

# Nanoaggregates and Selforganization Phenomena in Polyurethane Coumarin Film

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*The spectroscopic and photochemical properties of polyurethane coumarin (PUC) in solid state were investigated at room temperature under once-photon excitation. One photon induced photocycloaddition of PUC was investigated and the AFM and spectroscopic FTIR analysis confirmed dimer formation. The AFM analysis shows that the fotodimerization process occurs at the surface of polymer films. The polyurethane coumarin film on CaF<sub>2</sub> unirradiated and irradiated underline both the fotodimerization of the polymer films as well as the photocleavage of the polyurethane coumarin*

**Keywords:** polyurethane coumarin; photophysical properties; photochemical properties; selforganization phenomena; nanoaggregates

Coumarins and many of its derivatives have important applications in biological and medical treatments. Perhaps of the greatest fundamental biochemical interest is the photo-sensitizing effect on human cells [1-5]. Analysis of photosensitive materials containing an aromatic fluorophore very sensitive to an external stimulus has a particular importance for obtaining new functional devices with applications in optoelectronics [6-7].

The stability of polymer micelles, which affects the stability of encapsulation of guest molecules, may be a crucial condition for some controlled delivery applications.

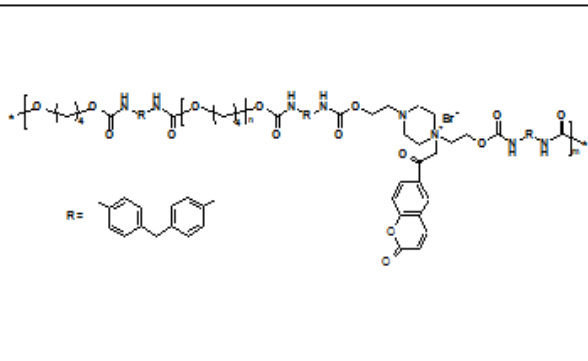
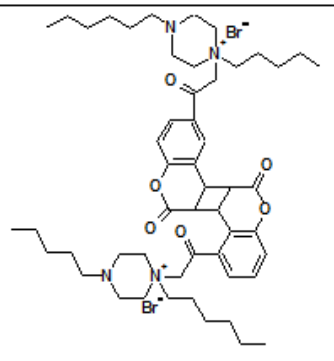
Under these conditions the study of nature and of the nanoaggregate formation mechanisms in polymers containing fluorophores can provide information both about their structure and conformational properties of polymer in the form of films and solution [8-19].

The paper presents the photopolymerization and photocleavage properties of the polyurethane coumarin. The methods of atomic force microscopy and FTIR

spectroscopy are used. The results confirm the existence of the phenomena of nanoaggregation and self-organization in the coumarin polyurethane films.

## Experimental part

The used solvents were found to be transparent and non-fluorescent in the range of excitation and fluorescence emission. All solvents [dimethylformamide (DMF), dimethyl sulf-oxide (DMSO), tetra hydro furan (THF)] (Merck reagent grade) were used without further purification. The polymer was prepared by the poly-addition reaction of classical poly (tetra methylene oxide) diol of molecular weight 2000, 4, 4'-diphenylmethane diisocyanat and N, N-dihydroxietilpiperazine, using the molar ratio 2:3:1. In the next step, the formed polymer was treated with bromine-methyl coumarin, to lead the polyurethane quaternized in proportion of 10%. The investigated polyurethane, the photopolymer block copolymer and the photocycloaddition of polyurethane coumarin side groups are given in table 1, together with the main spectral

polyurethane	photopolymer block copolymer
	
<i>FTIR Spectra (cm<sup>-1</sup>):</i> 3293 (NH); 2941-2857 (CH); 1729 (CO); 1599 (Aromatic); 1513 (amide); 1223 (C-O)	
<i>RMN Spectra, ppm (DMSO):</i> 8.5 (NH); 7.9 (CH=); 7.4-7.7 (Aromatic from coumarine); 7.34; 7.1 (MDI); 4.3; 4.4 (CH <sub>2</sub> from urethane groups); 1.5 (CH <sub>2</sub> CH <sub>2</sub> )	

