



*Dedicated to Professor Bogdan C. Simionescu
on the occasion of his 70th anniversary*

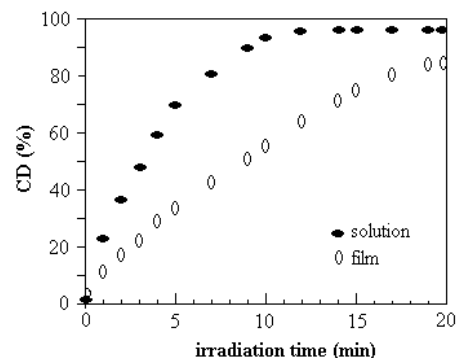
SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF AROMATIC POLYESTERS CONTAINING PENDANT CINNAMATE GROUPS

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Received July 28, 2017

Six alternating polyesters were synthesized from 5-cinnamoyloxyisophthalic acid and differently linked naphthalene diol units through a direct condensation polymerization. All the polymers were characterized by Fourier transform infrared, ^1H and ^{13}C -NMR spectroscopy, gel permeation chromatography, differential scanning calorimetry, wide-angle X-ray diffraction and thermogravimetric analysis. The polymers were soluble in polar aprotic solvents and displayed a good thermal stability. Their onset of degradation temperature was higher than 325 °C and char residue more than 48% at 600 °C in nitrogen atmosphere. The glass transition temperatures ranged between 146 and 187 °C. Wide-angle X-ray diffractometry confirmed the amorphous nature of the polymers. The influence of the cinnamate units directly linked to the lateral phenyl rings on the photochemical behavior of the polymers under UV light exposure was monitored by UV and IR spectroscopy that evidenced the photosensitive properties of the polymers. The irradiated polymer films were hard, transparent, and insoluble in organic solvents



INTRODUCTION

Aromatic polyesters have presented considerable scientific and commercial interest due to their excellent mechanical properties, chemical resistance and thermal stability. Nevertheless, high melting, softening or glass transition temperatures and limited solubility in organic solvents attributed to their rigid structures make most aromatic polyesters difficult to process into articles used in high-tech applications and general industries. Numerous studies have been reported on various methods of structural modifications adopted to improve the solubility and to modulate the thermal

properties of such stiff polymers. Among them, copolycondensation of monomers of various sizes and shapes,^{1,2} introduction of kinks and bends into the rigid straight chain,^{3,4} insertion of polar and flexible spacers into the main chain,^{5,6} appending bulky or non-symmetrical substituents to the polymer chain,^{7,8} introduce some disorder in the structure and symmetry of the polymer chains, produce a separation of chains, lower the chain packing and decrease the molecular mobility.

Polymers with naphthalene units in the main chain exhibit interesting properties due to various possible geometric arrangements of the naphthalene groups. The properties of the polymers, especially

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the ordering of the naphthalene units in adjacent polymer chains, can be affected by the structural variations in the polymer chains.⁹⁻¹⁶ Liquid crystalline properties of polymers containing naphthalene groups have been investigated.¹⁷⁻²⁰

