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Physical Chemistry

A Novel Method of Increasing the Photosensitivity of Spiropyran-Containing Systems

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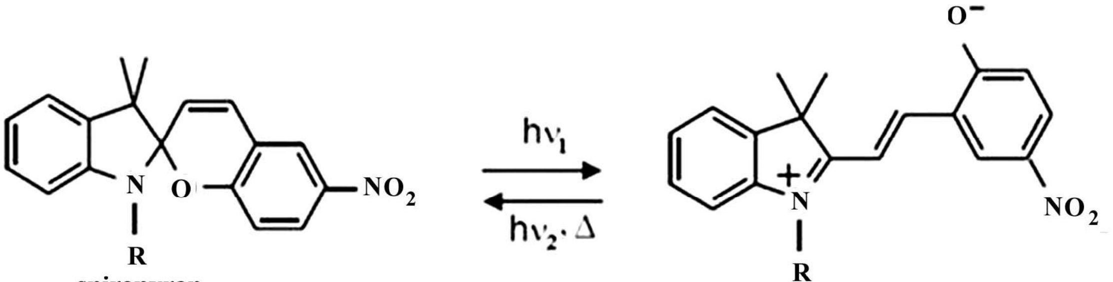
ABSTRACT. Our assumption that micellization process in compositions containing spiropyrans of certain type would increase efficient photosensitivity was confirmed experimentally. The efficient photosensitivity of the cholesteric liquid crystal composition doped with long-radical spiropyrans to ultraviolet radiation exceeded that of the composition doped with short-radical ones. This is likely to be caused by the fact that, in the presence of the long alkyl radical at the nitrogen atom, the merocyanine form of the spiropyran molecule with a lyophilic zwitterionic head and a lyophobic nonpolar tail is amphiphilic. Under certain conditions, molecules of this kind self-organize into micelles, which disturb the thermodynamic equilibrium in the basic solution. For restoring the thermodynamic equilibrium, merocyanine molecules add to the photoinduced merocyanine ones, which eventually increases the number of absorption centers. *© 2013 Bull. Georg. Natl. Acad. Sci.*

Key words: *spiropyran, merocyanine, liquid crystal, micelle, photochromism, nanoparticle.*

Spiropyrans (SP) are an important class of organic photochromic, bistable compounds. Bistable molecules and molecule ensembles can exist in two thermodynamic stable states divided by a certain energy barrier. Switching from one state to another occurs via external stimulation (light, heat, mechanical stress, electric and magnetic fields, etc.).Under the influence of ultraviolet light (UV) an uncolored spiropyran molecule with a bulky structure is transformed into a coplanar, colored merocyanine (MC) form with a high dipole moment. Such bipolar molecules under certain circumstances easily self-organize, i.e. create nanoparticles.

Spiropyrans are practically used in such lightcontrolled devices, as information-recording (including three-dimensional), memorizing and processing systems, nonlinear optical materials, molecular computers, filters with regulated optical density, optical switches, different types of sensors, medical instruments, ecology etc. Spiropyran among other parameters (stability, cyclicity, large cross section of two-photon absorption), must have high photosensitivity. Many scientific centers and companies worldwide carry out studies to increase the photosensitivity of spiropyrans which is evidenced by a large number of published works and patents in the field.



spiropyran

merocyanine

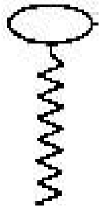
$R=CH_3$ (I)
$R = C_8H_{17}$ (II)
$R = C_{14}H_{29}$ (III)

Photosensitivity of Compositions Doped with Spiropyrans

It is possible to increase by modification of a molecule the photosensitivity of spiropyrans: 1) by varying the substitutes of different electronic natures (electrodonor and electroacceptor) in the indoline and chromen parts and their position in the molecule, and 2) by changing the molecule skeleton. By using this kind of approach, we have synthesized and studied several hundreds of spiropyrans. For instance, changing the indoline ring by azaindoline allowed us to gain spiropyrans with increased photosensitivity to the UV light as compared with the known analogues [1], and introduction of an additional fragment in the indoline part of the molecule (tetrahydrochinoline products) increased photosensitivity to visible light [2]. The spiropyrans gained on the basis of pyridoxal have demonstrated interesting photochromic properties [3].

