Polymers from Coumarines. Synthesis and Characterization of Polyamides Derived from 6-{[3-(Chloroformyl)-phenyl]ethynyl}coumarin-3-carboxylic Acid Chloride

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ABSTRACT: Coumarin-containing polyamides from 6-{[3-(chloroformyl)phenyl]ethynyl}coumarin-3-carboxylic acid chloride were prepared and characterized for the first time. They were soluble in common organic solvents such as *N*-methylpyrrolidone (NMP) and dimethyl sulfoxide (DMSO) and gave transparent and tough films on casting. In the presence of excess diamine, the polymers underwent chemical transformation at room temperature, producing polyazomethynes, as confirmed by the corresponding model reactions, and a possible reaction mechanism is proposed for this transformation. The coumarin containing polyamides showed emission and excitation maxima peaking at 464 and 398 nm, respectively, in solution and exhibited 10% weight loss above 400°C.

KEY WORDS Coumarin / Polyamides / Photoluminescence /

Coumarines (1,2-benzopyrones) and a class of heterocycles known for fluorescent properties. They are widely used as laser dyes^{1,2} due to high photostability and quantum yield of photoluminescence. The chemical modification of coumarines makes it possible to vary emission wavelength continuously throughout visible spectrum.³ Coumarines were also found to be electroluminescent. Thus, a dispersion of coumarin **6** in polymethylmethacrylate showed electroluminescence⁴ peaking at 554 nm.

Although many papers have been published on the synthesis and characterization of coumarines and various reviews are available^{3,5} very little attention has been paid to the incorporation of coumarines into polymers and only two papers have been published on this topic. The radical copolymerization of coumarin with styrene was studied by Yun.⁶ Polyesters containing a coumarin dimer were obtained by the photopolymerization of 7,7'-coumarinylpolymethylene dicarbonates.⁷ In these cases, the double bond of coumarin participates in the polymerization giving polymers containing derivatives of 3,4-dihydrocoumarin which do not have interesting optical properties because of the disturbing of the conjugation. On the other hand, polymeric materials containing emitter units have advantage over low molecular weight analogies, especially in making of electroluminescence devices; because of the absence of phase separation, and the possibilities of preparation of thin films of any desirable dimension with high optical quality by simple casting.

We published recently a series of studies on the synthesis of polymers containing discrete conjugated units of fluorescein,^{8,9} diethynylantracene,¹⁰ vinylphenylantracene,¹¹ and arylenevinylideneethynylene.¹² All these polymers gave films with good optical quality on casting. Fluorescein-containing polymers exhibited non-linear optical susceptibility of the third order of 3×10^{-10} esu, while anthracene-containing polymers showed electroluminescence at voltage as low as 6 V.

This work describes the synthesis and characterization of polyamides containing 3,6-disubstituted coumarine units for the first time.

EXPERIMENTAL

Materials

1,2-Dichlorobenzene was purified by simple distillation before use and 1,4-diaminobutane and 1,8-diaminooctane were distilled under reduced pressure. Other reagents were used as received (Aldrich). The synthetic route to the monomer and polymers is shown in Scheme 1. 3-Ethynylmethoxy benzoate (**9**) was prepared from 3-bromomethylbenzoate according to the literature.¹³

6-Bromo-3-carboethoxy coumarin (**2**) was prepared by refluxing 5-bromosalicylic aldehyde and malonic ester in ethanol in the presence of piperazine for 3 h in 67% yield. ¹H NMR (CDCl₃) 8.43 (s, 1H, (H⁴)), 7.80–7.70 (m, 2H, (H⁵, H⁷)), 7.28–7.22 (m, 1H (H⁸)), 4.44 (q, 2H, *J*=6.6 Hz, (CH₂)), 1.42 (t, 3H, *J*=6.6 Hz, (CH₃)) *T*_m=166°C (Lit¹⁴ 168°C).

