

# Synthesis and Properties of Novel Poly(coumarin-amide)s

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**ABSTRACT:** A novel monomer diacid, 6,6'-methylenebis(2-oxo-2H-chromene-3-carboxylic acid), was synthesized and used in a direct polycondensation reaction with various aromatic diamines in *N*-methyl-2-pyrrolidone solution containing dissolved LiCl and CaCl<sub>2</sub>, using triphenyl phosphite and pyridine as condensing agents to give a series of novel heteroaromatic polyamides containing photosensitive coumarin groups in the main chain. Polyamide properties were investigated by DSC, TGA, GPC, wide-angle X-ray scattering, viscosity, and solubility measurements. The copolymers were soluble in aprotic polar solvents, and their inherent viscosities varied between 0.49 and 0.78 dL g<sup>-1</sup>. The weight-average and number-average molecular weights, measured by gel permeation chromatography, were 27,500–43,900 g mol<sup>-1</sup> and 46,500–66,300 g mol<sup>-1</sup>, respectively, and polydispersities in the range of

1.48–1.69. The aromatic polyamides showed glass-transition temperatures (*T*<sub>g</sub>) ranging from 283 to 329°C and good thermal properties evidenced by no significant weight loss up to 380°C and 10% weight loss recorded above 425°C in air. All the polyamides exhibited an amorphous nature as evidenced by wide-angle X-ray diffraction and demonstrated a film forming capability. Water uptake values up to 3.35% were observed at 65% relative humidity. These polymers exhibited strong UV-vis absorption maxima at 357–369 nm in DMSO solution, and no discernible photoluminescence maxima were detected by exciting with 365 nm. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1450–1458, 2010

**Key words:** crosslinking; heteroatom-containing polymers; linear polymers; polyamides; synthesis

## INTRODUCTION

Coumarins, natural products well known for their diverse biological activities, have a broad range of applications in the pharmaceutical, perfume, and cosmetic industries. Synthetic coumarins are exploited as intermediates and building blocks in organic and polymer synthesis because they exhibit a high photosensitivity. Crosslinking by photodimerization of coumarin has been used for a variety of purposes such as preparation of biodegradable crosslinked materials, microfabrication of medical devices and drug encapsulation, and studies on reversible photocrosslinking and photocleavage of the coumarin polymers.<sup>1</sup> Aromatic polyamides, a class of high-temperature resistant engineering polymers, exhibit excellent thermal, mechanical, and electrical properties as well as outstanding chemical resistance. Usually, these polymers are infusible and soluble only in strong acidic media, and consequently, their potential applications are limited. Therefore, several modifications of their chemical structure have been performed to lower their transition temperatures and to enhance their solubility. One

approach used for increasing the solubility and processability of these polymers is the insertion of flexible linkages into the polymer backbone, such as, —O—<sup>2,3</sup>, —CO—<sup>4</sup>, —SO<sub>2</sub>—<sup>5</sup>, —S—<sup>6</sup>, —CH<sub>2</sub>—<sup>7</sup>, —C(CH<sub>3</sub>)<sub>2</sub>—<sup>8</sup>, and —C(CF<sub>3</sub>)<sub>2</sub>—<sup>9,10</sup>. These kinked and flexible bridging units are incorporated between aromatic units into the polymer chain on purpose to reduce the chain stiffness and lower the glass-transition temperatures. These linkages create bent bonds in the polymer chain and permit the rotation of aromatic rings. Generally, increased chain flexibility leads to the loss of thermal stability and significant decrease in tensile strength on heating. The incorporation of hexafluoroisopropylidene groups into polymer backbones enhances the polymer solubility with the retention of a higher thermal stability, due to the strong C—F bonds. In addition, —C(CF<sub>3</sub>)<sub>2</sub>— groups bring about increased glass-transition temperatures and flame resistance with a concomitant reduced crystallinity and water absorption. Structural modification plays an important role on the properties of aromatic polyamides and requires the use of different combinations of monomers to prepare them and the evaluation of their final properties.

Hence, the goal of a better solubility, together with the retention of a relative high thermal stability, could be achieved in preparing polyamides containing both methylene linkages introduced by the bis-coumarin diacid monomer, 6,6'-methylenebis(2-oxo-

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2H-chromene-3-carboxylic acid), and flexible ether and bulky  $-\text{C}(\text{CF}_3)_2-$  groups inserted into polymer structures by the aromatic diamines. It is expected that the incorporation of the bulky diacid group decrease the hydrogen bonding between amide groups and disrupt the coplanarity of aromatic units. Consequently, packing efficiency and crystallinity would be reduced. This should promote solubility while maintaining high glass-transition temperatures through controlled segmental mobility.

## EXPERIMENTAL

### Materials

2-Hydroxybenzaldehyde, 1,3,5-trioxane, and diethyl malonate were used as received. Reagent grade solvents were dried and purified as follows. *N*-Methylpyrrolidone (NMP) and pyridine (Py) were refluxed in an inert atmosphere in the presence of phosphorous pentoxide ( $\text{P}_4\text{O}_{10}$ ) and freshly powdered calcium hydride ( $\text{CaH}_2$ ), respectively, for 2 h, distilled under vacuum and stored over 4 Å molecular sieves. Triethylamine was distilled over potassium hydroxide (KOH) pellets and then stored over 5 Å molecular sieves. Reagent grade lithium chloride (LiCl) and calcium chloride ( $\text{CaCl}_2$ ) were dried at 170°C for 8 h under vacuum. Triphenyl phosphite (TPP) was purified by vacuum distillation. 4,4'-Oxydianiline (**7a**), 4,4'-(1,3-phenylenedioxy)dianiline (**7b**), 4,4'-(hexafluoroisopropylidene)dianiline (**7c**), 4,4''-(hexafluoroisopropylidene)bis(4-phenoxyaniline) (**7d**) were of high purity and used without further purification. All chemicals were purchased from Aldrich Chemical Co.

