JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 4, April 2007, p. 1014 - 1018

Synthesis and characterization of novel aromatic polyamides containing pendent coumarin groups

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A novel coumarin-containing monomer, 7-[2`-(1,3-diamino-5-benzoyloxy)ethyl]oxy-chromen-2-one, was prepared, characterized and used in a direct polycondensation reaction with different aromatic diacids to give polyamides having chromenyl side groups, which include an oxyethylenyloxy flexible spacer. These polyamides were obtained with inherent viscosities above 0.78 and up to 1.21 dL/g. The number-average molecular weights were in the range of 27.000-46.000 g/mol. All the resulting polymers were amorphous and soluble in polar solvents such as *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylacetamide (DMAc), *N,N*-dimethylformamide (DMF), dimethylsulfoxide (DMSO) and dioxane, and afforded strong, flexible and homogeneous films by solution-casting. The polyamides under study showed distinct glass transitions on the differential scanning calorimetry (DSC) curves ranging from 191 °C to 223 °C. Coumarin chromophores underwent [2+2] cycloaddition reaction under $\lambda = 313$ nm light irradiation to yield crosslinked network structures.

(Received November 2, 2006; accepted February 28, 2007)

Keywords: New monomer, Aromatic polyamides, Direct polycondensation, Coumarin pendent groups, Photocrosslinking

1. Introduction

Aromatic polyamides exhibit outstanding chemical, physical, and mechanical properties and are thus suited for their use as high-performance materials. The high-temperature properties of these polymers make them useful in a large number of applications in modern industries. One of the problems in high-temperature polymers consists in their poor processability caused by low solubility in common organic solvents and high melting or softening temperatures. These properties are attributable to the inherent macromolecular rigidity or semicrystallinity of the polymer backbone and to the presence of polar groups which give rise to strong interchain forces and formation of extended hydrogen bonding networks between aligned polymer chains. There are several methods employed to overcome the problem of poor processability. The main approach is to modify the chemical structure of aromatic polyamides in order to change their characteristics with respect to a specific application or to a particular property. The incorporation of flexible segments [1,2], the use of *N*-alkylation or *N*-arylation of the amide group [3,4], the substitution of the aromatic ring with methyl, phenyl, phenoxy, or naphthoxy groups [5-7], the attachment of bulky pendent groups [8-11] onto the rodlike polymer backbone were very successful synthetic routes to enhance the solubility and processing properties of polyamides without sacrificing their high thermal stability. Different combinations of monomers bearing various substituents are used to design new amorphous, thermally stable and high molecular weight polyamides with improved solubility and low glass transition temperature. The incorporation of certain functionalities as groups appended to the macromolecular chain generates new properties tailored for specific applications of the polymers.

Photoreactive polymers, especially photocrosslinkable ones, have received considerable interest due to their technological applications. Among them, cinnamoyl containing polymers are applied in the fields of microlithography, printing materials, liquid crystalline and nonlinear optical materials. One alternative route to the cinnamate chromophore is the coumarin chromophore, because it is known to undergo [2 + 2] cycloaddition on UV irradiation. Polymers with coumarin moieties have been useful in many fields such as fluorescence materials and laser dyes [12], nonlinear optical materials [13,14], photorefractive materials [15], photoresists [13], energy-transfer materials [16,17], alignment agents for liquid crystals [18], biological materials [19,20], electroluminescent materials [21], etc.

The aim of the present work involves the preparation and characterization of new aromatic polyamides containing pendent coumarin groups as photocrosslinkable units**.**

2. Experimental

2.1. Materials

7-Hydroxycoumarin (umbelliferone), ethylene carbonate, 4-dimethylaminopyridine (DMAP), *1,3*-dicyclohexylcarbodiimide (DCC) and other chemicals were commercially available and used without additional purification. 3,5-Diaminobenzoic acid and aromatic dicarboxylic acids such as isophthalic acid, terephthalic acid, 4,4`-biphenyldicarboxylic acid, 4,4`-oxybis(benzoic acid), 4,4`-sulfonyldibenzoic acid, 4,4`-methylenedibenzoic acid and 2,6-naphthalenedicarboxylic acid were used after purification by crystallization. Reagent grade solvents were dried and purified as follows. *N*-Methyl-2-pyrrolidinone (NMP), *N*, *N*-dimethylacetamide (DMAc), pyridine (Py), triphenyl phosphite (TPP), were dried by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Dichloromethane was dried by distillation over calcium hydride and stored over anhydrous potassium carbonate. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 180°C for 10 h before use.

