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Orientational properties of 1,3,4-oxadiazoles in liquid-crystalline materials determined by electronic absorption and fluorescence measurements

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Abstract

The electronic absorption and fluorescence spectra of two 4-donor/4′-acceptor substituted 2,5-diphenyl-1,3,4-oxadiazole derivatives in isotropic solvents (methanol, toluene), in a commercial mixture of low molecular mass liquid crystals – ZLI 1695 (MERCK, Darmstadt), and in a liquid-crystalline polysiloxane with 4-methoxy-4′-pentoxy-phenylbenzoate side-groups are presented and discussed. The orientational order parameters of the 1,3,4-oxadiazoles, dissolved in the liquid-crystalline films with uniform planar orientation of the mesogenic molecules and in aligned films of the polysiloxane, are determined. The possibility of application in OLEDs of the 1,3,4-oxadiazoles dissolved in homogenously oriented liquid-crystalline polymers is suggested.

Keywords: 1,3,4-Oxadiazole derivative; Liquid crystal; Liquid-crystalline polymer; Electronic absorption; Fluorescence; OLED

1. Introduction

Aromatic substituted 1,3,4-oxadiazoles are of great interest because of their possible applications as scintillators or laser dyes with high fluorescence intensity [1–3]. They are also known as efficient electron transporting and hole blocking materials in organic light-emitting diodes (OLEDs) [4–6]. Because of their luminescence properties 1,3,4-oxadiazoles can be used for preparation of the emission layer in OLEDs [7–9]. Some 1,3,4-oxadiazoles are mesomorphic and they can exist in smectic A or nematic phases [10–12]. The self-organizing capability of liquid crystals gives possibility to prepare OLEDs comprising emissive layers with anisotropic optical features. Some liquid-crystalline 1,3,4-oxadiazole derivatives in thin films composed of uniformly oriented molecules present linearly polarized electroluminescence or fluorescence emission [11]. On the other hand, the uniform orientation of nonmesogenic oxadiazoles can be obtained by using Langmuir–Blodgett technique and by vapour deposition [13,14]. An alternative way to obtain thin organic films with highly anisotropic fluorescence emission is dissolving the fluorescent molecules into low molecular mass liquid crystals or liquid-crystalline polymers [15,16]. In such a case, the anisotropic orientational distribution of the admixed fluorescent molecules is induced by the uniform planar orientation of the liquid crystal molecules or polymer's side-groups.

In the present paper, the possibility to obtain anisotropic absorption and fluorescence from two 1,3,4-oxadiazole derivatives, dissolved in macroscopically oriented matrices of low molecular mass liquid crystal and liquid-crystalline side-group polymer, is discussed in detail.

2. Experimental

Two aromatic substituted 1,3,4-oxadiazoles, 2-(4-nitrophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole (OXA11) and

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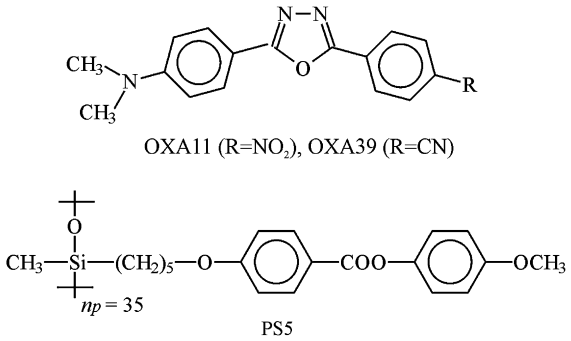

Fig. 1. Aromatic substituted 1,3,4-oxadiazoles and liquid-crystalline side-group polysiloxane.

2-(4-cyanophenyl)-5-(4-dimethylaminophenyl)-1,3,4-oxadiazole (OXA39), with the chemical structures given in Fig. 1, were investigated using electronic absorption and fluorescence. These derivatives were obtained from the Institute of Thin Film Technology and Microsensorics (Teltow, Germany). The chemical synthesis of the 2,5-substituted 1,3,4-oxadiazoles was described by Freydank et al. [17].

The 1,3,4-oxadiazoles were investigated in isotropic solvents of different polarity, toluene and methanol, in a commercially available liquid-crystalline mixture of *trans*-4-(*n*-alkyl)-4′-cyano-bicyclohexyles, ZLI 1695 (MERCK, Darmstadt), and also in a side-chain liquid-crystalline polymer with a siloxane backbone and 4-methoxy-4′-pentoxy-phenylbenzoate side-groups, PS5 (Fig. 1). The chemical synthesis of the polymer was performed in the Department of Chemistry, Warsaw Agricultural University (Warsaw, Poland), according to the procedure given in the literature [18].

