

Research Article

Spirooxazine Photoisomerization and Relaxation in Polymer Matrices

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9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3' [3*H*]naphtha[2,1-*b*]-1,4oxazine] (*SPO-7OH*) was used in studies of photochromic transformations in polymer matrices. Illumination with UV lamp caused opening the spirostructure of the oxazine with formation of open merocyanine species absorbing at ca. 610 nm. The kinetic studies of thermal relaxation of the open form showed that this process can be described with a biexponential function including both photochemical reaction and rheological behaviour of the polymeric environment. Basing on Arrhenius plot of the rate constant ascribed to the photochemical reaction, the activation energy was determined, which was 66.1 and 84.7 kJ/mole for poly(methyl methacrylate-*co*-butyl methacrylate) and poly(vinylpyrrolidone) matrix, respectively.

1. Introduction

Extensive research has been devoted to gain insight into transformation of photochromic molecules induced by light [1, 2]. Reversible rearrangement of bistable molecules occurs in photochemical or thermal way. Significantly different molecular states can exist as thermodynamically stable ones. The photoisomers differ in their physical properties such as absorption spectra, refractive indices, dielectric constants, geometrical structure, and oxidation/reduction potential [3]. Interests devoted to photochromic materials have been expanded because of their potential applications in optical devices and memories [4–6].

Among the most important categories of photochromic molecules there are spirocompounds which can induce excellent colouration during irradiation [7–9]. UV light excitation occurs to be relatively strong to cause photocleavage of the C–O spirobond of the spirooxazine which leads to the coloured merocyanine; the latter can exist in four isomeric forms [10–12]. The mechanism of the reversible photochromic transformation of spirooxazines involves the

photochemical process of ring opening of spirocompound yielding merocyanines and thermal or photochemical relaxation process of closing ring of the merocyanines [13]. The process of reversible isomerization is presented in Figure 1.

Studies on photochromism of spirooxazines have been carried out in various organic solvents as well as in different media, such as polymer matrices, liposomal membranes, monolayers, and bilayer-clay matrices [8]. The lifetimes of excited state of the spiroform and subsequent open form depend on temperature [14–16]. The polarity of polymer matrices is of great importance because of possible interactions between polymer chain and tautomeric form of merocyanine [12, 17].

In this paper the main attention was focused on investigation of the temperature influence on reversible isomerization of spirooxazine in polymer matrices. Two polymers with different glass transition temperature and polarity were used as matrices, and concentration of the dye was 30% by weight. The temperature dependence was controlled by measurement of UV-Vis absorption spectra. It is to mention