2.2. Equipment

FT-IR spectra at room temperature were recorded for polymer films using a FT-IR Bomem MB-104 spectrometer with a resolution of 4 cm^{-1}. ^1H NMR spectra were run on a a Bruker Avance DRX 400 spectrometer, using DMSO-d_6 or $CDCl_3$ as solvents. The chemical shifts were given as δ values from Me_4Si as the internal standard. Electronic absorption spectra were recorded on a SPECORD M42 Carl Zeiss Jena spectrophotometer. The inherent viscosities of polymer solutions (0.5% w/v) in NMP were measured at 25°C using an Ubbelohde suspended level viscometer. Thermogravimetric analyses (TGA) were performed in air at a heating rate of 10°C/min using a Q-1500 System (a derivatograph produced by MOM, Hungary). The glass transition temperatures were determined with a METTLER DSC 112E differential scanning calorimeter with heating and cooling rate of 10°C/min. Gel permeation chromatography was carried out on a PL-END 950 evaporative mass detector instrument using PL gel 5μm MIXED-D columns and DMF as solvent and monodisperse polystyrene samples with narrow polydispersity as calibration standards. A 500 W high-pressure mercury lamp with an optical filter to isolate the 313 nm line was used for the irradiation experiments at room temperature. The light intensity was about 15 mW/cm^2 at 313 nm. Qualitative solubility was examined on powder samples at a concentration of 10% (W/v) in a number of solvents. Water absorption measurements were determined gravimetrically at room temperature. Powdered polymer samples were dried at 120 °C for 24 h over P_2O_5, and then placed in a closed desiccator where a relative humidity of 65% is provided by an oversaturated aqueous solution of $NaNO_2$. During a few days interval the samples were allowed to humidify and periodically weighed until equilibrium with their surroundings was reached, as denoted by no weight change.

2.3. 7-[2`-(1,3-Diamino-5-benzoyloxy)ethyl]oxy-chromen-2-one

A solution of DCC (3.09g, 0.015 mol) and dichloromethane (50 mL) was added dropwise to a stirred solution of 3,5-diaminobenzoic benzoic acid (2.28 g, 0.015 mol), 7-(2-hydroxyethoxy)-chromen-2-one (3.09 g, 0.015 mol) and 4-dimethylaminopyridine (0.18 g, 0.0015 mol) in dichloromethane (50 mL), and the reaction was stirred at room temperature overnight. After addition of water, the organic phase was separated, washed with aqueous HCl (2M), saturated $NaHCO_3$, aqueous NaOH (10%) and water, and dried over Na_2SO_4. The solvent was removed by distillation and the product was recrystallized from ethanol. Yield 60%, m.p. 122-123°C.

Anal. Calcd for $C_{18}H_{16}O_5N_2$: N, 8.22%. Found: N, 8.15%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.53 (d, J = 9.5 Hz, 1H, H-4, coumarin), 7.30 (d, J = 8.3 Hz, 1H, H-5, coumarin), 6.85-6.77 (m, 2H, H-6 and H-8, coumarin, and 2H, diaminobenzoate protons), 6.23-6.17 (m, 1H, H-3, coumarin and 1H, diaminobenzoate proton), 4.45 (t, J = 4.8 Hz, 2H, CH_2OCO), 4.21 (t, J = 4.8 Hz, 2H, Ar-O-CH_2-), 3.60-3.70 (m, 4H, NH_2).