The zwitterionic MC form obtained as a result of photochemical isomerization of SP, in the presence of long alkyl radical at the nitrogen atom, is an amphiphilic molecule. This molecule consists of two

Polar head



Non-polar tail

parts: the lyophilic molecule head, readily soluble in liquid, and the unsoluble tail. The head (in our case zwitterion) is polar, while the tail (anchor) is a nonpolar alkyl radical. Molecules of this kind are surfactants and they self- organize into micelles under certain conditions. It is well known that micellization is characteristic of such surfactants that have an optimal lyophilic - lyophobic balance. It was revealed experimentally that the surfactants containing the $C_8 – C_{18}$ radical and the zwiterionic head exhibit the capability of micellization [4-6].

The physico-chemical properties of micelles, i.e. nanoparticles, differ dramatically from those of both separate atoms and molecules, and solid bodies. Separate molecules associated into stable super-molecular structures – supramolecules by means of intramolecular forces function as nanoreactors. In solution, they generate an intrinsic micropseudophase the properties of which differ from the characteristics of the main solution. Because of the increased concentration of the solution, the character of interaction with light in the nanoreactors changes. The nanoreactor-containing systems are one-phase and homogeneous at the macrolevel, and two-phase and microheterogeneous – at the nanolevel. Hence, based on the investigation of nanostructures, it is possible to compose and fabricate the nanomaterials with desired properties, better than the properties of natural materials. For instance, we can increase the efficient photosensitivity of the spiropyran-containing composition.

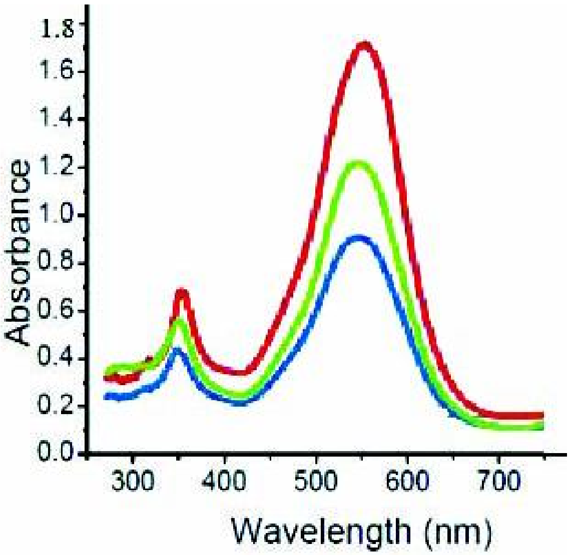


Fig. 1. Absorption spectra of compositions doped with spiropyrans: blue - doped with compound I, green - doped with compound II, red - doped with compound III

It is well known that, under certain conditions, amphiphilic molecules form lyotropic liquid crystals (LC). Thus, investigation of the process of micellization of spiropyrans in a liquid crystalline medium is of interest. Our choice of the liquid-crystal solvent was determined by the capability of self-organization, i.e. nanostructuring of the studied nematic-chiral liquid-crystal systems doped with spiropyrans. The latter is observed by the anomalies of Bragg's selective reflection band [7,8]. We chose the liquid crystal as a solvent, because living organism cells and intracellular organelles are covered with a thin high-order membrane. The membranes, in turn, represent lyotropic liquid-crystal structures. The size of spiropyran micelles in the LC decreases nearly by half under UV photoinduction. This fact gives the opportunity of purposeful delivery of medicines in the human organism. The delivered medicine is released with the help of UV light [9].