ZLI 1695 is characterized by positive dielectric anisotropy. Contrary to most of low molecular mass liquid crystals, ZLI 1695 is transparent to the UV irradiation. The nematic phase in ZLI 1695 was observed in the temperature range from 286 K to 345 K. In pure PS5 this phase was found between 350 K and 382 K. Below 350 K the polymer existed in the glassy state. The 1,3,4-oxadiazoles were dissolved in the isotropic solvents at concentration equal to 1×10^{-4} mol dm^{-3}. In ZLI 1695 and in PS5 the concentrations of the admixtures were greater than in the isotropic solvents, and they were equal to 1×10^{-2} mol dm^{-3} and 1×10^{-2} mol kg^{-1}, respectively. For the investigation of the 1,3,4-oxadiazoles in the isotropic solvents, some standard quartz cuvettes of 10 mm in thickness were used. The measurements of the 1,3,4-oxadiazoles in ZLI 1695 and PS5 were carried out in ''sandwich'' cells of 20 μm in thickness. The inner surfaces of the cells had been coated with a polyimide layer and, next, they were subjected to rubbing procedure. The cells were filled via capillary forces. In the case of ZLI 1695, this process was conducted at room temperature, and it took some seconds. As a result of anchoring forces on the polyimide layers, a uniform planar orientation of the mesogenic and nonmesogenic molecules was obtained. For PS5 the filling procedure took some hours, which was the result of greater viscosity of the liquid-crystalline polymer than that of the low molecular mass liquid crystal. In order to obtain the uniform planar orientation of the polymer's mesogenic side-groups and the admixed 1,3,4-oxadiazole molecules, the cells were annealed for some hours at temperature just below the clearing point of PS5. The obtained macroscopic orientation of the molecules was not destroyed in the glassy state of this polymer.

The absorption spectra of OXA11 and OXA39 in isotropic solvents and in liquid-crystalline layers were recorded in the UV–vis region by means of CARY 400 spectrophotometer. The setup was possible to be equipped with Glan or UV dichroic polarizers for the registration of polarized components of the spectra. The fluorescence measurements were carried out using a home-made photon-counting spectrofluorimeter. The exciting beam of polarized light was almost perpendicular to the cell surface, and the polarized fluorescence emission was detected in the direction perpendicular to this surface. The details of this setup and the information about the geometry of the experiment can be found elsewhere [19,20]. The spectrofluorimeter enables one to record four components of the polarized fluorescence spectra in the vis region, which gives opportunity to characterize orientational distribution of the molecules in the sample.

3. Results and discussion

3.1. Electronic absorption and fluorescence of 1,3,4-oxadiazole derivatives in isotropic solvents

The oxadiazole molecules, discussed in this paper, can be treated as structures composed of 2,5-diphenyl-1,3,4-oxadiazole (DPO) core substituted with electron-donating and electron-accepting groups in *para* position of the opposite phenyl rings. Calculations of electronic transitions in DPO, based on the quantum chemistry methods using semi-empirical π-electronic approach, show the possibility of four basic transitions ($S_0 \rightarrow S_i$, $i = 0,\ldots,4$) for this type of molecules [21]. The long-wavelength band ($S_0 \rightarrow S_1$) of the greatest intensity, with maximum at $\lambda_1 = 309.8$ nm, is connected with the transition of ππ* type delocalized on the π-electronic system of the whole molecule. The short-wavelength band ($S_0 \rightarrow S_4$, $\lambda_4 = 243.8$ nm) is of the same electronic nature but, in this case, the intensity is much less than for the long-wavelength one. Two other bands ($S_0 \rightarrow S_2$, $S_0 \rightarrow S_3$) with very small intensity and almost identical positions of maximum ($\lambda_2 = 271.6$ nm, $\lambda_3 = 271.3$ nm) are connected with the electronic transitions localized on π-electronic systems of the phenyl rings.

Introduction of electron-donating and electron-accepting groups into DPO molecule in *para* position of the phenyl rings results in bathochromic shift of electronic absorption and luminescence bands and in the increase of molar extinction coefficient [22]. The absorption spectra of OXA11 and OXA39 in toluene and methanol at room temperature are presented in Fig. 2. The spectra are cut off at the short-wavelength end because of the strong absorption of the solvents in this region. The maximum wavelengths of the separated bands and the respective molar extinction coefficients are presented in Table 1. The description of the maxima is given in analogy to that

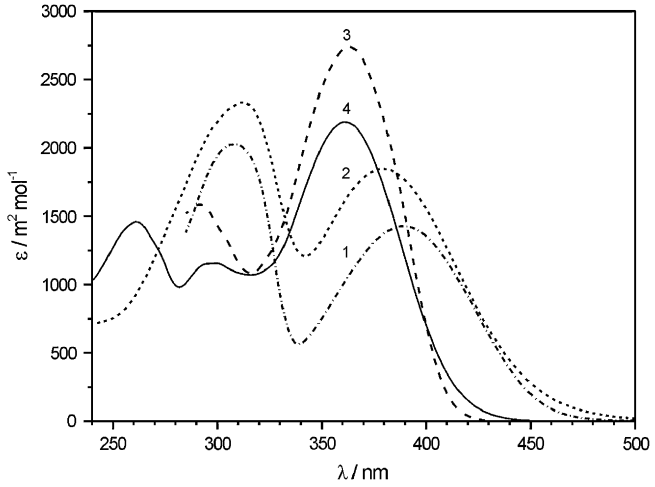

Fig. 2. Electronic absorption spectra of 1,3,4-oxadiazoles in toluene (1—OXA11, 3—OXA39) and in methanol (2—OXA11, 4—OXA39) at $T = 300$ K.

introduced in the theoretical predictions for DPO molecule. Because the absorption spectra of the investigated 1,3,4-oxadiazoles in the registration range contains two (OXA11) or, at most, three well separated bands (OXA39 in methanol), it can be assumed that the bands connected with the transitions on the phenyl rings cover each other. Thus, they are not analyzed separately. The measured maximum wavelengths and the molar extinction coefficients for OXA11 in toluene are in agreement with the literature data [22]. The data for OXA11 in methanol are not available in the literature (to our knowledge) but the maximum wavelengths can be found for this 1,3,4-oxadiazole in insensibly less polar ethanol: $\lambda_1 = 383$ nm, $\lambda_4 = 311$ nm [23].