2.4.Synthesis of diamine monomer

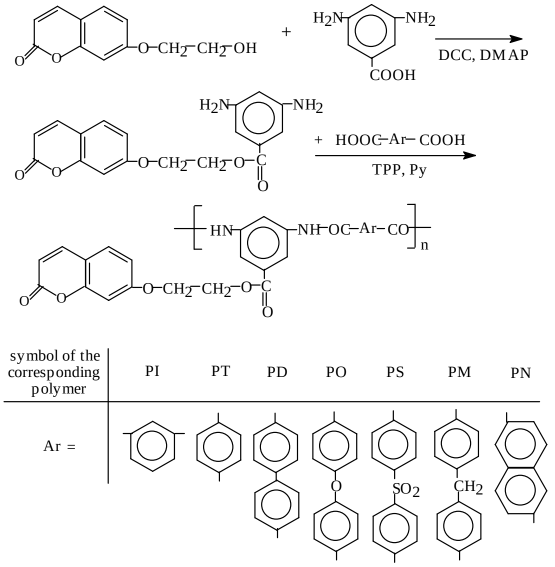
2.4.1. 7-(2-Hydroxyethoxy)-chromen-2-one

A spherical flask (100 mL), equipped with a reflux condenser, stirrer, thermometer, and nitrogen inlet, was charged with 7-hydroxycoumarin (4.86 g, 0.03 mol), ethylene carbonate (3.96 g, 0.045 mol), and potassium carbonate (6.21 g, 0.045 mol), as catalyst, in 50 mL of *N*, *N*-dimethylacetamide. The mixture was heated under reflux for 5h. The organic layer was washed with water to remove the catalyst and unreacted ethylene carbonate, and extracted with ether. The organic layer was dried over magnesium sulfate, followed by the removal of the solvent. The crude product was recrystallized from a hexane/ethyl acetate mixture (1/1 by volume), giving colorless crystals (mp 90-91 °C) in a 65% yield. Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.08%; H, 4.85%. Found: C, 63.99%; H, 4.89%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.63 (d, J = 9.3 Hz, 1H, H-4), 7.38 (d, J = 8.7 Hz, 1H, H-5), 6.90 (q, J = 2.6 Hz and 8.3 Hz, 1H, H-6), 6.84 (d, J = 2.6 Hz, 1H, H-8), 6.28 (d, J = 9.3 Hz, 1H, H-3), 4.16 (t, J = 4.6 Hz, 2H, Ar-O-CH_2-), 3.81 (q, J = 4.6 Hz, 2H, CH_2OH), 1.29 (s, 1H, -OH).

2.5 Synthesis of polyamides

Polyamide ***PT*** *from 7-[2`-(1,3-diamino-5-benzoyloxy)ethyl]oxy-chromen-2-one and terephthalic acid.* A mixture of 0.207 g (1.25 mmol) of terephthalic acid, 0.425 g (1.25 mmol) of as prepared diamine, 0.35 g of calcium chloride, 0.8 mL of triphenyl phosphite, 0.8 mL of pyridine, and 3.5 mL of NMP was heated with stirring at 120 °C for 3 h. As polycondensation proceeded, the solution became viscous gradually. After cooling, the reaction mixture was poured into methanol, producing a stringy precipitate that was washed thoroughly with methanol and hot water, collected on a filter, and dried at 100 °C under vacuum. The inherent viscosity of the polymer in NMP was 0.87 dL/g, measured at a concentration 0.5 g/dL at 25 °C.

^1H NMR (DMSO-d_6), δ (ppm): 10.4 (s, 2H, CO-NH), 8.63 (t, 1H, diaminophenyl proton), 8.05 (d, 2H, diaminophenyl protons), 7.88 (s, 4H, aromatic of terephthalic acid segment), 7.64 (d, J = 9.5 Hz, 1H, H-4, coumarin), 7.39 (d, J = 8.5 Hz, 1H, H-5, coumarin), 6.98 (q, 1H, H-6, coumarin), 6.92 (d, 1H, H-8, coumarin), 6.27 (d, 1H, H-3, coumarin), 4.53 (t, 2H, CH_2OCO), 4.27 (t, 2H, Ar-O-CH_2-). All other polyamides were prepared using a similar procedure.