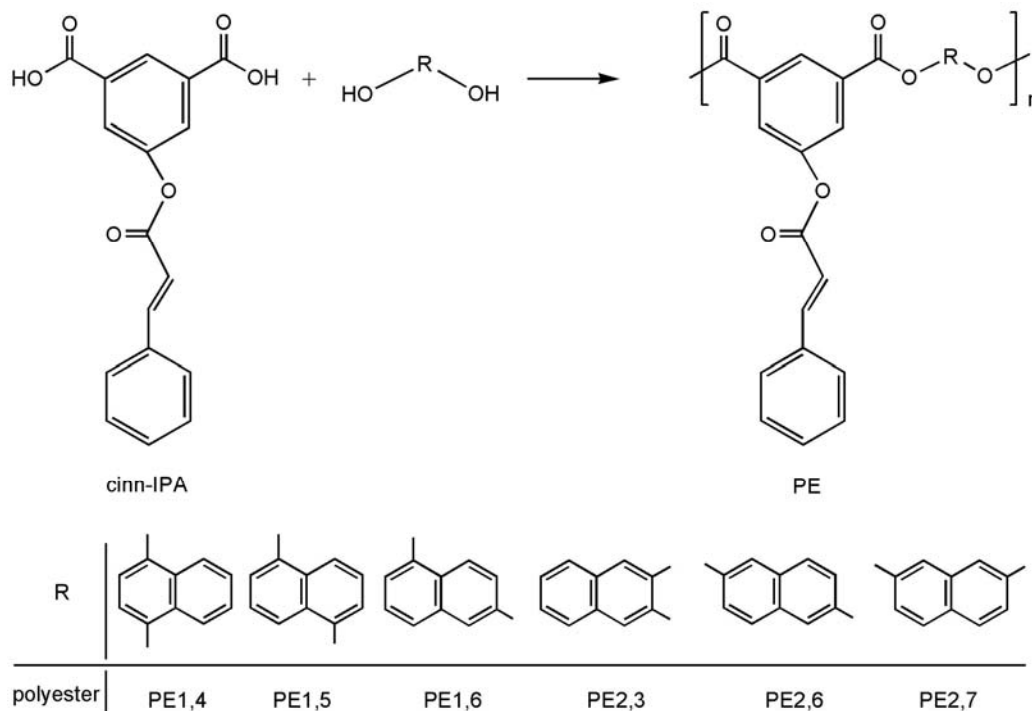
Photosensitive polymers with photocrosslinkable groups have received a widespread interest in recent years due to a large variety of applications in the field of microlithography, printing materials, holographic elements, liquid crystalline displays and non-linear optical materials.²¹⁻²³ Upon UV irradiation of the polymers containing cinnamate groups either in the backbone or in the side position of the chains, the carbon-carbon double bonds of the α,β -unsaturated carbonyl groups undergo $[2\pi + 2\pi]$ cycloaddition reactions. As a result, the crosslinking of the polymer chains takes place and an insoluble product is generated. These photosensitive polymers are regarded as negative type photoresists.²³

Because of mentioned particular characteristics, the present article reports on the synthesis and characterization of new aromatic polyesters containing naphthalene units in the main chains and cinnamate pendant groups with photosensitive properties. By introducing kinked and bulky isophthaloyl units into the main chains of the polymers it was envisaged to obtain amorphous polyesters with good thermal stability and relative high glass transition temperatures.

RESULTS AND DISCUSSION

5-Cinnamoyloxyisophthalic acid (cinn-IPA), an aromatic diacid monomer suitable for a step-growth reaction, was synthesized by condensation of cinnamoyl chloride and 5-hydroxyisophthalic acid. The photosensitive polyesters were prepared according to Scheme 1 by solution copolycondensation of 5-cinnamoyloxyisophthalic acid and various naphthalene diols in the presence of a tosyl chloride/dimethylformamide/pyridine condensing agent.²⁴

The structure information of polyesters was provided by FTIR, ^1H and ^{13}C -NMR spectroscopy. FTIR spectra of the polyesters showed characteristic absorption bands of ester carbonyl at around 3100-3050 (aromatic C-H stretching), 1750-1735 (C=O stretching), 1640-1630 (C=C stretching, vinylene), 1610-1600, 1575-1565 and 1500-1490 (C=C stretching, aromatic), 1325-1320, 1250-1240 and 1180-1170 (C=O stretching, acyl), 1090-1055 (C(=O)-stretching, acyloxy), 985-980 (C=C bending, *trans*-vinylene), 890-880 (out-of-plane C=C-H bending, aromatic) and 850 cm^{-1} (aromatic 1,3,5-trisubstituted, ring torsion). All polymers show absorption peaks at about 980 cm^{-1} corresponding to the out-of-plane bending mode of the *trans*-vinylene, which proves that the olefinic bond formation and the consequent polymerization reaction took place.



Scheme 1 – Synthesis of aromatic polyesters containing naphthalene moieties.