3-Ethoxycarbonyl-6-(3-methoxycarbonylphenyl)ethynylcoumarin (3)

To a solution of compound **2** (10 g, 33.7 mmol) and compound **9** (5.4 g, 33.7 mmol) in a mixture of triethylamine (TEA) (50 ml) and pyridine (150 ml) triphenylphosphine (TPP) (0.7 g), CuI (0.4 g), and PdCl₂ (TTP)₂ (0.5 g) were added under nitrogen. The reaction mixture was refluxed for 24 h under nitrogen, cooled and the precipitate formed was filtered off, washed with water,

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Scheme 1. Monomer synthesis.

Scheme 2. Polymer synthesis.

dried and crystallized twice from ethanol to give 3.5 g (27%) of compound **3**. $T_m = 143\text{--}144^\circ\text{C}$, IR (cm^{-1}) 3065 (CH, arom.), 2980, 2950 (CH, aliph.), 2215 ($\text{C}\equiv\text{C}$), 1755, 1722 ($\text{C}=\text{O}$, ester). ^1H NMR (CDCl_3) 8.49 (s, 1H, (H^4)), 8.22—8.20 (m, 1H, H^a), 8.05—8.00 (m, 1H, H^b), 7.80—7.73 (m, 2H, (H^5 , H^7)), 7.72—7.67 (m, 1H, (H^d)), 7.50—7.41 (m, 1H, (H^c)), 7.36—7.30 (m, 1H, (H^8)), 4.46 (q, 2H, $J = 7.14$ Hz, ($-\text{CH}_2-$)), 4.37 (s, 3H, ($-\text{OCH}_3$)), 1.42 (t, 3H, $J = 7.14$ Hz, ($-\text{CH}_3$)). ^{13}C NMR (CDCl_3)

166.2 (C^{18}), 162.8 (C^1), 156.1 (C^2), 154.7 (C^9), 147.7 (C^4), 137.1, 135.7, 132.8, 132.4, 130.6, 129.7, 128.7 (C^5 , C^7 , C^{14} , C^{15} , C^{16} , C^{17} , C^{19}), 123.0, 120.0, 119.1, 118.0 (C^3 , C^{10} , C^6 , C^{13}), 117.2 (C^8), 89.5, 87.9 (C^{11} , C^{12}), 62.2 ($\text{O}-\text{CH}_2-$), 52.4 ($\text{O}-\text{CH}_3$), 14.2 ($-\text{CH}_3$).

3-Carboxy-6-(3-carboxyphenyl)ethynylcoumarin (**4**)

Diester **3** was hydrolyzed to diacid **4** by heating 3.1 g (8.25 mmol) of **3** in 150 ml 10% NaOH in 50% aqueous ethanol at 60°C for 24 h. Ethanol was evaporated under reduced pressure, the reaction mixture was acidified and the yellow precipitate formed was filtered off, washed with water and dried *in vacuo*. Yield = 94% $T_m > 300^\circ\text{C}$. IR (cm^{-1}) 3400 (OH, free), 3120, 3080, 3060, 3040 (CH arom), 2207 ($\text{C}\equiv\text{C}$), 1745, 1725 ($\text{C}=\text{O}$), 1620 ($\text{C}=\text{C}$ arom).

Polyamides 6a and 6b

Diacid **4** (2.543 g, 7.614 mmol) was converted to diacid dichloride **5** by refluxing with a mixture of 250 ml benzene, 15 ml SOCl_2 and a few drops of DMF until the solution became clear (4 h). Excess of solvent was removed *in vacuo* at room temperature and compound **5** thus obtained was dried under reduced pressure until constant weight (2 h). Acid chloride **5** was dissolved in *o*-dichlorobenzene (75.0 ml) at 45°C. Half of it (37.5 ml) was added to a solution contained 0.6712 g (7.614 mmol) of 1,4-diaminobutane dissolved in 20 ml distilled water. The reaction mixture was vigorously stirred for 10 min,

the polymer precipitated was filtered off, washed with water and methanol and dried *in vacuo* at room temperature. Another 37.5 ml *o*-dichlorobenzene solution of compound **5** were reacted in the same way with 1.0984 g (7.614 mmol) 1,8-diaminooctane dissolved in 20 ml distilled water. The polymer was filtered off, washed with water and methanol and dried *in vacuo* at room temperature. Yields were 88 and 93% for polymers **6a** and **6b**, respectively.