Scheme 1. Synthesis of diamine monomer and aromatic polyamides.

3. Results and discussion

3.1. Polymer synthesis

As presented in Experimental Section and illustrated in Scheme 1, aromatic polyamides were synthesized in three major steps: functionalization of coumarin, synthesis of aromatic diamine monomer having a chromenyl substituent attached through an oxyethylene spacer group, and polymer synthesis. Polyamides were prepared by the direct polycondensation technique [22], which was carried out at 120 °C for 3 h by reacting the diamine monomer with various aromatic dicarboxylic acids in NMP containing dissolved $CaCl_2$ using triphenyl phosphite (TPP) and pyridine as condensing agents. All the reactions proceeded readily in homogeneous solutions and resulted in viscous and transparent polymer solutions. Tough, stringy precipitates were produced when the viscous polyamide solutions were trickled into stirring methanol. The results of polycondensation are given in Table 1. All the polymers were obtained in almost quantitative yields with inherent viscosities of 0.78-1.21 dL/g. The GPC curves indicated that the weight-average (M_w) and number-average (M_n) molecular weight values of the polyamides were in the range of 62.000-122.000 g/mol, and 27.000-46.000 g/mol, respectively, relative to polystyrene standards. The polydispersity indices were between 2.3 and 2.8, i.e., in the standard range for polycondensations. The molecular weights of these polyamides are sufficiently high to permit casting of flexible, transparent and tough films.

The structures of these new polymers were identified by IR and ^1H NMR spectroscopy. The presence in all the IR spectra of a wide absorption band around 3300 cm^{-1} and a sharp peak at 1540 cm^{-1} characteristic for N-H stretching and N-H deformation, respectively and another peaks at 1660 cm^{-1} due to C=O stretching and 1270 cm^{-1} assigned to C-N stretching and N-H bending confirmed the formation of amide structure. All polymers showed an strong absorption band at 1735 cm^{-1} characteristic to the stretching vibration of the C=O in the pyrone moiety and ester group of benzoate chain. The bands corresponding to the aromatic rings of polyamides associated to C-H and C=C stretching vibrations appear in the range of 3080-3060 cm^{-1} and at 1560, 1505, 1400 cm^{-1}. The absorption bands detected at 2940, 2860, 1460 and 720 cm^{-1} were attributed to the aliphatic part (-CH_2-) of side chains stretching vibration. The peaks observed at 1260 and 1120 cm^{-1} are due to C(C=O)O asymmetric and symmetric stretching, respectively, and at 1230 and 1060 cm^{-1} are characteristic to O=C-O-C asymmetric and symmetric stretching, respectively. Absorbances of the peak centered at around 1615 and 985 cm^{-1} are ascribed to C=C stretching vibration and C-H out-of-plane bending vibration, respectively in the vinylene linkage of the coumarin. A typical IR spectrum is shown in Fig. 1.

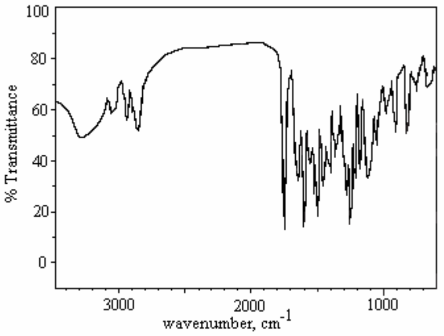


*Fig. 1. The IR spectrum of polyamide **PM***

^1H NMR spectra were also used to elucidate the structure of polymers. The ^1H NMR spectral data of polyamide **PT** are listed in the Experimental Section. Each proton of **PT** was assigned, and the integration values were in accordance with the expected structure (Fig. 2).

