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## Refractive index modulation in the films containing single and dual chromophore system

**Summary** — Photochromic properties of polymer films containing spirooxazine (SP) and copolymer containing diazo chromophores (IZO) were investigated. The SP underwent photoisomerization under exposure to UV light yielding open forms of merocyanines manifested by strong absorption band at *ca.* 600 nm. The spectra of SP film in transparent polymer matrix, recorded for a single component and for a mixture with IZO copolymer, revealed sensitivity of the materials to UV and visible light. The ellipsometric measurements showed a distinct change of refractive index of the UV treated films on bleaching by exposure to the red and green light. Treatment of the film in two-beam coupling arrangement with 532 nm linearly polarized laser light confirmed the formation of diffraction grating. The study of photoisomerization was accompanied by quantum chemical calculations of spectral and nonlinear optical properties of spirooxazine and merocyanine forms.

**Key words:** spirooxazine, photochromic copolymer, diazo sulfonamide dye, photoisomerization, diffraction grating.

### MODULACJA WSPÓŁCZYNNIKA ZAŁAMANIA ŚWIATŁA W FOLIACH ZAWIERAJĄCYCH POJEDYNCZY I PODWÓJNY UKŁAD CHROMOFORÓW

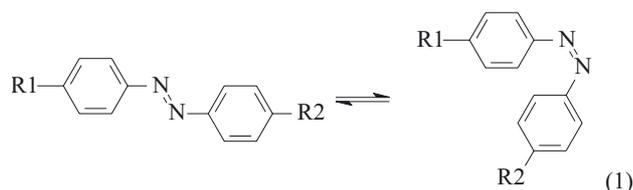
**Streszczenie** — Zbadano właściwości fotochromowe folii polimerowych zawierających spirooksazynę [SP, wzór (I)] oraz kopolimer zawierający diazowe grupy chromoforowe (IZO). SP ulegając fotoizomeryzacji pod wpływem naświetlania światłem ultrafioletowym, przechodzi w otwarte formy merocjanin [wzory (II)—(V), tabela 1], co skutkuje pojawieniem się silnego pasma absorpcji przy ok. 600 nm. Widma próbek zawierających SP w transparentnej matrycy polimerowej wykazały wrażliwość materiału na promieniowanie w zakresie UV-Vis (rys. 2 i 3, tabela 2). Pomiary elipsometryczne pozwoliły określić znaczące zmiany współczynnika załamania światła w stadium naświetlania światłem z zakresu UV oraz podczas wybielania, powodowanego naświetlaniem światłem zielonym. Zastosowanie światła laserowego o długości fali 532 nm w układzie sprzęgania dwóch fal umożliwia uzyskanie w folii siatki dyfrakcyjnej (rys. 4 i 5). Studium fotoizomeryzacji uzupełniono obliczeniami kwantowo-chemicznymi właściwości spektralnych i nieliniowo optycznych spirooksazyny oraz merocjanin (rys. 1).

**Słowa kluczowe:** spirooksazyna, kopolimer fotochromowy, barwnik diazo sulfonamidowy, fotoizomeryzacja, siatka dyfrakcyjna.

Photochromic processes seem to gain more and more importance due to expectations of a wide range of practical applications. An ease with which a laser beam causes changes of optical and dielectric properties within light sensitive materials indicates an opportunity to develop new optoelectronic devices basing on the light action. One of the best known photochemical reactions is reversible *trans-cis* isomerization of diazobenzene derivatives [1—3] according to eq. (1).