Model Compound Synthesis

Model compound synthesis is shown in Scheme 3.

Scheme 3. Model compound synthesis.

3-(n-Butylaminocarbonyl)-6-bromo Coumarin (12) was prepared by the hydrolysis of compound **2** in 10% NaOH at 40°C for 24 h to compound **10** ($T_m = 200^\circ\text{C}$, Lit¹⁵ 200°C) followed by reaction of **10** with excess SOCl_2 in CHCl_3 at reflux for 6 h. Excess solvent was removed under reduced pressure and two-fold excess *n*-butylamine dissolved in dioxane was added to the crude acid chloride **11** at room temperature. The reaction mixture was stirred for 10 min and poured into water. The precipitate formed was filtered off and chromatographed on SiO_2 (benzene). Overall yield 34% $T_m = 192^\circ\text{C}$. IR (cm^{-1}) 3344 (NH), 3051 (CH arom), 2955–2869 (CH aliph), 1713 (C=O, lacton), 1660 (C=O amide). ^1H NMR ($\text{DMSO}-d_6$) 8.80 (s, 1H, H⁴), 8.70–8.50 (m, 1H, NH), 8.30–8.20 (m, 1H, H⁵), 7.95–7.80 (m, 1H, H⁷), 7.52–7.40 (m, 1H, H⁸), 3.55–3.45 (m, 2H, HN-CH₂), 1.60–1.40 (m, 2H, HN-CH₂-CH₂-), 1.40–1.25 (m, 2H, -CH₂-CH₃), 0.95 (t, 3H, 7.5 Hz, -CH₃).

Model Reaction

1. To a solution of coumarin **2** (1.0 g, 3.37 mmol) or **12** (1.0 g, 4.10 mmol) in 20 ml of dioxane *n*-butylamine (0.88 g, 12.0 mmol) was added at 40°C and the reaction mixture was stirred until all starting material was consumed this was monitored by thin layer chromatography. It took 4 h for coumarin **2** and 24 h for coumarin **12** formation. The reaction mixture was poured into diluted HCl. The precipitate formed was filtered off, chromatographed on SiO_2 (benzene) and analyzed.

2. The reaction was carried out as in method 1, but instead of pouring the reaction mixture into diluted HCl,

Table I. Elemental analysis data

Compound	Formula	Found			Calcd		
		C %	H %	N %	C %	H %	N %
3	$\text{C}_{22}\text{H}_{16}\text{O}_6$	70.08	4.15	—	70.21	4.28	—
4	$\text{C}_{19}\text{H}_{10}\text{O}_6$	68.57	3.26	—	68.27	3.02	—
5	$\text{C}_{19}\text{H}_8\text{C}_{12}\text{O}_4$	60.91	2.11	—	61.48	2.17	—
6a	$(\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}_4)_n$	70.59	4.97	7.01	71.49	4.70	7.25
6b	$(\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_4)_n$	72.99	5.65	6.54	73.29	5.92	6.33
12	$\text{C}_{14}\text{H}_{14}\text{BrNO}_3$	51.81	4.33	4.29	51.87	4.35	4.32
14	$\text{C}_{11}\text{H}_{13}\text{BrNO}$	51.28	5.01	5.41	51.78	5.14	5.49
18	$(\text{C}_{48}\text{H}_{50}\text{N}_4\text{O}_4)_n$	76.34	7.12	6.89	77.18	6.75	7.50

the solvent was evaporated under reduced pressure and the residue was chromatographed on SiO_2 (benzene).

Elemental analysis data for new compounds are listed in Table I.

Measurements and Sample Preparation

Inherent viscosity was measured in NMP measured (0.5 wt% solution) at 25°C. DSC and TGA were performed at a heating rates of 10 and 5°C min⁻¹, respectively under nitrogen with a du Pont 2100 machine. FT-IR-spectra were taken using a Nicolet 510p spectrometer. UV-visible spectra were taken using a Shimadzu UV-260 spectrometer in NMR solution. ^1H NMR and ^{13}C NMR spectra were taken using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in $\text{DMSO}-d_6$ or CDCl_3 with TMS as the internal standard. Emission and excitation spectra were measured using a Perkin-Elmer 630-10S fluorimeter in NMR solution with excitation wavelengths of 398 and 389 nm, and emission wavelengths of 464 and 493 nm for polymers **6b** and **18**, respectively.