On the grounds of the collected data, it can be concluded that the introduction into DPO molecule of both electron-donating ($-N(CH_3)_2$) and electron-accepting ($-NO_2$, $-CN$) groups results in a considerable bathochromic shift of the long-wavelength and the short-wavelength bands maxima (λ_1 and λ_4, respectively). For OXA11 in toluene the respective shifts, with the reference to DPO, are equal to 79 nm and 65 nm. The band connected with the transitions localized on the phenyl rings is, in this case, covered by the much more intense short-wavelength one, which makes it impossible to determine $\lambda_{2,3}$. The same effect is observed for OXA11 in methanol. The nitro groups in OXA11 stabilize the intramolecular electronic energy of the molecule in a greater degree than the cyano groups in OXA39. The band maxima at λ_1 for OXA11 and OXA39 in methanol are shifted, with the reference to DPO, by 69 nm and 51 nm, respectively. Moreover, it can be observed that the replacement of the $-CN$ group with the $-NO_2$ one, characterized by stronger electron-accepting properties, results in the intensity increase of the short-wavelength band and in the decrease of the long-wavelength one. Similar relations were observed previously by Popova et al. in a series of DPO derivatives dissolved in toluene [22]. The data collected in Table 1 give also the information about the influence of the solvent polarity on the electronic structure of the 1,3,4-oxadiazoles. For OXA11 and OXA39, the increase of solvent polarity results in bathochromic shifts of the short-wavelength bands and the bands connected with the transitions on the phenyl rings. The long-wavelength bands are hypsochromically shifted.

For OXA11 and OXA39 in methanol, excited with the quasi-monochromatic light (Hg, $\lambda = 405.8$ nm), the fluorescence emission is not observed. On the other hand, an intensive fluorescence emission for OXA11 and a very weak one for OXA39 in toluene are registered. The small quantum efficiency in the second case is a result of a bad fitting of the exciting light wavelength to the maximum wavelength of the absorption band ($\lambda_1 = 364$ nm). Electronic absorption and fluorescence spectra of OXA11 in toluene, recorded at room temperature ($T = 300$ K), are presented in Fig. 3. The absorption and the fluorescence spectra cover each other insignificantly, which minimizes the reabsorption effect. The fluorescence maximum is found at $\lambda_F = 550$ nm, and, in this case, the Stokes shift is equal to 161 nm. Additional experiment, in which the exciting light wavelength is adjusted to the maxima of the absorption band of OXA39 in toluene and methanol, enables one to find the fluorescence maxima at $\lambda_F = 450$ nm and $\lambda_F = 576$ nm, and the Stokes shifts equal to 86 nm and 215 nm, respectively. The fluorescence intensity of OXA39 in methanol is about one hundred times less than in toluene. The extremely large Stokes shifts for dimethylamino substituted molecules with electron-accepting units could be a result of the photoinduced charge transfer (CT) states formation. The formation of CT states is described by several models [24,25]. Among them, the twisted intramolecular charge transfer (TICT) model is of primary importance [26,27].

Table 1
Maximum wavelengths and molar extinction coefficients of electronic absorption bands of 1,3,4-oxadiazole derivatives measured in isotropic solvents

Compound	Solvent	Absorption					
		λ_1 (nm)	ε_1 (m^2 mol^{-1})	$\lambda_{2,3}$ (nm)	$\varepsilon_{2,3}$ (m^2 mol^{-1})	λ_4 (nm)	ε_4 (m^2 mol^{-1})
OXA11	Toluene	389	1420	–	–	309	2030
	Methanol	379	1850	–	–	312	2330
OXA39	Toluene	364	2740	292	1590	–	–
	Methanol	361	2190	298	1150	261	1450
DPO[a]	–	309.8	–	271.6 271.3	–	243.8	–

[a] From calculations based on the quantum chemistry methods using semi-empirical π-electronic approach [21].

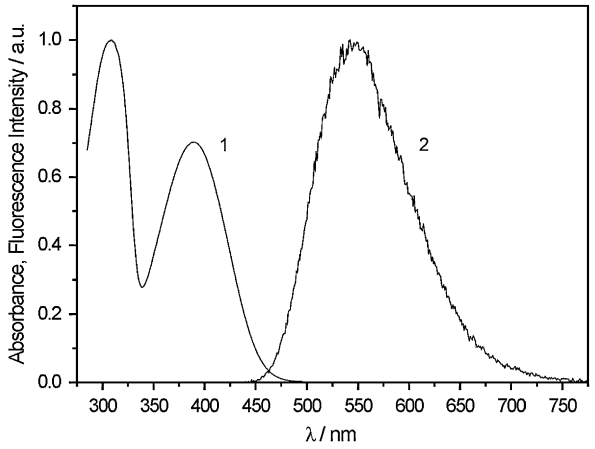

Fig. 3. Electronic absorption (1) and fluorescence (2) spectra of OXA11 in toluene ($T = 300$ K).