### Physical measurements

Spectral measurements of  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR were performed on a Bruker Avance DRX spectrometer at 400 and 100 MHz, respectively, using  $\text{DMSO}-d_6$  as solvent. Electronic absorption spectra were recorded using a SPECORD M42 spectrophotometer. Polymer films on quartz plate were prepared from all the polymers by controlled evaporation of the solvent from cast solutions. Polymeric films and solution samples were exposed to UV light irradiation from a 500 W high-pressure mercury lamp in the absence of a filter, at room temperature, at various exposure intervals. Film specimens of the synthesized polymers on KBr window were prepared from dimethylformamide (DMF) solution (2%). After the solvent was evaporated, the films were stored under vacuum at 150°C for at least 5 h to remove the residual solvent completely. Mass spectral data were obtained using an Agilent 6210 TOF LC/MS. The inherent viscosities of polymer solutions (0.5% w/v) in

NMP were determined at 30°C using an Ubbelohde suspended level viscometer. For all the aromatic polyamides, the infrared spectra were recorded on a Bruker Vertex 70 Fourier transform infrared spectrometer (FTIR). Solubility was determined at 1% (w/w) concentration. Elemental analyses were run in a Perkin Elmer 2400 CHNSO analyzer. Thermal stability was measured over 20–600°C in air at a heating rate of 10°C/min using a thermogravimeter Q-1500D system (F. Paulik, J. Paulik, Erdey). Differential scanning calorimetry (DSC) analyses were done on a Mettler DSC 112E instrument, with heating and cooling rate of 10°C  $\text{min}^{-1}$  in flowing nitrogen. The reported  $T_g$ 's were taken as the onset temperature of the glass-transition in the thermogram. Wide-angle X-ray scattering measurements were performed on a Bruker AXS-D8 Avance X-ray diffractometer using  $\text{CuK}_\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), at 36 KV and 30 mA, using samples as powders. The measurements were performed at  $2\theta$  between 5 and 60°. Weight-average molecular weights ( $M_w$ 's) and number-average molecular weights ( $M_n$ 's) were obtained via gel permeation chromatography (GPC) based on polystyrene calibration using a PL-EMD 950 evaporative mass detector instrument and DMF as the eluant. Water absorption measurements were determined gravimetrically at room temperature. Powdered polymer samples were dried at 120°C for 24 h over  $\text{P}_2\text{O}_5$ , and then placed in a desiccator containing a saturated aqueous solution of  $\text{NaNO}_2$ , which provided a relative humidity of 65%. The samples were allowed to humidify for 48 h until they had reached equilibrium, as denoted by no weight change.

### Monomer synthesis

#### 3,3'-Methylene-bis(6-hydroxybenzaldehyde) (3)

A solution of 2-hydroxybenzaldehyde (**1**) (30.5 g, 0.25 mol) and 1,3,5-trioxane (**2**) (2.7 g, 0.03 mol) in glacial acetic acid (15 mL) was heated to 80°C under stirring in nitrogen atmosphere. To this, a solution of concentrated sulfuric acid (0.1 mL) in glacial acetic acid (5 mL) was added dropwise. The temperature of reaction mixture was maintained at 80°C for 8 h, and then it was cooled and poured onto a large amount of ice water. The precipitate formed was filtered and washed with plenty of hot distilled water to remove acetic acid. The solid was extracted three times with diethyl ether to remove the excess of salicylaldehyde, then dried in a vacuum oven at room temperature, and crystallized twice from acetone to give 10.4 g (overall yield 45%) of compound (**3**); m.p. = 141–142°C. MS:  $m/z$  (%) = 256 ( $M^+$ , 100), 254 (91), 220 (12), 198 (27), 135 (67), 121 (16), 103 (9), 94 (11), 77 (14). Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{O}_4$  (256.256):

C, 70.31%; H, 4.68%. Found: C, 70.49%; H, 4.76%. IR (KBr,  $\text{cm}^{-1}$ ),  $\nu$ : 3463, 3328 (OH), 3105–3000 (C=CH arom), 2909 ( $\text{CH}_2$ ), 2885 (H—CO), 2760, 1655 (HC=O), 844, 810 ( $\text{CH}_2$ ).  $^1\text{H-NMR}$ :  $\delta$ , ppm = 10.85 (d, 2H, OH), 10.10 (s, 2H, CH=O), 7.75 (d, 2H, *ortho* to CHO), 7.60 (d, 2H, *meta* to OH), 7.00 (d, 2H, *ortho* to OH), 4.01 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C-NMR}$ :  $\delta$ , ppm = 197.6 (C=O), 161.0 (C6), 134.5 (C4), 132.8 (C3), 128.9 (C2), 121.1 (C1), 116.7 (C5), 42.3 ( $\text{CH}_2$ ).

#### 6,6'-Methylenebis(2-oxo-2H-chromene-3-ethoxycarbonyl) (5)

A solution of 5,5'-methylene-bis(salicylaldehyde) (3) (0.04 mol, 10.24 g), diethylmalonate (4) (0.088 mol, 14.08 g), 50 mL of absolute ethanol, 1 mL piperidine, and a few drops of acetic acid was stirred and heated to reflux for 5 h. Then the mixture was poured into 100 mL of ice-water mixture, and the precipitate was filtered and washed with distilled water. The product was dried under reduced pressure and purified by recrystallization from ethanol-water (1 : 2) to produce 11.45 g (64% yield) of dark orange crystals of the compound (5). M.p. = 123–124°C. MS:  $m/z$  (%) = 448 (M+, 23), 392 (25), 360 (11), 358 (100), 231 (14), 217 (16), 203 (12), 189 (17), 146 (29), 145 (21), 118 (12), 90 (9), 89 (8), 63 (13), 62 (10), 45 (7). Anal. Calcd. for  $\text{C}_{25}\text{H}_{20}\text{O}_8$  (448.425): C, 66.96%; H, 4.46%. Found: C, 67.16%; H, 4.59%. IR (KBr,  $\text{cm}^{-1}$ ),  $\nu$ : 3065 (C=CH arom), 2980, 2950 (CH aliph), 1755 (C=O ester), 1722 (C=O enone), 1620 (C=C), 850, 810 ( $\text{CH}_2$ ).  $^1\text{H-NMR}$ :  $\delta$ , ppm = 8.41 (s, 2H, H4), 7.80–7.70 (m, 4H, H5, H7), 7.30–7.25 (m, 2H, H8), 4.45 (q, 4H,  $J = 7.2$  Hz,  $\text{CH}_2$ ), 1.40 (t, 6H,  $J = 7.2$  Hz,  $\text{CH}_3$ ), 3.97 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C-NMR}$ :  $\delta$ , ppm = 162.7 (C=O), 156.0 (C2), 152.2 (C9), 149.3 (C4), 137.1 (C6), 132.3 (C7), 129.6 (C5), 118.8 (C10), 117.4 (C3), 111.9 (C8), 61.9 ( $\text{CH}_2$ ), 44.5 ( $\text{CH}_2$ ), 14.1 ( $\text{CH}_3$ ).

