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Aromatic polyesters with photosensitive side chains: Synthesis, characterization and properties

MARIOARA NECHIFOR*

"Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, Iasi, Romania

Abstract: New aromatic polyesters with photosensitive groups in their pendant chains were prepared from a diphenol carrying as substituent a cinnamoyl group extended with a flexible oxyethyleneoxy spacer and different aromatic dicarboxylic acids *via* direct polyesterification reaction in the presence of the tosyl chloride/pyridine/dimethylformamide system as condensing agent. The resulting polyesters were characterized using Fourier-transform IR, proton and carbon nuclear magnetic resonance and ultraviolet spectroscopy, differential scanning calorimetry, thermogravimetric analysis, wide-angle X-ray diffracto-metry, gel permeation chromatography, viscosity measurement and solubility tests. These polyarylates had moderate inherent viscosities ranging from 0.37 to 0.54 dL g^{-1}, good solubility in polar aprotic solvents, and afforded trans-parent, colorless and apparently tough films on casting from their solutions. Their glass-transition temperatures ranged from 136 to 154 °C. None of them showed significant decomposition below 320 °C and all retained 38–47 % of their weight at 700 °C in a nitrogen atmosphere. The presence of cinnamoyl chromophore endowed these polymers with the ability to interact with ultra-violet light, which resulted in photodimerization between the cinnamoyl side groups upon irradiation at λ = 365 nm and cross-linking of the polymers chains without the necessity of photo-initiators or photosensitizers. Consequently, the polymer films became insoluble in organic solvents.

Keywords: new diphenol monomer; direct polycondensation; cinnamoyl chro-mophore; photo-cross-linking.

INTRODUCTION

Aromatic polyesters are an important class of high performance and eng-ineering polymers due to their excellent mechanical, chemical and thermal pro-perties. Owing to their rigid structures, which confer them high glass transition, or melting temperatures, and limited solubility in nonaggressive organic solvents, most aromatic polymers are difficult to process. Considerable efforts have been

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devoted to the synthesis of organic-soluble polyarylates. There are several structural modifications used in the synthesis of stiff macromolecules aiming at decreasing the melting and glass transition temperatures, and improving the solubility without significant loss of their high thermal stability. All the methods introduce a disorder in the structure and symmetry of the polymer chain, which reduces the tendency of the polymer to crystallize. The interpolation of flexible spacers or kinked linkages into the backbone,[1,2] the insertion of heterocyclic and bulky units in the main chain,[3,4] the addition of bulky, non-symmetrical or solubilizing substituents,[5] the inclusion of non-linear or bent monomers,[6,7] and copolymerization of monomers of various sizes and shapes,[8,9] generate distortions and disruptions of the regularity and rigidity of macromolecular chains. The most commonly used method is the incorporation of bulky or non-polar pendent groups, which are known to reduce the strong intermolecular interactions of stiff chain polymers, produce a separation of chains and a lowering of chain packing. On the other hand, bulky side groups decrease molecular mobility, so that the overall effect is an increase in the glass transition temperature and an improvement of the solubility.[10–12]

Numerous studies were focused on the synthesis of multi-functional polymers, because of their potential use in applications where specific properties, such as thermal stability and photosensitivity, need to be combined in the same material. Photosensitive polymers with photo-cross-linkable functional groups have been an active field of research in polymer science because of their applications in high-tech and general industries. Among various photo-cross-linkable groups, the cinnamoyl chromophore has attracted extensive scientific interest due to its high photoreactivity under UV illumination with λ >280 nm. By a photo-induced initiation, this α,β-unsaturated carbonyl group undergoes two photochemical reactions, *viz*. a *trans*-to-*cis* isomerization and a bimolecular cycloidmerization. The latter reaction was exploited to induce cross-linking of different polymer structures according to the specific application envisaged. Photosensitive polymers containing cinnamoyl groups in the backbone or side chains have applications as photo-patterning materials,[13] optical photo-printing waveguides,[14] optical and electrical molecular devices,[15] in the alignment of liquid crystalline molecules,[16] tissue engineering and drug delivery,[17] degradable polymers,[18] cross-linked polymeric fibers,[19] *etc*. More often, cinnamate-based photosensitive polymers are regarded as negative type photoresists, as the [2π+2π] cyclo-addition of *trans*-cinnamoyl residues leads to polymer network structures and, consequently, insoluble products because of UV irradiation. These photopolymers have been used successfully for the manufacture of numerous industrial products in the field of photography, printing and microlithography.[20]

The present study reports on the synthesis and characterization of a new diphenol monomer and the corresponding aromatic polyesters obtained by its

direct polycondensation reaction with aromatic dicarboxylic acids. The aromatic diol monomer, namely 2-(cinnamoyloxy)ethyl 3,5-dihydroxybenzoate**,** was synthesized from α-resorcylic acid and 2-bromoethyl cinnamate in the presence of potassium carbonate. The aim of this investigation was to prepare new photosensitive polyesters containing cinnamoyl pendant groups attached to the dihydroxybenzoyl unit of the aromatic polyester main chains through an oxyethyleneoxy spacer, and their characterization. Some physical and photoreactive properties of the resulting polymers were investigated.

