Photophysical and Photochemical Properties of Polyurethane Coumarin Studied by Means of Electronic Spectra

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The spectroscopic and photochemical properties of polyurethane coumarine (PUC) in dimethyl sulf-oxide (DMSO), thetra hydro furan (THF), dimethyl formamide (DMF) and film state were investigated at room temperature under one photon excitation. Photodimer products were formed via UV irradiation. Syn head-to-head and syn head-to-tail photodimers were formed under one-photon (broadband UV) irradiation in polar solvents. The spectral investigation of the photochemical products of PUC revealed efficient fluorescence emission in the spectral region 300–400 nm, attributed to the syn-head-to-tail dimers of PUC. The results show that under irradiation of $\lambda > 310$ nm photodimerization process are increased and under UV irradiation with $\lambda < 260$ nm, photocleavage degree have been evidenced, too. Fluorescence spectra analysis of PUC in polar and film-based solvents reveals another very important result. The 375nm fluorescence wavelength of the PUC (exciting beam 310 nm) is about 30 times more intense than the same maximum in THF and in DMF. This result indicates a new method to confirm that PUC film photodimerisation occurs especially at its surface.

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

Coumarin 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 [1-8]. On the other hand, ordered supramolecular nanostructures that can be generated in block copolymer films were used as matrices for obtaining structured nanomaterials. In the process of separating microphases, supramolecular function of incompatible phases plays an important role in the formation of nanostructures, such as spheres, cylinders, lamellae [9-16]. Moreover, ordering a domain characterized by the existence of a single phase separation could induce microphase through complex mechanisms behind the incorporation of photoactive groups in the structure of block copolymers and supramolecular transfer order molecular level, getting the well-defined nanostructures. Usually, periodic ordered structures obtained from a series of specific copolymers have the dimensions in the range 3-50 nm [17-27]. From this perspective, we initiated a study of photopolymer block copolymer in which covalently attached coumarin about 4% exist. Coumarin and coumarin derivatives are most strongly fluorescent in solution and shows a solid state process extinguishing due fluorofor crystallization phenomenon.

Experimental part

All solvents dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetra hydro furan (THF) (Merck reagent grade) were used without further purification. They were found to be transparent and non-fluorescent in the range of excitation and fluorescence emission. Absorption spectra were recorded using Ocean Optics QE65000 spectrophotometer. The fused silica cells where used on 2mm, 5mm and 10mm, thickness of absorbent layer. ADVANTES spectrophotometer fitted with CCD detector was used to record the fluorescence spectra of the polyurethane coumarin under investigation. Polyurethane coumarin in film states were obtained by spin counting. AFM measurements were made by means of Easy Scan Nanosurf II device.

Moreover, various coherent and incoherent radiation have been used like, 310nm Hg; 365nm Hg, N_2 laser beam (337nm) and Nd-YAG 266 nm (QUANTEL).

All the measurements were taken at room temperature.

Syntesis

Polyurethane coumarin was synthetized 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 diizicianat and N, Ndihidroxietilpiperazine, 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 I, together with the main spectral features.

Results and discussions

Electronic absorption spectra

The spectra of polyurethane coumarin in some polar solvents and in film state have been studied. The positions of electronic bands and their shift on different solvents are

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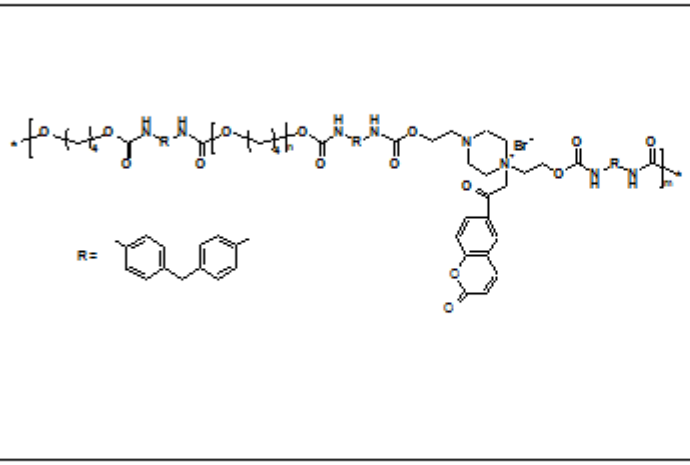
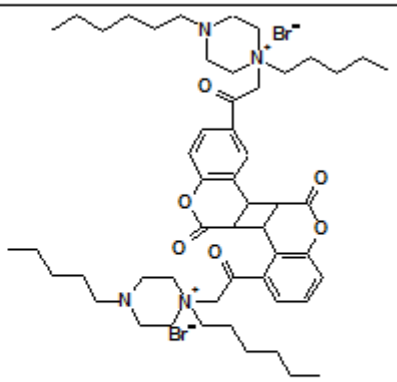
Table 1

