



## Fluorescent and photooptical properties of H-bonded LC composites based on stilbazole derivative

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### ABSTRACT

A novel series of H-bonded LC (smectic and nematic) composites and “model” mixtures without hydrogen bonding based on the stilbazole derivative were prepared. As the matrices of the composites following polymers were synthesized: smectic homopolymer containing p-oxybenzoic groups, nematic copolymer containing p-oxybenzoic and methoxyphenylbenzoic side groups, and nematic homopolymer with methoxyphenylbenzoate groups. The spectral properties of composite films were studied in detail. Significant differences in the fluorescence spectra of H-bonded LC composites and “model” mixtures were revealed. Mechanism of the processes occurring in the films of the LC composites under the action of the UV light was proposed. The mechanism includes a reversible proton transfer involved in the H-bonds formation. It was found that in the oriented films of the nematic composite degree of fluorescence polarization is higher than in the films of a similar mixture without H-bonding. The effect of linearly polarized light on the optical properties of the composite films was studied. It was shown that the highest values of the photoinduced dichroism are achieved in nematic liquid crystals composites. It was revealed that for the irradiated LC composites annealing leads to decrease of dichroism values (degree of polarized emission drops to zero), whereas for “model” LC mixture without hydrogen bonding a significant increase in these parameters was found.

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### 1. Introduction

First obtained in the middle of 1970s comb-shaped LC polymers still attract attention of scientists as one of the most interesting class of “smart” polymer materials easily changing their properties under the action of external fields due to a special “soft” nature [1].

Over the past few decades, scientists have developed approaches to obtain a sufficient wide variety of LC comb-shaped polymers. The preparation of such polymers is mainly limited by the rather complicated, time-consuming and expensive monomers' synthesis. Therefore, in the eighties a new way of preparation of LC polymer systems based on principles of molecular recognition and self-organization was suggested. This method deals with mixing the polymers (matrixes) with low-molar-mass substances (dopants), which are capable for specific noncovalent interactions, such as the formation of hydrogen bonds [2–6] (Fig. 1a). These mixtures successfully combine the properties of polymers (such as construction materials) and low-molar-

mass dopants (photochromism, optical activity, electro-sensitivity, etc.) [7,8].

This approach gives the extremely broad possibilities to obtain functional polymeric LC composites with desirable properties by using only one polymer matrix just varying the low-molar-mass dopants.

In a number of papers by Kato et al. [9,10] para-substituted derivatives of stilbazole promoted the formation of mesophase were used as low-molar-mass dopants capable of forming hydrogen bonds. Therein the phase behavior of H-bonded LC composites and the factors influencing on it were studied in details. But in the literature there is a very little information about other properties of these composites, such as optical, fluorescence. Therefore, this paper will specifically focus on the photo-optical and spectral properties of H-bonded LC composites based on stilbazole derivative and their comparisons with mixtures without hydrogen bonding.

Fig. 1 shows the scheme of the polymeric LC systems which have been prepared and studied in this work. Among them: the H-bonded LC composites in which each side group is able to be bound (Fig. 1a); LC composites consisting of matrixes in which (apart from the free carboxyl groups) mesogenic groups incapable for H-bonding are presented (Fig. 1b); LC mixtures containing only

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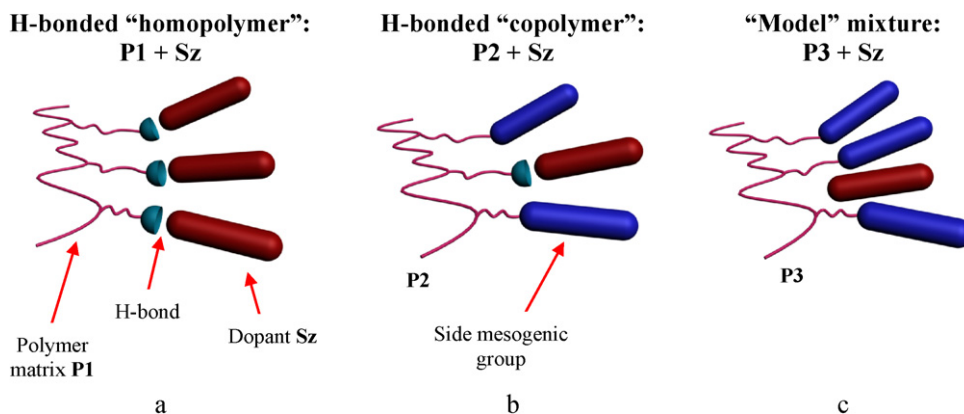


Fig. 1. Schematic model of LC composites prepared and studied in the paper.

mesogenic side groups without any functional groups capable for H-bonding (Fig. 1c).

In our work three different types of LC polymers as matrices have been selected. Their structural formulas, molar mass characteristics and the phase behavior are presented in Table 1.

Homopolymer [11] **P1** is characterized by smectic type of mesophase and contains carboxyl groups capable of forming hydrogen bonds. LC properties of this polymer arise from the formation of H-bonded dimers having a mesogenic (rod-like) shape. Copolymer [12] **P2** displays a nematic mesophase, because it contains 70 mol% of nematogenic methoxyphenylbenzoate fragments and 30 mol.% carboxylic side groups which are responsible for noncovalent hydrogen bonding.

Nematic homopolymer [13] **P3** was used in this work as a "model" compound non-forming H-bonds. As a low-molar-mass dopant, stilbazole derivative **Sz** was chosen. Nitrogen atom of the pyridine ring is responsible for strong H-bonding formation. Such ability is additionally strengthened by the presence of methoxy group in the *para* position with respect to the double C=C bond [9].