EXPERIMENTAL

Measurements

The ^{1}H- and ^{13}C-NMR spectra were run on a Bruker AC 400 instrument, at 400 and 100 MHz, respectively, at room temperature with deuterated chloroform (CDCl$_3$) or deuterated dimethyl sulfoxide (DMSO-d_6) as solvents, and tetramethylsilane as internal standard. The FTIR spectra were recorded using a Bruker Vertex 70 Fourier transform infrared spectrometer within the wavenumber range of 600–4000 cm^{-1} at 25 °C. Electronic absorption spectra were recorded on a SPECORD M42 spectrophotometer. A 500 W high-pressure mercury lamp was used as the source of UV light to irradiate polymer films without a filter, at room temperature, for various exposure periods. The polymer films were obtained by spin-casting solutions of polymers (10 mg mL^{-1} DMF) onto quartz plates and dried at room temperature for 12 h under vacuum. For FTIR spectral measurements, polymer solutions (20 mg mL^{-1} 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 completely the residual solvent. Inherent viscosity (η_{inh}) was measured with an Ubbelohde suspended level viscometer at a concentration of 0.5 g dL^{-1} in DMF as solvent at 25±0.1 °C. Elemental analysis was realized with a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer (Perkin-Elmer, UK). Quantitative solubility was determined using 0.05 g of the polymer in 0.5 mL of solvent. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer, under dynamic nitrogen (20 mL min^{-1}) at a heating rate of 10 °C min^{-1} from room temperature to 700 °C, using 3–5 mg of sample mass. Differential scanning calorimetry (DSC) analysis was performed on a Mettler DSC 112E instrument, with heating and cooling rate of 10 °C min^{-1} in flowing nitrogen. Wide-angle X-ray scattering (WAXS) measurements were conducted on a Bruker AXS-D8 Avance X-ray diffractometer using Ni-filtered CuK$_\alpha$ radiation (operating at 36 kV and 30 mA), using samples as powders; the scanning rate was 2° min^{-1} over a 2θ scattering angle range of 5–40°. Weight-average ($\overline{M}_w$) and number-average molecular weights ($\overline{M}_n$) were determined by gel permeation chromatography (GPC) in DMF/0.01 mol % of LiBr on a PL-EMD 950 evaporative mass detector instrument equipped with two PLgel MIXED columns based on a polystyrene calibration.

Materials

Triethylamine, 2-bromoethanol, cinnamoyl chloride, 4-toluenesulfonyl chloride (TsCl), 3,5-dihydroxybenzoic acid, *N*,*N*-dimethylformamide (DMF, 99.8 %) 5-*tert*-butylisophthalic acid (**3a**), 4,4′-oxybis[benzoic acid] (**3b**), 4,4′-(hexafluoroisopropylidene)bis[benzoic acid] (**3c**) and 4,4′-sulfonyldibenzoic acid (**3d**) were obtained from Sigma–Aldrich (Taufkirchen, Germany) and used without further purification. *N*-Methyl-2-pyrrolidone (NMP) was vacuum--distilled twice over phosphorus pentoxide under reduced pressure and stored over 4 Å

molecular sieves. Tetrahydrofuran (THF) was dried by refluxing with potassium and a small amount of benzophenone until a deep purple color developed and distilled before use. Pyridine (Py) was dried and distilled over CaH_2.

Synthesis of 2-bromoethyl cinnamate (1)

The synthesis of this product was performed according to a known procedure.[21] A three-necked round-bottomed flask equipped with a magnetic stir bar and a dropping funnel was charged with 2-bromoethanol (5.32 mL, 75 mmol), triethylamine (8.4 mL, 60 mmol) and dry THF (20 mL) and cooled to 0 °C in an ice bath. A solution of cinnamoyl chloride (8.33 g, 50 mmol) in dry THF (35 mL) was added dropwise under vigorous stirring over 1 h at 0–5 °C and the same temperature was maintained for an additional 3 h. The ice bath was removed and the reaction mixture was allowed to warm up to room temperature and kept for 24 h. The reaction was performed under an inert atmosphere to avoid humidity from air. The precipitated triethylamine hydrochloride salt was removed by filtration and the filtrate was concentrated under reduced pressure on a rotary evaporator. The residue was dissolved in dichloromethane and washed twice with aqueous sodium bicarbonate and water, and then dried over anhydrous $MgSO_4$. Finally, the solvent was evaporated under reduce pressure and the light yellow viscous liquid was loaded on a column of silica gel and eluted with ethyl acetate/*n*-hexane (vol. ratio 2:3). The intermediate product (**1**) was isolated as a colorless, viscous liquid, Yield: 69 %.