RESULTS AND DISCUSSION

Monomer and Polymer Synthesis

Polyamides **6a** and **6b** were prepared from acid dichloride **5** and aliphatic diamines by interfacial polycondensation (Scheme 1). This reaction should be carried out at 40–45°C due to the poor solubility of compound **5**. A key compound in the synthesis of the monomer is the coumarin-containing diester **3**. This diester was obtained by the Heck reaction of methyl (3-ethynyl) benzoate (**9**) and 3-carboethoxy-6-bromocoumarin (**2**) prepared by the Knoevenagel condensation of 5-bromosalicylic aldehyde (**1**) and malonic ester. The Heck reaction goes smoothly when electron withdrawing groups activate the halogen atoms. However, the bromine atom is strongly deactivated by the donor ether oxygen of the pyrone ring of compound **2**, thus hampering the reaction. Nevertheless, at large amount of catalyst and prolonged reaction time, compound **3** was obtained at 30%. This diester was carefully purified by repeated crystallizations from ethanol and hydrolyzed to diacid **4** which was converted to monomer **5** by treatment with SOCl_2 . Monomer **5** was used directly for the preparation of polymers without isolation and purification. The

monomer was pure enough to produce polymers of moderate molecular weight with inherent viscosities of 0.67 and 0.87 dl g^{-1} for polymers **6a** and **6b**, respectively. Spectroscopic data confirmed the general structure of the polymers. Figure 1 presents FT-IR and ^1H NMR spectra of **6b** as example. Absorption bands in the FT-IR spectra at 3348, 2932–2858, 1726, and 1653 cm^{-1} correspond to NH stretches of amide, CH stretches of octamethylene spacer, $\text{C}=\text{O}$ stretches of pyrone cycle, and $\text{C}=\text{O}$ stretches of amide carbonyl, respectively, and yet weak absorption was detected at 2215 cm^{-1} due to $\text{C}\equiv\text{C}$ group stretches. In the ^1H NMR spectrum, protons of the aliphatic spacer appeared at 3.05, 1.3, and 1.05 ppm. Protons H^4 of the coumarin moiety and NH of amide are seen at 8.59 and 8.4–8.2 ppm, respectively. The rest of the aromatic protons emerge in the range of 8.0–7.1 ppm.

Polymers were soluble in polar aprotic solvents such as NMP and DMSO. They slowly precipitated on standing. Transparent and tough films could be obtained by casting at 80°C from NMP solution.

In the case of polyamide synthesis by interfacial polycondensation excess amine only little affects the molecular weight of polymers.¹⁶ When 4-fold excess

Figure 1. ^1H NMR and FT-IR spectra of polymer **6b**.

Figure 2. ^1H NMR and FT-IR spectra of polymer 18.

1,8-diaminooctane was used to prepare **6b** which should have no terminal carboxy groups and the reaction mixture was left to stand for a overnight without isolation of the polymer, the resulting polymer was found different from **6b**. This polymer was yellow and showed green luminescence whereas polymer **6b** was white with blue luminescence. The polymer had better solubility in polar aprotic solvents and did not precipitate on standing; Intrinsic viscosity was 0.57 dl g^{-1} . Figure 2 shows FT-IR and ^1H NMR spectra of polymer obtained from monomer **5** with 4-fold excess 1,8-diaminooctane (**18**). The absorption band of $\text{C}=\text{O}$ stretches of pyrone at 1725 cm^{-1} disappeared almost completely and a new intense band appeared at 1639 cm^{-1} . In the ^1H NMR spectra, signal of H^4 proton at 8.59 ppm completely disappeared implying total disruption of pyrone cycle.

To investigate the reaction between coumarin-containing polymer and excess of amine, a model reaction of coumarins **2** and **12** with butylamine was studied (experimental part). In both cases the only isolated product was 6-bromosalicylic aldehyde (**1**) (method 1).

It is noteworthy that coumarin **2** was much more reactive in this reaction than coumarin **12**.