#### 6,6'-Methylenebis(2-oxo-2H-chromene-3-carboxylic acid) (6)

A solution of 6,6'-methylenebis(2-oxo-2H-chromene-3-ethoxycarbonyl) (5) (11.2 g, 0.025 mol), NaOH (20 g, 0.5 mol), ethanol (75 mL), and water (125 mL) was refluxed with stirring for 24 h. After cooling to room temperature, the mixture was poured into an aqueous solution of HCl with vigorous stirring, and the pale yellow precipitate was filtered off, washed with water, and recrystallized from ethyl acetate. The yield in biscoumaric acid (6) was 84% (8.2 g), m.p. = 211–213°C. MS:  $m/z$  (%) = 392 (M+, 27), 358 (90), 203 (33), 189 (21), 146 (100), 145 (18), 90 (17), 89 (12), 63 (9), 62 (7), 45 (6). Anal. Calcd. for  $\text{C}_{21}\text{H}_{12}\text{O}_8$  (392.318): C, 64.28%; H, 3.06%. Found: C, 64.19%; H, 3.17%. IR (KBr,  $\text{cm}^{-1}$ ),  $\nu$ : 3400 (OH free), 3065 (C=CH arom), 2980, 2950 (CH aliph), 1750 (C=O

enone), 1690 (C=O, COOH), 1615 (C=C), 850, 810 ( $\text{CH}_2$ ).  $^1\text{H-NMR}$ :  $\delta$ , ppm = 8.70 (s, 2H, H4), 7.48 (d, 2H, H8,  $J = 8.5$  Hz), 7.27 (d, 2H, H5,  $J = 2.0$  Hz), 7.17 (dd, 2H, H7,  $J = 2.0$  Hz,  $J = 8.5$  Hz), 4.03 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C-NMR}$ :  $\delta$ , ppm = 164.0 (C=O), 156.4 (C2), 148.6 (C4), 146.2 (C8), 143.7 (C9), 138.8 (C6), 121.1 (C7), 119.2, 118.8 (C3, C10), 116.5 (C5), 44.1 ( $\text{CH}_2$ ).

#### Polyamide synthesis

A mixture of dicarboxylic acid (6) (0.392 g, 0.001 mol), diamine (7b) (0.292 g, 0.001 mol), TPP (0.57 mL, 0.0022 mol), NMP (25 mL), Py (5 mL),  $\text{CaCl}_2$  (1.8 g), and LiCl (0.6 g) was heated at 115°C for 5 h under an inert atmosphere to avoid humidity and air. No precipitation of the polymers during the preparation was observed. After cooling, the reaction mixture was poured into 100 mL of methanol with constant stirring. The precipitate was collected on a filter and washed thoroughly with methanol and hot water. The solid was dried under vacuum to give 0.61 g of PA 2 (94% yield). The inherent viscosity of the resulting polyamide in NMP was 0.78  $\text{dL g}^{-1}$ , measured at 30°C at a polymer concentration of 0.5  $\text{g dL}^{-1}$ . The other polyamides were prepared by the same general procedure.  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectroscopic data for PA 1–4 are given below.

#### PA 1

$^1\text{H-NMR}$ :  $\delta$ , ppm = 10.70 (s, 2H, NH), 8.27 (s, 2H, H4 coum), 7.85–7.88 (d, 4H, arom diamine *ortho* to NH), 7.33 (d, 2H, H8 coum), 7.11–7.15 (dd, 4H, H5, and H7 coum), 7.04–7.08 (d, 4H, arom diamine *ortho* to ether), 4.40 (s, 2H,  $\text{CH}_2$ ).  $^{13}\text{C-NMR}$ :  $\delta$ , ppm = 160.4 (C2 coum), 159.8 (CO—NH), 151.9 (C9 coum), 151.5 (arom diamine adjacent to ether), 148.2 (C4 coum), 137.2 (C6 coum), 134.9 (arom diamine adjacent to NH), 133.0 (C7 coum), 126.5 (C5 coum), 121.8 (arom diamine *ortho* to NH), 120.1 (C10 coum), 119.3 (arom diamine *ortho* to ether), 116.2 (C3 coum), 112.4 (C8 coum), 44.5 ( $\text{CH}_2$ ).

#### PA 2

$^1\text{H-NMR}$ :  $\delta$ , ppm = (a) 10.78 (s, 2H, NH), (b) 8.49 (s, 2H, H4 coum), (c) 7.72 (d, 4H, arom diamine *ortho* to NH), (d) 7.33 (d, 2H, H8 coum), (e, f) 7.11–7.15 (dd, 4H, H5, and H7 coum), (g, h) 6.94–6.98 (d, 4H, arom diamine *ortho* to ether), and (i) 4.40 (s, 2H,  $\text{CH}_2$ ) (Fig. 1).