Synthesis of 2-(cinnamoyloxy)ethyl 3,5-dihydroxybenzoate (2)

This compound was prepared following a method reported in the literature.[22] Under a nitrogen atmosphere, 3,5-dihydroxybenzoic acid (4.7 g, 29 mmol) was dissolved slowly in DMF (35 mL), then dry potassium carbonate (4.0 g, 29 mmol) was added in one portion to the solution. Subsequently, a solution of 2-bromoethyl cinnamate (8.2 g, 32 mmol) in DMF (5 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 24 h under N_2. The reaction was quenched by adding 2 M HCl solution dropwise and the resulting solution was extracted with diethyl ether several times. The combined organic layers were dried over Na_2SO_4. The resulting solution was concentrated under vacuum and the solid residue was purified by column chromatography over silica using a mixture of ethyl acetate/hexane (vol. ratio 1/5) as eluent, and finally recrystallized from ethyl acetate/dichloromethane mixture to give the compound **2** as an off-white powder. Yield: 78 %

*Synthesis of polymers PE4(a–d) by direct polycondensation reaction*

Since all of the polymers were prepared by the same technique,[23] a representative synthetic procedure is given for the preparation of polymer **PE4b**. To a solution of TsCl (2.28 g, 12 mmol) in Py (5 mL), DMF (1.85 mL, 24 mmol) was added and the mixture was stirred at room temperature for 30 min. The resulting solution was added dropwise to a solution of dicarboxylic acid **3b** (0.619 g, 2.4 mmol) in Py (2.5 mL) at room temperature for 30 min and then at 50 °C for 10 min. To the resulting mixture, a solution of diphenol **2** (0.787 g, 2.4 mmol) in Py (2.5 mL) was added drop-wise over a period of 20 min and the reaction mixture was stirred at room temperature for 30 min and at 120 °C for 2 h. As the reaction proceeded, the solution became viscous and brown colored. The reaction mixture was poured into a large amount of methanol under vigorous stirring. The precipitate was collected on a filter and then dissolved in 1,1,2,2-tetrachloroethane, and again mixed with excess methanol. The resulting precipitate was washed with acetone and dried at 60 °C in a vacuum oven. Yield 81 %.

The analytical and spectral data for **1**, **2** and **PE4b** are given in the Supplementary material to this paper.

RESULTS AND DISCUSSION

Synthesis of monomer and polymers

Scheme 1 depicts the route for the synthesis of the diphenol monomer **2**. First, a flexible spacer was generated by a nucleophilic acyl substitution of cinnamoyl chloride with 2-bromoethanol to obtain the intermediate product **1**, which served to alkylate the carboxyl group of 3,5-dihydroxybenzoic acid. The resuled compound **2** was further used in a step-growth polymerization reaction according to a reported procedure[24] in which the TsCl/Py/DMF system was efficiently introduced as a proper condensing agent for the synthesis of aromatic polyesters from aromatic dicarboxylic acids and diphenols.
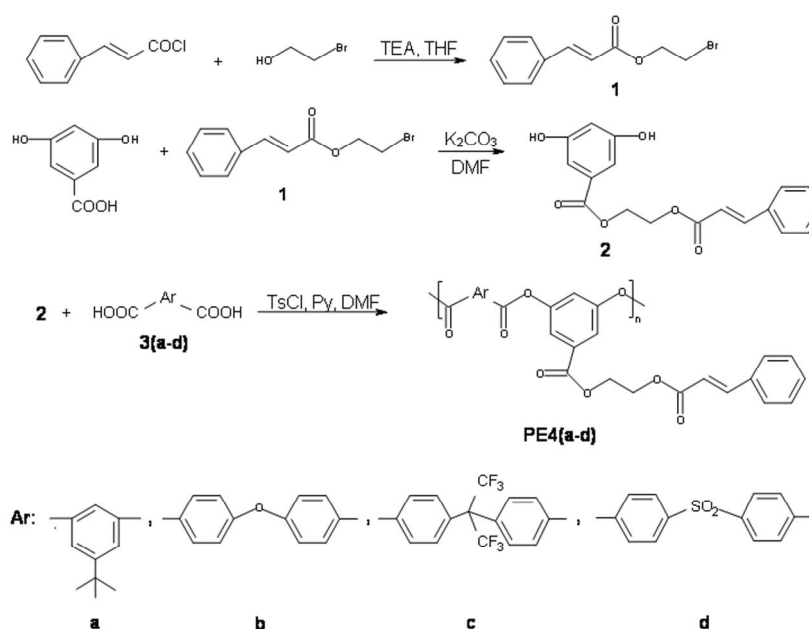
Scheme 1. Synthesis of diphenol monomer (**2**) and aromatic polyesters **PE4(a–d)**.

The structure of all polyesters was confirmed by FTIR and ^{1}H-NMR spectroscopy. The generation of polyesters was confirmed by the characteristic bands observed around 1740 (>C=O stretching in the ester groups), 1247 and 1165 (CO–C stretching absorptions, *α,β*-unsaturated ester and benzoate ester, respectively), 1590 and 1510 (aromatic in-plane ring C=C stretching vibration), 1630 (vinylene C=C stretch), 980 (bending frequency of *trans* olefinic group), 890 (out-of-plane C=C–H bend) and 850 cm^{-1} (aromatic 1,3,5-trisubstituted, ring torsion).