The ^1H and ^{13}C -NMR spectra confirmed the chemical structure of polymers. In the ^1H -NMR spectra were evidenced two distinctive doublets around 7.65 and 6.40 ppm characteristic to the two olefinic protons, and two peaks in the downfield around 8.55 and 8.20 ppm attributed to the H in the isophthalic ring. The coupling constant J had high values ranging between 15.9 and 16.2 Hz, which confirmed the presence of *trans* isomers of cinnamate group. The signals that appeared in the interval 8.0-6.7 ppm were ascribed to the aromatic protons from phenyl cinnamate and disubstituted naphthalene rings. In the ^{13}C -NMR spectra were identified two signals around 148 and 115 ppm characteristic to the two carbons of vinylene group. The two C atoms belonging to ester carbonyl groups had signals at 165-164 ppm. The peaks due to the aromatic carbons from phenyl and naphthalene rings were located between 160 and 105 ppm. According to FTIR, ^1H and ^{13}C -NMR spectra, the spectral assignments clearly supported the proposed structures.

Polyesters were tested for solubility at 5 wt.% concentration in different organic solvents. Most of them were soluble in organic solvents, particularly in aprotic polar solvents, either at room temperature or on heating depending on the structure of the naphthalene diols involved in the polyesters formation. The solubility was governed by both the structure of the diacid and diol monomers. The differently linked naphthalene units in the polymer backbone and the cinnamate pendant which decreased the chain-chain packing led to an amorphous morphology, which in turn increased solubility. The polymer solutions in NMP or DMF could be spin cast onto quartz plates to give homogeneous and transparent thin films.

The polymers had inherent viscosities ranging from 0.21 to 0.53 dL g $^{-1}$ (Table 1). The lowest value was registered for the polyester derived from asymmetrical naphthalene diol PE2,3 due to steric

hindrance at the adjacent hydroxyl groups on the naphthalene units.

The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polymers, determined by GPC using polystyrene standards, were in the range of 13900-34300 and 30600-70900 g mol $^{-1}$, respectively, with a polydispersity index (PDI) of 1.9-2.6 (Table 1).

The thermal analysis data are summarized in Table 2. All thermograms were quite similar and showed a one-step thermal degradation profile. The onset of thermal degradation occurred in the temperature range of 326–341°C and was associated with the decomposition of pendant cinnamate groups. The temperature at which 10 % weight loss occurred ranged from 371 to 393 °C. The temperature of the maximum decomposition rate as evidenced by differential thermogravimetry curves was above 425°C. The char yield of the polymers was in the range of 48–59 %. The glass transition temperature T_g of the polymers recorded in the second DSC scans evidenced that the values varied between 146 and 187 °C, depending on the main chain structure, namely the highly bent structure of isophthaloyl moiety, the presence of bulky pendant group and (a)symmetry introduced by the disubstituted naphthalene unit.

None of synthesized aromatic polyesters showed liquid crystal properties, despite the fact that naphthalene has a mesogenic character. Wide-angle X-ray diffractometry analysis supported the amorphous structure of the polyesters. The absence of sharp peaks in the WAXD spectra suggested the lack of crystallinity. Although the polyesters derived from symmetrical 1,5- and 2,6-naphthalene diols could exhibit a tendency toward crystallization, the step-like bent structure from these units and *meta*-catenation connected to a kinking carbonyl group suppress regular chain packing essential to form crystalline morphology.

Table 1

Inherent viscosities, yields and molar mass distributions of the polymers

Polymer	Yield (%)	η_{inh}^a (dL g $^{-1}$)	M_n^b (g mol $^{-1}$)	M_w^b (g mol $^{-1}$)	PDI c
PE1,4	80	0.44	29500	70900	2.4
PE1,5	74	0.33	25800	59300	2.3
PE1,6	84	0.53	34300	65200	1.9
PE2,3	71	0.21	13900	30600	2.2
PE2,6	77	0.36	21600	56200	2.6
PE2,7	79	0.35	23200	57400	2.5

^a measured in DMF (0.5 g dL $^{-1}$ concentration) at 25 °C; ^b referred to polystyrene standards in DMF; ^c the polydispersity index was obtained as M_w/M_n

Table 2
Thermal properties and spectroscopic data of the polyesters

Polymer	T _g ^a (°C)	IDT ^b (°C)	PDT ^c (°C)	Char yield ^d (%)	λ _{max} (nm)	
					solution ^e	film ^f
PE1,4	172	334	371	48	289	286
PE1,5	166	335	377	56	291	288
PE1,6	187	340	383	53	288	285
PE2,3	153	331	379	49	290	288
PE2,6	159	346	393	51	289	288
PE2,7	146	339	378	59	292	290