The  $^{13}\text{C-NMR}$  spectrum of polyamide PA 2 consists of coumarin peaks at 160.2 (C2), 151.9 (C9), 148.7 (C4), 137.2 (C6), 133.0 (C7), 126.5 (C5), 120.1 (C10), 116.6 (C3), 112.4 (C8) ppm, aromatic carbons from diamine moiety at 154.0 (C4'), 150.8 (C5'), 135.9 (C1'), 122.2 (C2'), 120.7, 120.2 (C3', C6') ppm, and

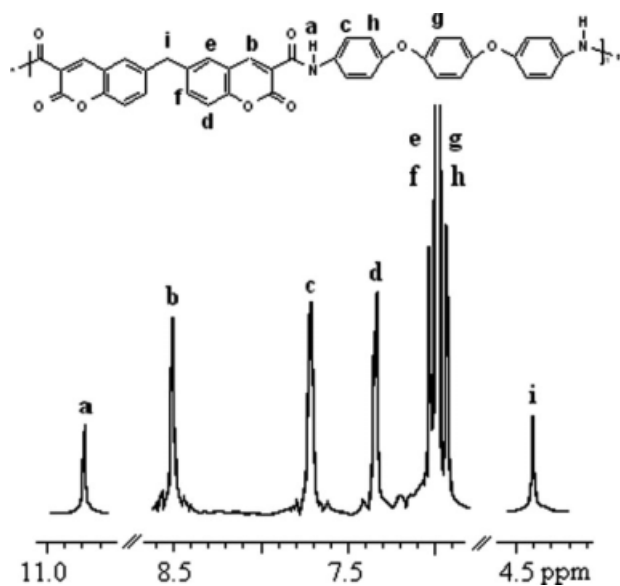


Figure 1  $^1\text{H-NMR}$  spectrum of the polyamide PA 2.

two signals at 160.2 and 44.5 ppm attributed to CO—NH and CH<sub>2</sub>, respectively (Fig. 2).

#### PA 3

$^1\text{H-NMR}$ :  $\delta$ , ppm = 10.93 (s, 2H, NH), 8.86 (s, 2H, H4 coum), 7.94 (d, 4H, arom diamine *ortho* to NH), 7.38–7.31 (m, 6H, arom diamine *ortho* to C(CF<sub>3</sub>)<sub>2</sub> and H8 coum), 7.11–7.15 (dd, 4H, H5, and H7 coum), 4.40 (s, 2H, CH<sub>2</sub>).  $^{13}\text{C-NMR}$ :  $\delta$ , ppm = 164.7 (CO—NH), 160.8 (C2 coum), 151.9 (C9 coum), 149.2 (C4 coum), 140.4 (arom diamine adjacent to NH), 137.2 (C6 coum), 133.0 (C7 coum), 127.6 (arom diamine *ortho* to C(CF<sub>3</sub>)<sub>2</sub>), 126.5 (C5 coum), 123.3 (arom diamine adjacent to C(CF<sub>3</sub>)<sub>2</sub>), 120.4, 120.1 (arom diamine *ortho* to NH and C10 coum), 116.2 (C3 coum), 112.4 (C8 coum), 44.5 (CH<sub>2</sub>); tetrasubstituted C and CF<sub>3</sub> were not observed.

#### PA 4

$^1\text{H-NMR}$ :  $\delta$ , ppm = 10.82 (s, 2H, NH), 8.65 (s, 2H, H4 coum), (c) 7.90 (d, 4H, arom diamine *ortho* to NH), 7.40 (d, 4H, arom diamine *ortho* to C(CF<sub>3</sub>)<sub>2</sub>), 7.33 (d, 2H, H8 coum), 7.19–7.09 (m, 12H, arom diamine *meta* to C(CF<sub>3</sub>)<sub>2</sub> and NH, and H5 and H7 coum), 4.40 (s, 2H, CH<sub>2</sub>).  $^{13}\text{C-NMR}$ :  $\delta$ , ppm = 162.6 (arom diamine *para* to C(CF<sub>3</sub>)<sub>2</sub>), 160.7 (CO—NH), 160.0 (C2 coum), 153.8 (arom diamine *para* to NH), 151.9 (C9 coum), 148.6 (C4 coum), 137.2 (C6 coum), 135.5 (arom diamine adjacent to NH), 134.7 (arom diamine *ortho* to C(CF<sub>3</sub>)<sub>2</sub>), 133.0 (C7 coum), 126.5 (C5 coum), 124.3 (arom diamine *ortho* to NH), 122.2 (arom diamine *meta* to NH), 120.1 (C10 coum), 118.4 (arom diamine *meta* to C(CF<sub>3</sub>)<sub>2</sub>), 116.0 (C3 coum),

112.4 (C8 coum), 44.5 (CH<sub>2</sub>); tetrasubstituted C and CF<sub>3</sub> were not observed.

## RESULTS AND DISCUSSION

### Monomer and polymer synthesis

A novel diacid monomer, 6,6'-methylenebis(2-oxo-2H-chromene-3-carboxylic acid) (6) was prepared from salicylaldehyde (1) as a starting material as shown in Scheme 1.

Bis(salicylaldehyde) (3) was synthesized by the reaction of salicylaldehyde (1) with trioxane (2) using a molar ratio salicylaldehyde:formaldehyde = 2.78 : 1.<sup>11</sup> The excess of salicylaldehyde reduces by-products formation. Then the condensation of 3 with diethyl malonate (4) through a Knoevenagel type reaction gave 6,6'-methylenebis(2-oxo-2H-chromene-3-carboxylic acid ethyl ester) (5), which was further hydrolyzed to obtain 6.<sup>12</sup>

Direct polycondensation of aromatic diamines with dicarboxylic acids in the presence of TPP and Py as condensing agents is a well known convenient method to prepare aromatic polyamides as TPP activates carboxylic acid by phosphorylation of the carboxylic acid, and the activated complex is attacked by nucleophiles.<sup>13</sup> Addition of the inorganic salts promotes the direct polycondensation and increases both the solubility of the polymers in reaction media and viscosity of resulting polymers, and consequently, the yield and molecular weight of polyamides.