In addition, the spectra exhibited absorption frequencies that distinguished the polyesters from each other, because of the involvement of the different dicar-

boxylic acids. The FTIR spectrum of polymer **PE4a** exhibited characteristic absorption bands at 2980 and 2870 cm^{-1} due to the asymmetrical and symmetrical stretching of CH$_3$ groups of *t*-butyl units. An absorption band at 1254 cm^{-1} ascribed to C–O–C asymmetric stretching vibration of the aryl–O–aryl group was seen in the spectrum of polymer **PE4b**. A strong absorption of the C–F stretching appear around 1327 cm^{-1} in the spectrum of **PE4c**. The IR spectrum of polymer **PE4d** showed strong absorption bands at 1147 (symmetrical –SO$_2$– stretching vibration) and at 1335 cm^{-1} (asymmetrical –SO$_2$– stretching vibration). The FTIR spectrum of polyester **PE4b** is illustrated in Fig. 1.
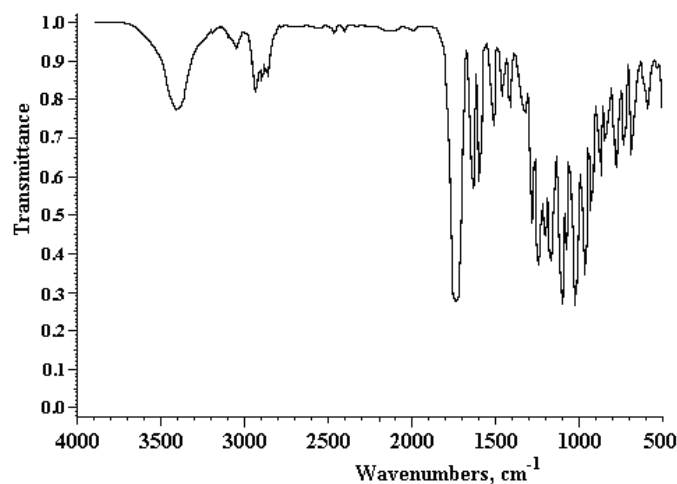

Fig. 1. FTIR spectrum of polyester **PE4b**.

The data obtained by ^{1}H-NMR spectral analysis supported the assigned structures of the resulting polyesters. Besides the peaks particular to the cinnamoyloxyethyl side chain and resorcylic acid, new signals appeared in the aromatic region of all spectra ascribed to the protons from the dicarboxylic acid structure (Fig. 2). In addition, the spectrum of **PE4a** presented a singlet at 1.33 ppm ascribed to the protons belonging to the *tert*-Bu substituent at the isophthalic acid ring. The structure of the repeat units in the polymer chain was also identified by ^{13}C-NMR (Fig. 3). The signals positioned at δ 63–64 ppm were attributed to the aliphatic carbons, those corresponding to carbons of the vinyl group were located around δ 145 and 117 ppm, those assigned to carbons of aromatic and aliphatic esters were observed at δ 164–167 ppm, while the aromatic carbons were evidenced between 118–162 ppm in the ^{13}C-NMR spectra of all polymers.
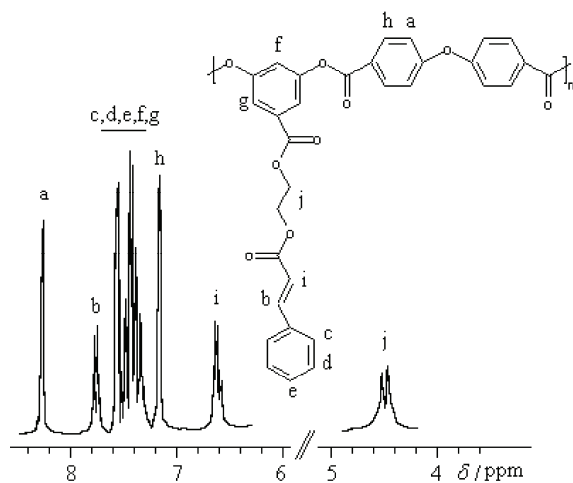
Fig. 2. ¹H-NMR spectrum of polyester **PE4b**.

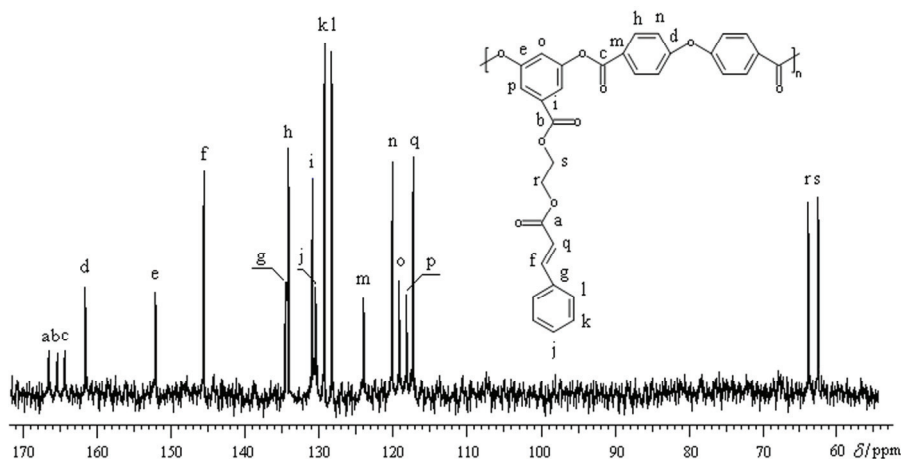Fig. 3. ¹³C-NMR spectrum of polyester **PE4b**.