3.2. Absorption anisotropy of 1,3,4-oxadiazole derivatives in ZLI 1695

Polarized absorption spectra of OXA11 and OXA39 in thin films of liquid-crystalline mixture ZLI 1695, with uniform planar orientation of the mesogenic molecules, at $T = 300$ K, are presented in Fig. 4. The parallel components of the absorption spectra of the investigated 1,3,4-oxadiazoles in ZLI 1695 are very similar in shape to the respective spectra registered in toluene and methanol. Particularly, well distinguishable absorption bands of OXA11 ($\lambda_1 = 397$ nm, $\lambda_4 = 311$ nm) and of OXA39 ($\lambda_1 = 372$ nm, $\lambda_{2,3} = 295$ nm, $\lambda_4 = 268$ nm) are observed. For OXA11 and OXA39 in ZLI 1695 a weak fluorescence emission with the maxima at $\lambda_F = 550$ nm and $\lambda_F = 450$ nm, respectively, is registered. In the investigated wavelength range, the absorbance of the parallel component is greater, in each point of the absorption spectrum, than the absorbance of the perpendicular component. This indicates that the absorption transitions of the investigated 1,3,4-oxadiazole molecules are polarized. Because of the type of long-wavelength band transitions in OXA11 and OXA39 molecules, the respective transition dipole moments can be almost parallel to the long molecular axis. The observed anisotropy of electronic absorption is also a result of the anisotropy of orientational distribution of the oxadiazole molecules in the liquid-crystalline matrix. The elongated shape of the 1,3,4-oxadiazole molecules and the intermolecular short-range interactions between them and the mesogenic molecules are of great importance for this effect. Statistical description of the molecular ordering is given by orientational distribution function f which, in the case of nematic liquid crystals, depends only on the polar angle θ [28]. In practice, this function can be determined from the X-ray scattering data. Another experimental method gives only partial information about this function. For example, in the case of cylindrical symmetry of the molecules ($C_{\infty h}$) and uniaxial symmetry of the phase, it is possible to determine the orientational order parameter $\langle P_2 \rangle$ from the absorption anisotropy S_A, using the following formula [28]:

$$S_A = \langle P_2 \rangle P_2(\cos \alpha) \tag{1}$$

where $P_2(\cos \alpha)$ is the Legendre polynomial of the second rank and α is the angle between the absorption transition dipole moment and the long molecular axis.

For OXA11 and OXA39, the long molecular axis can be defined as a line containing points corresponding to the *para* positions of the opposite phenyl rings in the molecule core. The 1,3,4-oxadiazole derivatives are, in fact, of banana-like shape but, in the first approximation, the molecules are assumed to be cylindrically symmetric. This assumption is rather rough but useful. Theoretically, the value of $\langle P_2 \rangle$ can be calculated for each band of the absorption spectra independently if the respective α angle is known. In practice, the bands cover each other more or less, and the determination of the order parameter of such bands from the absorption anisotropy is not very precise or, simply, impossible.

The absorption anisotropy as a function of wavelength for OXA11 and OXA39 in ZLI 1695 at temperature $T = 300$ K is presented in Fig. 5. The greatest values of the absorption anisotropy correspond to the long-wavelength bands of the investigated 1,3,4-oxadiazoles. For OXA11 and OXA39, at the maxima of these bands (397 nm and 372 nm, respectively), $S_A = 0.65 \pm 0.02$ in both cases. If one assumes, in accordance with the semi-empirical calculations [21], that the absorption transition dipole moment corresponding to the long-wavelength band of the 1,3,4-oxadiazole molecule is parallel to the long molecular axis ($\alpha = 0°$) then, from Eq. (1), $\langle P_2 \rangle = S_A$. Taking this assumption into account, it can be concluded that the type of end groups ($-NO_2$ or $-CN$) of the admixture molecules dissolved in ZLI 1695 is of less importance in the determination of the order parameter. It should be emphasized here that the long-wavelength bands are only slightly influenced by the other ones. In both cases, the absorption anisotropy decreases with the decrease of the wavelength. This indicates that non-zero values of the α angle for the absorption transition moments connected with the benzene rings, in particular, are possible. For this and also for the short-wavelength

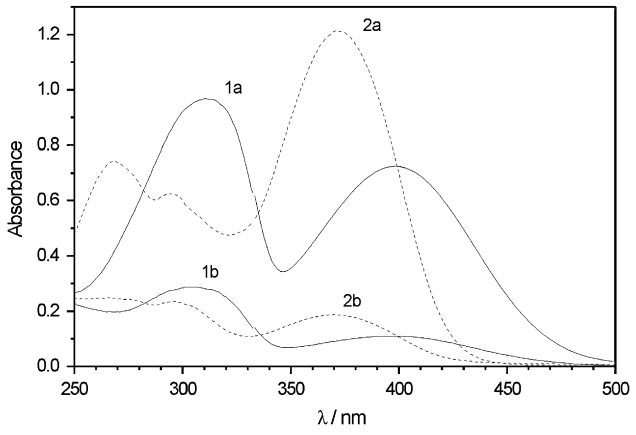

Fig. 4. Parallel (a) and perpendicular (b) components of polarized absorption spectra of OXA11 (1) and OXA39 (2) in thin films of ZLI 1695 ($T = 300$ K).

