easily dimerized and results in forming the corresponding cyclobutane derivatives associated with the disappearance of the double bonds. The chalcone unit is well known for its rigid-rod nature. The steric hindrance from the chalcone units increases aplanarity of the styryl phenyl ring and suppressed the *trans-cis* isomerization. The presence of an extended segment (e.g. oxyethylene) at the 4 position of chalcone unit favours the aplanarity as is reported in the literature (21). The polymer sample on irradiation for about 20 min was rendered insoluble in the solvents in which it was soluble before irradiation and this can be due to the crosslinking of the polymer chains through  $[2 + 2]$  cycloaddition of the C=C group of the pendant chalcone units and to the destroying of the conjugation in the entire  $\pi$ -electron system. The photocrosslinking rates of the polyamides in terms of the conversion of the carbon-carbon double bond with irradiation time are displayed in Figure 2.

The photochemical behavior of polyamides was also investigated by IR spectroscopy. The films on the KBr window cast from DMSO solution (1%) were subjected to UV rays for a designated time and the IR spectra were recorded before and after UV exposure and significant changes were observed. The  $>C=C<$  absorptions at about  $1600\text{ cm}^{-1}$  (stretching vibration) and  $975\text{ cm}^{-1}$  (out-of-plane deformational vibration for the *trans* chalconyl group) decrease considerably with UV irradiation time. The intensity of the C=O unsaturated ketone carbonyl stretching band at  $1665\text{ cm}^{-1}$  diminishes with the UV exposure time and a shift of this band to a higher wavenumber (at about  $1675\text{ cm}^{-1}$ ) associated to a saturated ketone carbonyl stretching vibration is observed in the spectra of the polymers after irradiation. This means that the conjugated system of the chalcone is broken and the main photoreaction of the chalconyl groups in our





**Figure 2.** Plot of relative decrease of absorbance  $1 - A_t/A_0$  for polyamides.

polymer films is attributed to the dimer structure formed between the side chains by irradiation. The photoirradiated polymer films were rendered insoluble in any organic solvents which confirms that the photocrosslinking reaction took place.

These observations are consistent with those already reported in the literature for polymers bearing  $\alpha,\beta$ -unsaturated carbonyl groups in side chains. The chalconyl unit has the absorption spectrum closely matched with the emission spectrum from a high-pressure mercury lamp (365 nm) that explains its high sensitivity to UV radiation (10–16).

Thermal properties of the polyamides were evaluated by TGA and DSC analyses and the results are presented in Table 2.

The thermogravimetric analyses (TGA) of the polymers were carried out in air/nitrogen in the 20 to 800°C temperature range. The thermal analysis data, namely the

**Table 2**  
Thermal behavior data of polyamides

Polymer	$T_g^a$ (°C)	PDT <sup>b</sup> (°C)		$Y_c^c$ (%)
		in air	in N <sub>2</sub>	
PI	216	379	388	52
PT	233	387	394	50.5
PD	254	393	403	56
PN	247	394	396	53

<sup>a</sup>Glass transition temperature determined from DSC measurements at a heating rate of 10°C/min in N<sub>2</sub> atmosphere.

<sup>b</sup>Polymer decomposition temperature at a 10% weight loss determined by TGA method at a heating rate of 10°C/min.

<sup>c</sup>Anaerobic residual weight at 800°C.

temperatures at a 10% weight loss (PDT) under both air and nitrogen atmospheres and char yield, are shown in Table 2. Thermogravimetric analysis revealed that the polyamides were stable up to the temperature above 320°C and heating at temperatures above 380°C was required to induce a loss of 10% of the initial polymer mass. The presence of the aromatic moieties in the structure of polyamides leads to a high amount of carbonized residue (char yield) in nitrogen ranging from 50.5 to 56% at 800°C. The thermal stability of the polyamides can be attributed to the presence of the aromatic groups included in their structures. It was observed that the polyamide with the *meta*-linked phenyl group (PI) has a lower ITD than those with symmetric groups (PT, PD, PN). The onset decomposition temperatures of all polymers can be associated to the decomposition of the ester moieties present in the side chains. The thermal stability of the alkyl-oxygen linkages in the side groups is lower than that of the phenyl-oxygen linkages and other predominately aromatic parts of the polyamide molecules and is explained by the well-known vulnerability of aliphatic chains towards the thermooxidative process. Figure 3 shows typical TGA curves of polyamide PD.