Polymeric materials containing azobenzene fragments in side chains are of particular interests as their properties can be easily optimized by proper choice of

the monomeric species subjected to polymerization and copolymerization and by eventual modification of prepolymers. The polymers of moderate molecular weights like polymethacrylates [4—10], polyurethanes [11—13] can be easily deposited onto a solid support in a form of a transparent film by spin-coating or casting, and as those, they can be used for various optical and optoelectronic experiments. One of the expectations is a possibi-

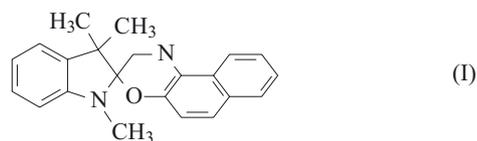


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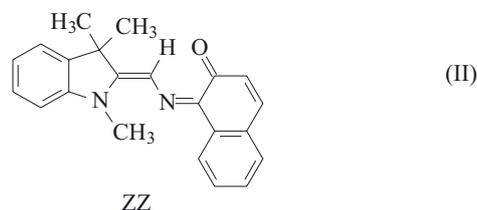
lity to record the data by holographic technique [3, 12, 13]. Using crossed laser beams focused on the polymer film one involves interference of the beams to generate dark and bright domains in the photosensitive material. Isomerization of the diazo group in the bright domains creates changes of dielectric properties of the polymer and it causes modulation of refractive index which results in a formation of a diffraction grating. Authors of this paper contributed to this subject developing series of sulfonamide containing diazobenzene monomeric and polymeric materials showing good photochromic properties [13—18]. All they contained heterocyclic sulfonamide fragments and their maximum absorption band was at *ca.* 450 nm, *i.e.*, it was blue shifted as compared with that of nitro derivatives of the Disperse Red type [7, 11]. The isomerization of these derivatives (the *trans* form is stable at room temperature) takes place under exposure to visible light, from *ca.* 400 nm up to *ca.* 560 nm wavelength. The *cis* isomer formed during this process shows maximum absorption band at *ca.* 385 nm. The reverse *cis-trans* reaction proceeds as a thermal relaxation or it can be accelerated by exposure to UV light.

Another class of reversible photochemical reaction is that which proceeds through ring opening-ring closing of cyclic chemical species. Good examples can be the derivatives of spiropyrans and spirooxazines. This class of chemical compounds has been widely investigated on the premise that they can be used to create new optical and optoelectronic devices [19—21]. The most frequently cited spiran derivatives are those of spirobenzopyran [20, 22—27], but other compounds of this type are also very interesting. Among them, the compounds belonging to spirooxazine group may be listed. In closed form they are nearly colorless, both in solutions as well as in a solid state, but under exposure to UV light, the formation of open merocyanine form is followed by appearance of strong absorption band in visible region [28—36]. Similar behavior was observed when spirooxazines were tested in guest-host systems and the hosts were polymeric materials. These systems were also found to be sensitive towards laser light [37—42].

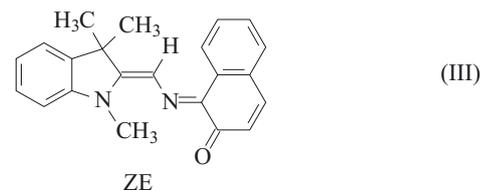
The aim of this study was to use the dual system chromophores containing previously mentioned diazo



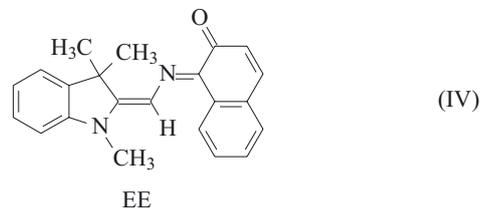
Spirooxazine (SP)



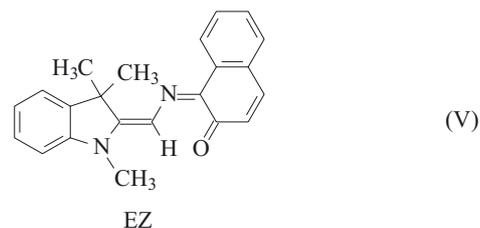
ZZ



ZE



EE



EZ

derivatives of sulfonamide type and spirooxazine [spirooxazine — formula (I), merocyanines — formulas (II)—(V)]. Such system was expected to show compatibility when exposed alternatively to UV light or visible region light. This might result in an enhanced sensitivity of the photochemical reactions involved in the process of holographic recording, carried out by two beam coupling arrangement.

## EXPERIMENTAL

### Materials

Spirooxazine (SP) [formula (I)] was purchased from Sigma Aldrich and it was used as received.

