

The Study of Photoreversibility, Photopolymerization and Photocleavage Properties of Polyurethane Coumarin by Means of Electronic Spectrometry and AFM Methods

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The spectroscopic and photochemical properties of polyurethane coumarin (PUC) in dimethyl sulf-oxide (DMSO), tetra hydro furan (THF), dimethyl formamide (DMF) and film state were investigated at room temperature under one photon excitation. The results show that under irradiation of $\lambda > 310$ nm photodimerization process are increased and under UV irradiation with $\lambda < 260$ nm, photocleavage of polymer have been evidenced, too.

Keywords: polyurethane coumarin; photophysical properties; photochemical properties; one-photon excitation

In 1902 Ciamician and Silber found that coumarin dimerized on photoirradiation with $\lambda > 300$ nm in ethanol or in aqueous medium. Since then, the photocyclo-dimerization of coumarin has received a lot of attention among organic chemists and has been studied extensively by several groups both from the synthetic and mechanistic points of view [1-4].

There are a lot of papers which show the ultraviolet light-triggered photodimerization of coumarins [5-9]. We must underline that photocleavage allows some dimers to revert to their original structure. In the case of polymer coumarin, cyclobutane ring that are derived from polymer coumarin dimers reverses under the action of electromagnetic radiation on 254 nm wavelength. This paper reports the characterization of polyurethane that is grafted with coumarin chromophores. In this, conditions we have studied the photopolymer block copolymer in which covalently attached coumarin about 4% exist.

Experimental part

All solvents dimethylformamide (DMF), dimethyl sulf-oxide (DMSO), tetra hydro furan (THF) (Merck reagent grade) were used without further purification. Absorption spectra were recorded using Ocean Optics QE65000 spectrophotometer. The fused silica cells were used on 2mm, 5mm and 10mm, thickness of absorbent layer. Polyurethane coumarin in film states were obtained by spin coating. AFM measurements were made by means of EasyScan Nanosurf II device.

The photodimerization of the polyurethane coumarin was performed with 200W high-pressure Hg lamp for up to two hours, while the photocleavage reaction was accomplished with 254nm Hg irradiation for min. Moreover, various coherent and incoherent radiation have been used like, 310nm Hg; 365nm Hg, N₂ laser beam (337nm) and Nd-YAG 266nm (QUANTEL). All the measurements were taken at room temperature.

Synthesis

The polyurethane coumarin was synthesized at Petru Poni Institute of Macromolecular Chemistry from Iasi,

Romania. The polymer was prepared by the poly-addition reaction of classical poly (tetra methylene oxide) diol of molecular weight 2000, 4, 4'-diphenylmethane diisocyanate and N, N-dihydroxyethylpiperazine, using the molar ratio 2:3:1. The investigated polyurethane [10, 11], the photopolymer block copolymer and the photocycloaddition of polyurethane coumarin side groups are given in table 1, together with the main spectral features.

Results and discussions

The results confirm that the speed of photodimerization process depends on the position and the nature of substituent in the coumarin rings (fig. 1). In figure 2 absorption electronic spectra of the polymer coumarin studied in film state, in DMF and THF when the substance was under the action of electromagnetic radiation with wavelengths, $\lambda > 310$ nm, are given.

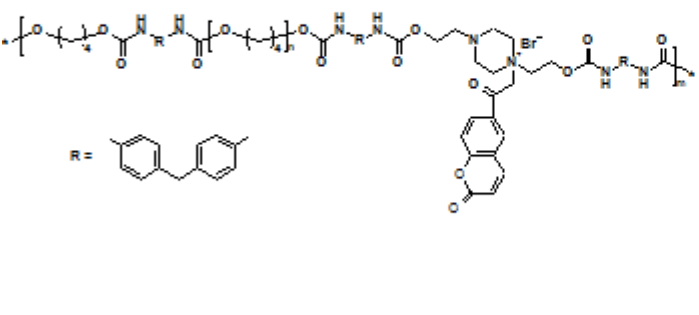
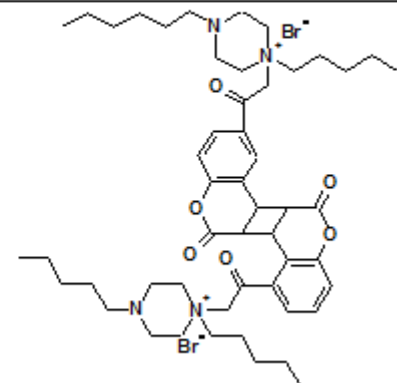
The results show that under irradiation with wavelengths $\lambda > 310$ nm, increase photodimerization process is evidenced (the absorption values of the electronic bands is decreased). In figure 3a and 3b, we can see that under UV irradiation with wavelengths $\lambda < 260$ nm, take place of photocleavage of polymer. Although, the results show, the photocleavage of polyurethane coumarin dimers appeared incomplete. The results confirm that coumarin dimers formed on irradiation depends not only on the solvent but also on the coumarin concentration [3]. If we take in consideration the concentration of coumarin in our studied polyurethane coumarin (about 4%), then we may admit that at low concentration, inefficient intersystem crossing produces the triplet coumarin and the anti head-to-head dimer is formed [1-3]. In figure 4 the chemical structure of the photopolymer block copolymer and the photodimerization of coumarin side groups are given. We underlined, too, that in polar solvents the singlet state is favored, resulting in the formation of mostly syn head-to-tail photodimers.

