



## Optical properties of coumarins containing copolymers



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### ABSTRACT

We investigate the optical properties such as absorption coefficient, refractive index, real and imaginary parts of dielectric function and energy band gap of coumarin-containing copolymers thin films by means of spectroscopic ellipsometry (SE) combined with transmittance measurements (T) and atomic force microscopy (AFM). We found that the optical properties of coumarin-containing copolymers strongly depend from length of alkyl spacer as well as the type of substitution in coumarin moiety. In our case the refractive index as well as the energy band gap of coumarin-containing copolymer decrease with increase the length of alkyl spacer. Additionally, the lengthening of the alkyl spacer brings the bathochromic shifts of the absorption spectra towards longer wavelengths.

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### 1. Introduction

Coumarins belong to the class of heterocyclic compounds known as benzopyrones. They consist of fused pyrone and benzene rings with the pyrone carbonyl group at position 2. Coumarins are considered among the most important classes of organic heterocyclic molecules with versatile applications in various fields of science and technology. Due to inherent photo-chemical characteristics, reasonable stability, good solubility and relative ease of synthesis, coumarin derivatives have been extensively investigated for electronic and photonic applications such as charge-transfer agents, solar energy collectors [1] and potential application in organic light-emitting diodes (OLEDs) [2]. They are useful in many fields such as photoalignment of liquid crystalline molecules [3,4], photoactive surface application [5], electroluminescent materials [6], fluorescence materials and laser dyes [7], two photon absorption materials, reversible optical data storage [8,9], organic-inorganic hybrid materials [10], nonlinear optical materials [11], as well as holographic elements [12]. Appropriately substituted coumarins find application as fluorescent dyes for synthetic fibers and as daylight fluorescent pigments, which impart vivid brilliance to paints and printing inks [1].

However, coumarins represent also the class of organic compounds which occur naturally in a number of plants. Therefore, coumarin derivatives have also attracted scientific interest because

these compounds possess biological and medical activities [1,13,14].

In this paper, we present the optical properties of coumarins containing copolymers thin films using spectroscopy, spectroscopic ellipsometry (SE) combined with transmittance measurements (T) and atomic force microscopy (AFM). The photosensitive copolymers were synthesized by radical copolymerization of corresponding methylcoumarin or coumarin derivatives with comonomers methyl methacrylate (MMA) using azobisisobutyronitrile (AIBN) as radical initiator.

The aim of this work was to show how the introducing of a methyl group (CH<sub>3</sub>) to the 4-position of coumarin and lengthening of the alkyl spacer between the polymer backbone and the coumarin moieties lead to the change of the optical properties. These chemical modifications allow to vary optical properties of coumarins containing copolymers continuously throughout the UV–vis–IR spectra.

### 2. Sample preparation

The copolymers P1–P4 have been synthesized by free radical polymerization coumarin based methacrylic monomers and methylmethacrylate in 10% DMF solution with AIBN as radical initiator at 80 °C (argon atmosphere).

N,N-Dimethylformamide (DMF) was vacuum distilled off from calcium hydride just prior to use. 2,2-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from absolute methanol. Methylmethacrylate (MMA) was washed with aq NaOH to remove inhibitors, dried with CaCl<sub>2</sub> under nitrogen at reduced pressure. All

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other reagents and solvents were commercially available and used as received [15,16].

Methacrylic monomers based on 4-methylcoumarin were obtained by adapting procedure described for the non-methylated coumarin parent [17,18]. Methacryloyl chloride is reacted with the suitable hydroxy derivative of 4-methylcoumarin or methylcoumarin in the presence of triethylamine.

### 2.1. 7-Methacryloyloxy-4-methylcoumarin [19–21]

Recrystallization from ethanol alcohol gave colorless plates m.p. 177 °C, 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 2.05 (s, 3H), 2.41 (s, 3H), 5.80 (s, 1H), 6.23 (d, 1H), 6.35 (s, 1H), 7.09 (t, 2H), 7.60 (d, 1H).

### 2.2. 7-Methacryloylcoumarin

The synthetic road is the same as for 7-methacryloyloxy-4-methylcoumarin and described previously. Recrystallization from ethanol alcohol gave colorless plates m.p. 146–147 °C, 80%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 2.0 (s, 3H), 5.9 (s, 1H), 6.5 (d, 1H), 6.35 (s, 1H), 7.2 (d, 1H), 7.3 (s, 1H), 8.1 (d, 1H), 7.8 (d, 1H).

### 2.3. 7-(2-Hydroxyethoxy)-4-methylcoumarin

A solution of bromoethanol (1.36 ml, 19 mmol), 7-hydroxy-4-methylcoumarin (2.2 g, 13 mmol), potassium carbonate (8.32 g, 60 mmol), and acetone (50 ml) was heated at 80 °C for 30 h. The cooled reaction solution was filtered to remove inorganic material and then evaporated under vacuum. The crude product was purified using column chromatography on silica gel with ethylacetate, yield 91%.

### 2.4. 7-(2-Methacryloyloxyethoxy)-4-methylcoumarin

The crude product was recrystallized from ethanol to afford colorless powdery crystals in 80% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.96 (s, 3H), 2.4 (s, 3H), 4.28 (t, 2H), 4.53 (t, 2H), 5.60 (s, 1H), 6.15 (s, 1H), 6.8–6.9 (m, 2H), 7.5 (d, 1H).

