

# Synthesis and Properties of New Polyamides Based on a Hydroxyethyl Cinnamide Extended from 3,5-Diaminobenzoic Acid

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**ABSTRACT:** A series of new aromatic polyamides containing cinnamide pendent units were prepared from 2'-(cinnamide)ethyl-3,5-diaminobenzoate and various aromatic dicarboxylic acids by the direct polycondensation reaction, with triphenyl phosphite and pyridine as condensing agents. The polyamides were characterized by  $^1\text{H}$  NMR, IR, and UV spectroscopy, and gel permeation chromatography. Their thermal stability was studied by thermogravimetric analysis in air, and differential scanning calorimetry. These polymers were readily soluble in polar aprotic solvents and can be cast from their solutions in flexible and tough films. Glass transition temperatures

( $T_g$ s) of these polyamides were observed in the range of 225–245°C. Their inherent viscosities varied from 0.77 to 1.12 dL/g that corresponded to weight-average and number-average molecular weights of 39,000–72,700 and 18,800–29,000, respectively. These polymers can be photochemically crosslinked. The photochemical aspects were revealed by means of UV-vis and IR analyses onto thin films. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2013–2020, 2007

**Key words:** polyamides; polycondensation; new monomer; cinnamide pendent group; photocrosslinking

## INTRODUCTION

Polyamides are among the most important synthetic polymers. They present excellent physical and chemical properties, and thermal and oxidative stability that make them useful as high-performance materials for advanced technologies. Most aromatic polyamides are rigid rod polymers and their processing either from the melt or solution is difficult because of their high transition temperatures and their poor solubility in common organic solvents. Useful approaches to improve the processability without changing their outstanding properties are by introducing bulky side groups, by incorporating groups such as  $-\text{O}-$ ,  $-\text{SO}_2-$ ,  $-\text{S}-$ ,  $-\text{C}(\text{CH}_3)_2-$ , or by both along the backbone so as to increase the overall chain flexibility.<sup>1–7</sup> Different combination of monomers containing various rigid and voluminous substituents are used to design new predominantly amorphous, thermally stable, and high molecular weight polyamides with enhanced solubility and lower glass transition temperature than that of unsubstituted polyamides.

Depending on the specific properties of the pendent groups and the characteristic properties of the

polymeric molecules, reactive functionalized polymers have recently attained much attention for their wide range of applications in different technological fields.<sup>8–13</sup>

Photosensitive polymers containing photo-crosslinkable groups have gained a considerable interest in recent years and are widely used for several applications in the field of microlithography, printing materials, photocurable coatings, liquid crystalline and nonlinear optical materials, energy exchange materials, photosensitizers, etc.<sup>14–17</sup> Polymers with  $\alpha,\beta$ -unsaturated carbonyl groups either in the backbone or in pendent position have attracted particular attention because of their excellent photoreactivity at UV absorption wavelength.<sup>18–20</sup> They undergo crosslinking upon UV light irradiation and are regarded as negative-type photoresists.

This article deals with the synthesis, by a direct polycondensation reaction, and characterization of a series of new polyamides bearing cinnamoyl side groups based on a new aromatic diamine, 2'-(cinnamide)ethyl-3,5-diaminobenzoate. The attachment of voluminous pendent groups onto the rodlike polymer backbone is a successful alternative route to enhance the solubility and processing properties of aromatic polyamides. In general, the introduction of asymmetrical *m*-phenylene unit into the main chain leads to improved solubility. The presence of pendent side groups in polyamides derived from 2'-(cinnamide)ethyl-3,5-diaminobenzoate and of a short oxyethylene chain

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as a flexible spacer into the side chains should be effective in increasing solubility and reducing hydrogen bonding by the disrupting effect on polymer chain symmetry and the increasing side chain flexibility, respectively. The effect of the introduction of cinnamide-ethoxy unit as a bulky pendent group into the polymer chain on the solubility, crystallization, and thermal properties will be described herein. The incorporation of certain functionalities as groups appended to a macromolecular chain generates new properties tailored for specific applications of the polymers. In the present study, cinnamoyl group was employed as a photosensitive group because it is known to undergo efficient  $[2\pi + 2\pi]$  cycloaddition on UV irradiation, which causes insolubilization of the crosslinked polymer. The photochemical behavior of the resulting polymers was investigated by UV and IR spectroscopy.