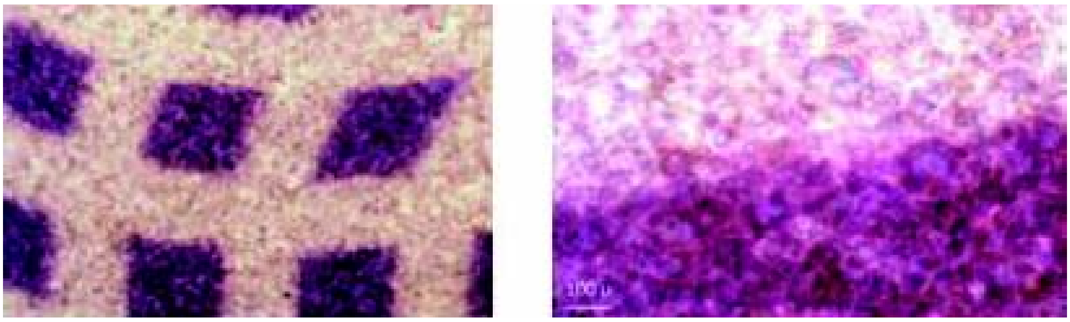
Experiment

We studied the process of micellization in the composition that represented a nematic-chiral LC matrix doped with R-3,3- dimethylindolino- 6'-nitrobenzopyrylospiran's following analogs: R=CH_3 (I), C_8H_{17} (II), and $C_{14}H_{29}$ (III), synthesized by us. The nematic-chiral matrix consisted of Merck's certified components: nematic substance ZLI-1939, containing the cyanic biphenyl group, and optically active substance MLC-4572 or MLC-4571. The experimental sample was made in the following way: the equimolar solutions of the composition under study were placed between flat-parallel glass plates. The sample thickness was determined by the teflon bedding. The samples were placed into a thermostatic chamber. They were irradiated with the same dose of energy by using interference filter (λ =365 nm) under the condition of constant temperature. The electron absorption spectra were detected by means of fiber optics spectrometer Avantes 2048.

We studied three compositions: **1**-doped with compound I, **2**-doped with compound II, and **3**-doped with compound III of equimolar concentration. The absorption spectra of the samples were detected prior to irradiation and after irradiation with the same dose of UV radiation under the condition of constant temperature (Fig.1).

From Fig.1 it is evident that along with the radical length, the absorption peak height increases. A hypsochromic shift of peak **2** in respect to peaks **1** and **3** was observed. A similar shift was observed in the ethanol solutions of those substances [10].

For practical application the spiropyran-doped compositions were integrated into a polymer matrix by an improved method of microcapsulation we developed [11,12]. The use of the microcapsulation method and icy acetic acid as suitable emulsifying agent allowed us to obtain a stable dispersive system in the polyvinyl alcohol matrix. The obtained system contained a dispersed phase – separated compositions, aggregates in the form of capsules in the dispersive medium of the polymer solution, which preserved at most the initial properties of the dispersive composition doped with spiropyran and conditioned the production of polymer films with high photosensitivity. By controlling all stages of microcapsulation we obtained process-perfect uniform, elastic films meeting the requirements of practical application.



a b

Fig. 2. Recorded images on the polymer films with **a** - 60x and **b** - 200x magnifications respetively

Microscopic investigation of the films confirmed that the polymer matrix consisted of microcapsules. Fig. 2. demonstrates the UV-irradiated and non-irradiated sections of the film, which show that the disperse phase of the polymer matrix in the form of microcapsules did not suffer disintegration as the result of irradiation, and hence the properties of spiropyran-doped compositions did not change.

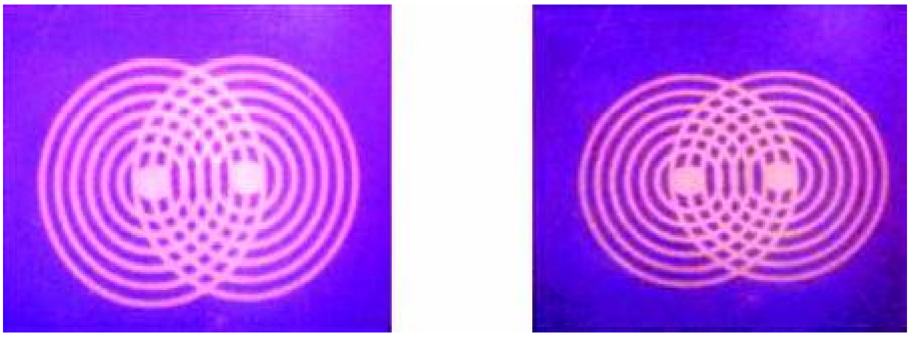
Optical investigation of the films showed that in the films we observed the same correlation as in the compositions, i.e. along with the SP radical length, the absorption peak height increased. This pointed to the fact that, as the result of microcapsulation of the polymer matrix, the composition retained its initial properties.

Results and Discussion

We suppose that the correlation of the efficient photosensitivity of long-radical spiropyran-doped nematic-chiral LC with the radical length is associated with the fact that the MC form of the spiropyran molecule with a zwitterionic lyophilic head and lyophobic alkyl radical at the nitrogen atom represents a surfactant amphiphilic molecule. The so-called Gordon parameter of the nematic-chiral LC of the polar solvent satisfies the conditions of micellization. Therefore, the micellization must occur in spiropyran-doped LC, under certain conditions.