### 2.5. 7-(6-Hydroxyhexyloxy)-4-methylcoumarin [18–20]

The crude product was purified by column chromatography on silica gel (hexane: ethylacetate, 4:6), obtained as white crystals m.p. 81–82 °C, 82%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.40–1.85 (m, 8H), 2.38 (s, 3H), 3.66 (t, 2H), 4.00 (t, 2H), 6.17 (d, 1H), 6.81 (t, 2H), 7.48 (d, 1H).

### 2.6. 7-(6-Methacryloyloxyhexyloxy)-4-methylcoumarin [18,19]

7-(6-hydroxyhexyloxy)-4-methylcoumarin (1.33 g; 4.8 mmol) was dissolved in anhydrous of methylen chloride 30 ml. The reaction mixture was kept at 0–5 °C then triethylamine (0.68 ml; 5 mmol) and methacryloyl chloride (0.48 ml; 5 mmol) were added gradually. The solution was 4 h reflux and washed (1 M hydrochloric acid, 10% sodium hydroxide) and dried over anhydrous magnesium sulfate. The crude oil was purified by column chromatography on silica gel using methylene chloride, yield 54%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 1.45–1.85 (m, 8H), 1.93 (s, 3H), 2.38 (s, 3H), 4.00 (t, 2H), 4.15 (t, 2H), 5.54 (s, 1H), 6.08 (s, 1H), 6.10 (d, 1H), 6.77–6.83 (m, 2H), 7.45 (d, 1H).

### 2.7. Polymerization

The copolymers P1–P4 have been synthesized by free radical polymerization coumarin based methacrylic monomers and

methylmethacrylate in 10% DMF solution with AIBN as radical initiator at 80 °C (argon atmosphere). The mixture was degassed with repeated freeze and thaw cycles and then heated for 24 h. The resulting viscous solution was added into methanol to precipitate polymeric material. The precipitation was repeated from DMF into methanol to give purified polymer.

### 2.8. Thin film formation

Polymer films of P1–P4 were spin-coated at 800 rpm during 60 s from 10 wt.% 1,1,2-trichloroethane solution previously filtered through a 0.4 μm pore size nylon syringe filter. Immediately after deposition, the thin films were dried in vacuum at 35 °C for 5 h to eliminate any remaining solvent.

## 3. Experimental details

<sup>1</sup>H NMR (500 MHz) spectra were recorded on Bruker Avance DRX-500. Differential Scanning Calorimetry: Q20 DSC model was used to determine the glass and phase transition temperatures (*T<sub>g</sub>*) of all polymers. The sample was initially stabilized and after the first scan was made at a heating rate of 10 °C/min up to 200 °C then cooled to 20 °C. Finally, a second scan was performed at a heating rate of 10 °C/min up to 200 °C giving the values of *T<sub>g</sub>*. The molecular weights of polymers were determined by Gel Permeation Chromatography (GPC) with polystyrene standards.

Ellipsometric azimuths Ψ and Δ were measured for three angles of incidence (65°, 70° and 75°) in the NIR-vis-UV spectral range (275–2000 nm; 0.6–4.5 eV) by V-VASE instrument (J.A.Woollam Co., Inc.). The transmittance spectra in the wavelength range from 275 nm to 2000 nm were recorded using spectrophotometer Cary 5000 (Agilent). IR ellipsometric measurements were performed for one angle of incidence (65°) in the spectral range from 1000 cm<sup>-1</sup> to 4000 cm<sup>-1</sup>.

To determine the thickness and optical constants of layers the four medium optical model of the sample was used: substrate (glass)/polymer layer (*d<sub>p</sub>*)/rough layer (*d<sub>r</sub>*)/ambient. The complex dielectric function ( $\tilde{\epsilon}$ ) of produced layers was parameterized using a sum of Gauss oscillators ( $\tilde{\epsilon}_G$ ). Additionally, a pole dispersion relation ( $\epsilon_p$ ) of real part of the complex dielectric function was applied in the non-absorbing wavelength range. The optical response of this system can be written in the following form:

$$\tilde{\epsilon}(E) = \epsilon_\infty + \epsilon_p(E) + \sum_j \tilde{\epsilon}_{G_j}(E), \quad (1)$$

where  $\epsilon_\infty$  is the high-frequency dielectric constant and was set as 1. The mathematical formulas of line shapes of particular oscillators used for reproducing the complex dielectric functions of the polymer films are presented below [22,23]:

$$\epsilon_p = \frac{A_0}{E_0^2 - E^2}, \quad (2)$$

$$\tilde{\epsilon}_G(E) = \epsilon_{1G}(E) + i\epsilon_{2G}(E). \quad (3)$$

where  $E_0$  is the pole oscillator position and  $A_0$  is its magnitude, the quantities  $\epsilon_{1G}$  and  $\epsilon_{2G}$  are real and imaginary parts of the Gaussian-type dispersion relation of the complex dielectric function, respectively and are defined as [22,23]:

$$\epsilon_{1G}(E) = \frac{2}{\Pi} P \int_0^\infty \frac{\xi \epsilon_{2G}(\xi)}{\xi^2 - E^2} d\xi \quad (4)$$

and

$$\epsilon_{2G}(E) = A_j \left[ \exp\left(-\left(\frac{E - E_j}{\sigma_j}\right)^2\right) - \exp\left(-\left(\frac{E + E_j}{\sigma_j}\right)^2\right) \right]. \quad (5)$$

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