## EXPERIMENTAL

### Materials

2-Aminoethanol, 3,5-diaminobenzoic acid, *N,N'*-dicyclohexyl carbodiimide (DCC), 4-dimethylaminopyridine (DMAP), 3,5-diaminobenzoic acid, terephthalic acid, isophthalic acid, 4,4'-biphenyldicarboxylic acid, 4,4'-oxybis(benzoic acid), 2,6-naphthalenedicarboxylic acid, and triphenyl phosphite (TPP) (Aldrich, Germany) were used as received. Tetrahydrofuran (THF) was distilled from sodium metal; pyridine (Py) and *N*-methyl-2-pyrrolidinone (NMP) were dried over calcium hydride for 24 h, distilled under reduced pressure, and stored over 4 Å molecular sieves in sealed bottles. Commercially-obtained anhydrous calcium chloride ( $\text{CaCl}_2$ ) was dried under vacuum at 180°C for 10 h before use.

### Analysis

Infrared spectra were recorded on a SPECORD M90 Carl Zeiss Jena spectrophotometer, using KBr pellet technique.  $^1\text{H}$  NMR spectra were run on a Bruker instrument operating at 400 MHz at room temperature with dimethyl sulfoxide- $d_6$  as a solvent and tetramethylsilane as an internal reference. UV-vis absorption spectra were recorded on a SPECORD M42 Carl Zeiss Jena spectrophotometer. The inherent viscosities were measured with an Ubbelohde suspended level viscometer for solutions of 0.5 g/100 mL in NMP thermostated at 25°C. Thermogravimetric analysis (TGA) was performed on a MOM-Budapest Q-1500 derivatograph at a heating rate of 10°C/min in air. The glass transition temperatures were determined with a METTLER DSC 112E differential scanning calorimeter at a heating rate of 10°C/min. Gel permeation chromatography was carried out on a

GPC PL-END 950 apparatus using PL gel 5  $\mu\text{m}$  MIXED-D columns and *N,N*-dimethylformamide (DMF) as solvent and monodisperse polystyrene samples with narrow polydispersity as calibration standards. Wide-angle X-ray diffraction powder patterns were obtained on a TUR-MG2 diffractometer by means of Ni-filtered  $\text{Cu K}\alpha$  radiation. A 500 W high-pressure mercury lamp with an optical filter was used for the irradiation experiments. Qualitative solubility was determined at a concentration of 10% (w/v) in a number of solvents.