Selection of low-molar-mass stilbazole dopant is explained not only by its ability to form stable (and strong:  $\sim 40$  kJ/mol) hydrogen bonds, but also its fluorescent properties. That opens the new perspectives for the creation and modification of LC materials with controllable spectral properties. This sort of control can be carried out not only by means of changes in the LC's structure [14], but also under the action of light, since the dopant molecules contain a photosensitive C=C bond.

The main goal of the paper are related to the study of photo-optical and fluorescent properties of H-bonded LC composites containing stilbazole moieties under the action of UV light, and comparison of their behavior with the "model" mixture without hydrogen bonding.

## 2. Experimental

### 2.1. Polymer synthesis

All polymers were synthesized by free radical polymerization of appropriate monomers which have been obtained according to procedures described in [7,8,13]. The reaction was carried out in anhydrous THF in a sealed tube under argon atmosphere for 100 h at 70 °C; the initiator – AIBN (2 wt.%). The resulting polymers were precipitated from THF with hexane to remove unreacted monomers and oligomeric products. After that, the polymers were dried under vacuum with heating for several hours. The yield was 60–80%. The composition of copolymer **P2** was set by portions of monomers (accepted that all the constants of copolymerization of

the monomers are equal). The polymerization was carried out to high conversions. Molecular weights were determined by GPC on chromatograph "Knauer" (UV detector, column type "LC-100" with a sorbent 1000 Å; solvent THF (1 ml/min, 25 °C, PS-Standard).

Phase transition temperatures were detected by polarized optical microscopy ("POLAM-R-112") equipped with heating stage ("Mettler FP-86"), as well as differential scanning calorimetry ("Mettler TA-4000") (heating rate 10 K/min, samples were prepared as tablets 5–10 mg).

### 2.2. Synthesis of low-molar-mass dopant Sz

Low-molar-mass dopant **Sz** was obtained as described before [15] in a yield of 23% as pale-yellow crystals, m.p. 130–131 °C. Found (%): C, 74.69; H, 6.24; N, 5.74.  $C_{15}H_{15}NO_2$ . Calculated (%): C, 74.67; H, 6.27; N, 5.81.  $^1H$  NMR (DMSO- $d_6$ ),  $\delta$ : 3.79 (s, 3 H, 4'-OMe); 3.84 (s, 3 H, 3'-OMe); 7.00 (d, 1 H, H (5'),  $J=8.6$  Hz); 7.15 (d, 1 H, CH=CHPy,  $J=16.3$  Hz); 7.17 (dd, 1 H, H (6'),  $J=8.6$  Hz,  $J=1.8$  Hz); 7.31 (d, 1 H, H (2'),  $J=1.8$  Hz); 7.48 (d, 1 H, CH=CHPy,  $J=16.3$  Hz); 7.52 (d, 2 H, H (3), H (5),  $J=5.9$  Hz); 8.52 (d, 2 H, H (2), H (6),  $J=5.9$  Hz).  $^{13}C$  NMR (DMSO- $d_6$ ),  $\delta$ : 55.42 (2 OMe); 109.45 (C (2')); 111.60 (C (5')); 120.46 (C (3), C (5)); 120.89 (C (6')); 123.55 (CH=CHPy); 128.94 (C (1')); 132.94 (CH=CHPy); 144.55 (C (4)); 148.89 (C (3')); 149.47 (C (4')); 149.86 (C (2), C (6)).

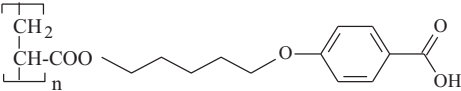
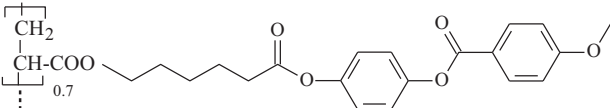
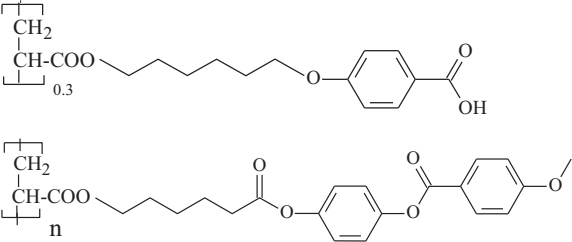
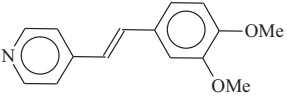
### 2.3. Composites preparation

Polymer mixtures were prepared by the standard procedure [9]. Samples of the polymer and the dopant were dissolved in a general solvent (pyridine or chloroform). After that the solvent was slowly evaporated and the residue was dried in a vacuum oven at heating for several hours.

### 2.4. Spectral techniques

Spectral measurements were made using UV-visible spectrometer "UNICAM UV-500". To investigate the photo-optical properties, Hg-lamp "DRSh-350" equipped with glass filter (365 nm) and polarizer Glan-Taylor Prizm was used as the light source. The light intensity was determined by the intensity meter "LaserMate\_Q" (Coherent). In the case of unpolarized light it was 1.5 mW/cm<sup>2</sup> for the band at 365 nm and 0.1 mW/cm<sup>2</sup> for a polarized light. Orientational order of polymer and their mixtures was studied by polarized UV-visible spectroscopy. For this purpose angular dependence of the polarized absorption was measured in increments of 10 by using of a photodiode spectrophotometer "Tidas" (J & M) equipped with a Polarizer Control Unit (Owis).

**Table 1**  
Chemical structures and properties of substances using in the work.

Substance	$M_w$ (kDa)	$M_w/M_n$	Phase behavior, °C
<i>Polymeric matrix</i>			
<b>P1</b> 	6.5	1.6	G 76 SmA 152 I
<b>P2</b> 	5.3	1.5	G 22 N 79 I
<b>P3</b> 	22.6	2.5	G 24 N 125 I
<i>Low-molar-mass dopant</i>			
<b>Sz</b> 	–	–	K 128 I

The value of dichroism  $D$  was calculated from spectral data using the following equation:

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}}$$

where  $A_{\parallel}$ ,  $A_{\perp}$  – polarized absorbance in directions along and perpendicular to the chromophores orientation, respectively.