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

	coumarin
	
FTIR Spectra (cm^{-1}): 3293 (NH); 2941-2857 (CH); 1729 (CO); 1599 (Aromatic); 1513 (amide); 1223 (C-O)	

in agreement with the theories and experimental data of the electronic absorption spectra of polyatomic molecules [20-22]. In agreement with usually numbering of atom carbons in a coumarin structure we underline that polyurethane chain is chemical bonded in 6-th position through a carbonyl one. Moreover, the chemical bond between coumarin and polyurethane chain (atomic group) acts as an electronic charge accepter (π_a*). The polyurethane coumarin spectra in the UV region may show a number of π - π* transitions and in addition of these may appear also n-π* in some cases. The n-π* transition would be mainly localized on the C=O chromophore. The C-O-C bond angle in coumarin is 122°, indicating a sp^2 hybridization of the ring-oxygen atom [28]. Figure 1 shows the electronic absorption spectra of polyurethane coumarin in film state and in solutions using DMF, THF and DMSO as solvents.

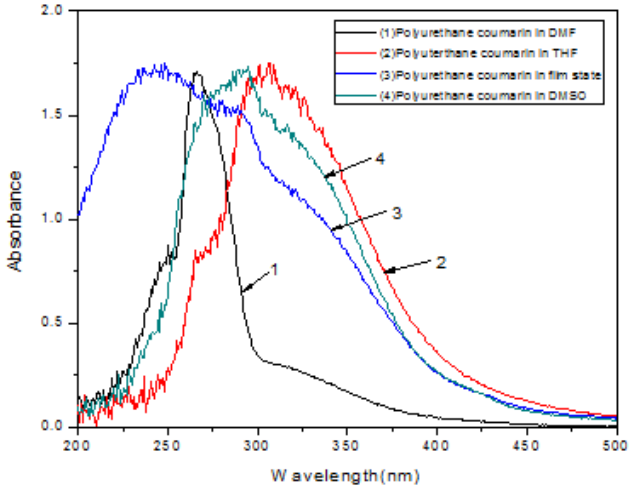


Fig. 1. Absorption electronic spectra of polyurethane coumarin: 1-DMF, 2-THF, 3-film state, 4-DMSO

In figure 2 is presented energy level scheme for polyurethane coumarin: π_a* a vacant π* orbital arising from chemical bond between coumarin and polymer chain.

Absorption electronic bands in polar solvents, suffered a red shift of band maxima. The polyurethane coumarin spectrum shows two absorption bands which correspond at π-π* transitions. This conclusion is sustained by the high

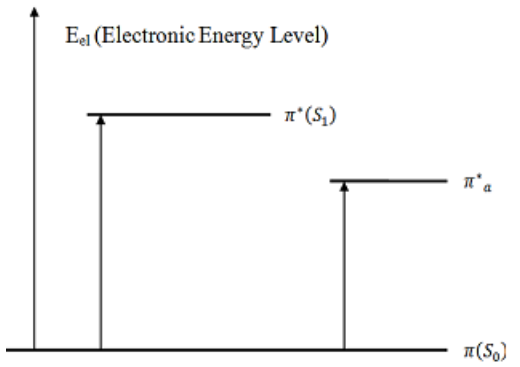


Fig. 2. Energy level scheme for polyurethane coumarin: π_a* a vacant π^* orbital arising from chemical bond between coumarin and polymer chain

intensity of the observed bands. Usually, n-π* transition is symmetry forbidden and the intensity is low. The analyzing of absorption spectra from figur e1 highlights the fact that they have at the small wavelengths (extreme UV bands) everyone one shoulder. This shoulder appears because of electronic absorption band of polyurethane (~ 244nm). Taking into consideration experimental data results from this paper and the result of some orbital molecular theories [29-34] we propose the next schematic electronic transitions between energy levels (fig. 2).

