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Aromatic polyamides containing chalconyl substituted
m-phenylenediamine segments

Summary — 4'(β-hydroxyethoxy)chalconyl-3,5-diaminobenzoate and three kinds of aromatic dicar-
boxylic acids were used as monomers in a direct polycondensation reaction for synthesis of some
polyamides containing chalconyl units in pendant groups. The presence of these units in the structure
of polyamides renders them photoreactive and this property was monitored by UV and IR spectro-
scopy. The polyamides show good thermal stability, glass transition temperature (T_g) values around
230 $^{\circ}$C and inherent viscosity in the range of 0.67—0.79 dLg^{-1}.
Key words: polyamides, polycondensation, chalconyl pendant groups, photocrosslinking.

POLIAMIDY AROMATYCZNE ZAWIERAJĄCE SEGMENTY CHALKONYLOWE PODSTAWIONE
m-FENYLENODIAMINĄ
Streszczenie — 4'-(β-hydroksyetoksy)chalkonylowy ester kwasu 3,5-diaminobenzoesowego i trzy
rodzaje kwasów dwukarboksylowych użyto jako monomery w reakcji polikondensacji w celu syntezy
trzech poliamidów zawierających segmenty chalkonylowe w grupach bocznych (Schemat A). Struk-
turę chemiczną zsyntetyzowanych poliamidów określono metodami spektroskopii FT-IR (rys. 1),
^{1}H NMR (rys. 2) i UV-VIS (rys. 3). Obecność segmentów chalkonylowych w strukturze poliamidów
sprawia, że są one zdolne do reakcji sieciowania pod wpływem światła, co potwierdzono za pomocą
badań spektroskopowych UV-VIS (rys. 3) i IR (rys. 4 i 5). Otrzymane poliamidy charakteryzowały się
średnimi wartościami logarytmicznej liczby lepkościowej (0,67—0,79 dL · g^{-1}) i absorpcji wody
(4,58—4,87 %), która jest związana ze zdolnością do tworzenia wiązań wodorowych dzięki grupom
amidowym (tabela 1). Analiza TGA wykazała dobrą stabilność termiczną poliamidów, których tem-
peratura zeszklenia (T_g) wynosi ok. 230 $^{\circ}$C (tabela 2, rys. 6). Stwierdzono także, że rozpuszczalniki
aprotonowe są zdolne do rozpuszczania tych poliamidów (tabela 3).
Słowa kluczowe: poliamidy, polikondensacja, chalkonylowe grupy boczne, fotosieciowanie.

The design of new polyamides that show good solu-
bility as well as other specific properties is a process of
growing importance for the researchers and end-users
worldwide. These polymers provide interesting systems
for multidisciplinary scientific studies and offer techno-
logical opportunities. It is well known that polyamides
are high temperature resistant and have a favourable
balance of other physical and chemical properties
[1—10]. The incorporation of bulky pendant groups
along the main chain of polyamides, either by a poly-
mer-analogue transformation of the substrate or using
a monomer with a substituent in the aromatic ring, in
polycondensation reaction is one of the various attempts
tested in order to enhance the solubility of polyamides in
organic solvents without significant modification of
their thermal properties. Moreover, these polymers may
be tailored to reach the desired requirements for specific
applications [11-18]. Numerous investigations have been
focused on the polymers with α, β-unsaturated carbonyl
groups of acryloyl type (acrylates, cinnamates, chal-
cones, coumarines) in the side or main chains due to
their well known photosensitivity to UV light which in-
duce *trans- cis-* photoisomerization and photocrosslink-
ing by intra- and intercatenary /2+2/ photocycloaddi-
tion reaction [19—25].

In this paper we present the synthesis of a new set of
polyamides bearing chalconyl substituted *m*-phenyle-
nediamine segments generated according to Yamazaki
and Higashi procedure [26]. This design is expected to
create new polymers which could be soluble in organic
solvents and photosensitive. The characteristic data re-
lated to these polyamides are discussed herein.

EXPERIMENTAL

Materials

3,5-Dinitrobenzoyl chloride, 2-chloroethanol, *N,N*-di-
isopropylethylamine (Hünig's base), 4,4'-biphenyldicar-

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boxylic acid and 4,4'-methylenedibenzoic acid were obtained from Fluka and used as received.

4-Hydroxychalcone [3-(4-hydroxyphenyl)-1-phenyl--2-propen-1-one] was prepared by reaction between acetophenone and 4-hydroxybenzaldehyde in the presence of sodium ethoxide, according to the procedure reported in the literature [27].

Diphenyl ether-4,4'-dicarboxylic acid was prepared as described in the literature [28].

Calcium chloride (Fluka) was dried in vacuum at temp. 200 $^{\circ}$C for 24 h.

Triphenyl phosphite (Fluka) was purified by distillation at reduced pressure and stored over CaH_2.