Analyze by means of AFM

It is also known that the photodimerization of coumarin polymers as film occurs especially at surface of thin layer

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Table 1
THE CHEMICAL STRUCTURE AND SOME SPECTRAL PROPERTIES OF THE POLYMER WITH COUMARIN UNITS

polyurethane	photopolymer block copolymer
	
<p>FTIR Spectra (cm⁻¹): 3293 (NH); 2941-2857 (CH); 1729 (CO); 1599 (Aromatic); 1513 (amide); 1223 (C-O)</p>	
<p>RMN Spectra, ppm (DMSO): 8.5 (NH); 7.9 (CH=); 7.4-7.7 (Aromatic from coumarine); 7.34; 7.1 (MDI); 4.3; 4.4 (CH₂ from urethane groups); 1.5 (CH₂CH₂)</p>	

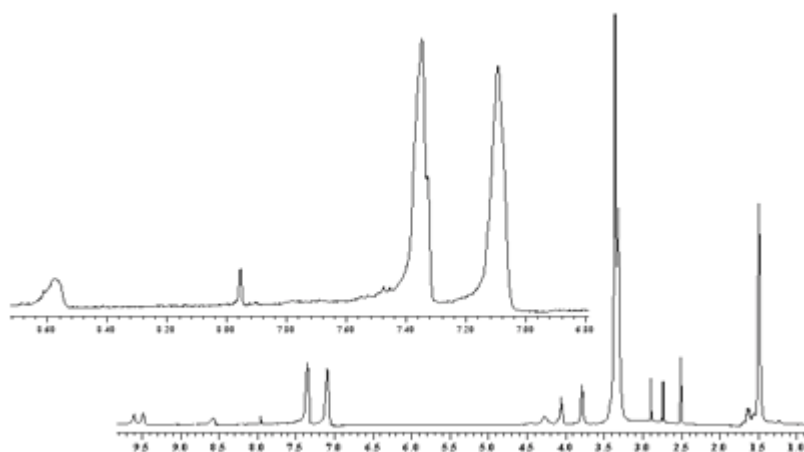


Fig. 1. The NMR spectrum of photopolyurethane coumarin

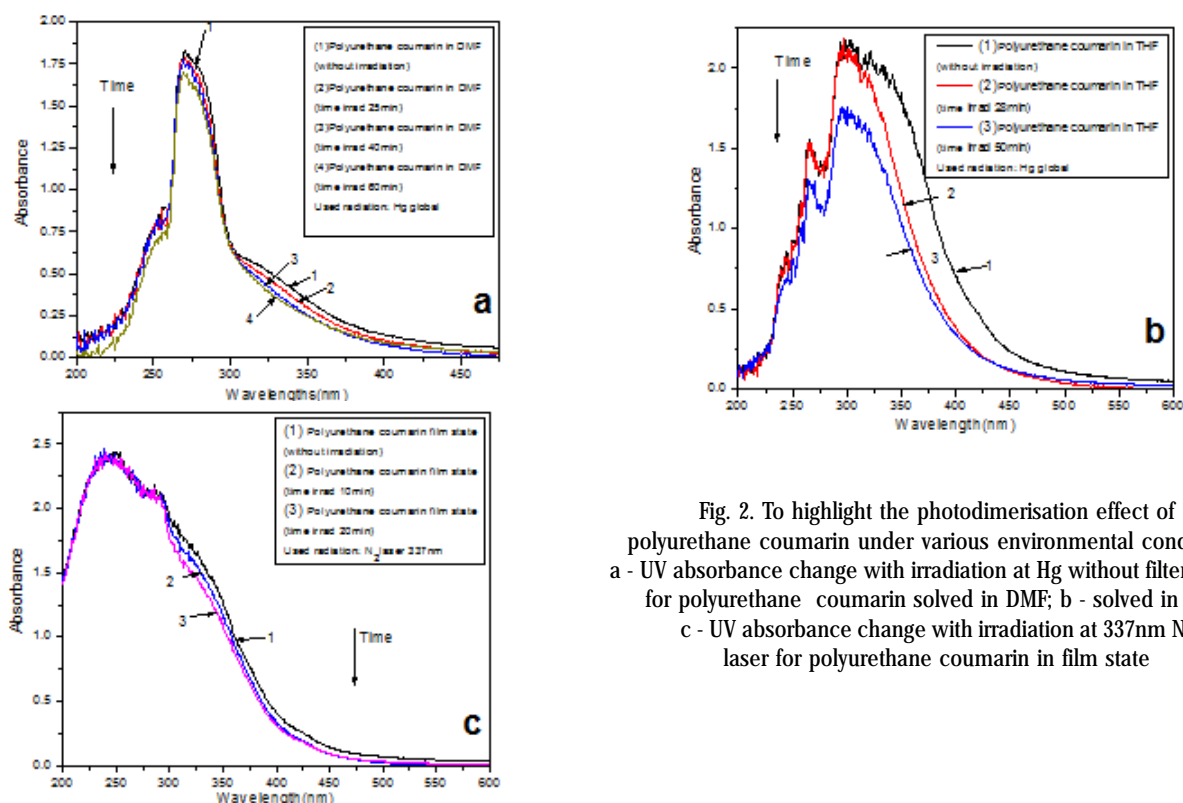


Fig. 2. To highlight the photodimerisation effect of polyurethane coumarin under various environmental conditions: a - UV absorbance change with irradiation at Hg without filter (Hg gl.) for polyurethane coumarin solved in DMF; b - solved in THF; c - UV absorbance change with irradiation at 337nm N₂ laser for polyurethane coumarin in film state