Fluorescence spectra

Emission of radiation phenomena are also of great interest in photophysics of new materials obtained on based of nanotechnologies. Generally, emission phenomena of polyatomic molecules are classified into processes of fluorescence and processes of phosphorescence. Experimental facts prove that the fluorescence spectra and phosphorescence spectra, emitted by pure substances, are not dependent on wavelength of exciting radiation. Our studies may elucidate some contributions of photoactive atomic groups from the chemical structure of a block copolymers to obtain a molecular-level ordering, because in the finally to obtain well-defined nanostructures. Fluorescence spectra of polyurethane coumarin have been obtained by using various experimental conditions as following, DMF, THF, DMSO and in film state. The results are shown in figure 3.

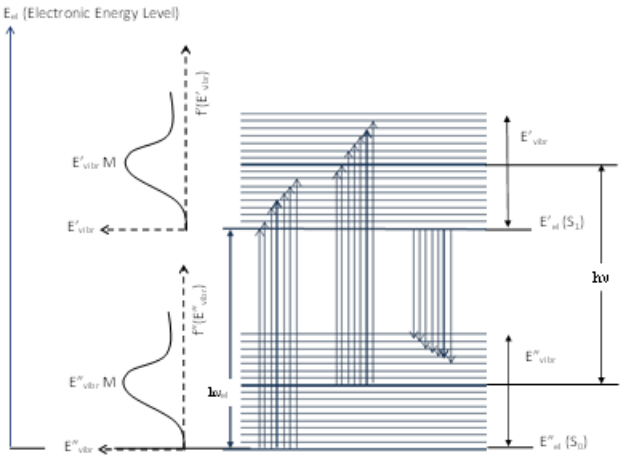


Fig. 3. Schematic representation of electronic transitions for studied polyurethane coumarin

Figures 1, 4 and 5 show that the shifts of fluorescence peaks with solvent polarity changes are more pronounced than the shifts of absorption electronic peaks. It indicates that excited state dipole moments, μ_e, are much higher than ground state dipole moments, μ_g, ($\mu_e > \mu_g$). We underline, too, that absorption and fluorescence bands exhibit bathochromic shift on increase of polarity of solvents which is in conformity with the fact that transitions involved in all these cases are π-π^*. One of the most widely used tool for theoretically evaluating excited-state energies is the time-dependent density functional theory (TD-DFT). By means of this theory we can rapidly provide accurate transitions energies, even for large molecular systems, which cannot be modeled otherwise. However, as long as analytic DT-DFT calculations are not yet available and as numerical vibration frequency calculations are impractically long to be performed for our polyurethane coumarin, it has been impossible to check that all our S_1 structures [35-36].

The analyzing of fluorescence spectra of polyurethane coumarin (figs. 4 and 5) shows that the intensity of emission peaks depends on the polarity of solvents and on the nature of film state. Moreover, the results show that the intensity of the fluorescence peaks depends on the intensity of the exciting beam and on the effect of interaction between excitation radiation and polyurethane coumarin. The results presented in the following section show that under irradiation of 310 nm photodimerization processes are increased and under UV irradiation with $\lambda < 260$ nm, photocleavage degrees have been evidenced too. Taking into account these processes, we can explain why the intensity of the fluorescence peak at 375 nm of PUC in the excited state of film with 310 nm Hg is ~ 30 times the intensity of the same peak of PUC in solution (THF).