All solvents were dried and distilled prior to use.

Methods

Infrared and ^{1}H NMR spectra were acquired using Bomem-MB-104 Type FT-IR spectrophotometer and Bruker AC 250 instrument, respectively.

UV-VIS absorption spectra were run using SPECORD M 42 Carl Zeiss Jena spectrophotometer.

Irradiation experiments were carried out using 500 W high-pressure mercury lamp.

The inherent viscosity of polymer solutions (0.5 % g/dL) in NMP was measured using Ubbelohde Suspended Level Viscometer thermostated at 25±0.1 $^{\circ}$C.

The thermal behavior of polyamides related to the glass transition temperatures and thermooxidative properties was monitored by DSC using METTLER DSC 112E and by TGA using F. Paulik Derivatograph.

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 casting a polymer solution [10 wt. % in dimethyl sulfoxide (DMSO)] on glass plates followed by drying in an oven at temp. 120 $^{\circ}$C for 12 h. Test samples were previously conditioned for 24 h at temp. 50 $^{\circ}$C before immersing them into deionized water at 23±1 $^{\circ}$C for 24 h in accordance to ASTM D 570.

The X-ray diffraction data were performed using PW 1830 Philips diffractometer (Ni-filtered Cu-K$_\alpha$ radiation of wavelength 0,1542 nm) in the reflection mode over the range of diffraction angles (2θ) from 5 to 35°, at room temperature. The voltage and tube current were 40 kV and 30 mA, respectively.

Synthesis of diamine

The *m*-phenylenediamine residue contains a chalcone group extended with oxyethylene spacer as substituent and is originated in the diamine monomer obtained in three steps (Scheme A). Initially, 4-(β-hydroxyethoxy)chalcone was obtained by Williamson etherification reaction between 4-hydroxychalcone and 2-chloroethanol. It is known that etherification of hydroxy aromatic compounds with alkyl halides proceeds to high
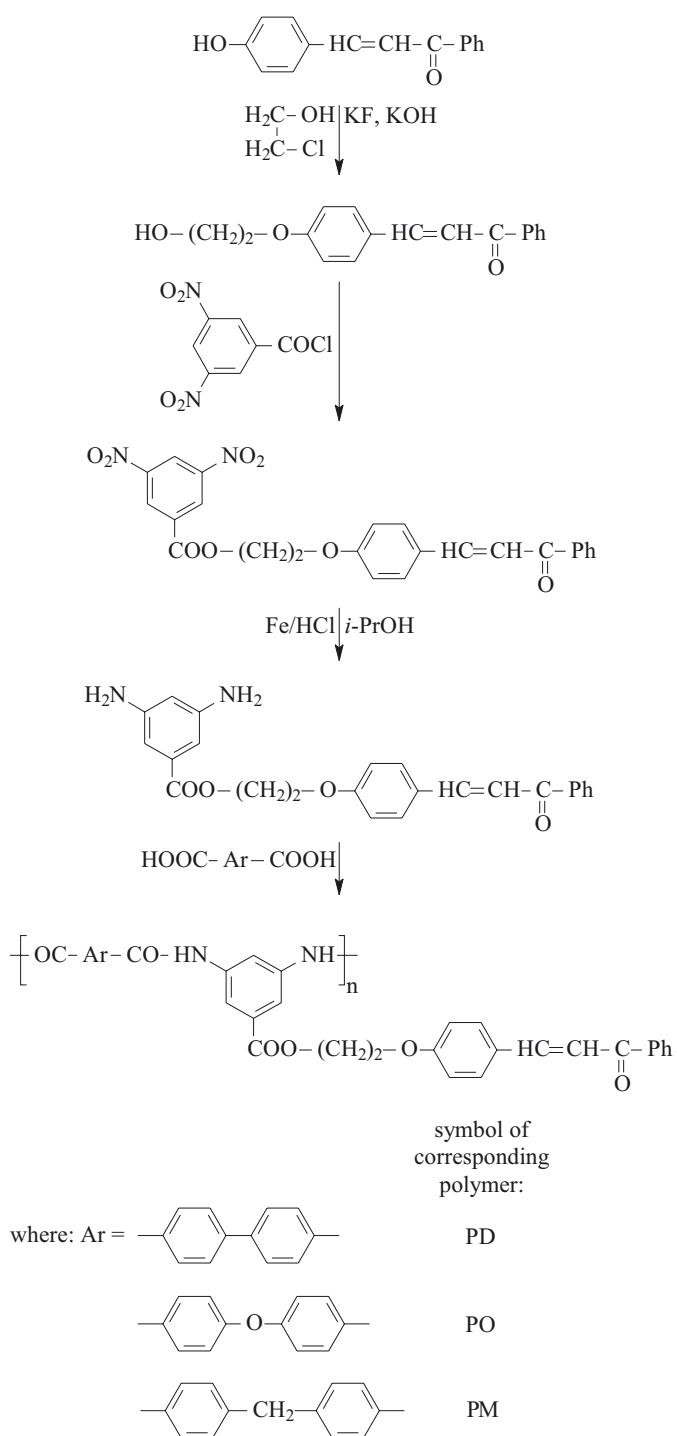
Scheme A. Course of three step synthesis of m-phenylenediamine and further Yamazaki-Higashi procedure to synthesis of aromatic polyamides

conversions to give the corresponding ethers under mild conditions using alkaline halides (KF, KI) in methanol or ethanol as catalyst [29].