**Table 1**  
THE CHEMICAL STRUCTURE  
AND SOME SPECTRAL  
PROPERTIES

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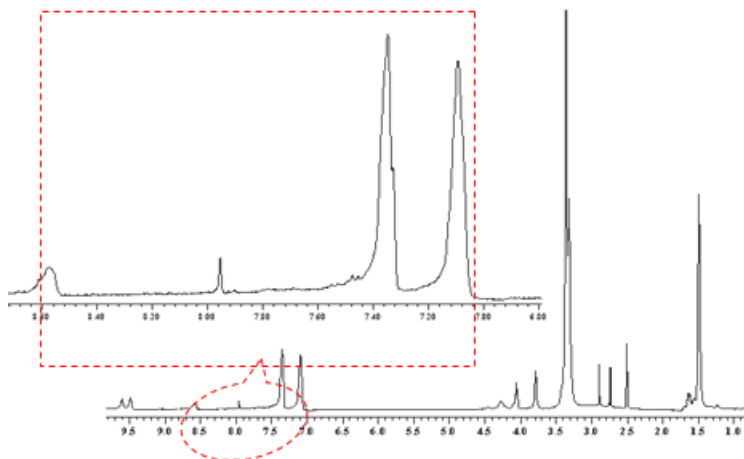


Fig. 1. The NMR spectrum of photopolyurethane with signal amplification in the 7.0-7.9 ppm

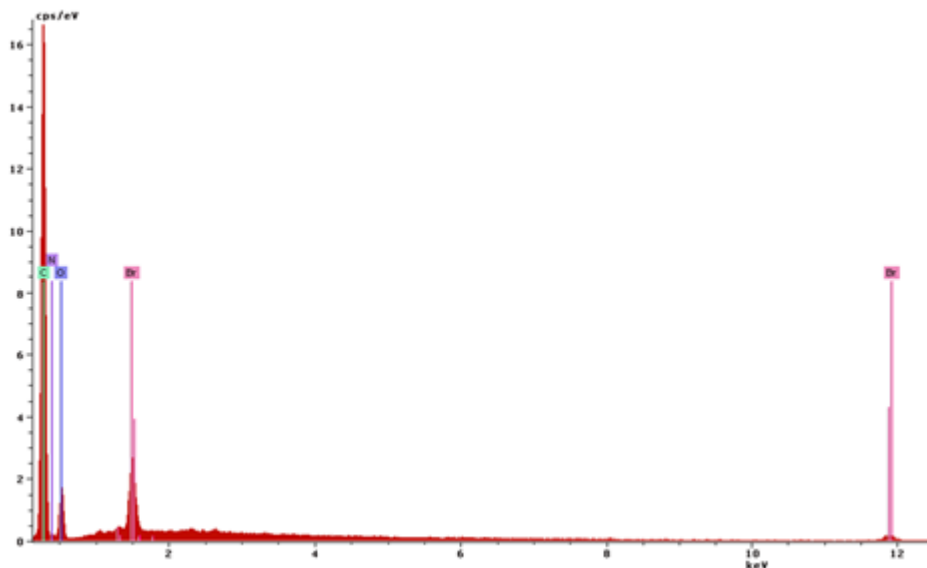


Fig. 2. Chemical composition of polyurethane coumarin

Element	AN	Net	[wt.%]	[norm.wt.%]	[norm.at. %]	Error in %
Oxygen	8	7818	68.4839	68.48595	64.88085	22.20715
Carbon	6	74615	18.9617	18.96227	23.9293	5.940214
Nitrogen	7	851	9.870188	9.870484	10.68123	3.750815
Bromine	35	2479	2.681214	2.681294	0.508622	0.112869
		Sum:	99.997	100	100	

**Table 2**  
BRUKER AXS MICROANALYSIS  
GMB, QUANTAX, GERMANY

features. To confirm the structure of the polymer, the NMR spectrum of photopolyurethane with signal amplification in the 7.0-7.9 ppm range is recorded (fig. 1).

These are assigned to aromatic protons of unsaturated coumarin and aromatic isocyanate used in the synthesis. Chemical composition of studied polyurethane coumarin was confirmed by Energy Dispersive X-ray Spectroscopy (EDS) analysis performed by means of a Bruker AXS Microanalysis facility Gmb, Quantax, Germany (fig. 2 and table 2).

AFM measurements were made by means of EasyScan Nanosurf II device. All the measurements were taken at room temperature (22°C).

## Results and discussions

The photodimerization of the polyurethane coumarin was performed using UV global radiation, while the photocleavage reaction was accomplished with 254 nm

irradiation. The photodimerization and photocleavage reactions of the polyurethane coumarin were followed using UV-Vis spectroscopy (Ocean Optics QE65000 spectrophotometer) and FTIR spectroscopy (BOMEN spectrophotometer). Investigations of surfaces thin layer of polyurethane coumarin obtained on CaF<sub>2</sub> shows that on the polymer surface nano-aggregates are formed, and these structures appear in greater numbers when the film is irradiated with 337nm N<sub>2</sub> laser radiation (figs. 3-6). Our results confirm the fact that photodimerization of coumarin polymers as film occurs especially at surface of thin layer [20].