Aromatic polyamides with coumarin units in the backbone were successfully synthesized by this

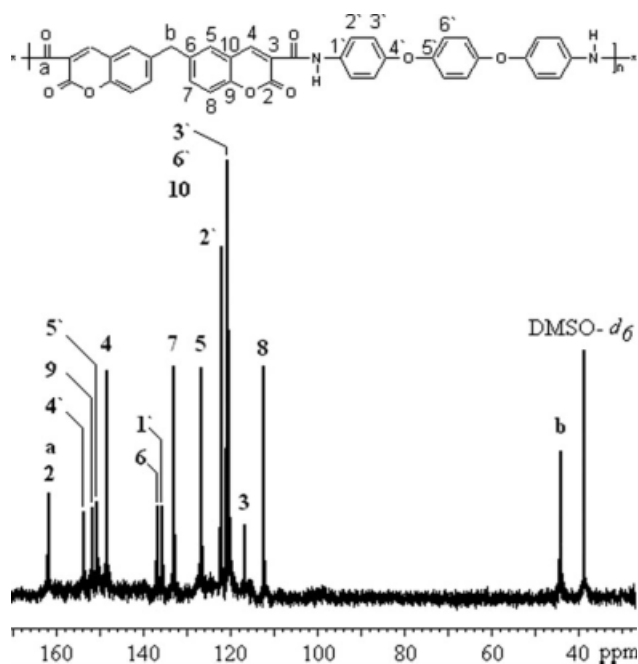
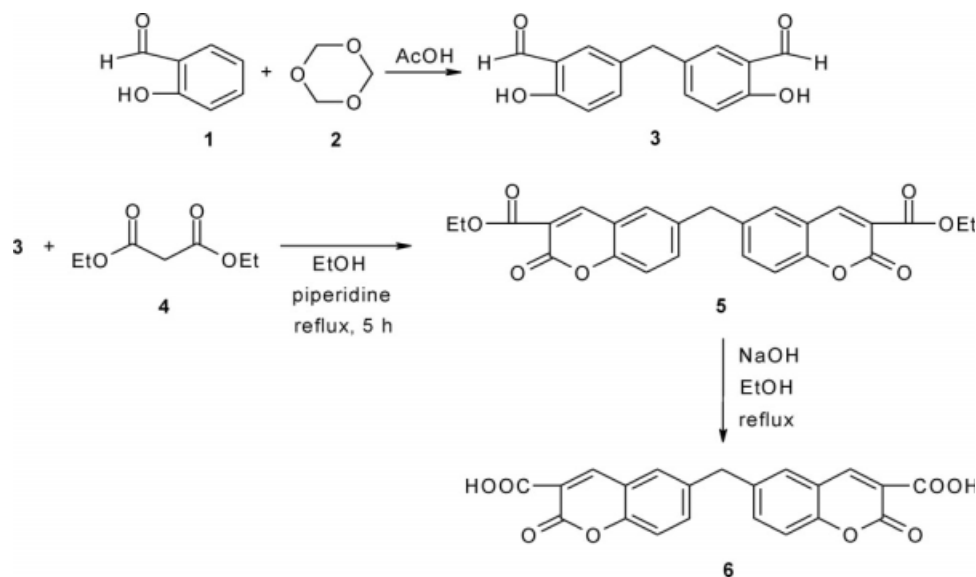


Figure 2  $^{13}\text{C-NMR}$  spectrum of the polyamide PA 2.

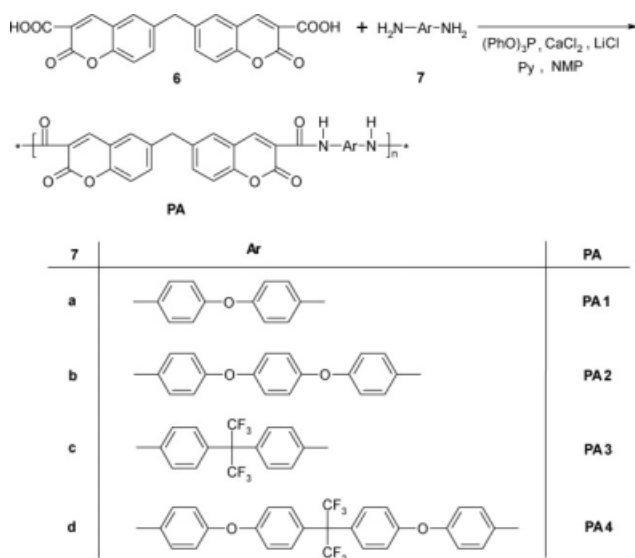


**Scheme 1** Synthesis of 6,6'-methylenebis(2-oxo-2H-chromene-3-carboxylic acid).

method using a mixture of NMP/Py ( $v/v = 5/1$ ) containing dissolved inorganic salts (8 wt % based on solvent and Py mixture), in the presence of a small excess of activator (TPP) (Scheme 2).

During polymerization reaction, all the systems remained homogeneous, and the polymers were isolated as powders in almost quantitative yields. As shown in Table I, the polyamides had inherent viscosities ranging from 0.49 to 0.78  $\text{dL g}^{-1}$  and number-average molecular weight ( $M_n$ ) values varying between 27,500 and 43,900  $\text{g mol}^{-1}$ , indicating that relative high molecular weights were achieved. GPC results also displayed low polydispersity values ranging from 1.48 to 1.69. As can be seen in Table I, the reactivity of the diamine moiety influences the

inherent viscosities and molecular weights of the polymers. The highest values of inherent viscosity and molecular weight belong to polyamide PA 2 derived from a reactive aromatic diamine (7b), whereas the lowest values pertain to polyamide PA 3 derived from a less reactive diamine (7c) which contains a strong electron-withdrawing group. The polymer structures were identified by FTIR,  $^1\text{H}$ -, and  $^{13}\text{C}$ -NMR spectroscopy. The IR spectra of the polymers show that the characteristic absorptions of amide groups occur around 3380–3280  $\text{cm}^{-1}$  and 1670–1640  $\text{cm}^{-1}$ , indicating N–H and C=O stretching, respectively. Strong absorptions of the aryl ether group and C–F stretching appear in the region of 1200–1250  $\text{cm}^{-1}$ , 1170–1180  $\text{cm}^{-1}$ , and 1200–1220  $\text{cm}^{-1}$ , respectively. The spectra exhibit characteristic absorption bands around 3050  $\text{cm}^{-1}$  (aromatic C–H), 1530  $\text{cm}^{-1}$  (N–H deformation), 1350  $\text{cm}^{-1}$  (mixed vibrations of OCN and NH groups), and 1150  $\text{cm}^{-1}$  (N–H bending). The presence of coumarin group in polyamide structures is evidenced by the appearance of characteristic absorption bands at 1730  $\text{cm}^{-1}$  due to carbonyl stretching and around