^{a)} Glass transition temperature from DSC measurements at a heating rate of 10 °C min⁻¹ in N₂ atmosphere; ^{b)} Onset decomposition temperature in TGA at a heating rate of 10 °C min⁻¹ in nitrogen; ^{c)} Polymer decomposition temperature at 10 % weight loss (T₁₀) in nitrogen at a heating rate of 10 °C min⁻¹; ^{d)} Residual weight at 600 °C in nitrogen; ^{e)} Absorption maximum of polymer solution in DMF; ^{f)} Absorption maximum of polymer thin film on a quartz slide.

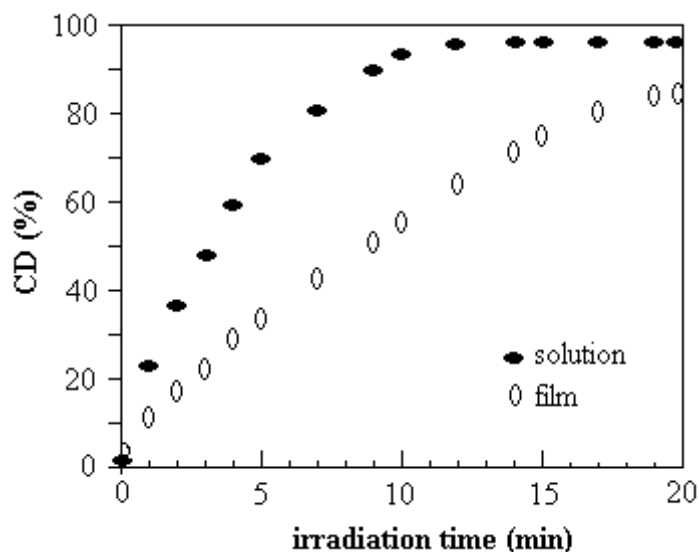


Fig. 1 – Time-dependent changes in crosslinking degree (CD) of polymer PE2,6 in solution and film upon UV irradiation.

Optical properties

The photosensitive properties of the new polyesters having pendant cinnamate groups were studied in DMF solution and solid state in the absence of photoinitiators by UV and FTIR spectroscopy. Thin polymeric films have been prepared on quartz substrates by spin-coating method using 1% polymer solution in DMF. All the films were heated at 60 °C under vacuum to remove the residual solvent. The irradiation was performed at ambient temperatures using a 500 W high-pressure mercury lamp (λ_{max} = 365 nm).

Before UV exposure the spectra exhibited absorption maxima near 285 nm (Table 2) attributed to π–π* transition of the olefinic double bond from cinnamate chromophore in the polymer structure. The intensity of the absorbance decreased gradually during increasing time of exposure to UV illumination. This phenomenon was attributed to the reduction of conjugation length and generation of cyclobutane rings by the olefinic π electrons redistribution.^{25,26} The electron absorption spectra of the film samples exhibited shape-similar absorption bands to those of the

corresponding solutions, but are slightly blue-shifted. Fig. 1 compares the rate of photocrosslinking of polyester PE2,6 in solution and thin film. The rate of photodimerization is much faster in solution than that in solid state.

The change of maximum absorbance at $\lambda_{\max}=288$ nm in solid state, revealed in the decrease of absorption intensity A_{288} , reflects the crosslinking degree of polymer PE2,6. The crosslinking density of polyester can be estimated by the following equation:

$$CD = \frac{(A_{288})_0 - (A_{288})_t}{(A_{288})_0} \times 100$$

where: DC (%) is the degree of crosslinking, $(A_{288})_0$ and $(A_{288})_t$ are the absorbance values of polymer at $\lambda_{\max}=288$ nm before irradiation ($t=0$) and after irradiation for t min, respectively. Fig. 1 depicts the dependence of CD values of polyester PE2, 6 in solution and polymer film on UV irradiation time t . The plots reveal that the fraction of crosslinked cinnamate groups was 70% in solution and 32% in solid state after 5 min of exposure, and a 83% crosslinking degree was accomplished upon 8 min of irradiation in solution and 20 min in polymer film.