Fluorescent properties were studied at 20 °C using a specially designed set up based on the spectrometer “AvaSpec-2048”. As a source of exciting radiation 365 nm LED was used; the light was directed at an angle of 30 degrees to the plane of the cell; the detector was placed perpendicular to the plane. The polarized emission was recorded using a spectrometer equipped with a rotating polarizer placed before the detector. The degree of emission polarization  $R$  was calculated using the formula:

$$R = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}}$$

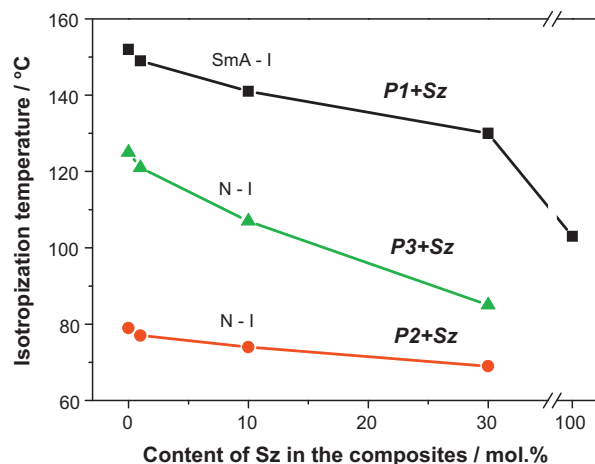
where  $I_{\parallel}$ ,  $I_{\perp}$  – polarized fluorescence intensities in directions along and perpendicular to the fluorophores orientation, respectively.

### 3. Results and discussions

At the beginning of the section the phase behavior of all LC polymers and its composites will be considered. Then the results of the spectral investigations of stilbazole **Sz** solutions and LC composite films will be presented. In the same section the fluorescent and the photooptical properties of oriented films of LC composites in the comparison with the “model” mixtures will be discussed. According to the main idea of the article, comparison of the studied properties of LC composites and “model” mixtures will be given in each section.

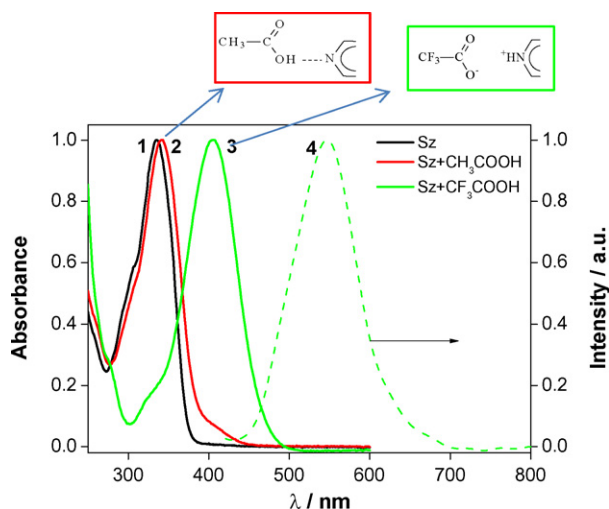
#### 3.1. Phase behavior of LC composites

First of all, let us consider the phase behavior of all polymer matrices with the varying concentration of **Sz**. We have prepared



**Fig. 2.** The isotropization temperature dependences on the content of low-molar-mass dopant **Sz** in the LC-composites.

composites based on matrices **P1**, **P2** and **P3** (their phase behavior is presented in Table 1) containing 1, 10, 30 mol.% of low-molar-mass dopant **Sz**. A mixture based on matrix **P1** with 100 mol.% of dopant (i.e., one **Sz** molecule is the share of each one of carboxylic side group) was also prepared. The presence of hydrogen bonds was confirmed by infrared spectroscopy method. All mixtures were stable and phase separation was not observed during the prolonged storage. Based on results of POM and DSC studies, it was shown that the introduction of low-molar-mass dopant does not effect on the mesophase type independently of the type of polymer matrices. Due to the nonmesogenic nature of the dopant isotropization temperatures of the composites decrease with increasing its content (Fig. 2). It should be noted that in the mixture based on the matrix **P3** (in which there is no hydrogen bonding at all) a temperature falling is observed in much more extent (Fig. 2). This effect can be explained by the fact that the anisometry of H-bonded complexes of **Sz** with side-hydroxybenzoic group of the polymer matrices is



**Fig. 3.** Absorption spectra of the solution of **Sz** (1), H-bonded complex with acetic acid (2), protonated form of **Sz** (3), and emission spectrum of the latter (4). Fragments of H-bonded complex of **Sz** and its protonated form are shown as insets.

higher than the anisotropy of the free **Sz** molecule. Thus, more anisometric (mesogenic) H-bonded complex disrupts the LC phase in a lesser extent, resulting in a slight decrease in the isotropization temperatures. Glass transition temperatures of the composites are not practically changed with the variation of dopant content ( $\sim 75^\circ\text{C}$  for composite **P1** + **Sz** and  $\sim 22\text{--}24^\circ\text{C}$  for composites based on **P2** and **P3**).