**Scheme 2** Synthesis of polyamides.

**TABLE I**  
Inherent Viscosity and GPC Values of Polyamides

Polymer code	$\eta_{\text{inh}}^{\text{a}}$ ( $\text{dL g}^{-1}$ )	$M_n^{\text{b}}$ ( $\text{g mol}^{-1}$ )	$M_w^{\text{b}}$ ( $\text{g mol}^{-1}$ )	$M_w/M_n$
PA 1	0.72	39,100	57,900	1.48
PA 2	0.78	43,900	66,300	1.51
PA 3	0.49	27,500	46,500	1.69
PA 4	0.61	34,300	54,900	1.60

<sup>a</sup> Measured in NMP at a polymer concentration of 0.5  $\text{g dL}^{-1}$  at 30°C.

<sup>b</sup> Relative to polystyrene standard, using DMF as eluant.

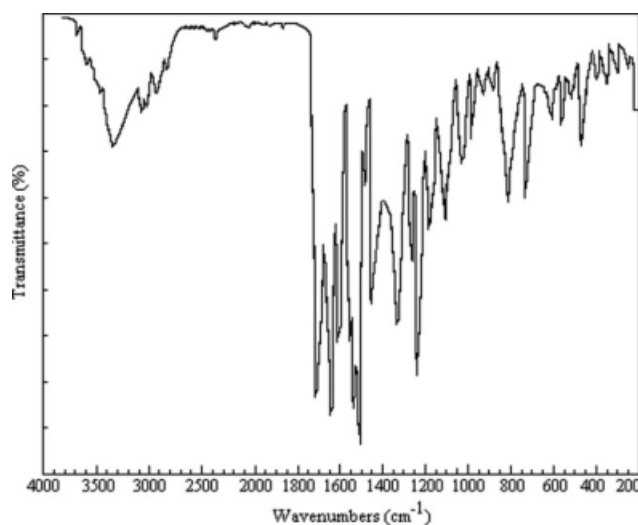


Figure 3 FTIR spectrum of the polyamide PA 2.

1615  $\text{cm}^{-1}$  ascribed to vinylene C=C stretching vibration. Figure 3 shows the FTIR spectrum of PA 2 as an illustrative example.

Figures 1 and 2 illustrate the  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR, respectively, spectra of polyamide PA 2, where all the peaks are readily ascribed to the protons and carbons, respectively, of the repeating unit.

### Polymer characterization

The solubility behavior of these polyamides was tested quantitatively, and the results are summarized in Table II. The polyamides dissolved in high polar solvents such as NMP, DMAc, DMSO, and DMF. In moderate polar solvents such as dioxane, *m*-cresol, Py, and THF they showed limited solubility. All the polymers were soluble in concentrated sulphuric acid and *o*-chlorophenol. The polymers are insoluble in chlorinated solvents such as chloroform, dichloromethane, tetrachloroethane, and other common organic solvents such as acetone or cyclohexanone. The substituted methylene linkages (i.e., hexafluoroisopropylidene groups) provide kinks in the backbone of the polymer, which lead to smaller

TABLE II  
Solubility Behavior of Polyamides<sup>a</sup>

Polymer code	Solubility							
	NMP	DMAc	DMSO	DMF	<i>m</i> -cresol	THF	Py	Dioxane
PA 1	+	+	+	+	+h	s	s	s
PA 2	+	+	+	+	s	–	s	–
PA 3	+	+	+	+	+	+	+h	+h
PA 4	+	+	+	+	+	+	+h	+h

(+) Soluble at room temperature; (+h) soluble on heating at 70°C; (–) insoluble; (s) swelling.

<sup>a</sup> Measured at a polymer concentration of 0.01  $\text{g mL}^{-1}$ .

TABLE III  
Thermal Characterization of Polymers PA 1–4

Polymer code	$T_g^a$ (°C)	$T_i^b$ (%)	$T_{10}^c$ (°C)	Char yield <sup>d</sup> (%)
PA 1	312	382	426	14
PA 2	290	395	437	16
PA 3	329	388	428	12
PA 4	283	401	442	18

<sup>a</sup> Glass transition temperature, from the second heating traces of DSC measurements.

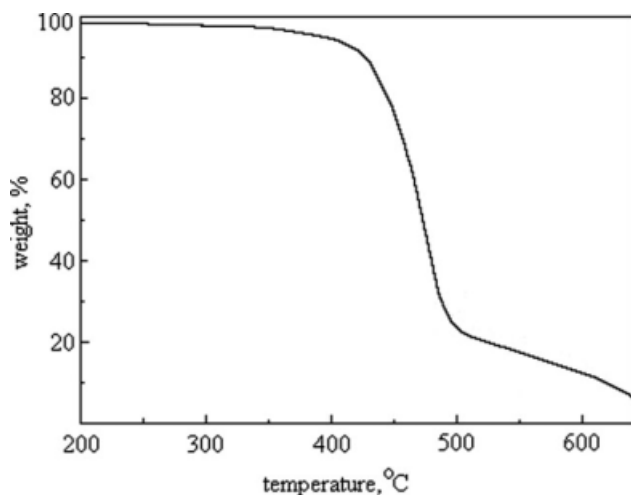
<sup>b</sup> Temperature at which the sample achieves 5% weight loss.