The polymers exhibit by differential scanning calorimetry (DSC) measurements conducted with a heating rate of 10°C/min, only the second order thermal transitions attributed to glass transitions. In the DSC thermograms are not indications of endothermic crystalline melting peaks, in accordance with the predominantly amorphous character of the samples. The chalconyloxyethyl pendant groups present in the polyamide structures increase the disorder in the main chain because they screen off attractive forces (H-bonds) between polymer chains and/or enlarge the spaced between polymer chains (4). It was assumed that the introduction of bulky chains along the polymer backbone would increase the polymer's free volume, resulting in decreased glass transition temperature ( $T_g$ ). The  $T_{g,s}$  of the substituted polyamides are influenced by the asymmetry and irregularity of polyamides introduced by the chalconyloxyethyl side chains which disrupt the chain interactions and determine the decrease of  $T_g$ . At the same time, the attachment of bulky side substituents on the aromatic units results in an increase in polymer

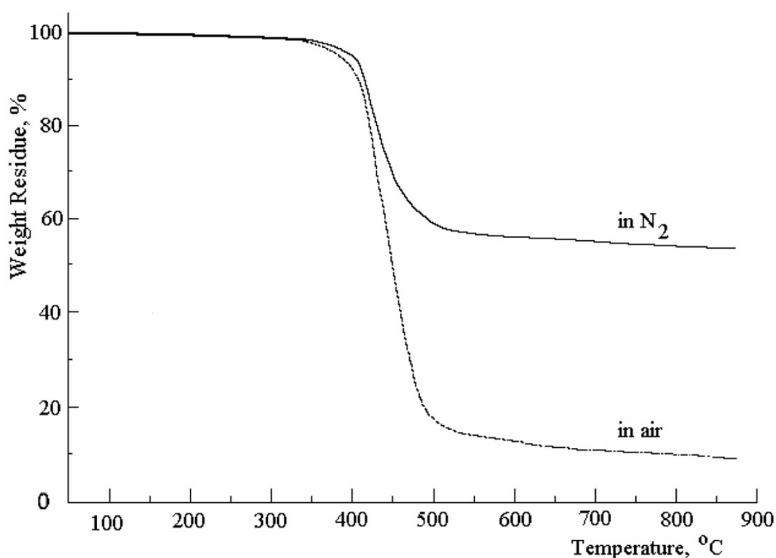


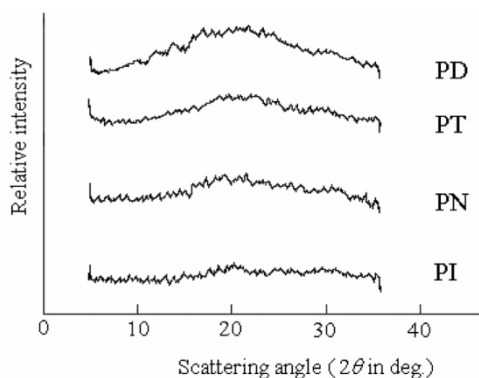
Figure 3. TGA curves of polyamide PD.

rigidity, which restricts the free rotation of the polymer backbone and the consequent hindrance determines the increase of the glass transition temperature. *Para*-linked phenyl substitution (*p*-phenylene, naphthalene-2,6-diyl, or biphenyl-4,4'-diyl) adds rigidity to the polyamide chains in comparison with the *meta*-linked phenyl one which seems to increase the flexibility because of the different possible positions of this group in the chain, resulting in a decrease of  $T_g$  (3). An increase of the number of *p*-oriented rings in the polyamide structure brings about an increase of the  $T_g$  as in case of polymers PD and PN. The oxyethylene units from the pendant groups chains disrupt the coplanarity of the styryl phenyl ring from the chalcone units and restrict the mobility contributing to a somewhat increasing of rigidity of the polymer side chains. The polymers present  $T_g$ 's values from 216 to 254°C as given in Table 2.

X-ray spectra of polyamides as films are shown in Figure 4. It is seen that diffractograms showed the same pattern and displayed weak reflection peaks near  $2\theta = 20^\circ$  and  $2\theta = 30^\circ$ . This fact reveals the amorphous character of polyamides and the presence of the olefinic bonds in the pendant chains.