Photodimerization of PUC in THF (generally in solution) occurs in the whole volume and consequently decreases the absorption of excitatory radiation so that the photodimers absorb in another spectral domain. In the case of PUC in the film state under the action of the excitation radiation of 310nm Hg takes place the photodimerization process of PUC in particular at the surface of the film [37-39]. In this case the fluorescence emission is due to all the PUC components on the depth of penetration of the excitatory radiation. The arguments presented for explanation of the results presented in figure 4 are confirmed by the experimental data in figure 5. In this figure are given normalized absorption spectra and fluorescence of PUC. Excitation of fluorescence radiation was done this time with 266nm radiation obtained from a laser with the active Nd YAG (Quantel) medium. The action of this

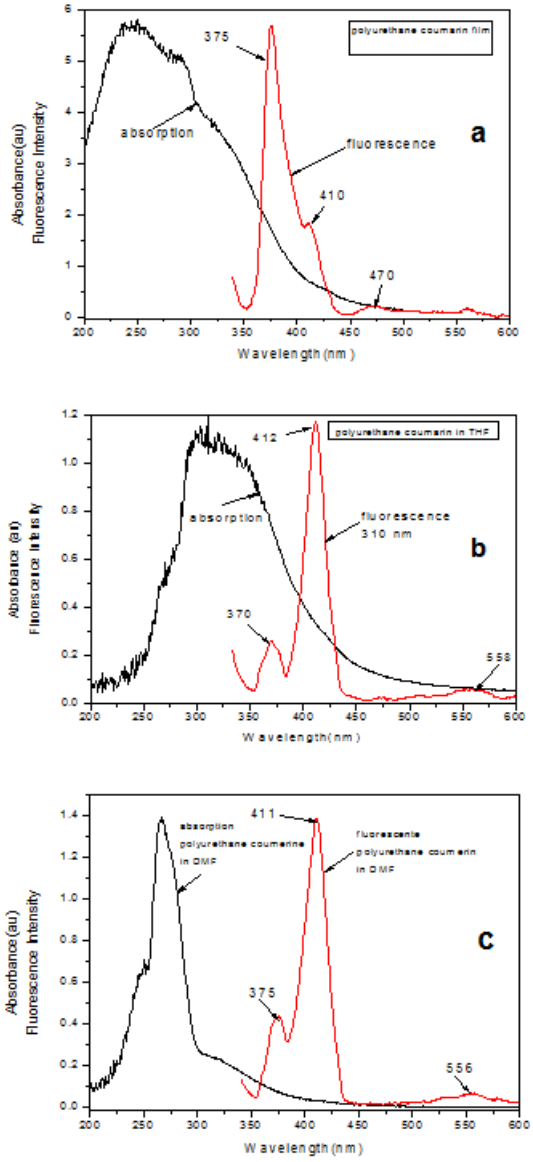


Fig. 4. Electronic absorption and emission spectra of coumarin polyurethane. Normalized absorption and fluorescence spectra of polyurethane coumarin in film state (a), in THF (b), in DMF (c), ($\lambda_{exc.}$ = 310 nm Hg)

radiation does not produce the photodimerization process of PUC studied in this paper. Consequently, the intensity of the fluorescence band with the maximum at ~ 315nm is quite large, and the differences in intensity (in film and solution) are due to the influence of the solvent and the intermolecular interactions that take place in the system. A prior knowledge of electronically excited species is often useful in describe of non-linear optical material and, of course, elucidation of any photochemical transformations. Moreover, taking into account the planary structure of the coumarin which produces strong intermolecular interactions, the behavior of coumarin from the polyurethane structure in the contact with electron donor molecules have been deeply studied, too. Thus, in the presence of aniline and diethylaniline (fig. 6a and b) there is a coumarin fluorescence quenching in small proportion with increasing amine concentration, which is attributed to amine as electron donor effect on species type coumarin fluorophore excited. It was also observed that at a certain amine concentration, the fluorescence intensity increases, the behavior is attributed to exciplex formation or involvement fluorescent amine as a species.