<sup>c</sup> Temperature at which a 10% weight loss was recorded by TGA.

<sup>d</sup> Aerobic residual weight at 600°C.

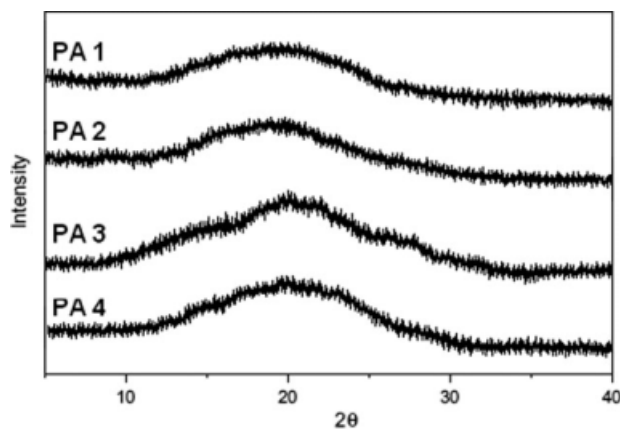
hydrodynamic volumes when compared with rigid-rod type systems. These kinks usually lead to the lower intrinsic viscosity values and increased solubility of these polymers. The introduction of the flexible ether bonds and methylene linkages improves the overall flexibility of the polymer chain and, consequently, the limited solubility exhibited by the polymers shows that the increase of flexibility is partly counterbalanced by the high rigidity induced by coumarin units.

The thermal behavior of the polymers was evaluated by DSC and thermogravimetric analysis (TGA). All the aromatic polyamides exhibited good thermal stability with insignificant weight loss up to 380°C in air. The temperatures of 5 and 10% weight loss, together with residual weight at 600°C were calculated from polymer thermograms and are tabulated in Table III. The TGA traces of all samples exhibited similar patterns of decomposition with a smooth, stepwise manner, suggesting a two-step thermal degradation. As an example, the TGA trace for polymer PA 3 is shown in Figure 4. A small weight loss in the temperature range from 100 to 300°C is due to residual solvent (NMP) and water evaporation (polyamides are known to absorb significant amounts of moisture because of hydrogen bonding with their polar amide linkages). A large weight loss at over 425°C is due to the heat decomposition of the polymers backbone. The weight loss in the region 100–300°C varied between 2.1% and 3.2%. It can be seen that  $T_i$ 's were quite similar, indicating that the weight loss upon heating was governed in the first step of degradation by the cleavage of methylene groups. Although the rigid nature of the coumarin-segment in the polymer main chain could impart its high thermal stability to the polyamides, the presence of the methylene linkage in the diacid structure brings about a moderately high thermostability. The  $T_g$  values of the polymers were observed in the range of 283–329°C and generally increased with decreasing conformational flexibility



**Figure 4** TGA curve of the polymer PA 3 recorded at a heating rate of  $10^{\circ}\text{C min}^{-1}$  in air.

of the diamine component's structure. Flexible linkages are frequently introduced into the polymer structure to improve the solubility of the polymer. Unfortunately, these flexible linkages tend to lower the glass-transition temperature. The polymer PA 3 exhibits the highest glass-transition temperature, which is attributed to the presence of the bulky rigid  $-\text{CF}_3$  group. The  $-\text{CF}_3$  group not only imparts good solubility but also imparts a high glass-transition temperature. The lower  $T_g$  values of the other polymers in this series can be explained in terms of flexible ether linkages from diamine moieties. All of the polymers indicated no clear melting endotherms or crystallization exotherms up to  $380^{\circ}\text{C}$ , the temperature at which the polymers began to decompose. This result supports the amorphous nature of these coumarin-containing polymers. Their X-ray diffractograms have wide peaks that are typical of amorphous polymers and showed no characteristic peaks of well-defined long-range order structure or crystallinity (Fig. 5).



**Figure 5** X-ray diffraction diagrams of polymers PA 1–4.

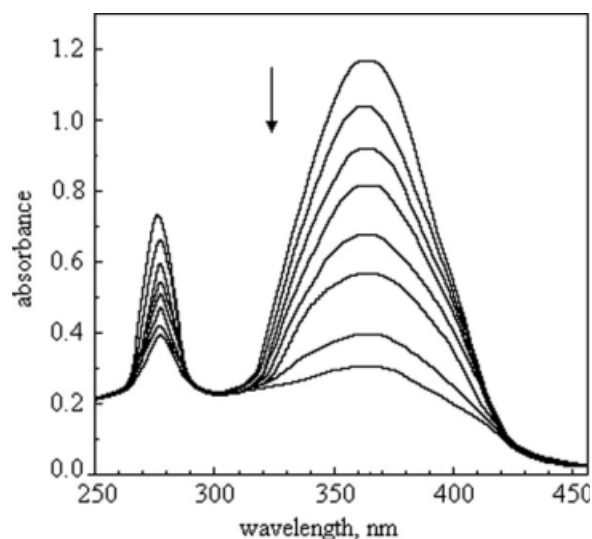
**TABLE IV**  
Water Uptake and Absorbance Maxima of Polyamides

Polyamide code	Water absorption (%)	Mol H <sub>2</sub> O/ repeat unit	Mol H <sub>2</sub> O/ equiv. amide	$\lambda_{\text{max}}$ (nm)	
				Solution	Film
PA 1	2.90	0.90	0.45	369	370
PA 2	3.35	1.20	0.60	357	359
PA 3	1.75	0.67	0.33	365	367
PA 4	2.25	1.10	0.55	361	364

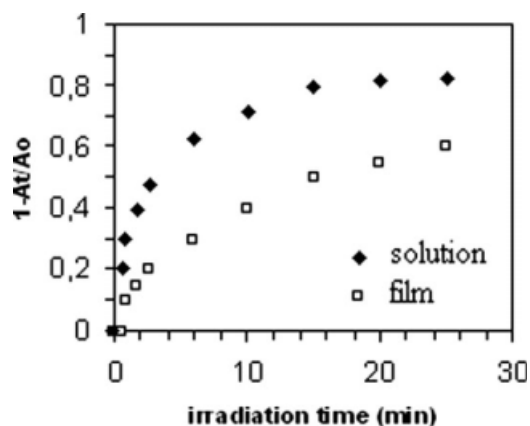
The isothermal water absorption for the novel polyamides is given in Table IV. As can be seen, except the polyamide PA 3, these polymers display a moderate to high hydrophilicity ascribed to the bulkiness and rigidity of coumarin units, which can cause less dense chain packing and increase water accessibility.