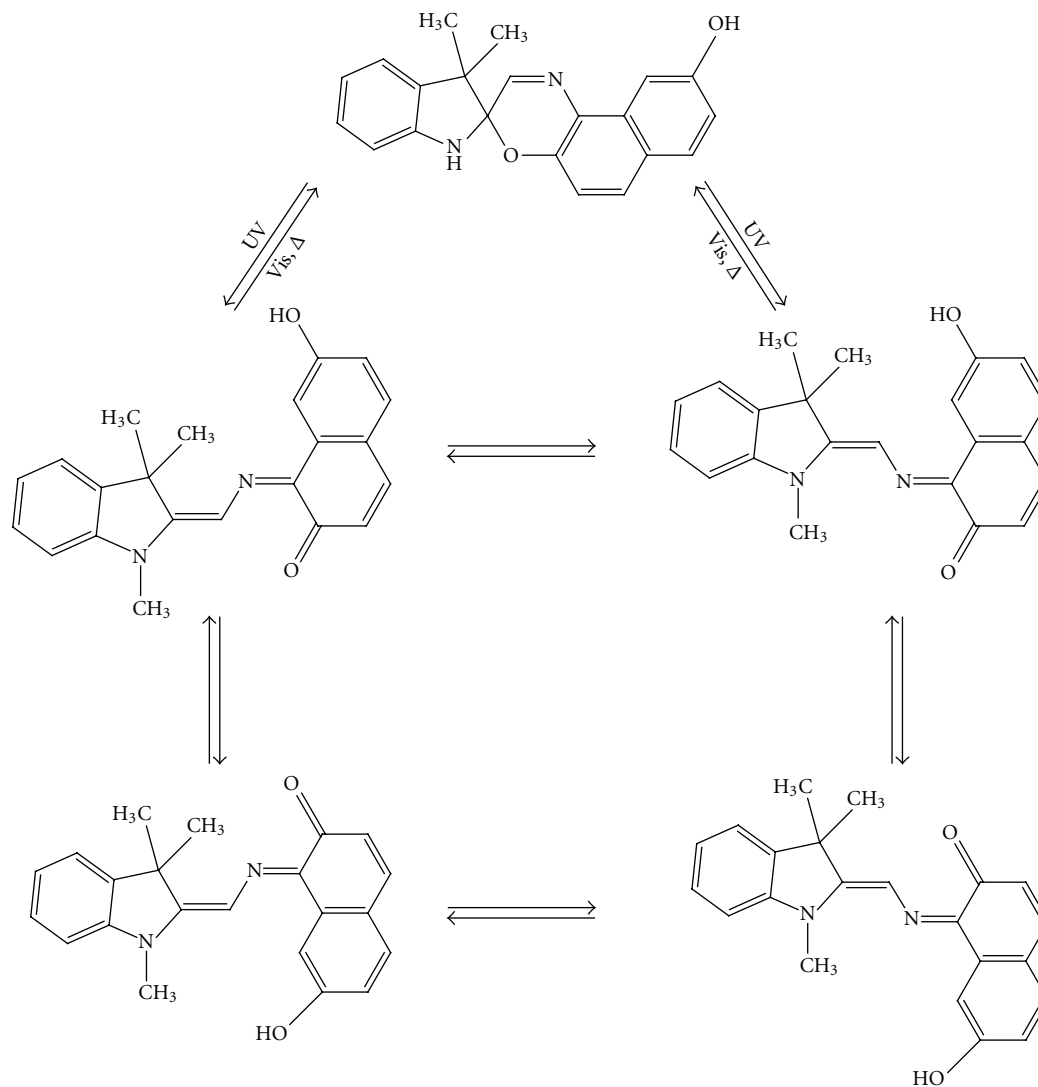


FIGURE 1: Mechanism of photochromic transformations of spirooxazine.

that spirooxazines belong to the photochromic dyes sensitive to UV range of radiation [10, 18, 19].

2. Experimental

2.1. Materials. 9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3' [3H]naphtha[2,1-b]-1,4oxazine] (*SPO-7OH*) was synthesized using previously described procedures [18, 19]. 1-Nitrosonaphthalene-2,7-diol (5.28 mmol, 1.00 g) was dissolved in 100 mL ethanol. 1,3,3-Trimethyl-2-methyleneindoline (4.80 mmol, 0.83 g) was added, and the reaction mixture was refluxed with stirring for 5 hours. The resulting product was purified by silica gel column chromatography using chloroform as an eluent. Yield of *SPO-7OH* was 41% (0.68 g).

Poly(methyl methacrylate-*co*-butyl methacrylate) (*P(MMA-BMA)*) and poly(vinylpyrrolidone) (*PVP*) were purchased from Sigma-Aldrich.

Polymer films containing spirooxazine dye (*SPO-7OH*) were prepared by spin coating technique. The materials were

deposited on glass plates using 6% solution of *P(MMA-BMA)* or 3% solution of *PVP* in chloroform. The concentration of photochromic compounds (*SPO-7OH*) in polymers was 30%. The samples were annealed at 423 K for 8 hours. The thicknesses of polymer films were in the range of 200–400 nm depending on concentration of polymer solutions. The resulting films were kept in dark before measurement.