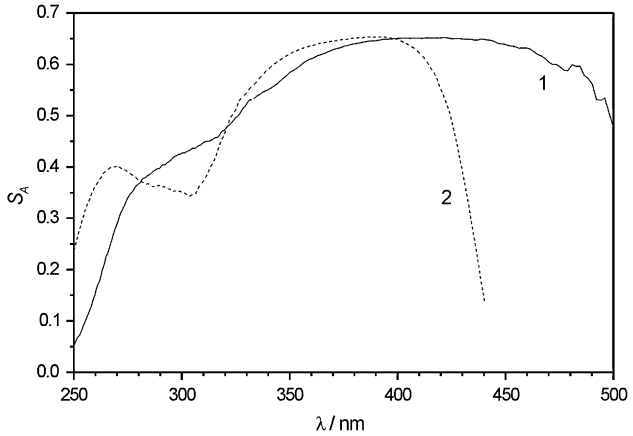

Fig. 5. Absorption anisotropy as a function of wavelength of OXA11 (1) and OXA39 (2) in ZLI 1695 at $T = 300$ K.

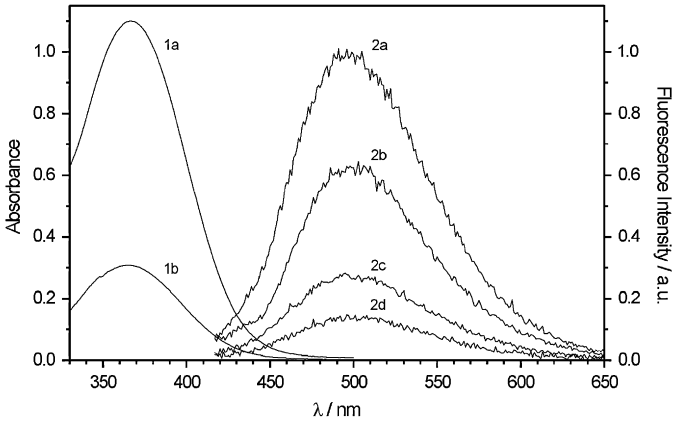

Fig. 7. Parallel (1a) and perpendicular (1b) components of polarized absorption spectra and four components of polarized fluorescence (2a—J_{zz}, 2b—J_{zy}, 2c—J_{yz}, 2d—J_{yy}) of OXA39 in PS5 ($T = 365$ K).

band, the determination of the α angle is much more complicated because of mutual covering of the bands and the increase of light scattering intensity.

3.3. Orientational distribution of 1,3,4-oxadiazole molecules in PS5

The shape of the electronic absorption spectra of 1,3,4-oxadiazoles in isotropic or anisotropic media depends strongly on the type of end groups. The components of polarized absorption and fluorescence spectra of OXA11 and OXA39 in PS5 at $T = 365$ K (nematic phase) are given in Figs. 6 and 7. The fluorescence emission is not observed for OXA11 if exciting the sample with light of the wavelength corresponding to $\lambda = 405.8$ nm mercury line. In the absorption spectrum of OXA11 in PS5, the individual bands are very hard to be distinguished, which is not the case in OXA39. The absorption spectra of the 1,3,4-oxadiazoles are cut off below 340 nm because of a strong absorption of the polysiloxane's phenylbenzoate side-groups. For this reason, the interpretation of the OXA11 spectrum in PS5 is difficult. The self-aggregation of OXA11 molecules resulting from the presence of the electrical dipoles or aggregation with the polymer's mesogenic groups could be proposed as a possible reason for the observed shape of the absorption spectrum. It is characteristic that the unusual shape of the spectrum is not found for OXA11 in both the isotropic solvents and ZLI 1695. On the other hand, a very similar spectrum to that of OXA11 in PS5 was registered by us for this 1,3,4-oxadiazole derivative dissolved in low molecular mass liquid crystal *trans*-4-(4-heptyl-cyclohexyl)-benzonitrile (PCH7). The position of the long-wavelength band maximum for OXA11 in PS5 is determined from the first derivative curve of the parallel component of the absorbance. The long-wavelength absorption band maxima of OXA11 and OXA39 in PS5 are found at λ_1 equal to 394 nm and 366 nm, respectively. These values are comparable with that registered for the 1,3,4-oxadiazoles in toluene. For OXA11 in PS5 the fluorescence is not observed. The fluorescence maximum of OXA39 in PS5 at room temperature is found at $\lambda_F = 481$ nm. The considerable Stokes shift of OXA39 in PS5, equal to 115 nm, indicates the presence of an efficient intramolecular energy conversion. The reabsorption effect is negligible and, consequently, the fluorescence can be very efficient. The significant difference in absorbance values of the parallel and perpendicular components, both for OXA11 and OXA39, is a result of the anisotropy of orientational distribution of the 1,3,4-oxadiazoles, dissolved in uniformly oriented liquid-crystalline polymer matrix. The anisotropy is also observed in the polarized fluorescence spectra of OXA39 in PS5.

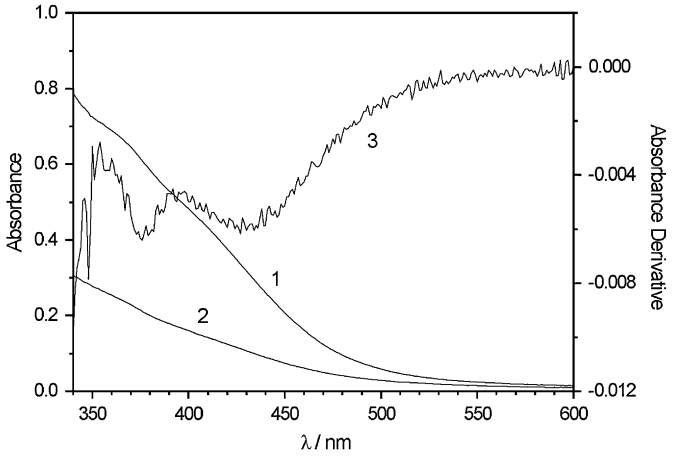

Fig. 6. Parallel (1) and perpendicular (2) components of polarized absorption spectra and the derivative of the parallel component (3) of OXA11 in PS5 at $T = 365$ K (nematic phase).