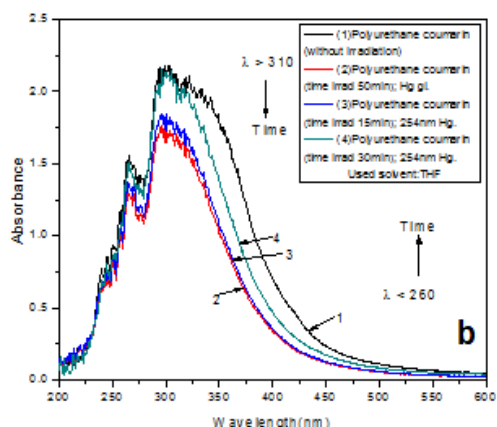
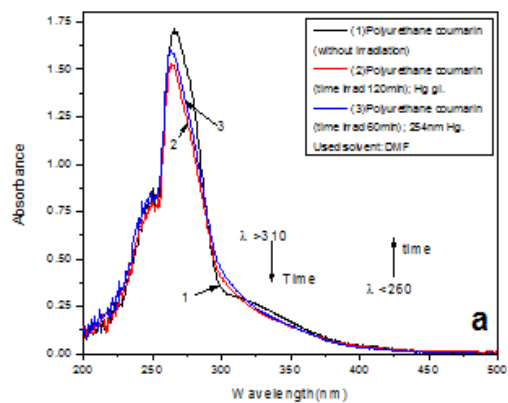


Fig. 3. To highlight the effects of photodimerisation and photocleavage of polyurethane coumarin in various environmental conditions: a - Photodimerization under Hg without filter (gl.) radiation and photocleavage under 254nm Hg of polyurethane coumarin in DMF; b - of polyurethane coumarin in THF

[4-5]. Moreover, because of these processes, amorphous film of a polymer can undergoes bending due photoinduction. This phenomenon is based on the process of the coumarin photodimerization when the coumarin is a pendant group occurring on one side of the film, which creates imbalanced surface stresses leading to the bending [4].

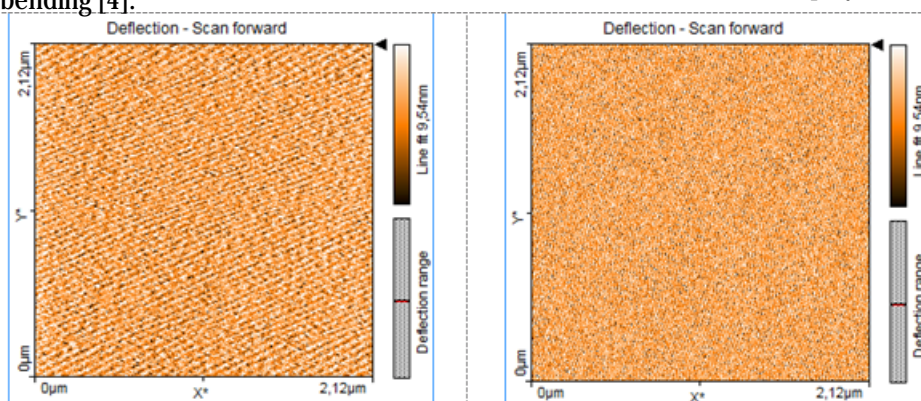


Fig. 5. Deflection image of polyurethane coumarin film state obtained by spin coating non-irradiated (left) and under irradiated with 337 nm Nitrogen laser (right)