A mixture of 5.04 g (22.5 mmol) of 4-hydroxychalcone, 2.52 g (45 mmol) of KOH and 1 mg of KF as catalyst were dissolved in 50 mL ethanol by heating. Then 1.8 g of 2-chloroethanol (25 mmol) was added dropwise. The reaction mass was refluxed under nitrogen for

about 12 h and afterwards cooled to room temperature. The mixture was acidified with concentrated HCl solution and poured into 300 mL of cold water. The precipitate was filtered off and recrystallized from chloroform. Yield was 79 % and the product melting temperature was 54 °C. The substance obtained was characterized by ^{1}H NMR (DMSO-d_6), and following chemical shifts corresponding to adequate groups of hydrogen atoms were observed: 6.74—8.14 ppm (m, 9H, aromatic), 7.35 ppm (d, 1H, -CH=CH-C(O)-), 7.70 ppm (d, 1H, Ph-CH=CH-), 4.15 ppm, 4.05 ppm (2t, 4H, Ar-O-CH$_2$- and -CH$_2$-OH).

Subsequently, the intermediate was treated with 3,5-dinitrobenzoyl chloride to give 4'-(β-hydroxyethoxy)chalconyl-3,5-dinitrobenzoate. It is preferred to perform esterification using acid chlorides because they frequently react quantitatively and rapidly. Dichloromethane was used as a solvent and *N,N*-diisopropylethylamine (Hünig's base) was added to neutralize the hydrogen chloride.

To the stirred solution of 4.02 g (15 mmol) of 4-(β-hydroxyethoxy)chalcone and 3.85 mL (22.5 mmol) of *N,N*--diisopropylethylamine in 25 mL of dichloromethane a solution of 4.14 g (18 mmol) of 3,5-dinitrobenzoyl chloride in 25 mL CH$_2$Cl$_2$ was slowly added at temp. 0 °C. The mixture was stirred at temp. 30 °C for 4 h and then washed with HCl solution (0.5 N, 50 mL), NaHCO$_3$ solution (10 %, 50 mL) and NaCl solution (10 %, 50 mL). The organic layer was dried over anhydrous MgSO$_4$ and after filtration the solvent was removed by distillation. The residue was recrystallized from ethyl acetate. Yield was 88 % and melting temperature 138 °C. Elemental analysis of obtained compound (C$_{24}$H$_{18}$N$_2$O$_8$, M = 462.418 g/mol) showed % N = 6.07 % (calculated 6.05 %). ^{1}H NMR (DMSO-d_6) gave following results: 7.10—8.45 ppm (m, 12 H, Ar), 7.75 ppm (d, 1H, -CH=CH-Ph), 7.40 ppm (d, J=16.1 Hz, 1H, -CH=CH-CO), 4.12 ppm (t, 2H, Ar-O -CH$_2$-), 3.9 ppm (t, 2H, -CH$_2$-OOC-).

In the third step in the reaction sequence dinitro compound was catalytically hydrogenated in the presence of iron to the corresponding diamine [30—32].

11.16 g (200 mmol) of iron powder was added portionwise under vigorous stirring to a warm solution of 3.62 g (10 mmol) of 4'-(β-hydroxyethoxy)chalconyl-3,5--dinitrobenzoate in 50 mL isopropanol containing 20 mL of concentrated hydrochloric acid. The reduction reaction was carried out at reflux for 6 h. The hot reaction mixture was quickly filtered off and the residue obtained after removal of isopropanol by means of a rotary evaporator was extracted with 3×100 mL of dichloromethane. The organic layer was washed thoroughly with NaOH solution (5 %) and NaCl solution (10 %) and dried over Na$_2$SO$_4$. Then, the solvent was removed under reduced pressure and the product was recrystallized from methanol. Yield of reaction was 65 %. Melting temperature of the product was 145 °C. Elemental analysis of this substance (C$_{24}$H$_{22}$N$_2$O$_4$, M = 402.456 g/mol) gave similar to calculated (6.96 %) value of % N = 7.06 %. ^{1}H NMR (DMSO-d_6) showed: 6.80—8.30 ppm (m, 12 H, Ar), 7.75 ppm (d, 1H, -CH=CH-Ph), 7.40 ppm (d, J=16.1 Hz, 1H, -CH=CH-CO), 4.0 ppm (t, 2H, Ar-O-CH$_2$-), 4.45 ppm (t, 2H, -CH$_2$-OOC-), 3.72 ppm (s, 4H, -NH$_2$).