The following mechanism is proposed for this reaction (Scheme 4). The reaction starts with the Michael addition of butylamine to the activated double bond of coumarin **2** or **12** with simultaneous cleavage of the pyrone ring giving adducts **13** or **15**, respectively. These adducts lose malonic acid derivatives giving rise to azomethyne **14** which hydrolyzes to 5-bromosalicylic aldehyde (**1**) during treatment of the reaction mixture. To prove this mechanism, reactions between coumarins **2** and **12** and butylamine were carried out with protection of the reaction mixture from water (method 2). In the latter case, a yellow oil instead of solid 5-bromosalicylic aldehyde was isolated. ^1H NMR and ^{13}C NMR spectra of this compound are presented in Figure 3. The spectra correspond to the structure of azomethyne **14**. The ^{13}C NMR spectra showed 6 signals corresponding to 6 different carbons of benzene ring in the region 160 – 110 ppm and four signal in the region of 60 – 14 ppm due to four carbons of *n*-butyl groups. The azomethyne

Scheme 4.

Figure 3. ^1H NMR and ^{13}C NMR of model compound 14.

carbon appeared at 163 ppm. In the ^1H NMR spectra two singlets at 8.13 and 7.31 ppm are due to OH and $\text{CH}=\text{N}$ -protons, respectively. The structure of 1,2,5-substituted benzene ring was confirmed by the multiplicity of signals of the aromatic protons. Proton H^3 appeared as a doublet at 6.79 ppm with a $J=8.7$ Hz due to interaction with H^4 . Proton H^4 appeared as a double doublet at 7.26 ppm with $J=2.4$ Hz due to interaction with meta H^6 and $J=8.7$ Hz corresponding to the *ortho* coupling with H^3 . Proton H^6 gives a doublet at 7.24 partially overlapping with multiplet of H^4 with $J=2.4$ Hz due to interaction with H^4 . *n*-Butyl group appeared as two triplets at 3.51 and 0.917 ppm with $J=6.9$ and 7.5 Hz respectively due to $=\text{N}-\text{CH}_2-$ and $-\text{CH}_3$ groups and two multiplets at 1.67–1.56 and 1.42–1.30 ppm corresponding two internal methylene groups of azomethyne **14**. The FT-IR spectra showed characteristic intense absorption bands at 1636 and 2959–2872 cm^{-1} due to $\text{HC}\equiv\text{N}$ - and CH stretches of azomethyne and *n*-butyl groups, respectively.

The above reaction have not been reported for coumarines to date. Ammonia does not add to coumarin even under pressure and at high temperature.¹⁷ However, coumarin reacts with stronger nucleophiles such as hydroxylamine to produce adduct **16**.¹⁸

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It is evident that strong activation of the double bond in coumarines bearing an electron withdrawing group

in 3 position, facilitates the Michael addition of primary amine and subsequent elimination of malonic acid derivative. This was confirmed by the fact that coumarin **2** containing ethoxycarbonyl group in the position 3 reacts with butylamine much quicker than coumarin **12** having a butylaminocarbonyl group due to the stronger acceptor properties of the former. Moreover, 3,6-dinitrocoumarin reacts with aqueous NaOH solution giving 5-nitrosalicylic aldehyde as the final product.¹⁹ It is obvious that, similar to coumarines **2** and **12**, the strong electron withdrawing nitro group in 3 position also facilitates the Michael addition of H_2O to the double bond of coumarin catalyzed by OH^- as the first step, giving 5-nitrobenzaldehyde as final product after losing nitroacetic acid.

Bearing in mind the data of the above model reactions, the chemical transformation of polymer **6b** under excess 1,8-diaminooctane can be presented as follows (Scheme 4). Once polymer **6b** is formed, it starts reacting with 1,8-diaminooctane producing polymer **17**. This reaction does not lead to the degradation of the polymer chain as seen from Scheme 5. The hydrolysis of azomethyne links by water in the reaction mixture, however, gives rise to polymer chain degradation resulting in polymer **18** having terminal salicylic aldehyde groups. However, hydrolysis is not very pronounced due to the insolubility of the polymer in water as judged from the viscosity and NMR data. The structure of polymer **18** is directly confirmed by the ^1H NMR and FT-IR spectra (Fig. 2). The signals of phenol OH, aldehyde proton and aromatic proton *ortho* to OH of terminal salicylic aldehyde moieties can be clearly seen at 11.1, 10.05, and 6.88 ppm as two singlets and a doublet, respectively. The proton of $-\text{OH}$ of azomethyne moiety overlapping with NHCO proton appeared at 8.35 ppm and a doublet of aromatic

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Scheme 5.