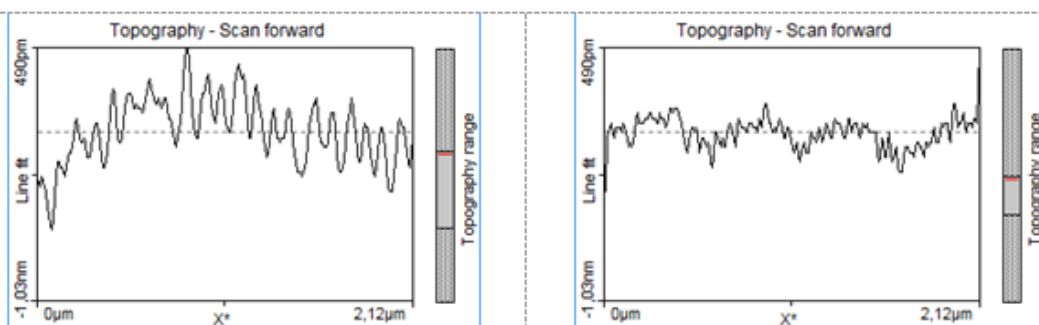


Fig. 6. Topography line of studied surface of the polymer coumarin obtained by spin coating non-irradiated (left) and under irradiated with 337 nm Nitrogen laser (right)

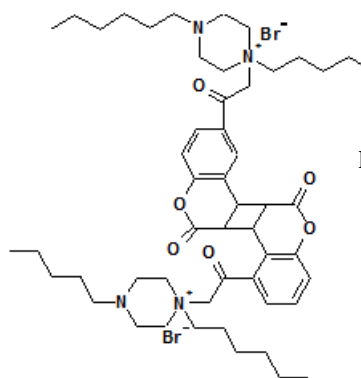


Fig. 4. Photocycloaddition of polyurethane coumarin

We have analyzed the surface of polyurethane coumarin film by means of AFM methods. In figure 5 the images of the surface of the polyurethane coumarin film are given in two cases: the surface of the film is non-irradiated (fig. 5-left) and then when the same surface is irradiated with N_2 laser beam ($\lambda = 337\text{nm}$) (fig. 5-right).

Three-dimensional image of the polymer film can be inferred that analyzed polyurethane coumarin is characterized by relatively homogeneous morphology, there is separation of specific nanophasic such polymers and aggregates formed have approx. 2- 3 nm in height. Exposing the film UV irradiation for 60 min, it is found that the polymer morphology is not significantly affected, keeping the aggregates formed in the same dimensional area. Our research results confirm that photodimerization of chemical structures of polyurethane coumarin under action of radiation with $\lambda > 310\text{nm}$ cause a decrease of the intensities of electronic absorption bands attributed to $\pi-\pi^*$ transitions when the polyurethane coumarin is in a film state or solved in DMF and THF. This phenomenon obviously causes a decrease of intensities of fluorescence bands of polyurethane coumarin, too. Investigations of surfaces thin layer of polyurethane coumarin obtained by spin-counting 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_2 laser radiation (fig. 6).

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

thin layer [5-8]. Nanoparticles can self-assemble as a result of their intermolecular forces. As systems look to minimize their free energy, self-assembly is one option for the system to achieve its lowest free energy thermodynamically. Nanoparticles can be programmed to self-assemble by changing the functionality of their side groups, taking advantage of weak and specific intermolecular forces to spontaneously order the particles. These direct interparticle interactions can be typical intermolecular forces such as hydrogen bonding or van der Waals forces, but can also be internal characteristics, such as hydrophobicity [10-15].

Conclusions

Under irradiation with wavelengths, $\lambda > 310\text{nm}$, increase photodimerization process take place, while under UV irradiation with wavelengths, $\lambda < 260\text{nm}$, take place of photocleavage of polymer. The photocleavage of polyurethane coumarin dimmers appeared incomplete.

The analysis of the polyurethane coumarin film surface by means of AFM methods show that when the surface is irradiated with N_2 laser beam ($\lambda=337\text{nm}$) the photodimerization process increases.

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