2.2. Optical Experiments. UV-Vis spectra were recorded using DT-MINI-2-GS Mikropack UV-VIS-NIR LIGHT-SOURCE. The polymer films were irradiated with 365 nm diode light (type H2A1-H365) providing 25 mW power. The samples were kept at constant temperature during illumination and thermal relaxation, and the temperature was controlled by DC HEATER SUPPLY.

3. Results and Discussion

3.1. Absorption Spectra of Spirooxazine Photochromic System. The measurements of UV-Vis spectra were carried out using

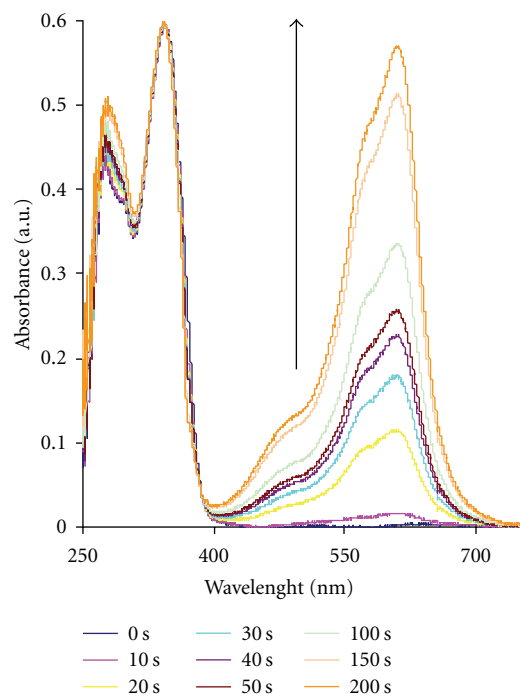


FIGURE 2: *SPO-7OH* in *P(MMA-BMA)* absorption spectra recorded before UV irradiation and after 200 s at 303 K.

thin polymer films containing spirooxazine (*SPO-7OH*) on glass plates. The absorption spectra of *SPO-7OH* in *P(MMA-BMA)* during illumination with UV diode light and thermal relaxation are presented in Figures 2 and 3, respectively.

Spirooxazine showed maximum absorption peak in the range of ca. 344–350 nm, depending on the polymer matrix. Upon UV light excitation, the spiro-carbon-oxygen (C–O) bond of colorless ring-closed form breaks and the subsequent isomerization leads to colored ring-open isomers (merocyanine). The maximum absorption peak of merocyanine is located at 610 nm for *PVP* and at 613 nm for *P(MMA-BMA)* guest host system. The photoisomerization of photochromic materials is reversible. The metastable colored form is changed into ground state colourless form. The route from open to closed form of spirocompound took place as a thermal relaxation process. Influence of temperature on relaxation process was investigated. The measurements were carried out within the range of 303–333 K in steps of 10 K under strict temperature control. The UV-Vis spectra were recorded during heating and periodic illumination with 365 nm diode light. Spectral parameters are presented in Table 1.

3.2. Kinetics of the Thermal Relaxation Process. Kinetic characteristics of thermal relaxation process of *SPO-7OH* were presented by recording the maximum absorption band decay in two different polymer matrices. The typical curves of absorption growth and relaxation processes are showed in Figure 4.

Several kinetic models are known and used to explain relaxation processes [14, 20, 21]. Biexponential function describes relaxation process sufficiently well, so (1) was