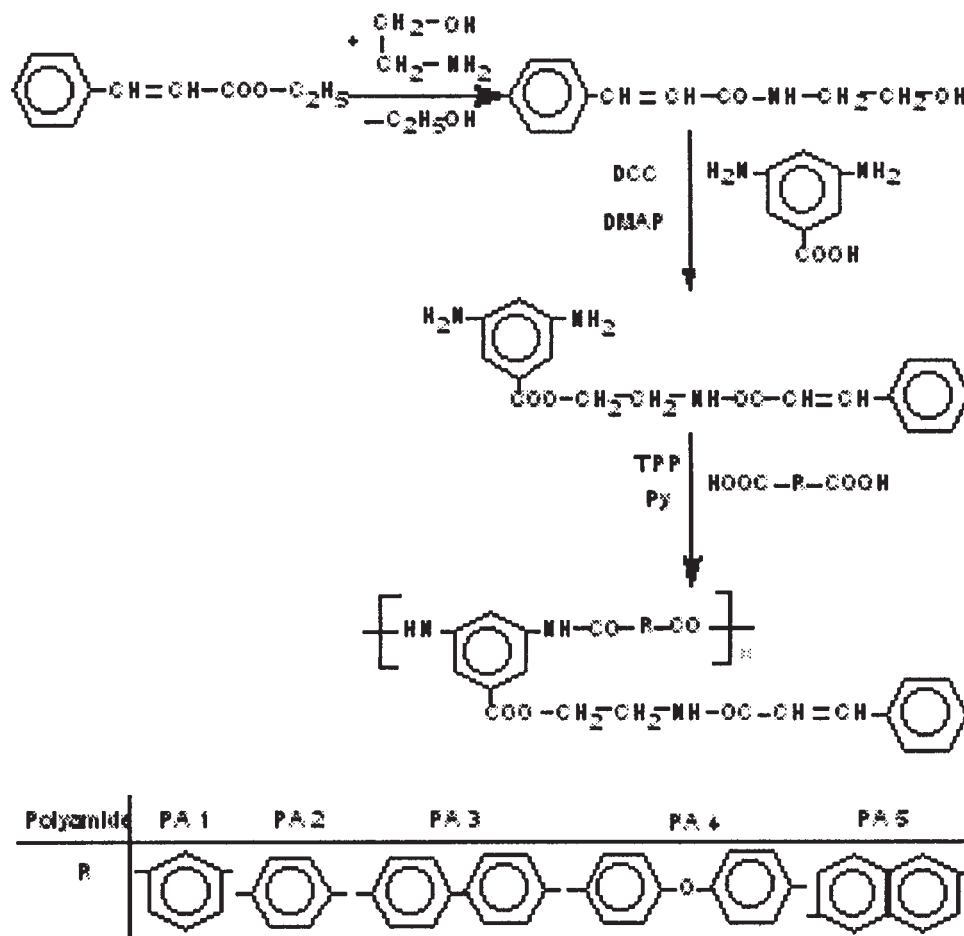
### Monomer synthesis

#### Preparation of *N*-(2-hydroxyethyl)cinnamide

A mixture of 4.40 g (0.025 mol) ethylcinnamate and 3.05 g (0.05 mol) 2-aminoethanol were heated for 10 h at 170°C. During amide-formation ethanol was distilled off. When the reaction was completed, the residual excess of 2-ethanolamine was stripped off in oil pump vacuum and the reaction mixture was poured into icy water, filtered off, and dried. Yield 4.63 g (97%). mp 104–105°C; elemental analysis of  $\text{C}_{11}\text{H}_{13}\text{NO}_2$  (191.2305) calc/found: % N 7.32/7.56.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , room temperature),  $\delta$  (ppm): 7.70–7.55 (m, CH=, Ar, 3H); 7.45–7.35 (m, Ar, 3H); 6.85 (s, NH, 1H); 6.40 (d, =CH–CO, 1H,  $J = 16.1$  Hz); 3.80 (s, 1H, OH); 3.70 (t,  $\text{CH}_2\text{O}$ , 2H); 3.45 (t,  $\text{CH}_2\text{N}$ , 2H).

#### Preparation of 2'-(cinnamide)ethyl-3,5-diaminobenzoate

*N*-(2-hydroxyethyl)cinnamide (4.59 g, 0.024 mol) and 3,5-diaminobenzoic acid (3.04 g, 0.020 mol) were dissolved in THF (20 mL) at 30°C. A solution of DCC (12.38 g, 0.060 mol) in dry THF (10 mL) was added to the mixture, followed by addition of a solution of DMAP (0.24 g, 0.0020 mol) in dry THF (10 mL); the mixture was stirred for 48 h at 30°C, then the solvent was evaporated under reduced pressure. The resulting residue was combined with 30 mL dichloromethane and the solid urea was filtered off. The solution was washed with water, aqueous HCl solution (10%), saturated  $\text{NaHCO}_3$  solution, and aqueous NaOH solution (5%). The organic solution was dried over anhydrous magnesium sulfate, the solvent was evaporated, and the resulting oil solidified while drying under vacuum pressure to give a solid, which was recrystallized from MeOH to give 2'-(cinnamide)ethyl-3,5-diaminobenzoate. Yield 4.22 g (65%); mp 137–139°C; elemental analysis of  $\text{C}_{18}\text{H}_{19}\text{N}_3\text{O}_3$  (325.368) calc/found: % N 12.91/13.17.  $^1\text{H}$  NMR ( $\text{DMSO}-d_6$ , room temperature),  $\delta$  (ppm): 7.70–7.55 (m, CH=, Ar, 3H); 7.45–7.35 (m, Ar, 3H); 6.90 (s, NH, 1H); 6.85 (s, 2H, Ar); 6.40 (d, =CH–CO, 1H,  $J = 16.9$  Hz); 6.30 (s, 1H, Ar); 4.55 (t,  $\text{CH}_2\text{O}$ , 2H); 4.25 (t,  $\text{CH}_2\text{N}$ , 2H); 3.70 (s, 4H,  $\text{NH}_2$ ).



Scheme 1 Synthesis of 2'-(cinnamide)ethyl-3,5-diaminobenzoate and cinnamide-pendent polyamides PA 1–5.

## Polymer synthesis

### Preparation of polyamide PA 1

A flask was charged with a mixture of diamine (0.65 g, 2 mmol), terephthalic acid (0.33 g, 2 mmol), triphenyl phosphite (1.05 mL, 4 mmol), pyridine (4 mL), *N*-methyl-2-pyrrolidinone (10 mL), and calcium chloride (0.55 g, 5 mmol). It was refluxed under argon atmosphere for 3 h. The viscosity of the solution increased during the reaction. After cooling, the reaction mixture was poured dropwise into a large amount of methanol with constant stirring, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried to give 0.87 g of polyamide PA 1 (96% yield). All of the other polyamides were prepared using similar procedure.