The maximum wavelength of the absorption band, λ_1, of OXA11 and OXA39 and also the maximum wavelength of the fluorescence, λ_F, of OXA39 in PS5 as a function of temperature are presented in Fig. 8. The blue shift of the absorption maximum and the red shift of the fluorescence maximum with the increase of temperature is a typical effect. These shifts correspond with the electronic distribution on the vibrational levels of the ground and excited states at a given temperature.

The $\langle P_2 \rangle$ order parameter as a function of reduced temperature, $T^* = T/T_{NI}$, for OXA11 and OXA39 in PS5 is presented

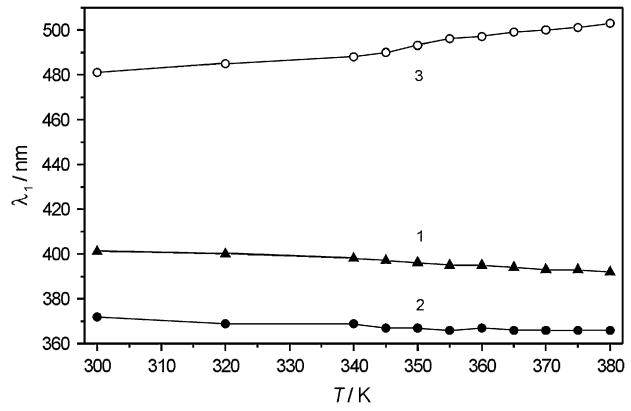

Fig. 8. Long-wavelength absorption band maximum, λ_1, of OXA11 (1) and OXA39 (2) and wavelength of fluorescence maximum, λ_F, of OXA39 (3) in PS5 as a function of temperature.

in Fig. 9. The order parameter was obtained from Eq. (1) by taking $\alpha = 0°$. At $T = 300$ K, the values of $\langle P_2 \rangle$ for OXA11 and OXA39 in PS5 are equal to 0.47 ± 0.02 and 0.57 ± 0.02, respectively, and they are less than that in ZLI 1695 at the same temperature. The difference in the $\langle P_2 \rangle$ values is still greater if considered at the same reduced temperature $T^* = 0.870$ corresponding to $T = 300$ K for ZLI 1695 and $T = 332$ K for PS5, for example. The lower values of $\langle P_2 \rangle$ for the 1,3,4-oxadiazoles in PS5 than in the low molecular mass liquid crystal are the result of the perturbing influence of the polymer main chain on the uniformly oriented mesogenic groups. The $\langle P_2 \rangle$ order parameter for OXA11 and OXA39 decreases with the increase of temperature, both in the glassy state and in the nematic phase of the polymer, as it was previously observed for 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene (DMANS) in PS5 [16]. The determination of the $\langle P_2 \rangle$ order parameter values for liquid-crystalline polymers at temperature just below T_{NI} is not possible because of the coexistence of nematic and isotropic phases in this region. For PS5 with the 1,3,4-oxadiazole admixtures the width of the two-phase region, ΔT_{NI}, is equal to 1 K. Contrary to the liquid-crystalline polymers, the two-phase region for pure low molecular mass nematics is very narrow. The $\langle P_2 \rangle$ value at T_{NI}, predicted by the Maier–Saupe theory of nematics [29], is greater than zero, in this case. The lower values of the order parameter for OXA11 than for OXA39 can be a result of the presence of the bulky nitro group in the molecular structure of OXA11. Thus, the OXA11 molecules in PS5 are prevented to orient themselves parallel to the direction of the preferred orientation of the mesogenic groups in a greater degree than the OXA39 ones. On the other hand, the values of $\langle P_2 \rangle$ for OXA11 and OXA39 in ZLI 1695 are equal to each other, which suggests the absence of such dependence in this case.

The $\langle P_2 \rangle$ order parameter gives only approximate information about the orientational distribution of cylindrical molecules in a uniaxial phase. More precise description is possible if the subsequent $\langle P_4 \rangle$ parameter is known. The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters can be determined from the intensities of polarized fluorescence components. On the assumption that the fluorescence lifetime τ_F is much less than the rotational diffusion times τ_{mn} of the emitting molecule ($\tau_F \ll \tau_{mn}$), the order parameters can be determined from the following system of equations [30,31]:

$$\begin{aligned}&[2r_1P_2(\cos\alpha) - P_2(\cos\beta) - 3B]\langle P_2\rangle - 18C\langle P_4\rangle = 3A - r_1\\ &[r_2P_2(\cos\alpha) + P_2(\cos\beta) + 3Br_2]\langle P_2\rangle - 3C\left(\frac{7}{2} + r_2\right)\langle P_4\rangle\\ &= 3A(1 + r_2) + r_2\end{aligned} \quad (2)$$

where α and β angles describe the directions of the absorption and fluorescence transition dipole moments, A, B and C are functions of α and β, and r_1, r_2 are the emission anisotropies.