The trigger (switch) of micelle or nanoreactors origination in this case is the UV light ($\lambda = 365$ nm). At the given temperature, prior to irradiation, the solution is made up of the matrix and spiropyran and merocyanine-form molecules, which are in thermodynamic equilibrium with spiropyran. The constant of thermodynamic equilibrium K_T is less than the constant of photochemical equilibrium K_{PH} ($K_T<K_{PH}$). In the case of exposure to UV light, the thermodynamic equilibrium of the composition is disturbed and shifts to the merocyanine-form molecules, and the color of solution gets more intensive. In the process of irradiation, the origination of merocyanine form molecules and growth of their concentration is followed by their structuring as micelle. The critical concentration of micellization is low for substances containing the long alkyl radical C_8H_{17} - $C_{14}H_{29}$. The processes of photoinduction and micelle formation are noninertial, i.e. they are initiated as soon as the trigger is started. There is one more pseudophase - the micelle originated at the microlevel in the base solution. In the process of micelle formation, the base solution is depleted with merocyanine molecules and the spiropyran molecules start to transform to the merocyanine ones to restore the thermodynamic equilibrium. To MC molecules formed photochemically, MC molecules formed for restoring the thermodynamic equilibrium are added. The given process increases the number of absorbing centers in the composition, which in the final account increases the effective photosensitivity of the system. We observed this process experimentally by the increase in the R=C_8H_{17} – $C_{14}H_{29}$ absorption peak in respect to C_1.

The increase in peak **3** in respect to peak **2** in both the composition and the films on their basis (Fig.1) can be attributed to the increase in the micelle radius with increasing alkyl radical length. Accord-



a b

Fig. 3. Photo- imprinted images on the polymer films using the mask with two partially intercrossed concentrated rings. **a**- doped with compound I, **b**- doped with compound II.

ingly the surface area of micelles and the number of molecules arranged on them increased. To restore the thermodynamic equilibrium, an additional quantity of SP molecules were converted into the MC form, and then the absorption peak height increased.

The increase of photosensitivity, along with the radical length, is well defined upon information recording in the polymer films (Fig.3). The violet and white colors correspond respectively to irradiated and nonirradiated parts of the films. The contrast strengthening between irradiated and nonirradiated areas of the film **b**, shows the increase of photosensitivity.

Thus, we may conclude that as a result of UV light induction of liquid crystal compositions doped with spiropyran, merocyanine molecules similar to surfactant molecules originate, which are structured as micelle (nanoreactors). In the process of micelle origination, in order to restore the thermodynamic equilibrium, spiropyran molecules transform to merocyanine molecules increasing the effective photosensitivity of the material. In the case of further increase of spiropyran concentration the concentration of micelle will be increased in the solution as a result of photoinduction and the pseudophase may become liquid crystal.

Conclusion

By choosing the nematic-chiral liquid-crystal solvent possessing the properties contributing to the micellization allowed us to improve the efficient photosensitivity of long-radical spiropyrans. We observed this process in both the composition and the films obtained on their basis by microcapsulation.

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ფიზიკური ქიმია

სპიროპირანების შემცველი სისტემების ფოტომგრძნობიარობის გაზრდის ახალი მეთოდი

კ. ჯაფარიძე*, ლ. დევაძე, ჯ. მაისურაძე**, გ. პეტრიაშვილი**, ც. ზურაბიშვილი**, ი. მჟავანაძე**, ნ. სეფაშვილი****

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ჩვენი მოსაზრება, რომ მიცელირების პროცესი გარკვეული ტიპის სპიროპირანების შემცველ კომპოზიციებში გაზრდიდა ეფექტურ ფოტომგრძნობიარობას, დადასტურდა ექსპერიმენტულად. ქოლესტერულ თხევადკრისტალურ კომპოზიციას, დოპირებულს გრძელი ალკილის რადიკალის შემცველი სპიროპირანით, უფრო მაღალი ეფექტური ფოტომგრძნობიარობა ახასიათებს ულტრაიისფერი გამოსხივებისადმი, ვიდრე კომპოზიციებს მოკლერადიკალიანი ანალოგებით. სავარაუდოდ ეს განპირობებულია იმ ფაქტით, რომ აზოტის ატომთან გრძელი ალკილის რადიკალის არსებობისას სპიროპირანის მეროციანინული ფორმა ამფიფილურია — ლიოფილური ცვიტერიონური თავით და ლიოფობური არაპოლარული კუდით. გარკვეულ პირობებში ასეთი მოლეკულები თვითორგანიზდებიან მიცელებად, რომლებიც არღვევენ თერმოდინამიკურ წონასწორობას ძირითად ხსნარში. წონასწორობის აღსადგენად წარმოქმნილი მეროციანინული მოლეკულები ემატება უკვე არსებულ ფოტოინდუცირებულ მეროციანინულ მოლეკულებს, რაც საბოლოო ჯამში ზრდის მშთანთქმელი ცენტრების რაოდენობას.

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