Poly(methyl methacrylate-*co*-butyl methacrylate) (PMMA-BM) delivered by Sigma Aldrich, was equimolar copolymer characterized by  $\overline{M}_w \approx 75\,000$ .

Diazo containing chromophore, which was copolymer (IZO) contained 20 % of butyl methacrylate (BM) *co*-monomer [formula (VII)], was synthesized and characterized as it was described elsewhere [18].

### Methods

The UV-Vis spectra were recorded using Diode Array Hewlett Packard Spectrophotometer 8452.

Spectral and nonlinear optical properties of SP and merocyanine species were calculated at Wrocław Supercomputer Center using GAUSSIAN g98 program with DFT B3LYP/6-31g\* basis set. The UV-Vis spectra were calculated with ZINDO option using optimized molecular coordinates from DFT calculation [43].

Ellipsometer EL X-02C of DRE Ellipsometerbau GmbH (Germany) was used for the determination of refractive indices. A probing beam was linearly polarized

laser beam of 632 nm wavelength and 3 mW power at incident angle of 70°.

The formation of diffraction grating was determined by TBC procedure according to [13]. The material was deposited on the glass plates by spin-coating using *ca.* 2 % solutions in tetrahydrofurane and only diffraction signal of the first order was recorded.

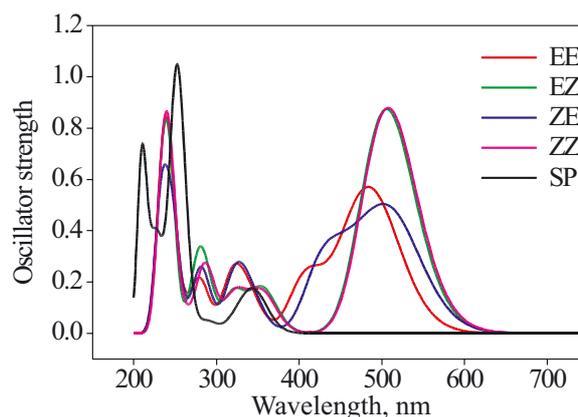
## RESULTS AND DISCUSSION

The *trans-cis* isomerization of the diazobenzene derivatives can proceed *via* inversion or (and) rotation around double N=N bond and yields single product, *i.e.*, the *cis* derivative. The quantum chemical calculation carried out previously made it possible to determine the absorption spectrum of the *cis* form. Because of the reverse *cis-trans* reaction which is caused by thermal relaxation at room temperature, the *cis* isomer can not be isolated from the reaction mixture. The maximum absorption band of the *cis* form of the sulfonamide dyes in question was found at *ca.* 385 nm, whereas the *trans* form absorbed at *ca.* 450 nm [14]. Both absorption spectra were close to each other and overlapped, so that, the real exposure effect was a decrease in the absorption band at 450 nm with shoulder ascribed to the *cis* form at *ca.* 385 nm. It is worth mentioning that isomerization yield for solutions and thin films was usually below 50 %.

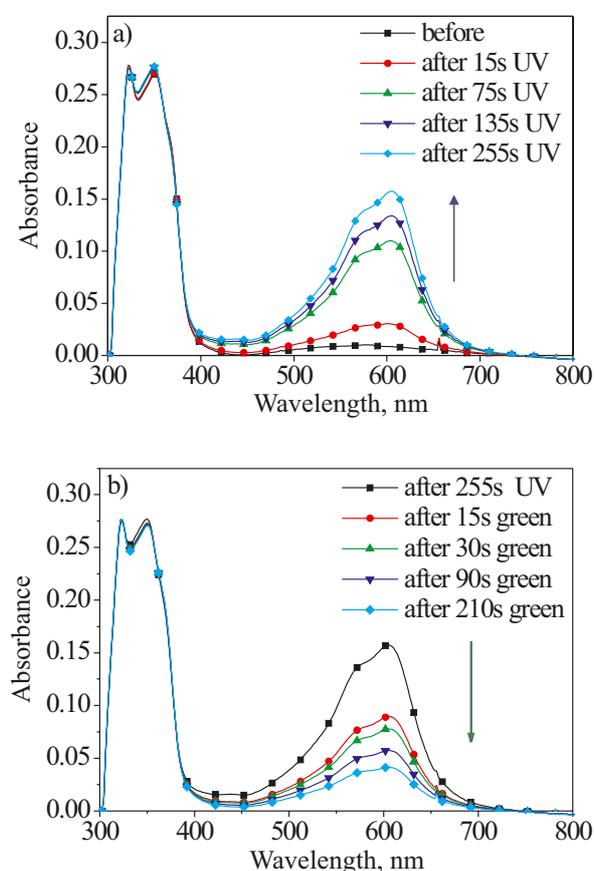
**Table 1.** Properties of spirooxazine merocyanine forms