Syntesis of photosensitive polyamides

The polyamides under study were synthesized according to Yamazaki-Higashi procedure which has been known to be a convenient method of the preparation of aromatic polyamides in a laboratory scale (Scheme A). The reaction preceeded homogeneously under nitrogen atmosphere at temp. 120 °C and polyamides characterized by moderate inherent viscosities were quantatively obtained. Metal salts, such as CaCl$_2$ have been chosen to facilitate polyamides generation in polycondensation reaction activated by triphenylphosphite/pyridine system. The polyamides contain in their main chain repeating segments coming from *m*-phenylenediamine and dicarboxylic acid.

As example of the preparation of all the polyamides the synthesis of polyamide (PD) is presented. 2.41 g (7.5 mmol) of 4'-(β-hydroxyethoxy)chalconyl-3,5-diaminobenzoate, 6 mL of triphenyl phosphite and 20 mL of NMP were quickly added to the mixture of 1.81 g (7.5 mmol) of 4,4'-biphenyldicarboxylic acid, 3 g of lithium chloride and 6 mL of pyridine in 20 mL of NMP. Then the solution was kept at temp. 120 °C for 4 h under a nitrogen atmosphere. The resulting viscous solution was poured slowly into 250 mL of stirring methanol to precipitate the polymer which was collected by filtration. The product was washed with a large amount of methanol and hot water and dried. The yield was almost quantitative.

RESULTS AND DUSCUSSION

Some data obtained from characterization of polyamides related to their nitrogen content, inherent viscosity, water absorption and thermal stability were pressed in Table 1 and Table 2.

The elemental analyses reveal that the nitrogen content in the polyamides is in good agreement with the theoretical amount as is presented in Table 1. Inherent viscosity of polyamides exhibited moderate values ranging from 0.67 to 0.79 dL·g^{-1} (see Table 1).

T a b l e 1. Characteristics of polyamides under study

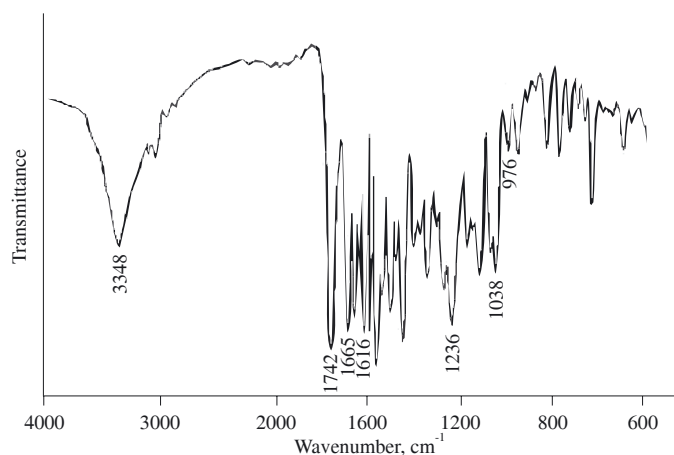| Symbol of polymer	Nitrogen content: found/calculated wt. %	Inherent viscosity dL/g	Water absorption wt. %	Amide group content wt. %
PD	4.67/4.60	0.79	4.58	14.112
PO	4.53/4.48	0.72	4.87	13.768
PM	4.58/4.49	0.67	4.65	13.811

Fig. 1. FT-IR spectrum of polyamide PO

The chemical structures of the polyamides were confirmed by FT-IR, ^{1}H NMR and UV-VIS spectroscopy. Typical infrared spectrum for polyamide PO is presented in Figure 1. The absorption bands displayed in FT-IR spectra of polyamides reflect the presence of the chromophore [-CH=CH-C(=O)-] from chalconyl segments and of the secondary amide structures. The typical FT-IR bands which show that polymers belong to the polyamides class appear near 3350 cm^{-1} (amide A, N-H), 1650 cm^{-1} (amide I, C=O stretch), 1540 cm^{-1} (amide II, N-H bend and C-N stretch) and 1340 cm^{-1} (amide III, C-N stretch and N-H bend). The amide III band is weaker than I and II ones. The polymers show C=O stretching bands characteristic to unsaturated ketone carbonyl at about 1665 cm^{-1} (strong) and 1635 cm^{-1} (weak). Near 1740 cm^{-1} C=O vibration associated with ester group appears. The absorption band around 1610 cm^{-1} is due to >C=C< group flanked by ketone and phenyl group. FT-IR spectra of the samples evidenced

the presence of *trans* -C=C- group (980 cm^{-1}). No absorption attributed to the *cis*-vinyl group was detected around 700 cm^{-1}. FT-IR spectra show also absorption corresponding to the ether group at about 1236 cm^{-1} and 1038 cm^{-1}. The bands corresponding to the aromatic parts of polyamides associated to -CH-and >C=C< stretch vibration appear in FT-IR spectra in the range of 3080—3060 cm^{-1} and 1560—1450 cm^{-1}, respectively. All polymers show absorption associated with *p*-disubstituted aromatic ring around 820 cm^{-1}. The representative bands corresponding to the aliphatic parts of side chain associated to -CH$_2$- stretch vibration are present in FT-IR spectra around 2940 cm^{-1} and 730 cm^{-1}.