### 3.2. Spectral (absorbance and fluorescence) properties of low-molar-mass dopant **Sz** and LC polymer composites

#### 3.2.1. Spectral properties of dopant **Sz**

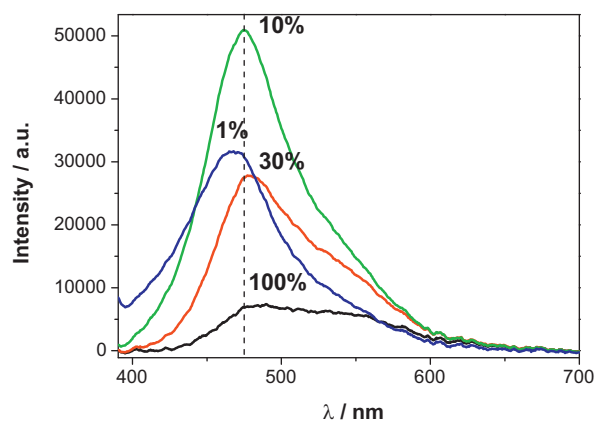
Before we shall start with consideration of the optical properties of LC composites, let us consider spectral properties of the **Sz** solutions in dichloromethane. The absorbance spectrum of the pure dopant is shown in Fig. 3. The absorbance peak at 335 nm corresponds to  $\pi\text{--}\pi^*$  electronic transition of conjugated aromatic system of stilbazole chromophore (Fig. 3, curve 1). It should be noted that this solution does not possess fluorescent properties. The addition of the weak acid such as acetic acid ( $\text{pK}_a \sim 4.8$ ) to solution of **Sz** leads to a shift of the absorption maximum to longer wavelengths of the spectrum by 7 nm, indicating the formation of H-bonded complex (see Fig. 3, curve 2). An increase in acid strength leads to a protonation of the pyridine ring. On addition of trifluoroacetic acid ( $\text{pK}_a \sim 0.3$ ) to the **Sz** solution a bathochromic shift of the absorption maximum by 70 nm was observed (see Fig. 3, curve 3). The resulting protonated form of **Sz** fluoresces at  $\sim 550$  nm (excitation wavelength 365 nm). Normalized emission spectrum is shown in Fig. 3 (curve 4). Such a large Stokes shift indicates a strong redistribution of the electron density in the excited molecules [16].

Thus, the formation of hydrogen-bonded complexes shifts the absorption band of **Sz** to a long-wave region. And only the charged (protonated) form of stilbazole in solution has fluorescence.

#### 3.2.2. Spectral properties of LC polymer composites films

In this section the absorption spectra of the LC composites in the comparison with ones of the **Sz** solutions are presented. Particular attention is given to the fluorescent properties of the LC composites as well as the “model” mixtures, demonstrating a role of hydrogen bonding.

First of all, it should be noted that the absorption maxima of all LC composites films under investigation are shifted by  $\sim 10\text{--}12$  nm to the longer wavelengths of the spectrum with respect to the



**Fig. 4.** Emission spectra of composite films based on polymer matrix **P1** with different concentration (mol.%) of the dopant **Sz** ( $T = 20^\circ\text{C}$ ).

absorption peak of **Sz** in the solution (see Fig. S1). A larger value ( $10\text{--}12$  nm compared to 7 nm) of bathochromic shift in comparison with H-bonded complexes “**Sz**– $\text{CH}_3\text{COOH}$ ” in the solution is observed due to the greater acidity of para-alkoxybenzoic acid ( $\text{pK}_a \sim 4.2$ ) that leads to the formation of hydrogen bonds in the composites. It was recently shown [14,17] that an increase in the acidity of the polymer matrix as well as an increase in the basicity of pyridine type dopant leads to bathochromic shift of the absorption and fluorescence bands.

Contrary to the solutions of the dopant **Sz** which do not display fluorescence, all prepared composites possess fluorescent properties; the origin of this phenomenon will be discussed below in the next section. To study the fluorescent properties the cells with thickness of  $10\ \mu\text{m}$  were prepared. Then they were filled by LC-composites at temperatures slightly below the clearing temperatures, and then the filled cells were annealed for several hours until the formation of the typical LC texture (a typical fan-shaped texture for **P1** + **Sz** composites and the marble textures for **P2** + **Sz** and **P3** + **Sz**).

Fig. 4 shows the emission spectra of the LC composites based on the polymer matrix **P1** with different molar ratio of the dopant **Sz**.

Almost identical concentration dependence of fluorescence was observed for LC composite based on matrices **P2** and **P3** (see Fig. S2).

Fig. 4 shows that the main emission band of the LC composites is located at 475 nm. A significant increase in fluorescence intensity is observed with the decreasing in the dopant content up to 10%. Further reducing concentration gave rise to a decrease of the emission intensity. The observed dependence can be explained by the inner filter effect [18]. At the high concentrations of dopant **Sz** (starting with  $\sim 10\%$ ) reabsorption of emission takes place and as a consequence the decrease of the fluorescence intensity is observed.

Fig. 5 shows the emission spectra of the LC composites based on different polymer LC matrices containing 10 mol.% of dopant **Sz**. It is clearly seen, that the fluorescence peaks of H-bonded composites based on the **P1** and **P2** are almost identical, differing only in their intensity. In the case of blends based on the matrix **P3**, where hydrogen bonding is absent, a significant difference in the fluorescence spectra is observed: the main emission band is strongly ( $70$  nm) shifted to the shorter wavelengths of the spectrum. The nature of this difference will be discussed below.

Thus, all LC composites and the model compound in the solid state display fluorescence properties. However the fluorescence spectra of H-bonded LC composites significantly differ from “model” mixture.