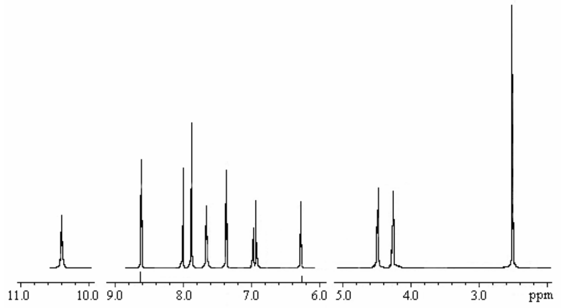


*Fig. 2. ^1H NMR spectrum of polyamide **PT** in DMSO–d_6.*

3.2. Polymer characterization

All the resulting polyamides were highly soluble at room temperature in polar aprotic solvents such as DMF, DMAc, NMP, DMSO and dioxane. These polymers dissolved also in less polar solvents like Py, *o*-chlorophenol, methanesulfonic acid and *m*-cresol; however, polymers **PT**, **PD** and **PN** with *p*-phenylene and biphenyl structure, respectively, had somewhat limited solubility, while polymers **PI**, **PO, PS** and **PM** were even soluble in THF. The isothermal water absorption for the new polyamides is given in Table 1. Their highly soluble nature and hydrophilicity are attributed to the presence of asymmetrical *m*-phenylene unit into the polymer backbone and also to the introduction of the bulky pendent chromenyl group which disturbs the coplanarity of the aromatic units, lowering the chain packing, increasing water accessibility and improving solubility. The good solubility makes these polymers potential candidates for practical applications in spin coating and casting processes.

Table 1. Inherent viscosities (η_{inh}) GPC data, and fraction of absorbed water for the polyamides.

	PI	**PT**	**PD**	**PO**	**PS**	**PM**	**PN**
η_{inh} (dL/g)[a]	0.98	0.87	0.85	1.17	1.21	1.09	0.78
M_w x10^{-4} (g/mol)[b]	10.6	7.6	7.2	12.2	11.9	11.4	6.2
M_n x10^{-4} (g/mol)[b]	4.2	3.2	3.0	4.6	4.4	4.1	2.7
M_w/M_n	2.52	2.37	2.40	2.65	2.70	2.78	2.29
Water absorption (%)	5.67	4.56	4.83	5.98	6.15	5.42	4.42

[a] Measured at a concentration of 0.5 g/dL in NMP at 25°C.
[b] Determined by gel-permeation chromatography (GPC), using DMF as eluent and polystyrene as standards.

Thermal properties of all the polyamides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The values of glass transition temperature (T_g), initial decomposition temperatures (T_d`s), 10% weight loss temperature and char yield at 600 °C in air of the polymers are summarized in Table 2. Glass transition temperatures, determined from the second heat scan at the midpoint of the glass transition endotherm, ranged from 191 to 223 °C, depending on the structure of the aromatic diacid moiety, and decreased with the decreasing rigidity and symmetry of the polymer backbone. The introduction of rigid naphthalene and biphenyl structure, and polar sulphonyl group led to increase T_g, e.g. polyamides **PN**, **PD** and **PS** exhibited relatively higher T_gs. All the polyamides were highly amorphous, their DSC curves showed no endotherms in the region 20-250 °C that could be assigned to melting.

All the polyamides exhibited reasonable thermal stability and they start to decompose from the weaker ester linkages at around 275 °C.

Table 2. Thermal properties of polyamides.

Polymer	T_g (°C)[a]	T_d (°C)[b]	T_{10} (°C)[c]	Char yield (%)[d]
PI	199	278	317	36
PT	211	277	315	37
PD	223	280	326	38
PO	195	276	320	31
PS	218	281	321	34
PM	191	279	319	32
PN	221	278	323	39

[a] DSC measurements with a heating rate of 10°C/min in N_2 atmosphere.
[b] Onset temperature of initial decomposition, recorded by TGA at a heating rate of 10°C/min in air.
[c] Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 10°C/min in air.
[d] Residual weight percentage at 600 °C in air.

The crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams obtained by the powder method with the use of nickel-filtered CuK_α radiation. The results indicated that all the polymers were completely amorphous. This could be attributed to the introduction of the packing-disruptive bulky coumarinyloxyethyl lateral group, which resulted in increased chain distances and polymer free volume, and decreased chain interactions. Therefore, the amorphous nature of these polymers was reflected in their excellent solubility.