Figure 2 shows ^{1}H NMR spectrum of polyamide PD. In ^{1}H NMR spectra of the polyamides two doublet signals appear, present up around chemical shift δ = 7.54 and 7.80 ppm with a coupling constant $J_{Hα-Hβ} ≈ 16$ Hz, characteristic for >C=C<$_{trans}$ bonds of the chalconyl part. The two triplets at about 3.96 ppm (-O-CH$_2$-) and around 4.40 ppm [-CH$_2$-OC(O)-] are associated with the presence of extended segment in the pendant chain. The peak at about 7.92 ppm is attributed to the aromatic proton between -NH-gropus of the substituted *m*-phenylenediamine unit and the multiplet observed in the range 6.80—830 ppm due to the hydrogens in the phenyl rings of all polyamides.

The attachment of the chalcon unit to the polymer chain was also evidenced by the presence of a major absorption band with maximum at about 330 nm in UV-VIS spectra, attributed to the π−π* transition originated in the chromophore [-CH=CH-C(=O)-] of the pendant chalcone moieties. The mesomerism of α, β-unsaturated carbonylic groups from chalcones favours the transference of electronic deficiency from C carbonylic atom to C$_β$ atom. UV-VIS spectra of polyamides are characterized by a major absorption band with maximum at about 332 nm due to the π−π* transition originated in the

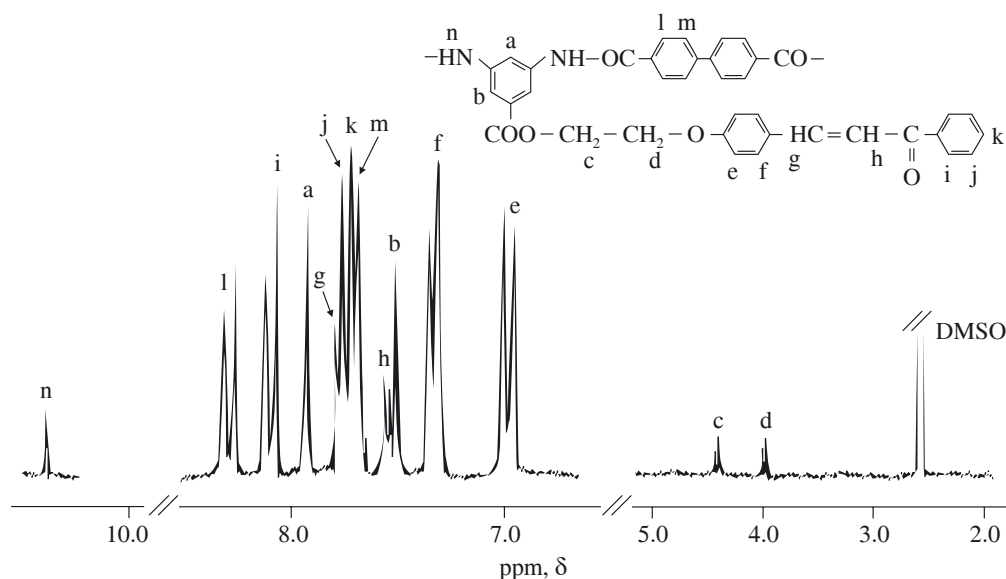*Fig. 2. ^{1}H NMR spectrum of polyamide PD*

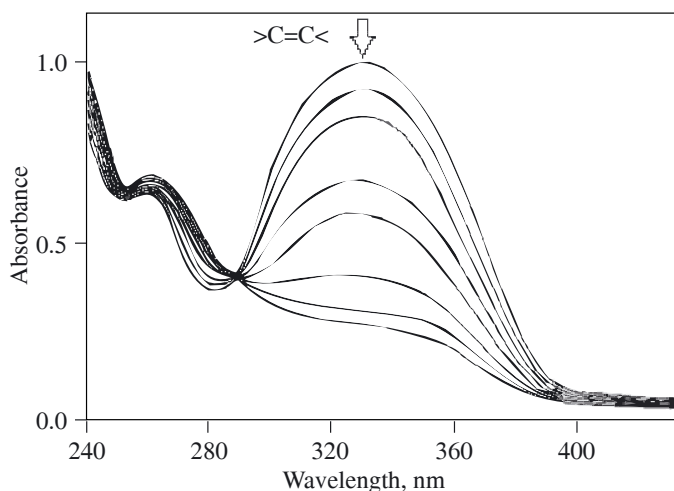Fig. 3. *Absorption spectral changes in the polyamide PD film during UV irradiation*

Fig. 4. *Changes of the relative absorbance A_t/A_o ($\lambda = 332$ nm) versus time of irradiation describing the photocrosslinking of the polymers in films*

photoactive chromophore [-CH=CH-C(=O)-] from the chalconyl moieties.