The polyesters showed reasonable molecular weights according to the GPC analysis and inherent viscosity measurements. The inherent viscosity was found to lie between 0.37 and 0.54 dL g^{-1}, the weight-average molecular weights ($\bar{M}_\text{w}$) varied in the range of 52,800–76,600 g mol^{-1} and the number-average molecular weights ($\bar{M}_\text{n}$) were between 18,200–33,300 g mol^{-1} (Table I). Accordingly, the polydispersity index (*PDI*) values of the polymers were in the range of 2.3–2.9. Transparent and apparently tough films of the polyesters, pale to slight yellow in color, could be cast onto glass plates from their solutions in DMF.

The solubility of polyesters was tested quantitatively in various solvents and all of them were soluble in polar solvents, such as DMF, *N,N*-dimethylacetamide, DMSO and NMP, as well as in the less polar *p*-chlorophenol, *m*-cresol, Py and

H$_2$SO$_4$ at room temperature, and they were insoluble in common organic solvents, such as THF, chloroform, dichloromethane, methanol, ethanol and water. Their good solubility could be attributed to the introduction of the bulky, packing-disruptive cinnamoyloxyethylene units. In addition, the diacid moieties with asymmetrical aromatic units **(PE4a)**, flexibilizing linkages –O– **(PE4b)** and –C(CF$_3$)$_2$– **(PE4c)** or polar –SO$_2$– group **(PE4d)** between the aromatic units contributed to their enhanced solubility. Polyester **PE4c** exhibited the highest solubility among the polymers of this series and it was soluble in pyridine and THF due to the presence of the hexafluoroisopropylidene group –C(CF$_3$)$_2$–, into the polymer structure.

TABLE I. Inherent viscosities, yields and molar mass distributions of the synthesized polymers

Polyester	η_{inh}[a] / dL g^{-1}	Yield, %	$\bar{M}_n$[b] / g mol^{-1}	$\bar{M}_w$[b] / g mol^{-1}	PDI[c]
PE4a	0.43	86	21,100	59,100	2.8
PE4b	0.54	81	33,300	76,600	2.3
PE4c	0.49	79	25,800	64,400	2.5
PE4d	0.37	74	18,200	52,800	2.9

[a] Inherent viscosity measured in DMF (0.5 g dL^{-1} concentration) at 25 °C; [b] Number-average and weight-average molecular weight ($\bar{M}_n$ and $\bar{M}_w$) were determined by GPC based on polystyrene standards; [c] the polydispersity index (*PDI*) was obtained as $\bar{M}_w/\bar{M}_n$

The thermal behavior and glass transition temperatures T_gs of the polymers were evaluated by TGA and DSC, respectively. The values are summarized in Table II. The TGA curves showed one-step decomposition process and indicated that no mass loss of the polymers occurred below 320 °C and the values for 10 % weight loss were in the region of 373–398 °C in nitrogen. The initial decomposition temperatures were not very different and occurred at about 320 °C when the ketoethylenic groups in the polymers underwent thermal decomposition. The maximum decomposition temperature ranged from 417 to 457 °C and the anaerobic char yield at 700 °C varied between 38 and 47 wt. %. The polyester **PE4d**

TABLE II. Thermal properties and spectroscopic data for polyesters **PE4(a–d)**

Polyester	T_g[a] °C	IDT[b] °C	T_{10}[c] °C	T_{max}[d] °C	Char yield[e] %	λ_{max} / nm	
						Solution[f]	Film[g]
PE4a	136	321	373	417	38	275	273
PE4b	143	325	380	424	43	274	270
PE4c	149	326	387	433	41	271	268
PE4d	154	329	398	457	47	270	267

[a]Glass transition temperature from DSC measurements at a heating rate of 10 °C min^{-1} in an N$_2$ atmosphere; [b]onset decomposition temperature in TGA at a heating rate of 10 °C min^{-1} under nitrogen; [c]polymer decomposition temperature at 10 % weight loss (T_{10}) under nitrogen at a heating rate of 10 °C min^{-1}; [d]temperature of the maximum rate of polymer decomposition; [e]residual weight at 700 °C under nitrogen; [f]absorption maximum of polymer solution in DMF; [g]absorption maximum of polymer thin film on a quartz slide