The introduction of the bulky pendant groups and *meta*-oriented units in the polyamide structures increases the disorder in the chain, prevents close chain-packing, allows solvent molecules to diffuse into the polymer chains and consequently, increases hydrophilicity, solubility and water absorption with respect to an unsubstituted analogue (22, 23). It is expected that the incorporation of the voluminous pendant chalconylox-yethyl groups into the polyamide backbone to enhance solubility by decreasing polymer interchain interactions. The presence of the oxyethylene units in the side chains lead also to improve solubility because they disrupt the coplanarity of the styryl phenyl ring from the chalcone units and reduce packing efficiency of macromolecular chains. In addition, the introduction of *meta*-linked units by diamino monomer in the structure of our polyamides results in increased free volume between the polymer chains and decreased intermolecular interactions. The solubility being an important requirement for a polymer, both from synthesis and ability of forming films point of view, we tested qualitatively this property of the obtained polyamides as films in various organic solvents and the results are summarized in Table 3.

It was found that all polyamides were readily soluble in aprotic polar solvents such as DMAc, NMP, DMF and DMSO and smooth, flexible and tough films can be obtained by casting from solutions of polyamides in these solvents. The hydrophilic behavior is an important characteristic of polyamides because of the existence of H-bonding sites on



**Figure 4.** X-ray spectra of the aromatic polyamides synthesized.

**Table 3**  
The solubility behavior of the polyamides

Polymer	Solubility						
	NMP	DMAc	DMF	DMSO	<i>m</i> -Cresol	Pyridine	THF
PI	+	+	+	+	+	h	s
PT	+	+	+	+	h	s	–
PD	+	+	+	+	s	–	–
PN	+	+	+	+	s	–	–

(+) soluble at room temperature; (s) swelling; (h) soluble on heating; (–) insoluble.

amide groups. The water absorption values of polyamides were in the range of 4.89–5.85 and are presented in Table 1.

## Conclusions

A series of polyamides have been readily prepared in good yields and high purity from a new chalconyloxyethyl—containing diamine and various aromatic dicarboxylic acids via the direct phosphorylation polycondensation. Because of the presence of the bulky chalconyloxyethyl units and *m*-linked amino groups in monomer structure all the polymers were amorphous, had good solubility in polar aprotic solvents and exhibited excellent thin-film-forming ability. The polyamides obtained present a reasonable level of thermal stability. The films of polymers after irradiation became insoluble in solvents from they were cast, which demonstrates that chalcone groups easily underwent photodimerization.

## References

1. Kang, S.J., Hong, S.I., and Park, C.R. (2000) Preparation and properties of a new aromatic polyamide with an ethoxycarbonyl pendant group: poly(4,4'-diamino-2'-ethoxycarbonyl-benzanilide terephthalamide). *J. Polym. Sci. Part A: Polym. Chem.*, 38: 936–942.
2. Suh, D.H., Ju, S.Y., Park, S.H., and Lee, J.W. (2001) Synthesis and properties of novel aromatic polyamides having pendant N,N-diphenyl imide groups. *J. Macromol. Sci. Part A: Pure Appl. Chem.*, 38: 751–760.
3. Pali, R., Loria-Bastarrachea, M., Aguilar-Vega, M., Angulo, J.L., and Vazquez, H. (2002) Synthesis and characterization of aromatic polyamides obtained from 4,4'-(9-fluorenylidene) diamine, 4,4'-(hexafluoro-isopropylidene) diamine and 4,4'-diamine-benzophenone. *High Perform. Polym.*, 14: 77–91.
4. Liou, G.-S. and Hsiao, S.-H. (2002) Polyterephthalamides with naphthoxy-pendent groups. *J. Polym. Sci.: Part A: Polym. Chem.*, 40: 1781–1789.
5. Onciu, M. and Rusu, E. (2002) Synthesis and characterization of some polyamides incorporating modified isophthalic acid units. *Polym. Int.*, 51: 488.
6. Hsiao, S.-H. and Huang, Y.-H. (2004) Synthesis and properties of novel aromatic poly(1,3,4-oxadiazole)s and poly(amide-1,3,4-oxadiazole)s having ortho-phenylenedioxy units. *High Perform. Polym.*, 16: 21–37.
7. Yamazaki, N., Higashi, F., and Kawabata, J. (1974) Studies on reactions of the n-phosphonium salts of pyridines. XI. Preparation of polypeptides and polyamides by means of triarylphosphites in pyridine. *J. Polym. Sci. Polym. Chem. Ed.*, 12: 2149–2154.