In the present study, coumarin was employed as a photosensitive group because it is known to undergo [2 + 2] cycloaddition on UV irradiation, without any side reaction. The *trans-cis* isomerization of the carbon-carbon double bond (in conjugation with the enone carbonyl function within the coumarin ring), which occurs in cinnamates, is not possible for coumarins.[18-22] The photodimerization of coumarin groups in the polymer films was traced by their absorption change. Before irradiation, the spectra exhibit an absorption band at around 320 nm, assigned to the absorption of the conjugated chromophore. Irradiation with 313 nm light resulted in a gradual decrease in absorbance at λ_{max}, assigned to π-π^* transition of the coumarin unit, whereas a slight increase in absorbance at wavelength shorter that 250 nm was observed, as shown in Fig**.** 3**.** This photoreaction can be explained by the reduction in conjugation length due to the [2+2] cycloaddition at the C=C double bond of coumarin moieties to give a benzenoid absorption band. This dimerization of the coumarin moieties causes photocrosslinking in the polymer film so that all the polymers after 30 min photo-irradiation became insoluble in ordinary organic solvents.

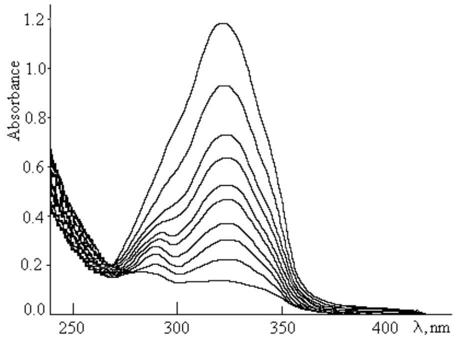


*Fig. 3. Absorption spectra of **PI** as film at irradiation times of 0, 1, 2, 3, 5, 6, 10,15, 20, 30 min from top to bottom, at 319 nm.*

Further information concerning the photochemistry of coumarin polymers was obtained by FT-IR measurements. Both the unirradiated and irradiated polymer films show sharp IR transitions and the differences between them can mostly be attributed to the [2 + 2] cycloaddition process. On exposure of the sample, the carbonyl peak (C=O) at 1735 cm^{-1} became broader and, on prolonged illumination with UV light, a new carbonyl peak appears at 1765 cm^{-1} as a shoulder, suggesting the formation of a nonconjugated carbonyl group in the cyclobutane photoproduct as a consequence of the breaking of the C=C bond and cyclization reaction. In addition, absorbances of the peaks centered at around 1615 cm^{-1} and 985 cm^{-1} due to the C=C bond decreased in intensity upon photoirradiation for each polymer, indicating the loss of coumarin chromophores as a result of UV-light-induced photodimerization.[18]

4. Conclusions

A new derivative of *m*-phenylenediamine bearing an ethyloxychromenyl group as substituent was prepared and successfully used as a condensation monomer in the solution direct polycondensation with aromatic dicarboxylic acids, *via* the Yamazaki-Higashi phosphorilation technique, to generate high molecular weight polyamides. The resulting polymers showed T_g's in the 191-223 °C range, depending on the monomers used in the synthesis and decreased with decreasing rigidity and symmetry of the polymer backbone. Because of the length and bulkiness of the coumarinyloxyethyl pendent group no crystallinity was observed for any of these polyamides. Thus, the amorphous nature of these polymers was in line with their enhanced solubility, which agrees with the general rule that the solubility increases with decreasing crystallinity. In the UV-visible spectra, the coumarinated polyamides revealed a maximum absorption at around 320 nm, which diminished remarkably with increasing UV exposure time, exhibiting the crosslinking (dimerization) between the coumarin moieties in the side chains and transformation of the polymer film from soluble to insoluble. High solubility and film forming properties, high photosensitivity, moderate T_g`s values and relative high hydrophilicity and thermal stability made these coumarinated polyamides promising polymeric materials.

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