We confirmed that photochemical dimerization of the coumarin pendants of polyurethane chain takes place in the solid state. Upon exposure to a UV (> 310 nm), a cast film on a CaF<sub>2</sub> plate displayed the appearance of a new C=O stretching vibration (1757 cm<sup>-1</sup>) due to the coumarin functionality, next to its original vibration (1728

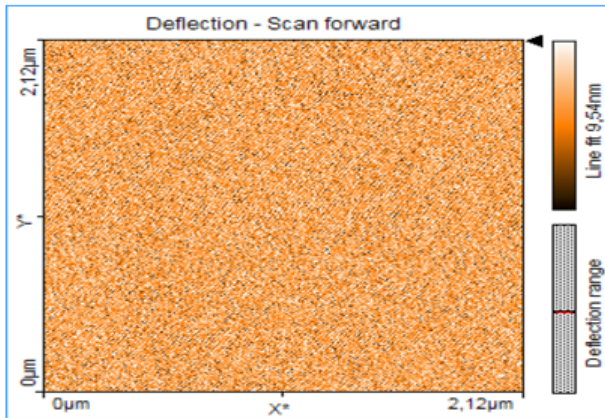


Fig. 3. Deflection image of polyurethane coumarin film state obtained on  $\text{CaF}_2$

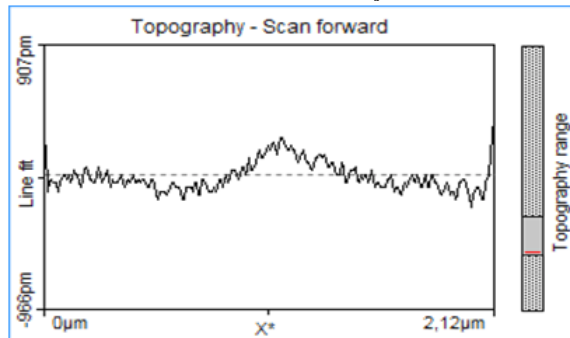


Fig. 4. Topography line of studied surface of the polymer coumarin obtained on  $\text{CaF}_2$

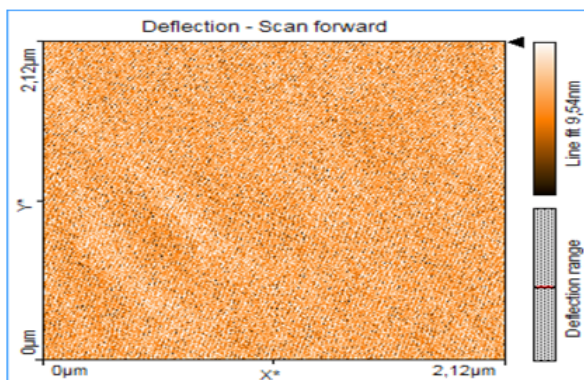


Fig. 5. Deflection image of polyurethane coumarin film state obtained on  $\text{CaF}_2$  under irradiated with 337 nm Nitrogen laser

$\text{cm}^{-1}$ ), and a decrease in intensity of the  $\text{C}=\text{C}$  stretching vibration ( $1600 \text{ cm}^{-1}$ ) (fig. 7). The spectral change subsided in 170 min, where the integral value of the  $\text{C}=\text{C}$  group vibration dropped to  $\sim 70\%$  of the initial one.

FTIR spectra of polyuretan coumarin film on  $\text{CaF}_2$  unirradiated and irradiated with UV radiation

We must underline that our substance is a photopolymer block copolymer in which covalently attached coumarin about 4% exists. Under these circumstances new band appears in the film after irradiation belongs to the carbonyl group ( $\text{C}=\text{O}$ ) of the chemical structure of coumarin ( $1758 \text{ cm}^{-1}$ ). We also underline the fact that the band at  $1728 \text{ cm}^{-1}$  is attributed to the carbonyl group forming chemical bonds between the fluorophore and the polyurethane polymeric chain.