8. Higashi, F., Ogata, S.I., and Aoki, Y. (1982) High-molecular-weight poly(p-phenyleneter-ephthalamide) by the direct polycondensation reaction with triphenylphosphite. *J. Polym. Sci. Polym. Chem. Ed.*, 20: 2081–2087.
9. Fan, S.-C., Schwarz, G., and Kricheldorf, H.R. (2004) Cyclic aromatic polyamides via the tri-phenylphosphite method. *J. Macromol. Sci. Part A: Pure Appl. Chem.*, 41: 779–790.
10. Song, D.-M., Jung, K.-H., Moon, J.-H., and Shin, D.-M. (2002) Photochemistry of chalcone and the application of chalcone-derivatives in photo-alignment layer of liquid crystal display. *Optical Mater.*, 21: 667–671.
11. Balaji, R. and Nanjundan, S. (2002) Studies on photosensitive homopolymer and copolymers having a pendant photocrosslinkable functional group. *J. Appl. Polym. Sci.*, 86: 1023–1037.
12. Mihara, T., Tsutsumi, M., and Koide, N. (2002) Photoreaction of new chalcone-based side chain type liquid crystalline polymers and alignment behavior of liquid crystal on the irradiated films. *Polymer Journal*, 34: 347–355.
13. Rusu, E. and Onciu, M. (2003) Polyamides with pendant cinnamoyloxyethyl units. *High Perform. Polym.*, 15: 197–206.
14. Rusu, E. and Onciu, M. (2003) Polymers with amide groups in the main and side chains. *Rev. Roum. Chim.*, 48: 565–569.
15. Kim, J.H., Ban, S.Y., Kaihua, S., and Choi, D.H. (2003) Photochromic behavior of new bifunc-tional copolymer containing spiroopyran and chalcone moiety in the side chain. *Dyes and Pigments*, 58: 105–112.
16. Selvam, P., Victor Babu, K., Penlidis, A., and Nanjundan, S. (2004) Copolymers of 4-(3,4-dimethoxycinnamoyl)phenyl acrylate and MMA: Synthesis, characterization, photocrosslinking properties, and monomer reactivity ratios. *J. Macromol. Sci., Part A: Pure Appl. Chem.*, 41: 791–809.
17. Liaw, D.J. and Chen, P.S. (1996) Preparation and properties of polyesters derived from 4,4'-sulfonyl dibenzoyl chloride by solution polycondensation. *J. Polym. Sci. Part A: Polym. Chem.*, 34: 885–891.
18. [www.huntsman.com/performance\\_chemicals/Media/Reactive Applications of Cyclic Alkylene\\_Carbonates.pdf](http://www.huntsman.com/performance_chemicals/Media/Reactive_Applications_of_Cyclic_Alkylene_Carbonates.pdf), John H. Clements, January 15 (2003).
19. Ram, S. and Ehrenkauffer, R.E. (1984) A general procedure for mild and rapid reduction of aliphatic and aromatic nitro compounds using ammonium formate as a catalytic transfer agent. *Tetrahedron Lett.*, 25: 3415–3418.
20. Gowda, D.C., Mahesh, B., and Gowda, S. (2001) Zinc-catalyzed ammonium formate reductions: rapid and selective reduction of aliphatic and aromatic nitro compounds. *Indian Journal of Chemistry, Section B: Organic Chemistry*, 40B: 75–77.
21. Sadaful, D.S. and Panda, S.P. (1979) Photocrosslinkable unsaturated polyesters. *J. Appl. Polym. Sci.*, 24: 511–521.
22. Yang, C.-P., Chen, R.-S., and Hung, K.-S. (2001) Synthesis and properties of soluble colorless poly(amide-imide)s based on N,N'-bis(3-carboxyphenyl)-4,4'-oxydiphthalimide and various aromatic diamines. *Polymer*, 42: 4569–4577.
23. Lozano, A.E., de Abajo, J., de la Campa, J.G., and Preston, J. (1995) Synthesis and properties of aromatic polyamides with oligobenzamide pendent groups. I. Poly-5-(4-benzoylamino-1-benzoylamino) isophthalamides. *J. Polym. Sci. Part A: Polym. Chem.*, 33: 1987–1994.