Form	Dipole moment C · m/10 <sup>-30</sup>	Polarizability m <sup>3</sup> /10 <sup>-30</sup>	First hyperpolarizability m <sup>4</sup> /(V · 10 <sup>-40</sup> )	Difference of potential energy kJ/mol
Spirooxazine	0.83	31.8	4.4	—
EZ	3.67	37.6	141.7	13.29
EE	4.88	36.8	96.97	46.62
ZZ	4.30	37.9	118.1	19.78
ZE	4.44	37.5	89.9	48.95

In the case of spirooxazine, the absorption spectra showed absorption only within UV range for both solutions and crystalline forms. Exposure of SP to UV light causes opening of the spirooxazine ring yielding four open isomeric merocyanine forms [formulas (II)—(V)]. The quantum chemical methods bring us an opportunity to do the structure optimization and try to determine certain preferences of isomer formation. For this reason we made the calculation using Gaussian g98 program using DFT option with B3LYP/6-31g\* basis set. Table 1 shows the properties of the isomers such as dipole moment, polarizability and first hyperpolarizability calculated for the molecules in an isolated state. Additionally, the potential energy difference between open merocyanines and SP was tabulated. Calculated UV-Vis spectra of SP and merocyanine structures are presented in Fig. 1.



**Fig. 1.** UV-Vis spectra calculated for SP and merocyanine structures optimized with Gaussian B3LYP/6-31g\* basis set. Calculation carried out for the molecule in isolated state



**Fig. 2.** UV-Vis spectra of spirooxazine SP in PMMA-BM: a) UV exposure, b) green light exposure

The data in Table 1 and spectra indicate that there are distinguishable pairs of merocyanine isomers: EZ and ZZ show lower absorbance expressed as oscillator strength and their maximum absorption peaks are slightly blue shifted, whereas EE and ZE are very similar according to peak shapes and their potential energy difference towards SP is of close value (46.62 kJ/mol for EE and 48.95 kJ/mol for ZE). For static hyperpolarizability values one may observe the same tendency.

The reverse isomerization of SP in polymer matrix, being copolymer of methyl and butyl methacrylate (PMMA-BM), was presented in Fig. 2. The exposure of the film to UV lamp caused an appearance of the absorption band at *ca.* 606 nm ascribed to merocyanines (Fig. 2a). The shape of the absorption band might indicate that the mixture of the isomers was formed and this assumption might result from comparison of the experimental spectra with those calculated by quantum chemistry method. Is it worth mentioning that the maximum absorption of experimental spectra are shifted to longer wavelengths as compared with calculated ones and it is normal as the calculations have been made for isolated molecule. The stationary state of the isomerization caused by UV light was reached in *ca.* 4 minutes, and afterwards the exposure green light was started. The reverse reaction: merocyanines-SP is illustrated by Fig. 2b, showing gradual disappearance of the 606 nm absorption band with exposure time.