The polyamide films were exposed to UV light in order to confirm their photosensitivity and insolubility after irradiation. The behavior of the polymers under irradiation was monitored by UV-VIS and FT-IR spectroscopy using thin films prepared from DMSO solution (25.0 mg in 1 cm^3 of DMSO). The intensity of the absorption maximum at about 332 nm in UV spectra of the polymer films diminished rapidly with the time of exposure to UV rays. The changes in UV absorption spectrum of the polyamide PM before and after irradiation are illustrated in Figure 3.

This behavior was used to monitor the progress of crosslinking and revealed that the chalcone moieties could be easily dimerized and resulted in forming of the corresponding cyclobutane derivatives associated with the disappearance of the double bonds in the chalcone units. Figure 4 compares the photocrosslinking rates of the polyamides in terms of the conversion of the carbon--carbon double bond with irradiation time.

The chalcone unit is well known for its rigid-rod nature and transfers this characteristic to the pendant group of the polyamide structure. The steric hindrance from the chalcone unit increases aplanarity of the styryl phenyl ring and supresses the *trans-cis* isomerization. The presence of an extended segment (*e.g.* oxyethylene) at the position 4 of chalcone unit favours aplanarity as is reported in the literature [27]. The polymer films were rendered insoluble in the solvents from which they were cast upon about 20 min of irradiation and this behavior is due to the crosslinking of the polymer chains through cycloaddition of >C=C< double bonds and to the destroying of the conjugation in the entire π-electron system.

FT-IR spectra of the films cast on KBr pellets from DMSO solution were recorded before and after UV exposure and significant changes were observed. The
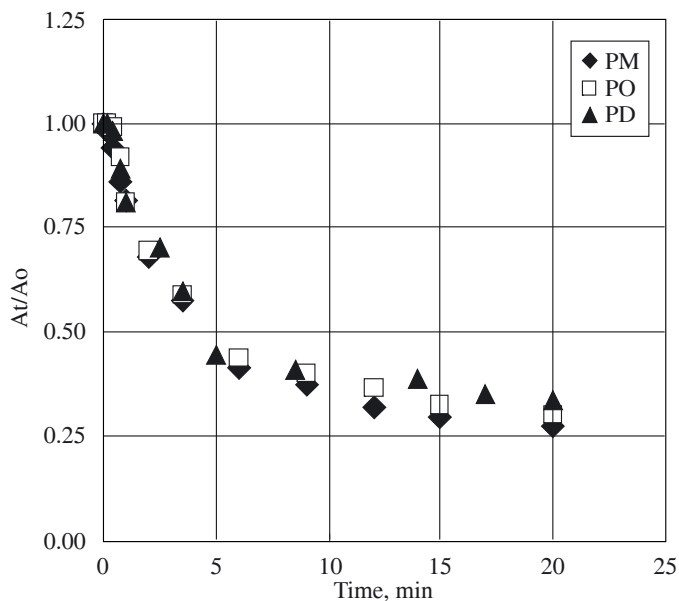
changes in IR spectra of polymer PO in the range from 1600 to 1700 cm^{-1}, observed as a function of UV exposure time at room temperature are shown in Figure 5. The >C=C< absorptions at about 1610 cm^{-1} (stretching vibration) and 980 cm^{-1} (out-of-plane deformational vibration
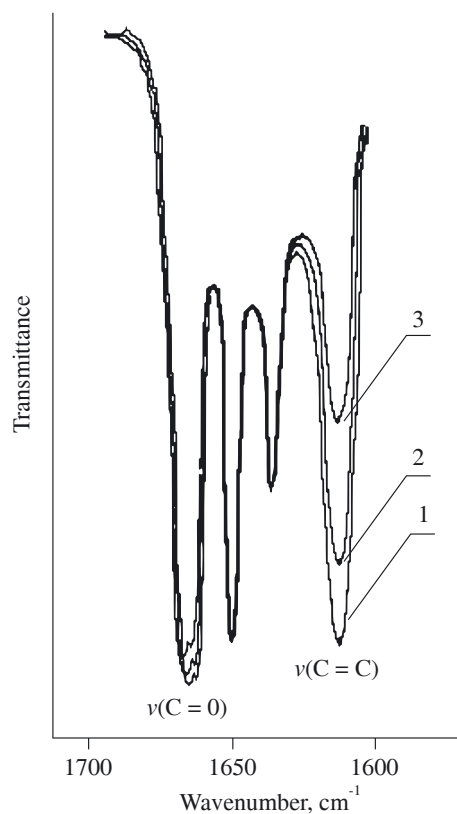