In order to monitor the photochemical reaction underwent by cinnamate polymers, the changes recorded in the FT-IR spectra before and after UV light illumination of the polymer films were analyzed. The IR transitions observed in the spectra can be attributed to the $[2\pi+2\pi]$ cycloaddition process. Thus, the shift of carbonyl band from the conjugated position (1735 cm^{-1}) to the un-conjugated position (1767 cm^{-1} , cycloaliphatic carbonyl) was consistent with transformation from a α , β -unsaturated carbonyl group and proved the dimerization reaction of cinnamate groups by UV irradiation because the carbonyl band position depended on the conjugation in the polymer. We also confirmed the dimerization reaction from the decrease in intensity of stretching vibration of C=C (1640 cm^{-1}) in the vinylene linkage from cinnamate unit, which took place due to the destruction of the conjugation within cinnamate during photoirradiation. Additionally, the insolubilization in organic solvents of irradiated polymeric films indicated the development of an intermolecular process. This was a further evidence for the occurrence of a $[2\pi + 2\pi]$ photo-crosslinking reaction of the cinnamate group.

EXPERIMENTAL

Materials. Cinnamoyl chloride, 5-hydroxyisophthalic acid, 1,4-dihydroxynaphthalene, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 2,3-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 4-toluenesulfonyl chloride (TsCl), *N,N*-dimethylformamide (DMF, 99.8 %) were obtained from Sigma-Aldrich (Taufkirchen, Germany) and used without further purification.

Synthesis of *O*-cinnamoyl-5-hydroxyisophthalic acid (cinn-IPA). To 9.1 g (0.05 mol) of 5-hydroxyisophthalic acid dissolved in 40 mL of anhydrous 1,4-dioxane, 5 mL of pyridine was added and the mixture was stirred for 30 min at room temperature under a dry nitrogen flow. A solution of 10 g (0.06 mol) of cinnamoyl chloride in 20 mL of 1,4-dioxane was slowly dropped and stirred overnight. Finally the mixture was heated at 50–60 °C for 30 min. The reaction mixture was filtered off and the filtrate was poured into distilled water. The resulted precipitate was filtered off, washed with water, and recrystallized from a mixture of water and ethanol, and dried in a vacuum oven at room temperature to give 12.6 g of the dicarboxylic acid monomer in 81% yield. Elemental analysis (%): Calcd. for $C_{17}H_{12}O_6$: C, 65.38; H, 3.87; Found: C, 65.51; H, 3.98. FTIR (ν , cm^{-1}): 3443 (acid O–H stretching), 3089 (aromatic C–H stretching), 2659 (OH, carboxylic acid), 1737 (C=O stretching, ester), 1637 (C=C stretching, vinylene), 1603, 1567 and 1503 (C=C stretching, aromatic), 1476 (aryl stretching), 1322, 1244, 1171 (–C=O stretching, acyl), 1074 (–C(=O)– stretching, acyloxy), 982 (C=C bending, *trans*-vinylene), 887, 849 and 711 (C–H bending, aromatic). $^1\text{H-NMR}$ (δ , ppm): 13.23 (s, 2H, COOH), 8.51 (t, 1H, isophthalic ring), 8.24–8.19 (d, 2H, isophthalic ring), 7.69–7.65 (d, 1H, =CH-Ph, $J = 16.1$ Hz), 7.57–7.52 (m, 2H, Ph), 7.47–7.33 (m, 3H, Ph), 6.45–6.40 (d, 1H, =CH-CO, $J = 16.1$ Hz). $^{13}\text{C-NMR}$ (δ , ppm): 168.8 (C=O, carboxyl), 164.6 (C=O, ester), 156.5 (C5, isophthalic ring), 147.4 (CH=, β), 135.1 (C1'), 132.1 (C1, isophthalic ring), 130.8 (C4'), 129.7 (C3'), 128.7 (C2'), 127.6 (C2, isophthalic ring), 122.8 (C4, isophthalic ring), 115.7 (CH=, α).