## RESULTS AND DISCUSSION

### Monomer and polymer syntheses

Scheme 1 outlines the synthetic route for diamine monomer and polyamides prepared therefrom. The

diamine monomer, 2'-(cinnamide)ethyl-3,5-diaminobenzoate, was synthesized by a three-stage procedure. The first step was an acid-catalyzed condensation reaction of cinnamic acid with excess ethyl alcohol producing ethyl cinnamate.<sup>21</sup> The latter was used in the second step in the reaction with 2-aminoethanol to produce *N*-(2-hydroxyethyl)cinnamide. In the final step, the chain-extended cinnamide derivative, containing oxyethylene spacer group, was reacted with 3,5-diaminobenzoic acid in the presence of DCC and DMAP.<sup>22</sup>

The direct polycondensation by using condensing agents to activate acid groups *in situ* is an attractive route to synthesize polyamides, since carboxylic acid chlorides or isocyanates are highly reactive, and therefore, sensitive to moisture. The phosphorylation polyamidation technique developed by Yamazaki et al.<sup>23</sup> was used to prepare the novel polyamides PA 1–5 from 2'-(cinnamide)ethyl-3,5-diaminobenzoate and a series of aromatic dicarboxylic acids in the presence of NMP as solvent and using triphenyl phosphite and pyridine as condensing agents. All the polycondensation reactions readily proceeded in homogeneous solution.

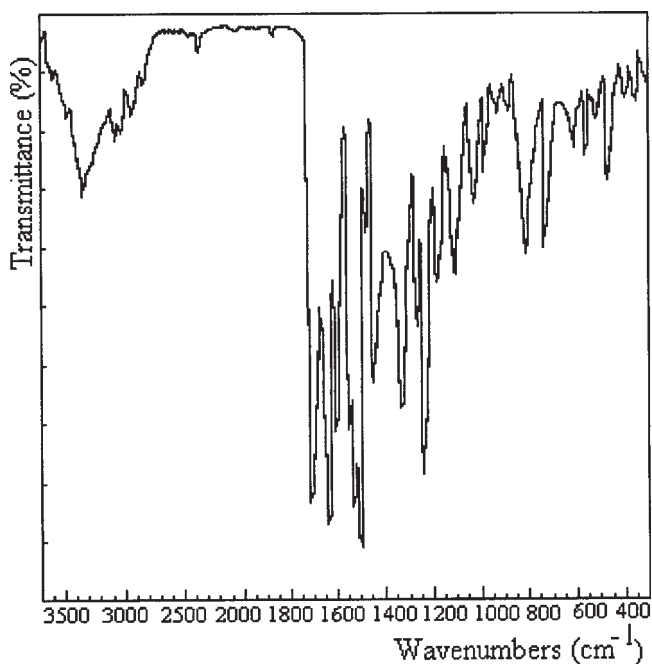


Figure 1 IR spectrum of polymer PA 4.

The structure of polyamides was confirmed by IR and  $^1\text{H}$  NMR spectroscopy. The IR spectra of polyamides exhibited characteristic bands due to amide N–H stretching around  $3350\text{ cm}^{-1}$ , amide bonds at  $1650$  (C=O stretching, amide I) and around  $1540$  and  $1340\text{ cm}^{-1}$  (N–H bending and C–N stretching, amide II and amide III, respectively), aromatic C–C stretching at  $1600$ ,  $1510$ , and  $1485\text{ cm}^{-1}$ , conjugated C=O stretching vibration at about  $1725\text{ cm}^{-1}$  and C–O–C ester linkage in the range  $1260$ – $1100\text{ cm}^{-1}$ , vinylenic C=C stretching vibration at  $1640\text{ cm}^{-1}$ , and *trans*-vinylenic C–H out-of-plane bending at about  $980\text{ cm}^{-1}$ . All the IR spectra showed two absorption bands around  $2940$  and  $730\text{ cm}^{-1}$  due to  $-\text{CH}_2-$  stretch vibration. Figure 1 presents the IR spectrum of polyamide PA 4.

$^1\text{H}$  NMR spectra were also used to identify the structure of polymers. Figure 2 illustrates the  $^1\text{H}$  NMR spectrum of polyamide PA 2. Solution  $^1\text{H}$  NMR spectra in  $\text{DMSO}-d_6$  confirmed the chemical structures of PA 1–5 with aliphatic amide proton chemical shifts observed at about 6.90 ppm and farthest downfield shifts of aromatic amide proton around 10.50 ppm. All  $^1\text{H}$  NMR spectra of polyamides present characteristic resonances corresponding to aromatic protons: two multiplets at 7.45–7.35 and 7.55–7.60 ppm (aromatic H of cinnamoyl segment) and two singlets at 7.50 and 7.95 ppm (aromatic H of 3,5-diaminobenzoate moiety). The additional resonances or splitting of above signals reflect the different neighborhoods of aromatic rings from dicarboxylic acid moiety. The *trans* isomerism of the

double bond from cinnamoyl group was confirmed for all polyamides of this work by the presence of a doublet at 7.70 ppm characteristic to  $=\text{CH}-\text{Ar}$  and another at 6.40 ppm due to  $=\text{HC}-\text{CO}$  with a coupling constant of 15.7 Hz. A reduction in the peak area of the methylene adjacent to the amide at 4.25 ppm was observed in addition to the corresponding appearance of the methylene resonance adjacent to an ester linkage at  $\sim 4.55$  ppm. Both  $^1\text{H}$  NMR and IR spectra were in good agreement with the proposed structures.