Because the process of fotodimerization carbonyl band at  $1728 \text{ cm}^{-1}$  shifted to lower wave numbers ( $\sim 1717 \text{ cm}^{-1}$ ). Conversely position stretching vibration band belonging to the group of  $\text{C}=\text{C}$  ( $\sim 1600 \text{ cm}^{-1}$ ) remains unchanged. Explaining the production process fotodimerization surface polymer films using FTIR spectra is given in the works [13]. The photocleavage of the polyurethane coumarin was

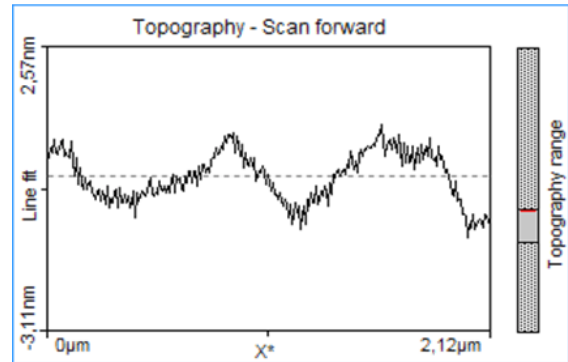


Fig. 6. Topography line of studied surface of the polymer coumarin obtained on  $\text{CaF}_2$  under irradiated with 337 nm Nitrogen laser

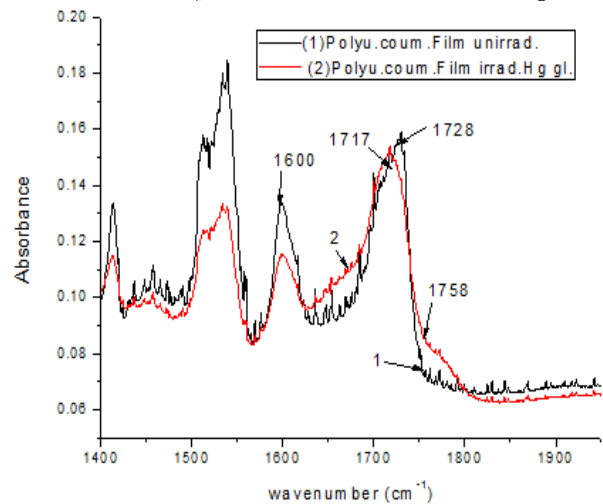


Fig. 7. To emphasize the effect of photo dimerization on infrared spectroscopy methods. FTIR pectra of polyuretan coumarin film on  $\text{CaF}_2$  unirradiated and irradiated with UV radiation

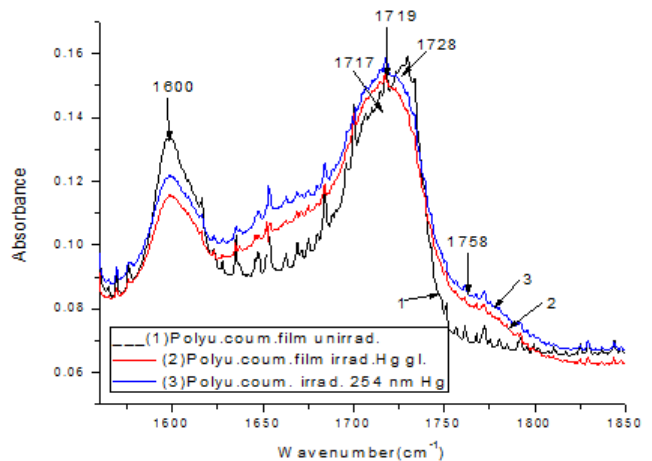


Fig. 8. To highlight the effect of photo-cleavage with infrared spectroscopy methods. FTIR pectra of polyuretan coumarin film on  $\text{CaF}_2$  unirradiated and irradiated with 254 nm Hg radiation

accomplished with 254 nm Hg irradiation for 300 minutes. The results are given in figure 8.

FTIR spectra of polyurethan coumarin film on  $\text{CaF}_2$  unirradiated and irradiated with 254 nm Hg radiation.

The analysis reveals that the band carbonyl moving toward higher wavenumber ( $\sim 1719 \text{ cm}^{-1}$ ). This movement, though small, shows us that some of fotodimers underwent a process of photo cleavage under the action of radiation of 254 nm. Interesting to note is the fact that the  $\text{C}=\text{C}$  band positions remain unchanged.

## Conclusions

The results confirmed that photochemical dimerization of the coumarin pendants of polyurethane chain takes place in the solid state.

Investigations of surfaces thin layer of polyurethane coumarin obtained on CaF<sub>2</sub> by means of AFM shows that on the polymer surface nano-aggregates are formed, and these structures appear in greater numbers when the film is irradiated with 337 nm N<sub>2</sub> laser radiation.

Our results confirm the fact that photodimerization of coumarin polymers as film occurs especially at surface of thin layer.

The photocleavage properties of photodimerization of coumarin polyurethane film have been studied by means FTIR spectra. These processes are confirmed by the shifted carbonil bands (C=O, 1728 cm<sup>-1</sup>) and the appearance of new bands at 1758 cm<sup>-1</sup>, band belonging to the carbonyl group of the coumarin chemical structure.

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