The isomerization of diazobenzene derivatives can be compatible process to spirooxazine ring opening-ring closing reaction. For the diazobenzene derivatives, the UV exposure accelerates the *cis-trans* reaction and visible light exposure promotes *trans-cis* isomerization. It was reasonable to check the behavior of mixtures of these two classes of compounds. Previous studies on mixtures of polymeric diazobenzene derivatives with nitrospiroxazine were promising [44], so the films of spirooxazine and IZO polymer [formula (VI)] were prepared by spin-coating deposition in proportion 1:1 by weight. The IZO polymer belonged to the family of diazo sulfonamide chromophores described in details in [45]. The UV-Vis spectra (Fig. 3) show two distinct absorption bands: the first of merocyanines at *ca.* 610 nm and the second ascribed to the IZO polymer at *ca.* 450 nm. The effect of UV exposure shows Fig. 3a. An increasing absorption at 610 nm with time is a result of merocyanines' formation. At nearly stationary state the exposure source was changed and action of green light caused reverse isomerization of merocyanines into SP and at the same time the *trans-cis* isomerization of diazo groups in the polymer. A consequence of this step was gradual disappearance of the 610 nm band and a decrease in absorbance at 450 nm.

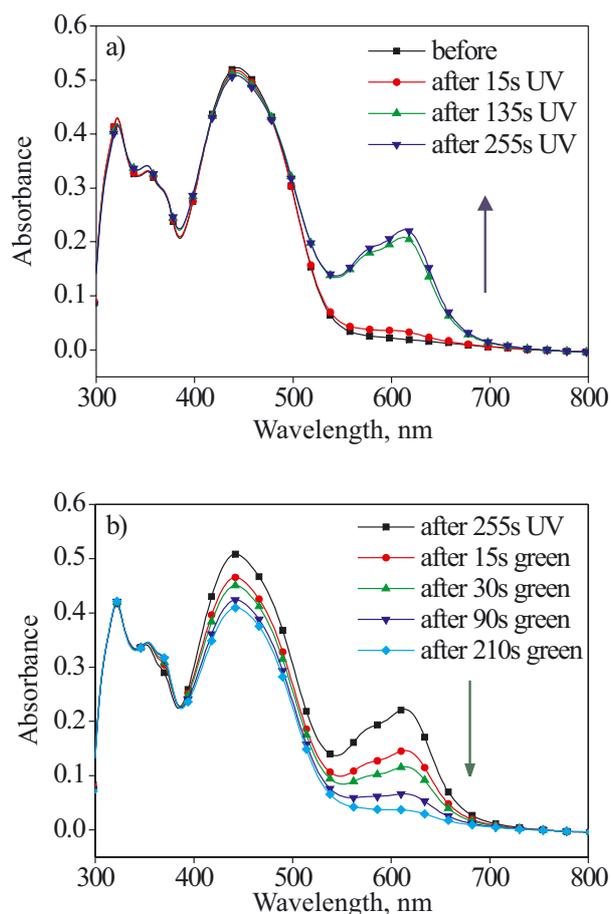
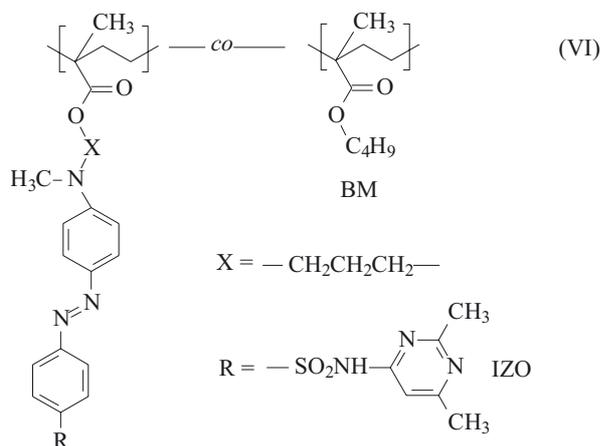


Fig. 3. UV-Vis spectra of SP + IZO (1:1 by weight) polymer chromophore: a) UV exposure, b) green light exposure