### Polymer characterization

It has been recognized that one of the successful approaches to increase solubility and processability of polyamides is the introduction of voluminous pendent groups into the polymer backbone to minimize crystallization and forming a noncoplanar structure, thereby making crystallization impossible. The presence of bulky extended cinnamide moieties can interrupt the intermolecular hydrogen bonding of the polyamides and reduce the stacking efficiency and crystallinity. This leads to an enhanced solubility and to a relatively high  $T_g$  through decreased segmental mobility due to steric hindrance.

The solubility behavior of these polyamides was tested qualitatively and listed in Table I. They were generally observed to be soluble in polar aprotic solvents, such as *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), and *N*-methyl-2-pyrrolidinone (NMP) at ambient temperature and even in less-polar solvents like methanesulfonic acid, dioxane, *m*-cresol, and *o*-chlorophenol. The pendent group had a positive effect on the solubility because the cinnamide-

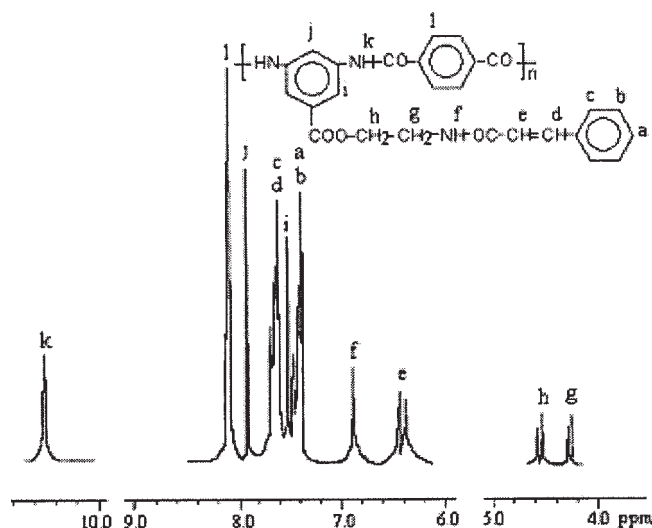


Figure 2  $^1\text{H}$  NMR spectrum of polyamide PA 2 in  $\text{DMSO}-d_6$ .

TABLE I  
Solubility Behavior of Polyamides in Various Solvents<sup>a</sup>

Polyamide	Solubility						
	DMSO	DMF	NMP	DMAc	<i>m</i> -Cresol	Py	THF
PA 1	+	+	+	+	+	+/-	+/-
PA 2	+	+	+	+	+	+h	+h
PA 3	+	+	+	+	+	+h	+h
PA 4	+	+	+	+	+	+/-	+/-
PA 5	+	+	+	+	+	+/-	+/-

<sup>a</sup> Symbols: +, soluble at room temperature; +/-, partially soluble at room temperature; +h, soluble on heating at 100°C.

containing polyamides were more soluble than poly(*m*-phenyleneisophthalamide) as a reference polyamide, which dissolved only in amide-type polar solvents (DMF, DMSO, and NMP) and only upon heating. The incorporation of bulky pendent groups produces a chain separation effect lowering the chain packing, which increases water accessibility and improves solubility. The best solubility range was observed for PA 1 and PA 4, incorporating an asymmetrical *m*-phenylene unit and a diphenyl ether linkage, respectively, as a bridging group in each repeating unit of the backbone, which demonstrated partial solubility in common organic solvents, such as tetrahydrofuran, cyclohexanone, and pyridine. Polymers PA 2 and PA 3 with *p*-phenylene and biphenyl structure, respectively, had somewhat limited solubility.

The thermal behavior of the polyamides was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), the results of which are summarized in Table II. In every case, no crystalline transition temperature was observed but a wide endotherm appeared between 50 and 160°C in the first run of DSC curves. The latter was attributed to the loss of water associated with the polymer and therefore, two runs were required to obtain consistent DSC traces. Quenching from the elevated temperature (about 350°C) to room temperature in air yielded more amorphous samples so that the glass transition temperatures ( $T_g$ ) within the 225–245°C range were recorded in the second heating traces of DSC, these values demonstrating a good correlation with similar systems.<sup>24,25</sup> These values are lower than that of other related polyamides without pendent groups.<sup>25</sup> For example, poly(*m*-phenylene isophthalamide) has a  $T_g$  value of 275°C unlike PA 1, which has a  $T_g$  value of only 225°C. Such behavior of the present polymers could be attributed to the higher free volume determined by the presence of pendent groups. Apparently, the voluminous side chains increased the disorder in the repeating unit and the chain packing. As expected, the  $T_g$  values were dependent on the structures of the carboxylic acid components. The polyamides PA 2, PA 3, and PA 5, having symmetric *p*-phenylene units,

showed the highest  $T_g$  values, polyamide PA 4, derived from 4,4'-oxydibenzoyl component with an ether linkage, exhibited the second highest, and the polymer PA 1, having a unsymmetrical isophthaloyl structure, showed the lowest among these polyamides.