displayed the highest thermal stability and T_g value, as well. This behavior could be a consequence of the sulfone group present in the main chain of the polymer. The TG and DTG curves of polyester **PE4b** are presented in Fig. 4.
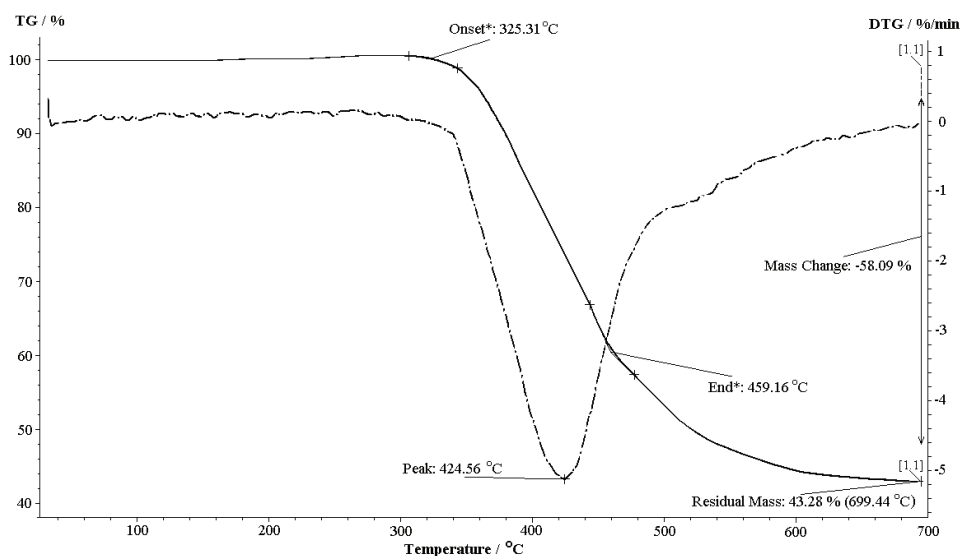

Fig. 4. TG and DTG curves of polyester **PE4b**.

None of the polyarylates showed melting endotherms on the DSC thermo-grams up to the decomposition temperatures. The T_g values of these polyarylates, obtained from the second heating DSC experiments, were recorded in the range of 136–154 °C (Table II and Fig. 5). **PE4a** exhibited the lowest T_g value, which could be explained in terms of the increased flexibility and low rotation barrier of its diacid moiety (*meta*-linked). These results also supported the amorphous nature of these polyarylates.
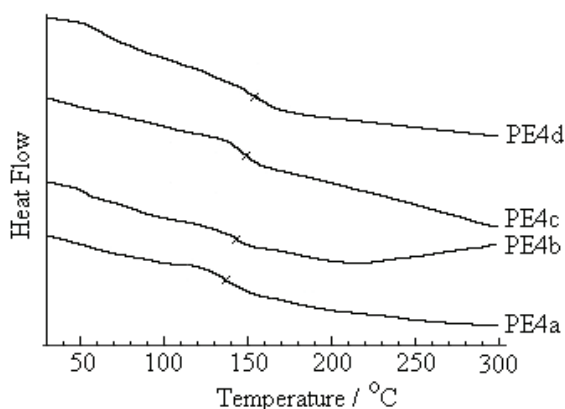

Fig. 5. DSC curves of polyesters **PE4(a–d)**.

Wide-angle X-ray diffraction measurements recorded at room temperature showed amorphous patterns for all the polymers (Fig. 6). This evidence could be explained by the presence of the flexible pendant cinnamoyloxyethyleneoxy groups, which resulted in poor chain packing, and through the distortions introduced by linking some aromatic rings in the *meta* position. The good solubility of polyesters was also favored by their amorphous structure.
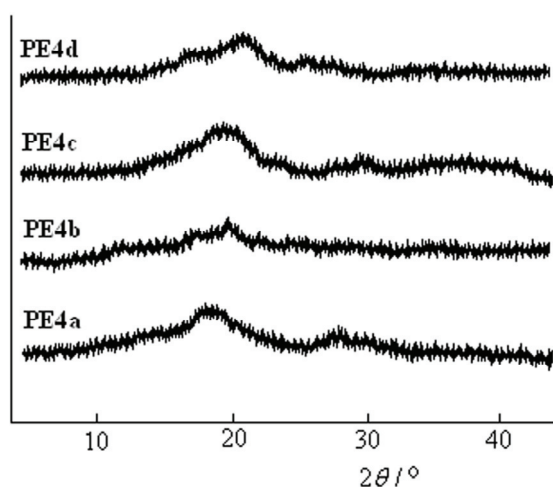

Fig. 6. X-ray diffraction diagrams of polymers **PE4(a–d)**.

Photochemical behavior

Upon irradiation in the ultraviolet-B (UVB) region of the electromagnetic spectrum, the cinnamoyl chromophore undergoes a *trans–cis* photoisomerization, which is favored in the early stages of illumination, and [2π+2π] cycloaddition, which results in the generation of cyclobutane rings and cross-links when the chromophore is inserted into a polymer backbone or side chains. It is generally accepted that the *trans–cis* photoisomerization is the minor photoprocess, while the photodimerization is the dominant photoreaction.[25,26]

The changes in the UV spectral patterns of polyester **PE4b** in the solid state for various exposure times at room temperature in the absence of triplet sensitizers are presented in Fig. 7. As can be seen, the polymer showed a maximum UV absorption at 270 nm, due to π→π* transitions of >C=C< in the pendant cinnamoyl moiety. The absorption maximum of polymer solution in DMF was 274 nm, which indicated a slight red shift compared with that of the polymer film. UV-exposure to 365 nm light induced spectral changes accompanied at the beginning of irradiation by the appearance of an isosbestic point at 224 nm, which implies the predominant occurrence of *trans–cis* photoisomerization with a concomitant increase in the absorbance at a shorter wavelength due to the generation of the cyclobutane ring through [2π+2π] addition of the pendant *α,β*-