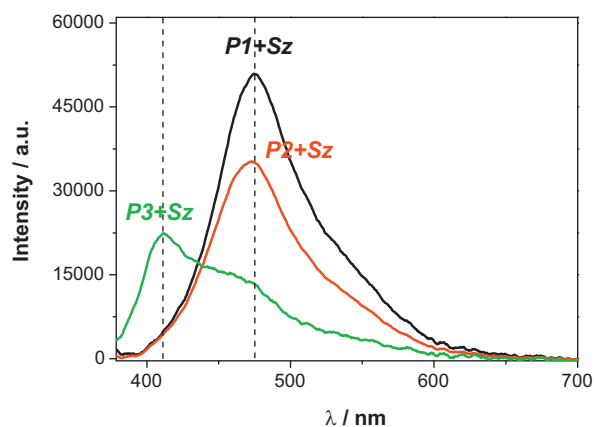


Fig. 5. Fluorescence spectra of the different LC composites containing 10 mol.% of dopant **Sz**.

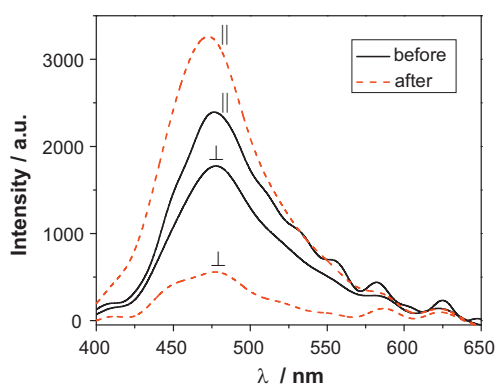


Fig. 6. Polarized fluorescence spectra of LC composite **P2+Sz-10%** (along and perpendicular to the chromophore orientation) before and after annealing.

### 3.2.3. Fluorescence properties of oriented films of the LC composites

Formation of N or SmA mesophases allows one to use LC ordering for uniaxial chromophore orientation, that can be induced by the external fields or special substrates treatment and, as a consequence, it can give the possibility to control fluorescence in some extent. We have used latter approach in order to obtain LC composite samples displaying the polarized fluorescence. For these purpose thin films of the LC composites were prepared by spin-coating on the glass substrates with rubbed polyimide coating (ZLI-2650 “Merck”). Spin-coating technique enables to make only amorphous films which could be annealed to form a LC phase.

Fig. 6 shows the fluorescence spectra of the films **P2+Sz-10%** before and after annealing at 50 °C (above the glass transition temperature of the polymer matrix). The difference in the parallel and perpendicular components of the polarized fluorescence intensity of the LC composite film shows that the fluorescing molecules are in the oriented state. Additionally, the increase in the degree of the emission polarization is evident after annealing.

The estimated values of fluorescence polarization degrees (**R**) obtained during the experiments are listed in Table 2. We did not observed any polarization of the fluorescence for the composites based on matrix **P1** probably due to poor orientation of the LC-domains of smectic phase by using the rubbed polyimide coating. In addition, we have observed homeotropic orientation of side group of **P1** after annealing by means of “out of plane” polarized spectroscopy (see Fig. S4). The latter fact also hinders “in plane” orientation of molecules. Non-zero values of **R** for the fresh prepared nematic systems (**P2** polymers) suggest that even at the

Table 2

Degrees of fluorescence polarization (**R**) of fresh prepared and annealed oriented films of the LC composites.

Type of LC phase	LC composites containing 10 mol.% of <b>Sz</b> , based on following matrices:		
	<b>P1</b>	<b>P2</b>	<b>P3</b>
Fresh prepared film	0	0.15	0.05
Annealed film	0	0.70	0.45

Table 3

Kinetic parameters of E-Z isomerization ( $k_{E/Z}$ ) and fluorescence decrease ( $k_f$ ) for photoprocesses in **Sz** solution and LC composites films.

Sample		Quasi constant rates	
		$k_{E/Z}, \times 10^3 \text{ s}^{-1}$	$k_f, \times 10^3 \text{ s}^{-1}$
<b>Sz</b>	Solution in $\text{CH}_2\text{Cl}_2$	98.4	–
<b>P1+Sz-30%</b>	Film	3.2	1.4
<b>P2+Sz-30%</b>		3.5	1.2
<b>P3+Sz-30%</b>		7.9	10.6

$k_{E/Z}$  – E-Z isomerization quasi rate constant.  $k_f$  – quasi rate constant of fluorescence decrease.

experimental conditions (room temperature) the composites films are slightly oriented, because their glass transition temperatures approximately correspond to the ambient temperature.

Comparison of H-bonded and “model” nematic LC-composites allows one to reveal a significant difference in degree of the fluorescence polarization (Table 2). One can suggest that the fluorescent molecules of dopant **Sz** in the H-bonded nematic LC composites are much better ordered than in mixtures without hydrogen bonding. This can be explained in the same way as in the case of the phase behavior (see above); H-bonded complexes of **Sz** with side alkylbenzoic groups have larger anisotropy in comparison with free **Sz** molecules in the nematic matrix.

Thereby, due to the mesomorphic nature of nematic composites (mixtures), we can easily control the characteristics of fluorescence, in particular, the degree and direction of the polarized fluorescence.

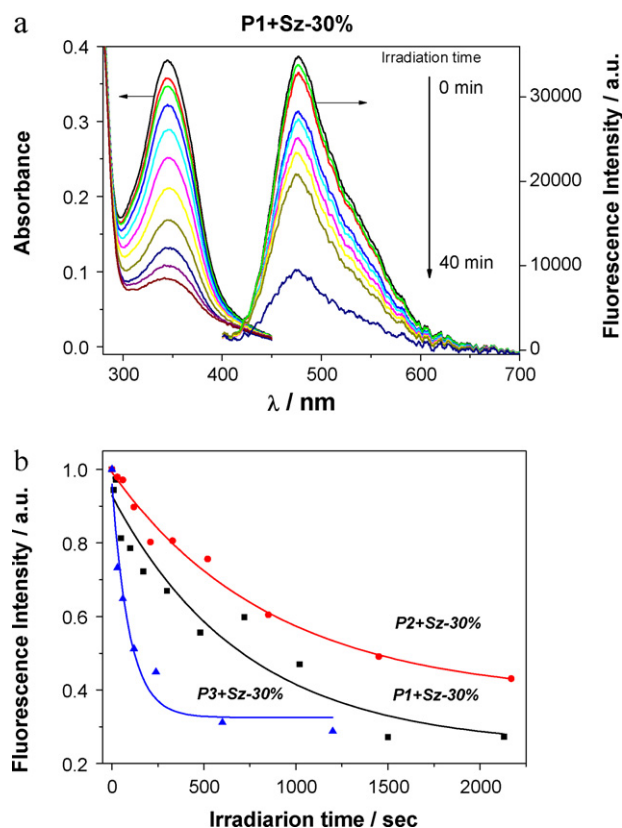
### 3.3. Photooptical properties of LC composites films