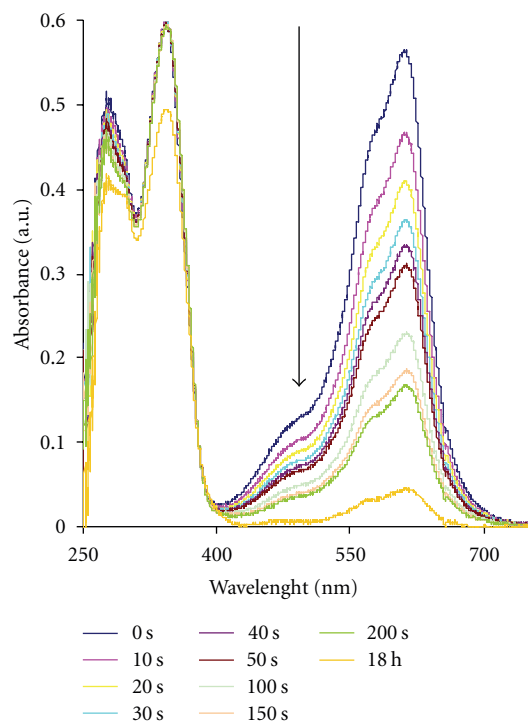


FIGURE 3: Absorption spectra of *SPO-7OH* in *P(MMA-BMA)*—thermal relaxation process at 303 K.

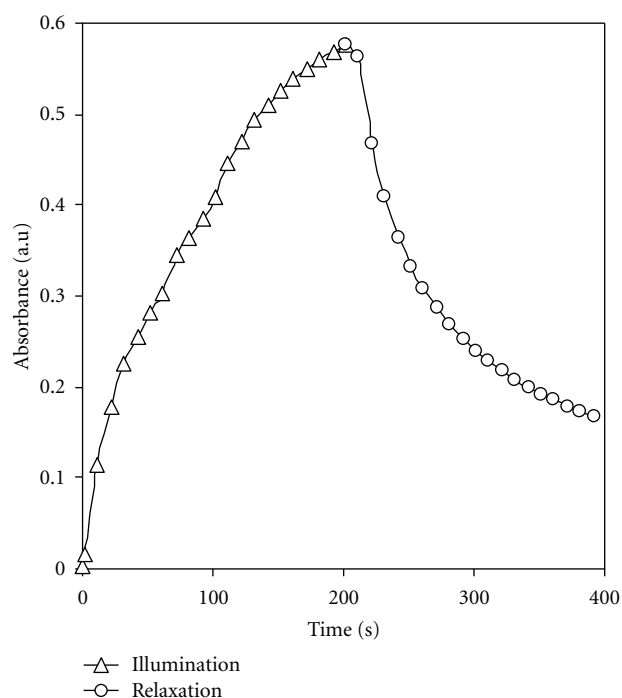


FIGURE 4: Typical growth and relaxation process of photoinduced absorbance modulation of *SPO-7OH* in *P(MMA-BMA)* at 303 K.

chosen to optimize thermal bleaching reaction converting merocyanines to their ground state ring-closed form:

$$A(t) = ae^{-k_a t} + be^{-k_b t}, \quad (1)$$

TABLE 1: Spectral parameters of *SPO-7OH* in polymers matrices.

Sample	Temperature (K)	λ_{\max} (nm)	$A(t)_i$ (a.u.)	t_i (s)	$A(t)_r$ (a.u.)	t_r (s)
<i>SPO-7OH P(MMA-BMA)</i>	303	613	0.569	200	0.167	200
<i>SPO-7OH P(MMA-BMA)</i>	313	613	0.402	200	0.078	200
<i>SPO-7OH P(MMA-BMA)</i>	323	613	0.020	200	0.015	200
<i>SPO-7OH P(MMA-BMA)</i>	333	613	0.084	200	0.000	80
<i>SPO-7OH PVP</i>	303	610	0.194	200	0.115	200
<i>SPO-7OH PVP</i>	313	610	0.170	200	0.110	200
<i>SPO-7OH PVP</i>	323	610	0.126	200	0.083	200
<i>SPO-7OH PVP</i>	333	610	0.084	200	0.058	200

$A(t)_i$: absorbance of merocyanine measured after time t_i during illumination with light;

$A(t)_r$: absorbance of merocyanine measured after time t_r during thermal relaxation.