-unsaturated carbonyl groups. Prolonged irradiation resulted in the disappearance of the isosbestic point and gradual vanishing of the absorption band centered at 270 nm, suggesting that the chromophores suffered from photodimerization. After completion of the photo-cross-linking, the film became insoluble in any organic solvent and did not show liquid–crystalline property attributed to restricted molecular mobility and flexibility in the polymer backbone.
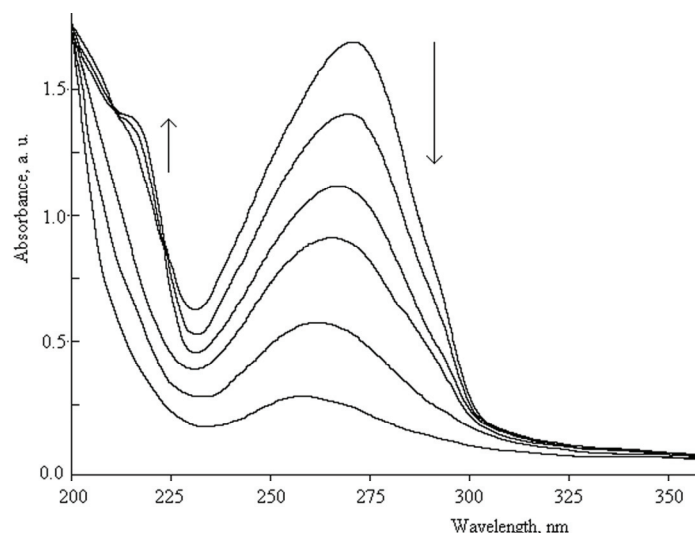

Fig. 7. Change in the UV spectrum of **PE4b** thin film upon UV irradiation at exposure times of 0, 5, 7, 15, 25 and 35 min, from top to bottom (λ_{max} = 270 nm).

The photodimerization reaction of the cinnamoyl group in the polymer **PE4b** was analyzed using IR spectroscopy, as well. The FTIR spectrum of the unexposed polymer film presented bands at 1639 and 980 cm^{-1} ascribed to vinylene C=C stretching and *trans*-vinylene CH deformation vibrations of the cinnamoyl groups, respectively. The intensities of the two bands decreased during UV irradiation because of the photodimerization, and *trans–cis* photoisomerization and photodimerization of the cinnamoyl groups, respectively. Simultaneously, it was expected that the intensity drop of the absorption band at 1740 cm^{-1}, attributed to C=O non-conjugated and C=O conjugated stretching vibration of the aliphatic and aromatic ester groups in the polymer structure, would originate principally from the photoreaction of the cinnamoyl chromophores. These changes could be correlated with the loss of conjugation by the cycloaddition reaction of the carbon–carbon double bond, and interchain cross-linking upon irradiation with UV light and consequent generation of new unconjugated carbonyl groups in the cyclobutane rings.

CONCLUSIONS

A series of novel photosensitive polyesters containing bulky cinnamoyloxy-ethyleneoxy side chains were prepared by direct polycondensation of the diphenol 2-(cinnamoyloxy)ethyl 3,5-dihydroxybenzoate and aromatic dicarboxylic acids in the presence of TsCl/Py/DMF as the condensing agent. The structure of the polymers was confirmed by FTIR, ^{1}H- and ^{13}C-NMR spectroscopy. The resulting polyesters were characterized by good solubility in organic solvents, the potential to form thin films, moderate inherent viscosity and satisfactory thermal stability up to 320 °C. The glass transition temperatures varied in the range 136–154 °C, allowing a large interval between the glass transition and thermal decomposition. The degradation process of all polymers exhibited only one decomposition maximum in the range 417–457 °C. WAXS analysis and the absence of endothermic peaks in DSC indicated that the polymers were amorphous. The voluminous and flexible pendant cinnamoyloxyethyleneoxy groups and aromatic rings linked in the *meta* position in the backbone led to poor chain packing and distortions, respectively. As a result, the polymers lacked crystallinity, which explained their specific properties presented above, *i.e.*, solubility in aprotic polar solvents, good thermal stability and molecular weights high enough to form films from their solutions. The aromatic polyesters reported herein exhibited a high degree of photosensitivity due to the high content of cinnamoyl chromophore groups, and resistance to solvents after cross-linking, which could make them potential candidates for application as negative-type photoresists.

SUPPLEMENTARY MATERIAL

Analytical and spectral data for **1**, **2** and **PE4B** are available electronically from http:////www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

АРОМАТИЧНИ ПОЛИЕСТРИ СА ФОТО-ОСЕТЉИВИМ ГРУПАМА У БОЧНИМ ЛАНЦИМА: СИНТЕЗА, КАРАКТЕРИЗАЦИЈА И СВОЈСТВА

MARIOARA NECHIFOR

''Petru Poni'' Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, Iasi, Romania