All the polymers exhibited reasonable thermal stability but with their  $T_d$ s (taken at the initial weight loss onset of TGA curves) very similar, about 275°C, indicating that the weight loss upon heating was governed in the first steps of degradation by the thermal breaking of the ethylene (–CH<sub>2</sub>–CH<sub>2</sub>–) and cinnamoyl groups (–HC=CH–), as was observed by TGA measurements made in air. The temperature for 10% weight loss,  $T_{10}$ , which is an important criterion for evaluation of the thermal stability of polymers, was at about 340°C and their char yields at 600°C were in the range of 27–34%.

The crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams. As shown in Figure 3, they have generally amorphous character, which is due to the presence of bulky pendent groups that significantly increase the disorder in chains and, therefore, cause less chain packing. However, polyamides PA 2 and PA 3 exhibited somewhat or moderately crystalline patterns probably due to a better packing of the rigid and symmetrical

TABLE II  
Thermal Behavior of Polyamides PA 1–5

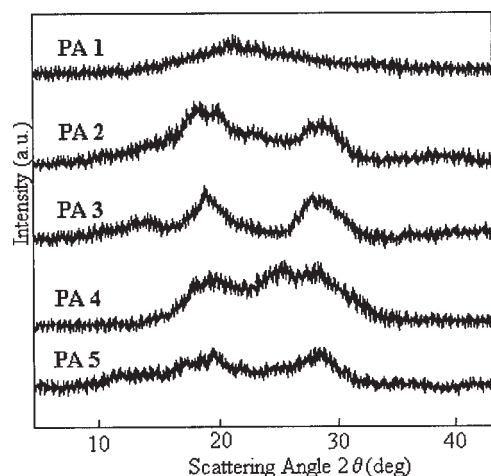
Polymer	$T_g$ (°C) <sup>a</sup>	IDT (°C) <sup>b</sup>	$T_{10}$ (°C) <sup>c</sup>	Char (%) <sup>d</sup>
PA 1	225	279	329	27
PA 2	243	277	340	28
PA 3	238	275	338	32
PA 4	230	273	331	31
PA 5	245	279	348	34

<sup>a</sup>  $T_g$  from the second heating traces of DSC measurements conducted at a heating rate of 10°C/min in air.

<sup>b</sup> IDT (initial decomposition temperature), Temperature at which a 5% weight loss was recorded by TGA at a heating rate of 10°C/min in air.

<sup>c</sup>  $T_{10}$ , Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 10°C/min in air.

<sup>d</sup> Char, Residual yield in TGA at 600°C in air.



**Figure 3** Wide-angle X-ray diffractograms of polyamides.

aromatic rings (*p*-phenylene and biphenyl-4,4'-diyl units, respectively) into the polymer backbones. All the polyamides showed weak diffraction peaks near  $2\theta = 20^\circ$  and  $2\theta = 30^\circ$ , which reveal the presence of the olefinic bonds in the pendant chains but in the case of the two polymers **PA 2** and **PA 3**, they also could indicate a little crystalline order, reflected in their limited solubility.

Spectroscopic data, together with intrinsic viscosity measurements and molecular weights, are given in Table III. Molecular weight determinations were carried out by GPC. In general, high molecular weights were achieved, with weight-average ( $M_w$ ) and number-average ( $M_n$ ) molecular weight values ranging from 39,800 to 72,700 g/mol and 18,800 to 29,000 g/mol, respectively, and a polydispersity index varying between 1.93 and 2.51. The introduction into the polymer chain of unsymmetrical aromatic rings (**PA 1** and **PA 5**), which causes a decrease of crystallinity, or a flexible ether unit (**PA 4**), which reduces the rigidity of the polymer chain, led to higher molecular weight polymers. The molecular weights of polyamides were sufficient for casting transparent, tough, and flexible films. As shown in Table III, the resulting polymers had moderate to

high inherent viscosities of 0.77–1.12 dL/g measured at 0.5 g/dL concentration in NMP at 25°C.

Because of the presence of the amide groups in the molecular chains, the polyamides **PA 1–5**, like all the polyamides, absorb moisture reversibly from the environment until they reach equilibrium. Water absorption is used to determine the amount of water absorbed under specified conditions, such as temperature and length of exposure in water or humid environments. For the water absorption test, the polyamide samples were dried in an oven at 120°C for 8 h and then exposed to a humid environment that is a desiccator where 65% relative humidity was maintained by means of an oversaturated aqueous solution of  $\text{NaNO}_2$  at room temperature. Immediately upon cooling, the specimens were periodically weighed until equilibrium was reached. The amount of absorbed water of these polyamides was in the 4.15–5.24% range and the corresponding values are given in Table IV.