The low-molar-mass dopant **Sz**, apart from the fluorescent properties is also capable of undergoing a number of photochemical reactions (E/Z-isomerization, [2+2]-cycloaddition, etc.) due to the presence of unsaturated double bond C=C. In this regard, a question about the effects of the nonpolarized and polarized UV light is particularly relevant and it will be thoroughly discussed in this section

The photooptical properties of LC composites have been studied on the example of the thin films of LC composites with 30 mol.% of **Sz** prepared by spin-coating (from a solution in  $\text{CHCl}_3$ ) on quartz substrates.

During UV-irradiation of either composite films (Fig. 7a) or **Sz** solutions (Fig. S3) E/Z-isomerization occurs, as evidenced by the decrease in the absorption peak intensity. Decrease in fluorescence intensity for the LC composite films also takes place because of a Z-isomer of **Sz** does not display any fluorescent properties.

Fig. 7b and Fig. S5 show the kinetic curves of the processes of the decrease of fluorescence and E/Z-isomerization, respectively during exposure of LC composites thin films by UV light (365 nm). The kinetic parameters of E/Z-isomerization ( $k_{E/Z}$ ), and the quasi rate constants of the fluorescence decrease ( $k_f$ ) are given in Table 3 (these “quasi constants” are valid only for specific experimental conditions, and they are only to identify the regularities of photoprocesses in the investigated systems). These data show that the



**Fig. 7.** Absorbance (a) and fluorescence spectral changes (b) of LC composites films during irradiation by Hg-lamp' light (365 nm,  $I \sim 1.5 \text{ mW/cm}^2$ ).

isomerization of the dopant in solution occurs more than 10 times faster than in the films. It seems to be due to the lack of steric hindrances impeding this process. It is noteworthy, that the quasi rate constants of both processes for a "model" mixture based on the matrix **P3** are comparable with each other (i.e., the rate of isomerization is directly proportional to the rate of fluorescence decrease) and significantly higher than in the H-bonded composites.

In other words, all photoprocesses for H-bonded LC composites are much slower. It is noteworthy, that the fluorescence decrease is slower than the isomerization that indicates the complex nature of emission decay.

To explain the observed spectral differences, we propose the possible mechanisms of the processes occurring under the action of light in the "model" mixtures (Fig. 8a) and H-bonded LC composites (Fig. 8b).

Fig. 8a shows the scheme of photoprocess in mixtures without hydrogen bonding (dichloromethane solutions of **Sz** and LC composite **P3** + **Sz**). After the photon ( $h\nu_1$ ) absorption, E-isomer of stilbazole, which quantitatively prevails, goes to the  $S^1$  excited state. From this excited state molecule can either isomerize or relax to the initial  $S^0$  state with releasing another photon ( $h\nu_3$ ). In solution (dichloromethane) due to the absence of steric hindrances, the absorption of light completely activates the E-Z isomerization of **Sz** molecules. The process of radiative relaxation (fluorescence) is completely suppressed. The fact that fluorescence can be caused by suppression of isomerization process is confirmed by the properties of the mixtures based on **P3** matrix (which can be regarded as a solid solution). In these mixtures the process of E/Z-isomerization is considerably slowed down (see Table 3) due to the high viscosity of the polymers, and thus rather intense fluorescence is observed (Fig. 5).

Thereby, the suppression E/Z-isomerization in systems containing dopant **Sz** is accompanied by increase of fluorescence efficiency.

This statement is valid for H-bonded systems; it will suffice to compare the fluorescence intensity of the composites based on **P1** and **P2** (Fig. 5). Fluorescence intensity of the composite **P1** + **Sz** higher than **P2** + **Sz**, since the glass transition temperature of the matrix **P1** ( $76^\circ\text{C}$ ) is much higher than the matrix **P2** ( $22^\circ\text{C}$ ), that increasingly slows down the isomerization process.

Now let us consider the mechanism of photoprocesses occurring in the LC composites without and with H-bonding (Fig. 8b). The presence of the hydrogen bonding in such systems affects their fluorescent properties. After the absorption of a photon ( $h\nu_1$ ) a molecule of **Sz** goes to the  $S^1$  electronically excited state. It is known that in the  $S^1$  state basicity of the pyridine derivatives increases more than 2-fold [19] (according to [19]  $pK_a$  for 4-methoxy-4'-styrylpyridine in 50% aqueous methanol increases with excitation from 5.17 to 13.55), that is caused by increasing charge on the nitrogen atom (it is marked by different colors of the nitrogen atom in Fig. 8b). Such a significant increase in the basicity of the dopant **Sz** in the excited state leads to the transfer of the hydrogen atom involved in the formation of H-bond to the pyridine ring. This is accompanied by protonation of the excited molecule of stilbazole. The protonated form can exist in multiple tautomeric forms (Fig. 8b). Further, the protonated form of **Sz** radiatively relaxes ( $h\nu_2$ ) in the ground electronic *trans*- $S^0$  state, simultaneously the reverse migration of hydrogen atoms to the oxygen atom of the carboxyl group with formation of H-bond occurs.