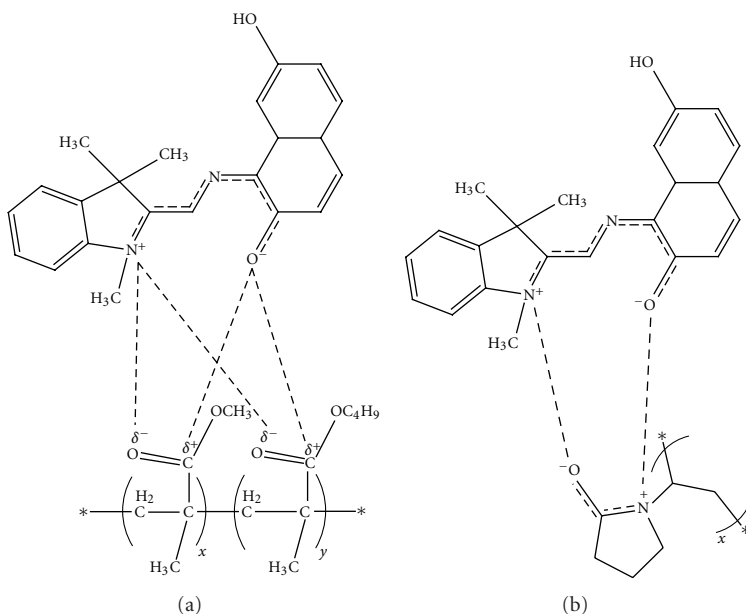


FIGURE 5: The dipole-dipole interaction between merocyanine and side chains of polymers (a) *P(MMA-BMA)* and (b) *PVP*.

where $A(t)$ is change of absorbance observed at time t ; k_a and k_b represent the rate constants ascribed to the amplitude of a and b , respectively. The first part of (1) is responsible for isomerization of chromophore, and the second part corresponds to material equilibration. The rate constants k_a and k_b determine the rate of *open-closed* isomerization and the rate of material reorientation, respectively.

The decay curves were fitted to biexponential decay model using a computer program. This biexponential model fits experimental points into calculated curve very well. All values of the constants are given in Table 2. Along with increase of temperature, there is observed an increase of rate constants and thereby relaxation process is significantly faster at higher temperature. Comparing the rate constants k_a and k_b , it can be noticed that the first process is considerably faster than the second one. This means that the main influence on the rate of relaxation process has *open-closed* isomerization. However, the suppressing environment

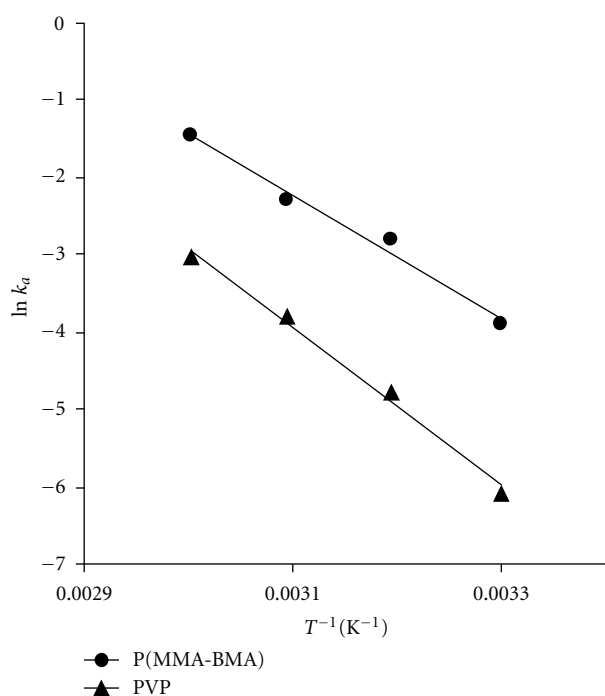
relaxation and kind of polymer matrices had a distinct effect that was evidenced by higher values of the rate constants in *P(MMA-BMA)* versus *PVP* in guest host system. The polarity of polymer matrices can influence the relaxation rate because of formation of the dipole-dipole interaction between merocyanine and side chains of polymers (Figure 5). The dipolar interactions are significantly stronger in *PVP* than in *P(MMA-BMA)*. The differences in dipolar interactions of the polymers with merocyanine have a distinct effect on difference in stabilization of merocyanine forms. The relaxation process appeared to be slower when the interactions were more pronounced owing to the presence of nitrogen atoms in *PVP* polymer.