Figure 4. UV-visible absorption spectra of NMP solutions of polymers **6b**, **18**, and model compound **14**.

Figure 5. Emission spectra of polymers **6b** (1) and **18** (2) (λ_{ex} = 398 and 389 nm, respectively) and excitation spectra of polymers **6b** (3) and **18** (4) (λ_{em} = 464 and 493 nm, respectively) taken in NMP solution. Coumarin **6**

proton *ortho* to OH group of repeating units was situated at 6.65 ppm. The signal of azomethyne proton ($\text{CH}=\text{N}-$) overlapping with aromatic protons appeared at 7.35 ppm similarly to model compound **14**. In the FT-IR spectra of polymer **18** (Figure 2) $-\text{C}=\text{NH}$ stretches appeared at 1639 cm^{-1} , close to those of model compound **14** (1635 cm^{-1}). The shoulder at 1655 cm^{-1} in the spectra of polymer **18** was due to the $\text{C}=\text{O}$ stretches of amide. The stretches of the internal triple bond appeared at 2210 cm^{-1} .

Polymer Properties

Figure 4 presents UV-visible absorption spectra of NMP solutions of polymers **6b**, **18**, and model compound **14** (spectra of **6a** are similar to those of **6b** and not shown). The spectra of **6a** showed no absorption in the region beyond 400 nm. The spectra of polymer **18** resembled those of compound **14** (peaks at 260, 326, and 423 nm) presenting a weak long wave absorption maximum beyond 400 nm due to the presence of the azomethyne group in polymer **18** and model compound **14** ($n \rightarrow \pi^*$ transition) giving one more indirect confirmation of the structure of polymer **18**.

All the polymers exhibited photoluminescence in solution and in the form of film. Figure 5 shows the emission and excitation spectra of NMP solutions of polymers **6b** and **18** (spectra of **6a** were identical to those of **6b**). As seen from the figure, polymers **6b** and **18** showed emission band peaking at 464 and 493 nm, respectively. The excitation spectra of the polymers **6b** and **18** showed single emission bands at 398 and 389 nm. In both cases, a large difference exists between the absorption and excitation maxima, probably due to the strong absorption of the incident light at the absorption maximum. Polymer **18** exhibited a 29 nm red-shifted emission band compared to **6b** due to the red-shifted absorption maximum of the former. It is noteworthy, that observed emission intensity of polymer **6b** was about one order of magnitude higher than that of polymer **18**.

The polymers were found rather thermostable. There was not much difference in thermostability among **6a**, **6b**, and **18**. All three polymers showed 10% weight loss at 425, 433, and 428°C under nitrogen, respectively. This is probably due to the thermal cross-linking of the polymers by triple bonds leading to network formation. This was confirmed by DSC data and FT-IR spectra. The DSC curves of all polymers showed an exotherm peaking at around $280\text{--}300^\circ\text{C}$. After this thermal treatment the polymers were no longer soluble and the absorption band at 2210 cm^{-1} disappeared from the FT-IR spectra.

In conclusion, coumarin-containing polyamides based on novel monomer 6-[[3-(chlorocarbonyl)phenyl]ethynyl]coumarin-3-carboxylic acid chloride were prepared and characterized for the first time. They were soluble in common organic solvents such as NMP and DMSO and gave transparent and tough films on casting. In the presence of excess diamine the polymers underwent chemical transformation at room temperature producing polyazomethyenes as confirmed by the model reactions and a possible reaction mechanism is proposed. The coumarin containing polyamides showed intense photoluminescence peaking at 464 nm in solution and films and showed 10% weight loss above 400°C .

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