The $\langle P_2 \rangle$ and $\langle P_4 \rangle$ order parameters as functions of reduced temperature for OXA39 in PS5, calculated from the polarized absorption and fluorescence components from Eqs. (1) and (2), are presented in Fig. 10. For the calculations, it is assumed that $\alpha = 0°$. Thus, the β angle can be calculated from the

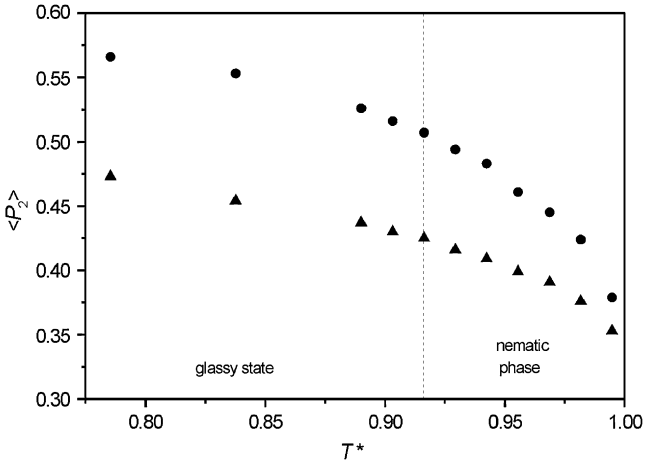

Fig. 9. $\langle P_2 \rangle$ order parameter as a function of reduced temperature for OXA11 (triangles) and OXA39 (circles) in PS5.

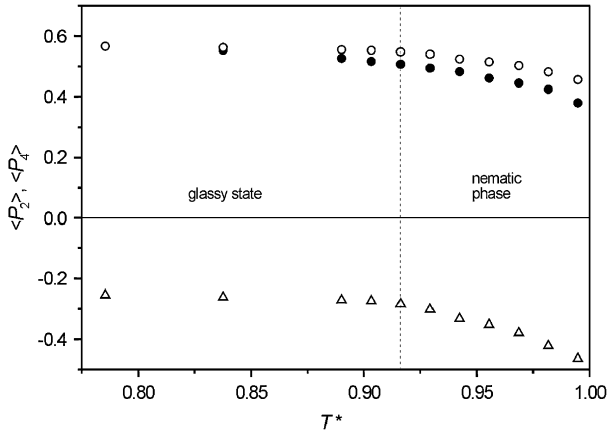

Fig. 10. $\langle P_2 \rangle$ (circles) and $\langle P_4 \rangle$ (triangles) order parameters as functions of reduced temperature for OXA39 in PS5, calculated from polarized absorption (filled symbols) and fluorescence (open symbols) components for $\alpha = 0°$ and $\beta = 39.6°$.

absorption and the fluorescence experimental data obtained at room temperature ($T = 300$ K). At this temperature PS5 exists in the glassy state and the rotational motions of the polymer's mesogenic groups and the admixed molecules are relatively slow ($\tau_F \ll \tau_{mn}$). Thus, the order parameters calculated independently from the absorption, $\langle P_2\rangle_A$, and from the emission, $\langle P_2\rangle_F$, anisotropies should be equal to each other. On these assumptions, the calculations give $\beta = 39.6°$ for OXA39 molecule. The large value of the β angle, in coincidence with the large Stokes shift, can be an additional argument for the significance of the intramolecular energy conversion in the deactivation of OXA39 molecule after absorption of light. For the determination of the order parameters at higher temperature, it is assumed that the β angle is temperature independent. As a consequence, the difference in the values of $\langle P_2\rangle_F$ and $\langle P_2\rangle_A$ increases with the increase of temperature, which can be a result of faster rotational motions of the molecules. This effect was observed previously for liquid-crystalline polymers with mesogenic side-groups [16] and for low molecular mass liquid crystals [32] with the fluorescent molecules admixed. The difference in $\langle P_2\rangle_F$ and $\langle P_2\rangle_A$ values arises from the fact that the molecular motions are not regarded in Eq. (2). The generalization is connected, however, with the necessity of independent measurements of τ_F and τ_{mn}. Another important feature of the molecular distribution of OXA39 in PS5 is negative values of $\langle P_4\rangle_F$ order parameter in the glassy state and in the nematic phase.

In Table 2 simulated values of β, $\langle P_2\rangle$, and $\langle P_4\rangle$ for given values of the α angle for OXA39 in PS5 at temperature in the range from 300 K to 380 K are collected. It is seen that the β angle is not very sensitive to the variation of the α angle. Considering the α angle to be less than 15°, which seems to be a reasonable assumption for OXA39 molecule, it can be found that the β angle variations are less than 7%. Also the changes of the $\langle P_2\rangle_F$ and $\langle P_2\rangle_A$ values are not very significant (less than 10%) for $0° < \alpha < 15°$. A different situation is found for the $\langle P_4\rangle_F$ order parameter, which is very sensitive to the variations of the α angle. For example, the increase in the α value from 0° to 10° causes the alteration of the $\langle P_4\rangle_F$ sign from negative to positive values, both in the glassy state and in the whole nematic phase of PS5.