Polymer synthesis. The isophthalic polyesters described in this study were synthesized by direct step-growth polymerization in the presence of tosyl chloride as described by Higashi.²⁴ Since all of the polymers were prepared by the same technique, a representative synthetic procedure is given for the preparation of polymer PE2,6. A mixture of TsCl (2.86 g, 0.015 mol) and DMF (2.3 mL, 0.03 mol) in Py (6 mL), prepared and aged at room temperature for 30 min, was added dropwise to a solution of dicarboxylic acid cinn-IPA (0.936 g, 0.003 mol) in Py (3 mL). To this mixture, stirred at room temperature for 15 min and at 60 °C for 15 min, a solution of 1,6-naphthalene diol (0.48 g, 0.003 mol) in Py (3 mL) was added dropwise over a period of 20 min at 60 °C. The solution was kept under stirring for 3 h at 120 °C, while it became viscous and brown colored. The solution was poured into methanol and the resulted precipitate was collected on a filter. It was washed with methanol and acetone and dried in a vacuum oven at 60 °C for 8 h. Yield 1.0 g (77%).

Measurements. The ^1H and $^{13}\text{C-NMR}$ measurements were performed on a Bruker 400 MHz spectrometer using deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) as solvent and tetramethylsilane as internal standard. The FTIR spectra were measured on a Bruker Vertex 70 spectrometer, by coating the

polymer solutions in DMF on KBr plates. The inherent viscosity (η_{inh}) of the polymers was determined at 25 ± 0.1 °C using DMF solutions of 0.5 g polymer per 100 ml concentration, with an Ubbelohde viscometer (Schott & Gen. Glasswerk, Mainz, Germany). The thermal stability of the polymers was investigated by thermogravimetric analysis (TGA) on a Q-1500 D (MOM Budapest, Hungary) derivatograph. The thermograms were recorded in the temperature range 25–600 °C under dynamic nitrogen atmosphere (20 mL min^{-1}), at a heating rate of 10 °C min^{-1} ; the weight of the sample was in the range of 45–50 mg. The onset on the thermogravimetric curve (the initial decomposition temperature) was considered as being the starting of thermal decomposition. The glass transition temperature (T_g) of the polymers was determined using a differential scanning calorimetry 12E calorimeter (Mettler-Toledo, Greifensee, Switzerland). Approximately 3–8 mg of each polymer were placed in aluminum pans and run in nitrogen with a heat-cool-heat profile from room temperature to 350 °C at 10 °C min^{-1} . The midpoint temperature of the change in slope of the DSC curve of the second heating cycle was considered the glass transition temperature value of the polymer. Weight-average (M_w) and number-average molecular weights (M_n) were measured by gel permeation chromatography (GPC) on a PL-EMD 950 evaporative mass detector instrument equipped with two PLgel MIXED columns. Measurements were carried out with 2 % polymer solutions in DMF/0.1 mol NaNO_3 as solvent and eluent, with a rate of 0.6 mL min^{-1} . Polystyrene standards of known molecular weight in solution of DMF/0.1 mol NaNO_3 were used for calibration. UV-vis spectra of coated films onto quartz plates at different exposure times using a 500 W high-pressure mercury lamp at the wavelength of 365 nm were collected by a Perkin Elmer Lambda 2 spectrophotometer. Wide-angle X-ray scattering (WAXS) measurements were conducted on a Bruker AXS-D8 Avance X-ray diffractometer using Ni-filtered $\text{Cu-K}\alpha$ radiation (operating 36 kV and 30 mA), using samples as powders; the scanning rate was 2 ° min^{-1} over a scattering angle $2\theta = 5\text{--}40 \text{ °}$.

CONCLUSION

The present work describes the synthesis of new copolyesters from various naphthalene diols and 5-cinnamoyloxyisophthalic acid *via* the direct reaction in the presence of tosyl chloride and their properties. The resulted polymers showed good solubility in various organic solvents, good thermal stability, and could be cast into transparent and flexible films. DSC measurements and WAXD analysis revealed the amorphous nature of these polymers which was attributed to the disturbance of the segmental movement and the destruction of the symmetry and regularity of the molecular chains due to the introduction of the pendant bulky cinnamate groups.

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