Нови ароматични полиестри са фото-осетљивим групама у бочним ланцима су добијени полазећи од дифенола, супституисаних цинамоил-групама на крајевима флексибилних окси-етиленоксидних сегмената, и различитих ароматичних дикарбоксилних киселина. Полимери су синтетисани директном полиестерификацијом у присуству ефикасног система за кондензацију: тозил-хлорид/пиридин/диметилформамид. Затим су синтетисани полиестри окарактерисани помоћу FTIR, ^{1}H- и ^{13}C-NMR спектроскопије, и UV-спектроскопије, диференцијалне скенирајуће калориметрије, термогравиметријске анализе, широкоугаоне рендгенске дифракције, гелпропусне хроматографије, вискозиметрије разблажених раствора, као и у погледу растворљивости. Добијени ароматични полиестри су показали средње вредности инхерентних вискозитетних бројева у опсегу од 0,37 до 0,54 dL g^{-1}, добру растворљивост у поларним апротичним растварачима, а њихови филмови су били прозирни, безбојни и жилави. Температуре остакљивања син-

тетисаних полимера су биле у опсегу од 136 до 154 °C. Добијени ароматични полиестри су термички стабилни до 320 °C, а остатак масе на 700 °C у атмосфери азота је износио од 38–47 %. Присуство цинамоил-хромофорних група у полимерним ланцима је омогућило њихову фото-димеризацију, под утицајем ултраљубичастог зрачења на таласној дужини $\lambda = 365$ nm, односно реакцију умрежавања без присуства фото-иницијатора. Као последица одигравања реакције фото-полимеризације и умрежавања, добијени полимерни филмови су нерастворни у органским растварачима.

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REFERENCES

1. D.-J. Liaw, P.-S. Chen, *J. Polym. Sci., A: Polym. Chem.* **34** (1996) 885
2. S.-H. Hsiao, J.-H. Chiou, *Polym. J.* **33 (**2001) 95
3. A. Rahmatpour, *J. Polym. Res.* **18 (**2011) 1813
4. S. Seesukphronrarak, S. Kawasaki, K. Kobori, T. Takata, *J. Polym. Sci., A: Polym. Chem.* **46** (2008) 2549
5. S. Watanabe, H. Murayama, M. Murata, Y. Masuda, M. Tanabe, Y. Imai, *J. Polym. Sci., A: Polym. Chem.* **36** (1998) 2229
6. R. Seto, T. Kojima, K. Hosokawa, Y. Koyama, G. Konishi, *Polymer* **51 (**2010) 4744
7. D.-J. Liaw, B.-Y. Liaw, J.-J. Hsu, Y.-C. Cheng, *J. Polym. Sci.: Part A: Polym. Chem.* **38** (2000) 4451
8. M. I. Loria-Bastarrachea, H. Vazquez-Torre, M. de J. Aguilar-Vega, *J. Appl. Polym. Sci*. **86 (**2002) 2515
9. V. B. Patil, M. Medhi, N. S. Bhairamadgi, P. P. Wadgaonkar, N. N. Maldar, *Mater. Sci. Eng., B* **168** (2010) 186
10. P. N. Honkhambe, M. V. Biyani, N. S. Bhairamadgi, P. P. Wadgaonkar, M. M. Salunkhe, *J. Appl. Polym. Sci.* **117** (2010) 2545
11. Z.-Z. Huang, X.-L. Pei, T. Wu, S.-R. Sheng, S.-Y. Lin, C.-S. Song, *J. Appl. Polym. Sci.* **119** (2011) 702
12. S. Mallakpour, S. Sepehri, *J. Appl. Polym. Sci.* **110** (2008) 2942
13. J. Chen, R A. Vaino, R. L. Smith, S. C. Collins, *J. Polym. Sci., A: Polym. Chem.* **46** (2008) 3482
14. I. Assaid, D. Bosc, I. Hardy*, J. Phys. Chem., B* **108** (2004) 2801
15. S. Furumi, A. Otomo, S. Yokoyama, S. Mashiko, *Thin Solid Films* **438**–**439** (2003) 85
16. S.-J. Sung, J. H. Yun, S. Lee, J.-K. Park, D.-H. Kim, K. Y. Cho, *React. Funct. Polym.* **70** (2010) 622
17. C.-M. Dong, X. Wu, J. Caves, S. S. Rele, B. S. Thoma, E. L. Chaikof, *Biomater.* **26** (2005) 4041
18. M. Nagata, E. Ioka, *React. Funct. Polym.* **63** (2005) 163
19. P. Gupta, S. R. Trenor, T. E. Long, G. L. Wilkes, *Macromolecules* **37** (2004) 9211
20. A. Reiser, *Photoreactive polymers: The Science and Technology of Resists*, Wiley, New York, 1989
21. N. Kawatsuki, K. Matsuyoshi, M. Hayashi, H. Takatsuka, T. Yamamoto, *Chem. Mater.* **12** (2000) 1549
22. M. Kato, K. Kanda, T. Kimura, H. Matsuda, H. Nakanishi, *Polym. Bull*. **36** (1996) 415
23. S. Mallakpour, E. Kowsari, *J. Appl. Polym. Sci*. **101** (2006) 455
24. F. Higashi, R. Hayashi, T. Yamazaki, *J. Appl. Polym. Sci*. **86** (2002) 2607
25. T. Kimura, J.-Y. Kim, T. Fukuda, H. Matsuda, *Macromol. Chem. Phys.* **203** (2002) 2344
26. B. Chae, S. W. Lee, M. Ree, Y. M. Jung, S. B. Kim, *Langmuir* **19** (2003) 687.