It was expected that the change of the dielectric properties of the materials in question would lead to change of refractive index. To prove this fact the thin films were deposited onto the glass plate. The glass plate was sand treated on the bottom side to avoid double reflection from glass planes. The SP in methyl methacrylate-butyl methacrylate copolymer film was exposed to UV light for 5 min and its ellipsometric parameters were measured with probe laser beam of 632 nm. As a result of UV exposure the increase by 0.0325 in refractive index ( $n$ ) was observed. The 632 nm laser beam was within absorption band of merocyanines formed by UV exposure so that with time of probing, *i.e.* within *ca.* 20 s, the decrease in  $n$  was recorded to be 0.0191. In this moment the green light exposure was switched on and after 5 min nearly initial value of the refractive index was obtained (Table 2). The mixture 1:1 by weight of SP and IZO chro-

Table 2. Change of refractive index ( $\Delta n$ ) under exposure, measured by ellipsometry

Film material	$\Delta n$		
	after 5 min UV	after 20 s measurement	after 5 min green light exposure
SP	0.0325	-0.0191	down to initial value

mophore was treated in the same way. The UV exposure resulted in  $n$  increase by 0.0355. The ellipsometer probing gave a decrease in  $n$  by 0.0204 and after green light exposure within 5 min yielded decrease in  $n$  by 0.0419. It is worth to mention that in the case of IZO itself the change of  $n$  under green light exposure was 0.0089.

The modulation of refractive index as a result of exposure could be a good indication to try to use the material for recording of diffraction grating. A two-beam coupling experiment with SP film in methyl methacrylate-butyl methacrylate copolymer film gave us a sign that the diffraction grating could be formed on bleaching of the film treated previously with UV light (Fig. 4). The diffraction signal was generated very fast on switching the laser beams on but its yield was rather small being in the range of fraction of percent. The combination of two dyes (SP + IZO) produced slightly better results although certain period of time for growing signal intensity was observed (Fig. 5); this could be ascribed to the presence of the polymer dye which reaction to exposure was slower as compared with that of the SP. In conclusion, one might say that the use of the dual chromophore system could be a good solution however proper adjustment of light source wavelength could be suggested in further studies.

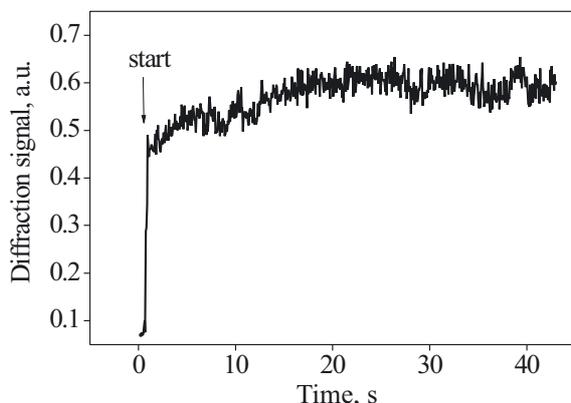


Fig. 4. Diffraction signal of spirooxazine SP in PMMA-BM film vs. time

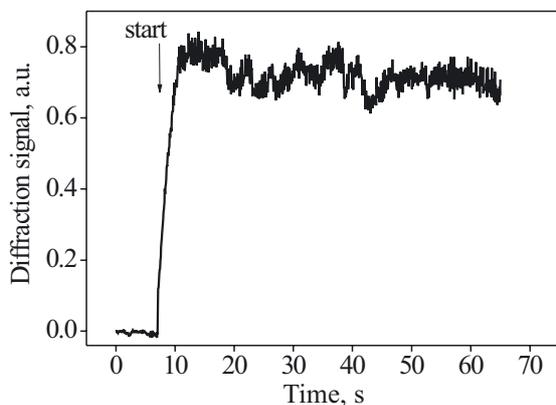


Fig. 5. Diffraction signal of SP + IZO (1:1 by weight) film vs. time

## CONCLUSIONS

The spirooxazine and IZO polymer dye could be used as dual chromophore system where mutual cooperation of the dyes in photochromic transformations was required. Both dyes could form isomeric structures when exposed to UV and visible light. The isomeric structures manifested difference of dielectric properties such as dipole moment and refractive index. The variation of the refractive index under exposure indicated possibility to use the dyes mixture in the devices in which the formation of diffraction grating was expected to produce holographic data recording.

## ACKNOWLEDGMENTS

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