Fig. 5. *Changes of infrared spectra of the polyamide film PO under the influence of UV irradiation: 1 — before (t = 0), 2 — after 1 min, 3 — after 10 min*

for the *trans* chalconyl group) decrease considerably with UV irradiation time. The decrease in the absorbance assigned to C=O unsaturated ketone carbonyl at about 1660 cm^{-1} and shift of this band to higher wavenumber (around 1670 cm^{-1}) during irradiation can be associated with the appearance of a saturated ketone carbonyl stretching vibration. This behavior means that the conjugated system of the chalcone is broken and the main photoinduced reaction of the chalconyl groups in our polymer films is attributed to the formation of cyclodimer structure between pendant chains. The photoirradiated polymer films became insoluble in any organic solvent which confirms that the photocrosslinking reaction took place.

The chalconyl unit has the absorption spectrum closely matched with the emission spectrum of a high--pressure mercury lamp (365 nm) that explains its high sensitivity of UV radiation. The observations are in accordance with those already published for polymers containing α,β-unsaturated carbonyl groups in the pendant chains [21—24].

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

T a b l e 2. Thermal behavior data of polyamides

Symbol of polymer	T_g[a], °C	IDT[b], °C	PDT[c], °C	Yc[d], %
PD	247	321	398	21
PO	236	327	411	24
PM	223	316	393	20

[a] Glass transition temperature determined from DSC measurements at a heating rate of 10 °C/min in N$_2$ atmosphere.
[b] Initial decomposition temperature at 5 % weight loss, in air, at heating rate of 10 °C/min.
[c] Polymer decomposition temperature at 10 % weight loss, in air, at heating rate of 10 °C/min.
[d] Residual weight at 600 °C, in air.

TGA measurements of the polymers were carried out in air at room temperature to 600 °C. It was evidenced that the polyamides showed a weight loss of 5 % at temperature around 316 °C and heating to temperature above 390 °C was required to induce a loss of 10 % of the initial polymer mass. The thermal stability of polyamides can be justified by the presence of the aromatic rings in their structures. The first stage of weight loss of all the polymers can be associated with the break of the alkyl-oxygen linkages present in the pendant groups. The thermal stability of the ester units in the side groups is lower than that of the aryl-oxygen linkages and aromatic parts. The amount of char yield of polyamides in air was in the range of 20—24 wt. % at 600 °C. Figure 6 shows TGA trace in air of polyamide PM.

The polymers exhibit in DSC measurements glass thermal transition temperature (T_g) and no endothermic
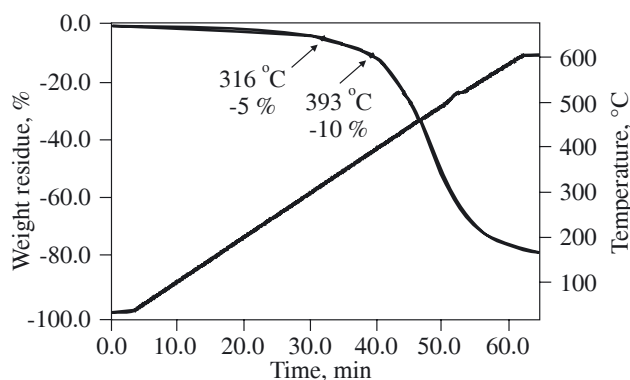
Fig. 6. TG trace of polyamide PM in air at a heating rate of 10°/min

crystalline melting peak is evidenced, in accordance with the substantially amorphous character of the macromolecules in the solid state. The presence of the bulky pendant chains influences T_g 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 presence of the chalconyloxyethyl groups in the polyamide structure increases the disorder in the main chain because they screen off H-bonds between polymer chains and/or enlarge the spaces between polymer chains. As a consequence the polymer's free volume increases resulting in decreased glass transition temperature [35]. On the other hand, the size of the chalconyloxyethyl pendant groups restricts the mobility of the polymer chain and contributes to an increase in T_g. p*ara*-Linked phenyl substitution adds rigidity to the polyamide chains, in comparison with the *meta*-linked phenylendiamine segments which seems to increase the flexibility because of the different possible positions of this group in the chain, resulting in a decrease in T_g. In the same time -CH$_2$- unit between phenylene rings from polyamide PM related to ether linkage brings a decrease in T_g. The oxyethylene units from the pendant
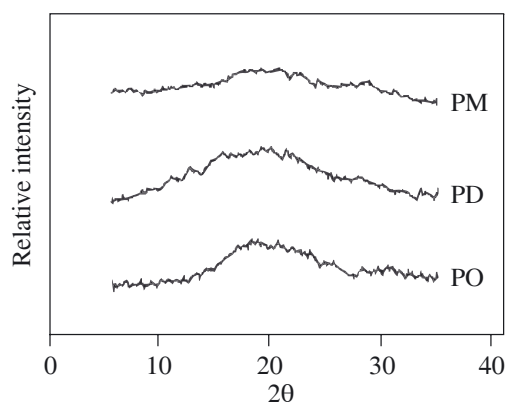
Fig. 7. X-ray diffractograms of polyamides syntesized