The cinnamoyl group in the side chain of the polymers can be exploited for photo-crosslinking process at wavelengths longer than 280 nm. Cinnamates have been widely employed as photo-crosslinkable units leading polymer backbones to insolubilization. Thus, these polymers can be employed as negative resists (the crosslinked areas become insoluble and remain upon wet development) that can be subsequently ablated (positive resist, the irradiated material is removed). To monitor the photochemical behavior, the film samples to be irradiated were prepared by casting from 10% DMF solutions onto quartz slides. The samples were dried under vacuum at 75°C to remove off the solvent completely. Thin films of cinnamide polymers were illuminated with 313 nm light and subjected to UV spectrum measurement at intervals. Figure 4 presents spectral changes of thin film of the polyamide **PA 3** upon UV irradiation. Before irradiation, the absorbance maxima of polyamide solutions bathochromically shifted by about 8 nm compared to the case of the corresponding polyamide films. This fact indicates that some alteration of spectral shape is induced by

**TABLE III**  
Characteristic Data for Polyamides PA 1–5

Polymer	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	$M_w$ (g/mol) <sup>b</sup>	$M_n$ (g/mol)	$M_w/M_n$	$\lambda_{\text{max}}$ (nm) <sup>c</sup>	$\lambda_{\text{max}}$ (nm) <sup>d</sup>
<b>PA 1</b>	0.77	56,200	23,800	2.36	285	277
<b>PA 2</b>	0.81	39,800	18,800	2.12	293	285
<b>PA 3</b>	0.98	54,600	28,300	1.93	289	282
<b>PA 4</b>	0.87	72,700	29,000	2.51	287	279
<b>PA 5</b>	1.12	60,500	24,800	2.44	290	281

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

<sup>b</sup> Molecular weights relative to polystyrene standards in DMF by GPC.

<sup>c</sup> Absorption maximum of polymer solution in 1,4-dioxane.

<sup>d</sup> Absorption maximum of polymer thin film on a quartz glass.

TABLE IV  
Moisture Absorption Data of Polyamides

Polyamide	Percent water absorption <sup>a</sup>	mol H <sub>2</sub> O/rep. unit	mol H <sub>2</sub> O/equiv. amide	Amide group (wt %)
PA 1	4.68	1.18	0.39	28.35
PA 2	4.83	1.22	0.40	28.35
PA 3	4.91	1.44	0.48	24.29
PA 4	5.24	1.59	0.53	23.58
PA 5	4.15	1.16	0.39	25.54

<sup>a</sup> Percent water absorption = [(wet weight – dry weight)/dry weight] × 100.

molecular interactions between cinnamide chromophores in solid films. The polyamide film, upon UV light irradiation, exhibits an absorption maximum at 282 nm ( $\lambda_{\max}$ ), which is due to the cinnamoyl chromophores in the side groups. An isosbestic point ( $\lambda_{\text{iso}} = 257$  nm) and an abrupt decrease in intensity were observed in the absorption spectral changes at the early stage of UV irradiation. The appearance of an isosbestic point confirms that the initial irradiation causes a cis–trans isomerization. Further photoirradiation brings about spectral changes with a slowly decrease of UV-absorption maximum, accompanied by a deviation from the isosbestic point. This implies that prolonged UV irradiation leads to the formation of cyclobutane rings through  $[2\pi + 2\pi]$  cycloaddition of the carbon–carbon double bond in the cinnamoyl unit. The rate of disappearance of carbon–carbon double bond of the pendent cinnamoyl group was monitored by measuring the UV absorption intensity of the polymer film after each exposure interval using the following expression:

$$\text{Rate of crosslinking (\%)} = \frac{A_0 - A_T}{A_0} \times 100$$

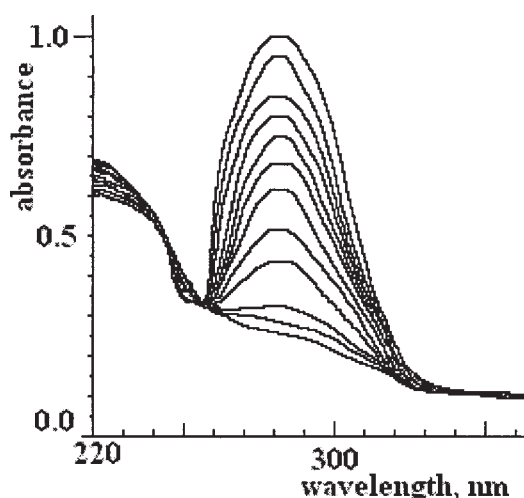


Figure 4 Absorption spectra of PA 3 as film, at irradiation times of 0.5, 1, 1.5, 2, 3, 4.5, 6, 10, 20, and 25 min, from top to bottom, at 282 nm.

where  $A_0$  and  $A_T$  are absorption intensities due to  $>C=C<$  chromophore after irradiation of times  $t = 0$  and  $t = T$ , respectively.