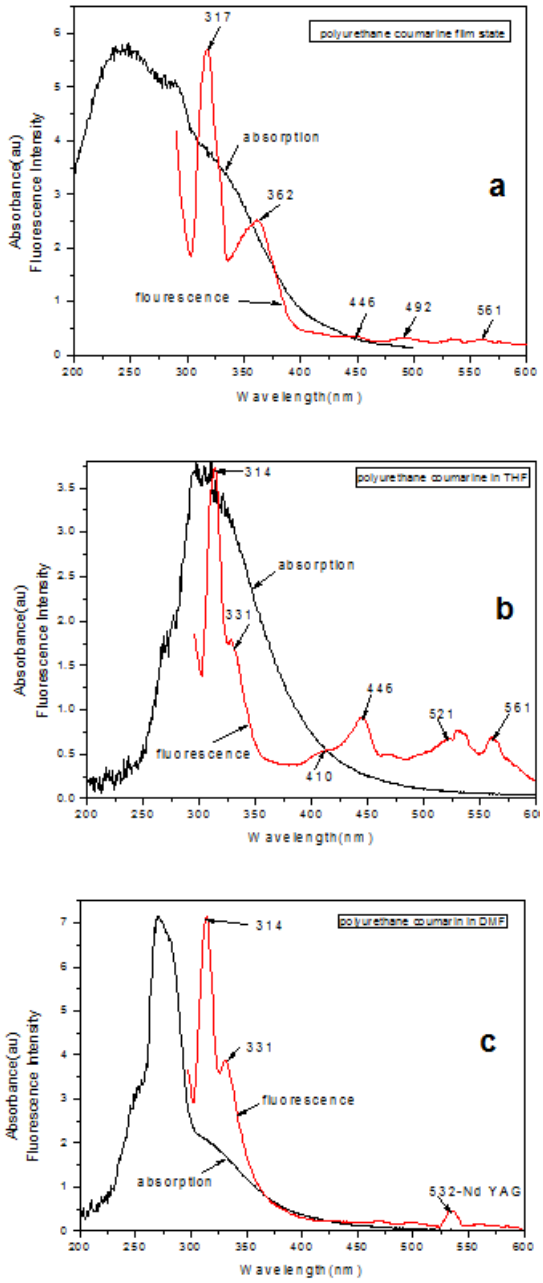


Fig. 5. Electronic absorption and emission spectra of coumarin polyurethane. Normalized absorption and fluorescence spectra of polyurethane coumarin in film state (a), in THF (b), in DMF (c); ($\lambda_{exc.}$= 266 nm Nd-YAG)

Conclusions

The electronic spectra of polyurethane coumarin correspond to π-π* transition. The large red shift of absorption and fluorescence spectra are obvious and suggest that in both the thin films, DMF and THF there are small aggregates of polyurethane coumarin. These small aggregates form especially on the base of dimerization process.

The decrease of intensity of fluorescence band of polyurethane coumarin with maximum at 375nm in DMF and 370nm in THF solution because photodimerization occurs in the entire volume during fluorescence excitation with radiation 310nm Hg. In the film state the fluorescence intensity of the same band in the same action exciter radiation is about 30 times higher because that photodimerization of coumarin polymers as film occurs especially at surface of thin layer.

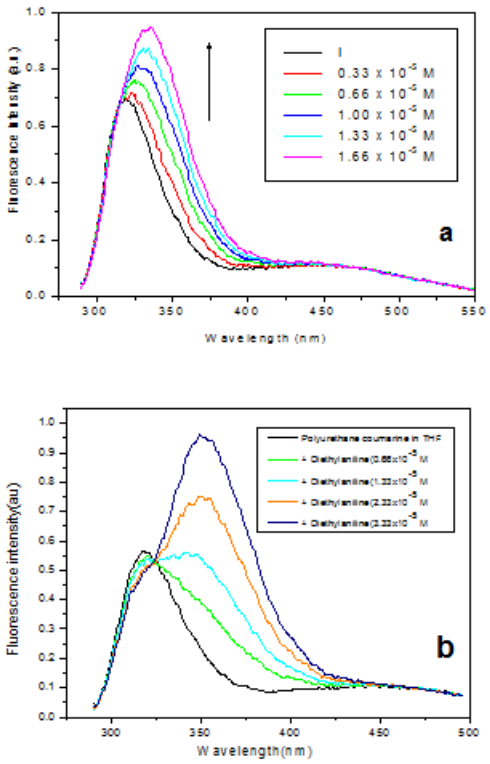


Fig. 6. Electronic emission spectra of coumarin polyurethane Fluorescence spectra of polymer with coumarin units solved in THF in the presence or absence of aniline (a) and in the presence or absence of diethylaniline (b), (λ_{exc}=280nm)

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Manuscript received: 12.01.2017