The Arrhenius equation (2) was used to determine activation energy (E_a) of relaxation process corresponding to the faster step:

$$\ln(k_a) = \ln k_0 - \frac{E_a}{R} \cdot \frac{1}{T}. \quad (2)$$

TABLE 2: Kinetic parameters for thermal bleaching reaction.

Sample	Temperature (K)	a	k_a	b	k_b	R
<i>SPO-7OH P(MMA-MBA)</i>	303	0.3798	0.0205	0.2240	0.0017	0.996
<i>SPO-7OH P(MMA-MBA)</i>	313	0.1992	0.0596	0.1930	0.0050	0.999
<i>SPO-7OH P(MMA-MBA)</i>	323	0.1245	0.1013	0.0607	0.0084	0.999
<i>SPO-7OH P(MMA-MBA)</i>	333	0.0467	0.2364	0.0363	0.0434	0.997
<i>SPO-7OH PVP</i>	303	0.1026	0.0023	0.1829	0.0001	0.999
<i>SPO-7OH PVP</i>	313	0.0364	0.0085	0.1345	0.0004	0.999
<i>SPO-7OH PVP</i>	323	0.0260	0.0225	0.1001	0.0011	0.999
<i>SPO-7OH PVP</i>	333	0.0116	0.0477	0.0693	0.0011	0.999

FIGURE 6: The Arrhenius plots for thermal bleaching of *SPO-7OH* in polymer matrices.TABLE 3: Activation energy (E_a) and the Arrhenius preexponential factor (k_0) for thermal relaxation process of *SPO-7OH* in polymer matrices.

Sample	k_0 [s^{-1}]	E_a [$kJ \cdot mol^{-1}$]
<i>SPO-7OH P(MMA-BMA)</i>	$5.46 \cdot 10^9$	66.10
<i>SPO-7OH PVP</i>	$1.03 \cdot 10^{12}$	84.72

The Arrhenius plots for thermal bleaching of *SPO-7OH* in polymer matrices were shown in Figure 6. The calculated values of rate constants (k_a) fit the Arrhenius plots with very good precision, so it was possible to determine values of energy barrier which were presented in Table 3. It can be noticed that activation energy in relaxation process of *SPO-7OH* in *P(MMA-BMA)* is lower than that in *PVP* which is consistent with expectation.

4. Conclusions

The illumination of spirooxazine containing polymer matrix resulted in formation of open merocyanine species absorbing at ca. 610 nm. The reverse process could be described as composed of two stages: first one as a photochemical closing of merocyanine form and the second one as the polymer matrix rheological cooperation response. The Arrhenius plot of the reaction rate constant of the first stage made it possible to determine activation energy of this process that was 66.1 and 84.7 kJ/mole in poly(methyl methacrylate-*co*-butyl methacrylate) and poly(vinylpyrrolidone) matrix, respectively.

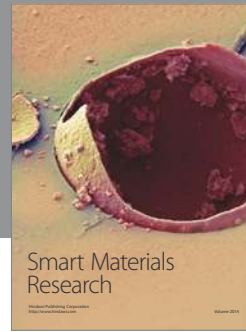
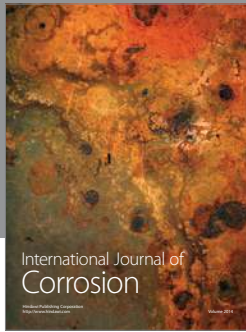
Acknowledgments

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