The width of the orientational distribution function, f, depends, in a considerable degree, on the value of $\langle P_4\rangle$ order parameter. For low negative values of $\langle P_4\rangle$, the minimum for the f function is found at $\theta = 0°$. In such a case, an oblique orientation of the fluorescent molecules with respect to the direction of macroscopic ordering of the surrounding mesogenic groups is preferred. From this point of view, the $\langle P_4\rangle$ order parameter is of critical meaning for the description of the orientational distribution of molecules. The simplified orientational distribution functions [28] for OXA39 in PS5 in the glassy state ($T = 300$ K) and in the nematic phase ($T = 365$ K), calculated for $\alpha = 0°$ and $\alpha = 10°$, are presented in Fig. 11. The examples illustrate clearly the relation between the $\langle P_4\rangle$ values and the f function characterizing the orientational distribution of OXA39 molecules in the liquid-crystalline matrix. Assuming that $\alpha = 0°$ for OXA39, it can be concluded from the shape of the f function that the admixture molecules prefer the oblique orientation with respect to the preferred orientation of the mesogenic groups. Such a distribution can also be a consequence of the slightly bent shape of the OXA39 molecules. For comparison, the results for rod-like molecules of DMANS ($\alpha = 0°$, $\beta = 12 \pm 2°$) in PS5 can be given here [16]. For DMANS in the glassy state ($T = 300$ K) the values of $\langle P_2\rangle_F$ and $\langle P_4\rangle_F$ are equal to 0.62 and 0.18, and in the nematic phase ($T = 365$ K), 0.35 and −0.15, respectively. According to the reported data, it is evident that the orientation of DMANS molecules in PS5 is more perfect than OXA39, which can be a result of the difference in molecular shape.

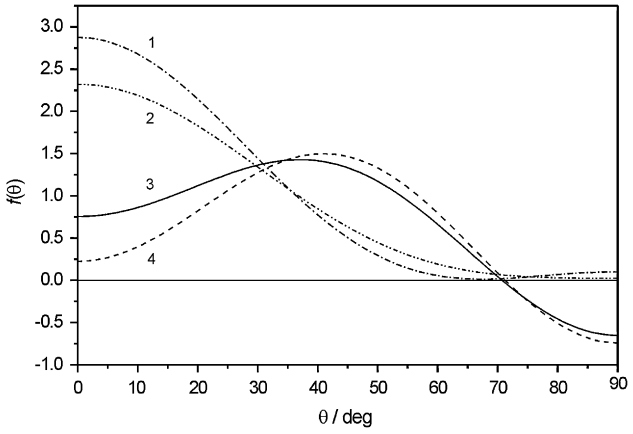

Fig. 11. Simplified orientational distribution functions in the glassy state and in the nematic phase for OXA39 in PS5, calculated for $\alpha = 10°$ (1—300 K, 2—365 K) and $\alpha = 0°$ (3—300 K, 4—365 K).

4. Conclusions

The 1,3,4-oxadiazole derivatives, OXA11 and OXA39, are soluble in isotropic solvents (methanol, toluene), in a commercial mixture of low molecular mass liquid crystals (ZLI 1695), and in polysiloxane liquid-crystalline side-group polymer

Table 2
Simulated values of β, $\langle P_2\rangle_A$, $\langle P_2\rangle_F$, and $\langle P_4\rangle_F$ for given values of α angle for OXA39 in PS5

T (K)	S_A	$\alpha = 0°$				$\alpha = 5°$				$\alpha = 10°$				$\alpha = 15°$			
		β (°)	$\langle P_2\rangle_A$	$\langle P_2\rangle_F$	$\langle P_4\rangle_F$	β (°)	$\langle P_2\rangle_A$	$\langle P_2\rangle_F$	$\langle P_4\rangle_F$	β (°)	$\langle P_2\rangle_A$	$\langle P_2\rangle_F$	$\langle P_4\rangle_F$	β (°)	$\langle P_2\rangle_A$	$\langle P_2\rangle_F$	$\langle P_4\rangle_F$
300	0.57	39.6	0.57	0.57	−0.26	40.4	0.57	0.57	−0.01	41.4	0.59	0.59	0.20	42.5	0.63	0.63	0.37
340	0.53	39.6	0.53	0.56	−0.27	40.4	0.53	0.56	−0.02	41.4	0.55	0.58	0.18	42.5	0.59	0.61	0.35
365	0.46	39.6	0.46	0.52	−0.35	40.4	0.47	0.52	−0.10	41.4	0.48	0.53	0.11	42.5	0.51	0.56	0.28
380	0.38	39.6	0.38	0.46	−0.46	40.4	0.38	0.45	−0.20	41.4	0.40	0.46	0.01	42.5	0.42	0.47	0.18

(PS5). The investigated 1,3,4-oxadiazoles absorb light mostly in the UV region, where two (OXA11) or three (OXA39) well separated bands are observed. The efficient fluorescence emission is observed for OXA39 in PS5 but not for OXA11 in this liquid-crystalline polymer. In uniformly oriented films of ZLI 1695 and PS5, both for OXA11 and OXA39, the orientation of the long molecular axis in the direction of macroscopic orientation of the liquid-crystalline matrix is preferred. For OXA11 and OXA39 in ZLI 1695, the values of $\langle P_2 \rangle$ orientational order parameter are determined at room temperature from the polarized absorption spectra. Both the $\langle P_2 \rangle$ and $\langle P_4 \rangle$ values for OXA39 in PS5 can be obtained from the analysis of the components of polarized absorption and fluorescence. The possibility to orient OXA11 molecules in PS5 matrix and the relatively high fluorescence efficiency of the 1,3,4-oxadiazole in the polysiloxane can be treated as the starting-points in consideration of this system to a matter of applications in OLEDs, for example.

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