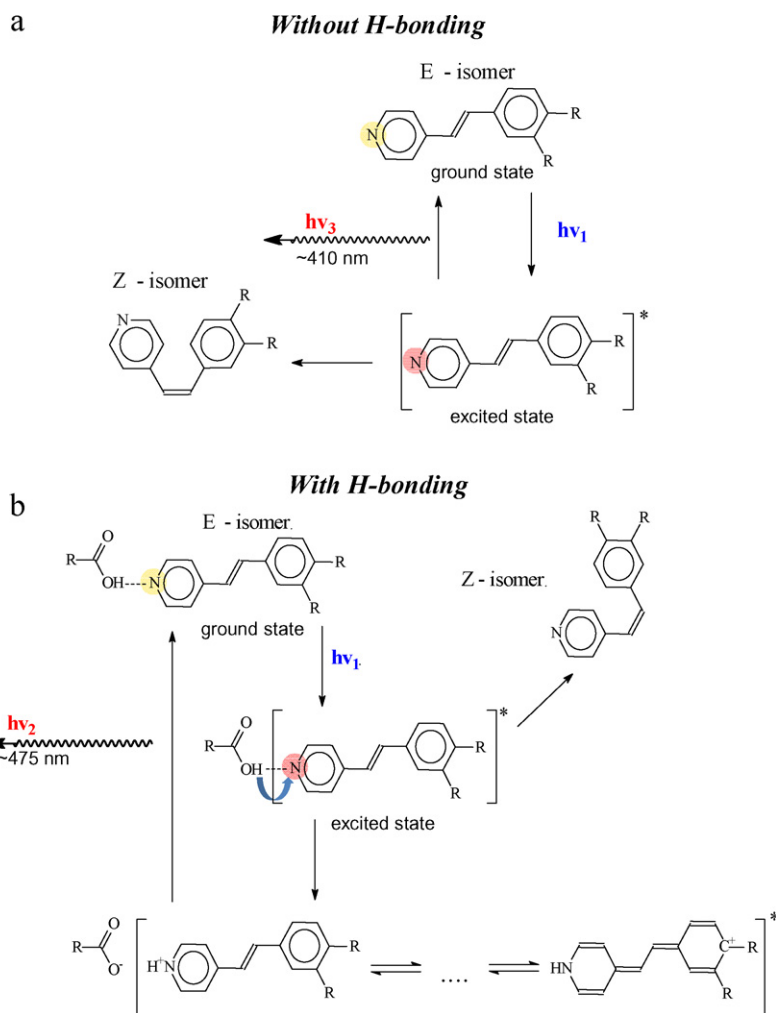
In other words, the molecule of dopant in the case of **P3** + **Sz** mixtures does not emit the light itself, but its protonated form possesses fluorescence with a strong bathochromic shift of the fluorescence peak. It's interesting to note that the absorption peak of stilbazole after protonation in solution is shifted to the long wavelengths by 70 nm ( $335 \text{ nm} \rightarrow 405 \text{ nm}$ ) (see Fig. 3), and the fluorescence peak in the composites is also shifted to the long wavelengths by 70 nm ( $405 \text{ nm} \rightarrow 475 \text{ nm}$ ) for going from systems without hydrogen bonding to the H-bonded systems. This fact once again confirms the plausibility of the proposed mechanisms of photoprocesses.

Thereby, the presence of hydrogen bonding in LC composites based on stilbazole derivatives dramatically changes the mechanism of fluorescence, and as a consequence, the fluorescence becomes more intense and peak position is shifted to the longer spectral region in comparison with the LC mixture without H-bonding. It also should be pointed out that the mesophase nature of polymer matrices does not play any role in photoprocesses mechanism, only the polymer matrix rigidity and hydrogen bonding are important.

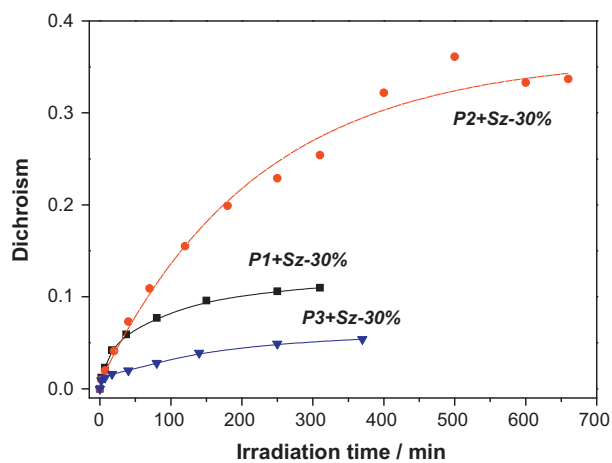
### 3.4. Photoorientation processes in the LC composites

Polarized light is very useful and promising tool for the manipulation of orientation and ordering of photochromic LC systems [20]. That is why we have drawn a special attention to the photoorientation phenomena in thin spin-coated films of H-bonded LC-composites induced by polarized UV light. To study the processes of photoorientation the thin films of LC composites were prepared by spin-coating on quartz substrates. The dichroism values (calculated at the absorption maxima) of the composite films as a time function upon the UV-irradiation with plane-polarized light (365 nm) are depicted in Fig. 9. Polarized absorbance spectra and polar diagrams of irradiated films are presented in Fig. S6 (Supporting information).