groups chains disrupt the coplanarity of the styryl phenyl ring from the chalcone units and restrict the mobility contributing to a somewhat increasing rigidity of the polymer side chains. From the values given in Table 2, it could be stated that all the polymers showed T_g about 220 $^{\circ}$C.

The amorphous character of polyamides is supported by very weak diffraction peaks as is presented in Figure 7 for polymer films. It is seen that diffractograms showed the same pattern and displayed weak peaks near $2\theta = 20^{\circ}$ and $2\theta = 30^{\circ}$, the latter being associated with the presence of the olefinic bonds in the pendant chains.

The presence of the bulky chalconyloxyethyl pendant groups and phenylenediamine segments in the polyamides increases the free volume between the polymer chains, decreases intermolecular interactions and prevents close chain-packing. Thus, the solvent molecules can diffuse into the polymer chains and consequently increase hydrophilicity, solubility and water absorption of polyamides in comparison with an unsubstituted analogue [33, 34]. The presence of the oxyethylene moieties in the pendant chains leads also to improvement in the solubility because they disrupt the coplanarity of the styryl phenyl rings from the chalcone units and reduce the packing efficiency of the macromolecular chains. The solubility is an important requirement for synthesis and ability of film forming of the polymers and we tested qualitatively this property of the obtained polyamides as films in various organic solvents and the results are displayed in Table 3.

T a b l e 3. The solubility behavior of the polyamides; the symbols in the Table mean: + — soluble at room temperature, s — swelling, h — soluble under heating, – — insoluble

Symbol of polymer	Solubility						
	N-methyl-pyrrolidone	N,N-dimethyl-acetamide	N,N-dimethyl-formamide	dimethyl sulfoxide	m-cresol	H₂SO₄ (98 %)	tetra-hydro-furan
PD	+	+	+	+	s	+	–
PO	+	+	+	+	h	+	s
PM	+	+	+	+	h	+	s

It was found that all the polyamides were readily soluble in aprotic polar solvents such as N,N-dimethylacetamide, N-methylpyrrolidone, N,N-dimethylformamide and dimethyl sulfoxide and exhibit film forming ability from these solvents.

The water absorption is characteristic for polyamides due to the existence of H-bonding sites in amide groups. The values related to water uptake were calculated from the weight differences between the films dried and immersed in water for 24h and are presented in Table 1.

CONCLUSION

A set of polyamides included m-phenylenediamine segments originate in a new diamine with a substituent of chalconyloxyethyl type which have been prepared quantitatively by direct phosphorylation polycondensation in the presence of CaCl₂ salt and triphenylphosphite/pyridine activation system. The presence of the voluminous chalconyloxyethyl unit and m-linked amino groups in monomer structure gives to all polymers an amorphous character and film-forming property. The chalcone group of the polymer easily undergoes intermolecular cycloaddition by UV irradiation and, as consequence of the photocrosslinking of polymer chains, insolubility of the polyamide films is usual organic solvents increases. The polyamides were stable up to the temperature above 316 $^{\circ}$C and the pendant groups contributed by their size and rigidity to T_g value around 230 $^{\circ}$C.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— Próby syntezy silseskwioksanów z różnymi podstawnikami organicznymi

— Synteza, fizyczne i chemiczne właściwości polieterouretanów modyfikowanych za pomocą naturalnych przeciwutleniaczy (*j. ang.*)

— Enzymatyczna i hydrolityczna degradacja poli(ε-kaprolaktonu) w warunkach naturalnych

— Biodegradacja starzonej kompozycji polietylenu z syntetycznym poliestrem

— Właściwości reologiczne polietylenu małej gęstości napełnianego włóknami węglowymi określane w warunkach równoległej superpozycji ustalonych i oscylacyjnych przepływów ścinających (*j. ang.*)

— Wieloparametrowa analiza żelowania poli(chlorku winylu).

— Właściwości mechaniczne usieciowanych polimetylowodorosiloksanami kauczuków silikonowych zawierających krzemionkę i węglan wapnia

— Właściwości mechaniczne wulkanizatów mieszanin NR/NBR spęcznionych olejem silnikowym