### Photochemical aspects

Photosensitive polymers based on the coumarin ring are extensively investigated because coumarin chromophore undergoes a simple photodimerization through a  $[2\pi + 2\pi]$  photocycloaddition reaction under direct irradiation ( $\lambda > 300 \text{ nm}$ ) resulting in cyclobutane-type dimers, which cause insolubilization of the polymer film. Although various reports have been published on the synthesis and characterization of coumarin containing polymers, very little attention has been paid to the incorporation of coumarins into polymer main chains to study their optical properties.<sup>14–16</sup> The photochemical property of the coumarinated aromatic polyamides presented in this report was investigated by UV-vis spectroscopy, in the absence of photoinitiators. Photodimerization reaction of polymers was studied in solution and



**Figure 6** UV-vis absorption spectra of polyamide PA 3 in DMSO; irradiation time: 0, 1, 2, 3, 6, 10, 12, 15, and 20 min.



**Figure 7** Plot of relative decrease of absorbance  $1 - A_t / A_0$  upon UV irradiation of polyamide PA 3 in solution ( $\lambda_{\max} = 365$  nm) and film ( $\lambda_{\max} = 367$  nm), respectively, versus irradiation time.

film state. Figure 6 illustrates the electron absorption spectra of a dilute solution of polyamide PA 3 irradiated with UV light at different time intervals and Table IV summarizes the spectral data of the synthesized polymers. It was found that the polymer PA 3 exhibited two absorption maxima at 365 nm and 277 nm, which were assigned to  $\pi\text{-}\pi^*$  transitions of the reactive olefinic double bond from coumarin ring. As expected, the methylene group has no influence on the absorption spectrum of the coumarin ring because the substituent at the sixth position of coumarin has no resonance effect with the coumarin unit. Taking into account that the coumarin chromophore undergoes only photochemical dimerization because of its fused ring structure, the intensity drop of the maximum absorbance during illumination with UV light can be primarily attributed to the loss of coumarin chromophores and generation of dimers. All of the four coumarinated polymers showed the similar trend of the decrease of UV absorbance with irradiation time in spite of the different chain flexibility from each other. UV-vis absorption peaks of the polyamides PA 1-4 in dilute DMSO solutions show absorption maxima slightly blue-shifted (3-4 nm) relative to the corresponding polymer films (Table IV), implying that there is no relevant  $\pi\text{-}\pi$  interaction aggregation between the polymer chains (at a concentration of  $1.5 \times 10^{-4} M$ ). Analogous to DMSO solutions, polymer films exhibited shape-similar absorption bands. Figure 7 compares the rate of photocrosslinking of polyamide PA 3 in solution and thin film. The rate of photodimerization is much faster in the solution than that in the form of polymeric film. It could also be observed that the UV-exposed polymer films became insoluble in organic solvents and this gave additional evidence for the occurrence of a  $[2\pi + 2\pi]$  photocrosslinking reaction of the coumarin group.

The crosslinking reaction was further substantiated by FTIR. It is well known that direct irradiation ( $\lambda > 300$  nm) of coumarin generates cyclobutane-type dimers by photocycloaddition without side reactions such as *trans-cis* isomerization. Therefore, the differences between IR transitions of the unirradiated and irradiated samples can be attributed to the  $[2\pi + 2\pi]$  cycloaddition process. The FTIR spectra evidenced the dimerization reaction through changes in the peaks at  $1730\text{ cm}^{-1}$ ,  $1615\text{ cm}^{-1}$ , and  $1570\text{ cm}^{-1}$  attributed to the stretching vibrations of C=O and conjugated C=C, respectively, in the pyrone moiety. Photoirradiation resulted in the emergence of a nonconjugated carbonyl group in the cyclobutane photo-product evidenced by a new peak positioned to higher frequency ( $1740\text{ cm}^{-1}$ ), as a consequence of the cyclization reaction. Concomitantly, the intensity of the two relevant bands at  $1615\text{ cm}^{-1}$  and  $1570\text{ cm}^{-1}$  decreased as the double bond was broken because of UV-light-induced photodimerization.

With respect to the photochemistry of coumarin derivatives, it is known that they exhibit strong fluorescence in the UV and visible region that makes them applicable in different fields of science and technology. Contrary to exception, by exciting with 365 nm, which is the absorption maximum of biscoumarin chromophore, the polyamides exhibited no emission peaks in both the solid and solution states.

## CONCLUSIONS

A novel monomer containing heteroaromatic rings, 6,6'-methylenebis(3-carboxy-coumaric acid), was synthesized and reacted with various aromatic diamines using Yamazaki classical phosphorylation method, which permits the direct amidation of aromatic acids and amines promoted by TPP, in the presence of Py and inorganic salts to give a series of novel aromatic polyamides containing coumarin groups in the main chain. The inherent viscosities of the resulting polyamides were between 0.49 and 0.78 dL g<sup>-1</sup> and the levels of water uptake ranged between 1.75% and 3.35% at 65% relative humidity. The polymers were soluble in aprotic polar solvents and thermally stable up to 380°C, and their  $T_g$ 's varied from 283 to 329°C. WAXD analysis revealed that all the polymers showed amorphous patterns without any evidence of crystalline order. The UV-vis absorption of these polymers exhibited strong absorption in both DMSO solutions and films, and no emission peaks were detected by exciting with  $\lambda = 365$  nm.

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