In all cases, the predominant orientation of chromophores is appeared in a direction perpendicular to the polarization plane of the incident light. Fig. 9 and the data of Table 4 show that for the hydrogen-bonded LC polymer systems, the maximum values of the photoinduced dichroism are much higher. For a composite based on matrix **P1**, characterized by the smectic type of mesophase and



**Fig. 8.** Schemes of the possible photoprocesses taking place in LC mixtures without hydrogen bonding (a) and in the H-bonded LC composites (b).



**Fig. 9.** Kinetic curves of photoinduced dichroism growth in composite film upon the irradiation with polarized UV-light (365 nm,  $I \sim 0.1$  mW/cm<sup>2</sup>, room temperature).

high glass transition temperature, the dichroism values are three times lower in contrast to the nematic type composite based on the matrix **P2**. In addition, Table 4 presents the maximum degree of polarized fluorescence ( $R^{\max}$ ), that is almost completely coincides with the values of dichroism. It is noteworthy that obtained values of  $D^{\max}$  are much lower in comparison with  $D^{\max} \sim 0.6$ – $0.8$  for

**Table 4**

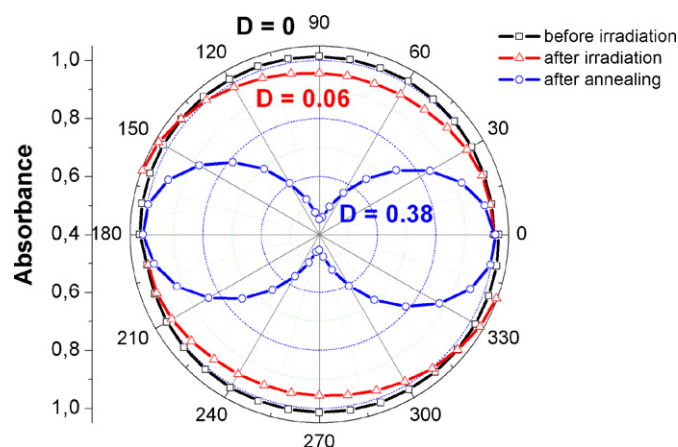
Maximum values of photoinduced dichroism ( $D^{\max}$ ) and degree of polarized fluorescence ( $R^{\max}$ ), values of dichroism and degree of polarization ( $D^a$  и  $R^a$ ) after annealing.<sup>a</sup>

Sample	$D^{\max}$	$R^{\max}$	$D^a$	$R^a$
<b>P1 + Sz-30%</b>	0.11	0.11	$\sim 0$	$\sim 0$
<b>P2 + Sz-30%</b>	0.34	0.35	0.01	0.07
<b>P3 + Sz-30%</b>	0.06	0.05	0.38	0.49

<sup>a</sup>Spin-coated films were irradiated with polarized UV light up to saturation then they were annealed.

azobenzene-containing LC polymers [21,22] and quite typical for cinnamoyl- [23] and stilbene-containing polymers [24]. It should be pointed out that the values of photoinduced dichroism in H-bonded mixtures are much higher that can be explained by an existence of the long mesogenic fragments consisting of H-bonded chromophore and carboxylic acid moiety. Another important fact is an increase of dichroism of **P2 + Sz-30%** film that is explained by photoselection process (this testifies similar behavior of polarized absorption components Fig. S7).

A very interesting feature of these systems was revealed after annealing at temperature above  $T_g$  of the polymer matrix. After annealing of the H-bonded LC composites the values of dichroism and degree of polarized emission decrease almost to zero values. It should be pointed out that we did not observe (by means of "out of plane" polarized spectroscopy) the appearance of the homeotropic orientation for systems based on either **P2** matrix or **P3**. In the



**Fig. 10.** Polar diagrams of relative absorbance at 340 nm and corresponding dichroism values for the “model” mixture film (**P3** + **Sz-30%**) before and after irradiation with polarized UV light (365 nm,  $I \sim 0.1$  mW/cm<sup>2</sup>) and after following annealing at 50 °C.

case of the “model” mixture after annealing enormous growth of dichroism (Fig. 10, the same graph but with the absolute absorption values is depicted in Fig. S8) takes place (more than 6 times). At the same time, even more substantial increase (approximately 10 times) of the degree of polarized fluorescence (Table 4) is found. An increasing of dichroism after annealing in comb-shaped polymers containing azobenzene [25] and stilbene [24] side groups was previously observed by many researchers.

Our observations can be explained as follows. In H-bonded systems oriented molecules of **Sz** “tied” to the unoriented polymer matrix through the relatively labile H-bonds. At temperatures above  $T_g$  the mobility of side groups increases and the non-oriented polymer matrix destroys the ordering of the H-bonded complexes of **Sz**. A situation is opposite for “model” mixtures: oriented molecules of **Sz** align the side mesogenic groups of the polymer matrix during annealing.

Thus, for the first time the photoorientation phenomenon was demonstrated for stibazole-containing H-bonded LC-polymer systems that opens wide opportunity for the photoregulation of their photochemical and photophysical properties.

#### 4. Conclusions

In the present paper, a series of LC composites with different types of the mesophase stabilized by the hydrogen bonds were obtained and a comparative analysis of their phase behavior and spectral properties with LC mixture without hydrogen bonding was presented. It is shown that the introduction of nonmesogenic dopant **Sz** in a polymer matrix **P3** which does not able to form H-bonds leads to a much more significant decrease in the isotropization temperatures than in the H-bonded composites. The

essential difference in the fluorescence spectra of H-bonded composites and “model” LC mixtures, namely, a significant shift of the emission band to long-wave region in the H-bonded composites was found. The processes taking place under irradiation with non-polarized and polarized UV light were studied in details and it was shown that the maximum degree of photoinduced orientation is achieved in nematic LC composites. These investigations demonstrate a crucial role of H-bonding in phase behavior and photooptical properties of stilbazole-containing LC-composites.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.04.017.

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