The crosslinking nature of the polymers suggests that the photoreactivity of all polyamides PA 1–5 was mainly confined to the photoreactive moiety in the polymer chain and not to the type of polymer. Figure 5 portrays the plot of percentage of crosslinking versus time. As is well known, the segmental mobility of the polymer main or side chain plays an important role in determining the photocrosslinking rate of photosensitive polymers, i.e., greater mobility renders faster reaction attributable to easy approach of photoreactive chromophores. The rates of crosslinking of the present polyamides containing extended photosensitive moieties are higher than that of similar polyamides without extended photosensitive units in the side chains.<sup>6</sup> The increased rate of crosslinking is ascribed to the oxyethylene spacer between the chromophore and the polymer backbone, which increases the flexibility of the pendent group and gives more free movements to that.

Polymers having cinnamate residues are known to be insolubilized by photoirradiation due to the photodimerization to form intermolecular crosslinkages. It was confirmed that thin films of all polymers presented in this work became insoluble upon UV irradiation with 313 nm light. Cyclobutane formation

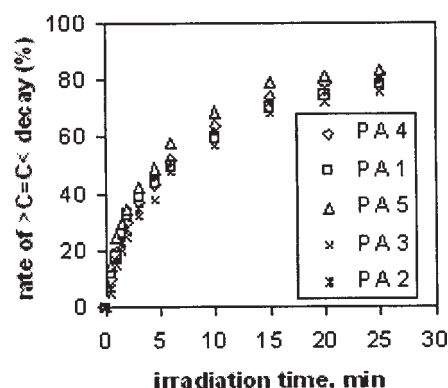


Figure 5 Rate of disappearance of  $>C=C<$  chromophore with time for the polyamide films.

in polyamides during the photocrosslinking reaction was also confirmed by IR spectroscopy. Polyamide films showed infrared absorption bands around  $1725\text{ cm}^{-1}$ , assignable to the conjugated C=O stretching vibration of the cinnamoyl moiety, and around  $1640$  and  $980\text{ cm}^{-1}$ , attributed to the vinylene C=C stretching vibration and the *trans*-vinylene C–H deformation vibration in the cinnamoyl moieties, respectively. As the exposure time increases, the intensity of the band at  $1725\text{ cm}^{-1}$  decreases and its position shifts to higher wavenumber. At longer exposure time, a new band, presumably originating from the nonconjugated C=O stretching vibration, is observed at around  $1735\text{ cm}^{-1}$ . The intensities of the bands at  $1640$  and  $980\text{ cm}^{-1}$  decreased with increasing exposure time, indicating that substituted cyclobutane rings were formed in the film by UV exposure. The intensity drop in the vinylene C=C stretching band might originate from the photodimerization of the cinnamoyl moieties, while the intensity drop in the *trans*-vinylene C–H deformation vibrational band could result from the consumption of the *trans*-vinylene linkage in the cinnamoyl moiety due to *trans*-*cis* photoisomerization and photodimerization.<sup>26,27</sup>

## CONCLUSIONS

A new derivative of 3,5-diaminobenzoic acid comprising an ethylene-cinnamide group as substituent was prepared and successfully used as a condensation monomer in reaction with aromatic dicarboxylic acids for the synthesis of certain new aromatic polyamides.

As expected, the presence of the bulky and extended cinnamide unit in the side chain renders the polymers soluble and photosensitive. All polyamides had good solubility in polar aprotic solvents and could be cast into strong, homogeneous, and flexible films. The polymers had weight- and number-average molecular weights in the range of  $39,000$ – $72,700$  and  $18,800$ – $29,000$ , respectively, and polydispersity index varying between  $1.93$  and  $2.51$ . The polymers had moderate  $T_g$  values ( $225$ – $245^\circ\text{C}$ ) and relatively high hydrophilicity. Cinnamoyl-based polyamides in the films were found to undergo the  $[2\pi + 2\pi]$  cycloaddition of the vinylene C=C in addition to the *trans*-*cis* photoisomerization of the cinnamoyl species during UV illumination. The absorption band at around  $280\text{ nm}$  decreased with the irradiation

time, exhibiting the crosslinking (dimerization) between the cinnamoyl moieties in the side chains. Good solubility, moderate  $T_g$  values, film forming, and their photocrosslinkable properties leading to insolubilization make these polyamides suitable for microelectronics applications.

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