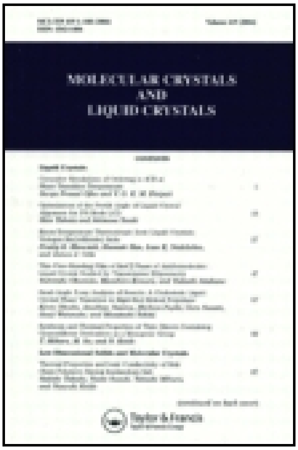

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Study of Orientational Order in Uniaxial Liquid Crystal Phases by Means of Optical Spectroscopy Methods

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Study of Orientational Order in Uniaxial Liquid Crystal Phases by Means of Optical Spectroscopy Methods

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The polarized absorption and emission spectra of dichroic fluorescent dye dissolved in two members of homologous series of alkoxy-cyanobiphenyls have been recorded as a function of temperature in the smectic A and nematic phases. From these spectra the order parameter and the orientational distribution function of the molecules in the dye-liquid crystal mixture have been estimated. The results have been compared with the data obtained from the optical birefringence measurements.

Keywords: liquid crystal; dichroic dye; absorption; fluorescence; order parameter

INTRODUCTION

The mechanical, optical, electrical and magnetic properties of liquid crystalline materials are strongly dependent on the molecular orientation. Therefore, the knowledge of the degree of order is of primary importance in understanding various aspects of physics of liquid crystals on the one hand and in most applications of these materials on the other. However, although liquid crystal phases are characterized by long-range order, this order does not usually extend over the whole sample. Liquid crystal samples are constituted by domains, in which the preferred direction of the molecules orientation varies from one domain to another. To obtain a single-domain sample the bulk alignment of the molecules must be induced, which can be achieved using the electric or magnetic fields or by treating the substrate surface by surfactant materials[1].

In a nematic phase the molecules are, on average, aligned with their long axes parallel to each other, which leads macroscopically to a preferred direction, described by the director **n** and the centres of mass of the molecules are placed randomly. Therefore, in this phase only a long-range orientational order occurs. In smectic phases the molecular centres of mass sit on the planes perpendicular to the preferred axis, leading to a layer structure, so not only orientational but also positional order occurs. Experimental determination of the degree of the molecular order in liquid crystal samples has been carried out extensively by a wide variety of methods. Among them, the classical methods of optical spectroscopy are well suited to study the long-range orientational order in the uniaxial (e.g. nematic and smectic A) liquid crystal phases. Doping the liquid crystal matrix with a fluorescent probe and utilizing the guest-host effect[2], the information concerning the molecular orientation can be obtained from both polarized absorption and fluorescence measurements[3-5].

In this paper we have studied the long-range orientational order of 4'-n-hexyloxy-4-n-cyanobiphenyl (6OCB) and 4'-n-octyloxy-4-n-cyanobiphenyl (8OCB) doped with dichroic fluorescent dye using the polarized light spectroscopy methods. Liquid crystals 6OCB and 8OCB, chosen for our studies, are of considerable importance in technological applications, because they, similar as other members of the alkoxy-cyanobiphenyl homologous series, form colorless, photochemically stable mesophases with strong positive dielectric anisotropy.

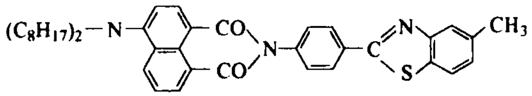
EXPERIMENTAL

The mesogens 4'-n-hexyloxy-4-n-cyanobiphenyl (6OCB) and 4'-n-octyloxy-4-n-cyanobiphenyl (8OCB) were synthesized in the Laboratory of Professor R. Dąbrowski at the Military Academy of Technology in Warsaw and were used without further purification. The temperatures of the phase transitions were in the agreement with the literature[6,7] and were as follows:

6OCB: C - 331.2 K - N - 349.7 K - I

8OCB: C - 327.7 K - S_A - 340.2 K - N - 353.2 K - I.

As a guest the dichroic dye, derivative of the bicarboxylic acid with the following chemical structure:



were used. The dye was synthesized and chromatographically purified in the Institute of Physics, Łódź University of Technology, Poland and was dissolved in liquid crystal matrices at a concentration of 10^{-2}M/l. It had been found[8] that it has brilliant yellow color and emits green fluorescence light with very high quantum yield.

The polarized absorption spectra were recorded by means of a double beam spectrophotometer SPECORD M40 (Carl Zeiss Jena, Germany). The polarized fluorescence spectra were obtained using a home-made photon-counting fluorimeter in the π geometry, i.e. the exciting light beam was perpendicular to the surface and the fluorescence light was monitored perpendicularly from the same side of the cell[4]. The 436 nm line of the high pressured mercury lamp was used as an excitation source. Corrections for the photomultiplier spectral sensitivity and for the different response of the device set with various directions of polarization were made. Both the spectrophotometer and fluorimeter were equipped with neutral UV polarizers. The measurements were carried out as a function of temperature using "sandwich" cells of 20 μm thickness. The planar orientation of the liquid crystal and dye molecules was achieved by treating the glass surfaces of the cells with polyimide and by additional rubbing process. This procedure gives a good homogeneous orientation of the molecules in a thin layer, which was controlled with a polarizing microscope. The temperature of the cells was regulated and controlled with an accuracy of ±0.1 K.

RESULTS AND DISCUSSION

In our considerations we have assumed for simplicity that the mesogenic molecules are both rigid and posses $C_{\infty V}$ symmetry and the fluorescence probe molecule is fairly rigid, at least in the ground state and has effective cylindrical symmetry with transition moments tilted away from the effective symmetry axis. Such assumptions, although satisfied only in the first approximation, give the possibility to obtain from the classical methods of optical spectroscopy not only the second-rank order parameter $<P_2>$, but also the fourth-rank order parameter $<P_4>$, which provides further information about the orientational order as it is more sensitive for the molecular fluctuations. $<P_2>$ and $<P_4>$ are, respectively, the averages of the second and fourth Legendre polynomials, which constitute a set of order parameters for the anisotropic matrix[9] and are defined as follows:

$$<P_L> = \frac{\int_0^{\pi/2} P_L(\cos\theta) f(\theta) \sin\theta \, d\theta}{\int_0^{\pi/2} f(\theta) \sin\theta \, d\theta}, \quad L = 2,4. \qquad (1)$$

θ denotes here the deviation of a molecular axis about which the rotational symmetry has been assumed with respect to the director **n**.

On the basis of the optical absorption anisotropy of the dye dissolved in liquid crystal matrix it is possible to calculate the order parameter $\langle P_2 \rangle$ from the following formula[10]:

$$\langle P_2 \rangle = \frac{A_\parallel - A_\perp}{A_\parallel + A_\perp} \, \frac{2}{3\cos^2\alpha - 1}, \qquad (2)$$

where $A_\parallel$ and $A_\perp$ are absorbances of the light polarized parallel and perpendicular, respectively, to the director and α is the angle between the direction of the absorption transition moment and the long molecular axis of the dye.

The method allowing to calculate the order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ from the polarized fluorescence measurements had been developed by Wolarz on the basis of the theory given by Zanoni[3] and is described in details in[5,11]. In order to use this method it is necessary to know the angle δ between the absorption and emission transition moment directions of the dye from the independent experiment. For the dye used in this paper it is equal to 28.1°[5]. However, the angle α has been calculated by using the procedure described in[5] and the experimental data of the fluorescence intensities and the absorbances of the appropriate polarized components obtained for the dye dissolved in 8OCB at the lowest temperature in the smectic A phase. We have supposed, that at this temperature, because of the high viscosity, the thermal molecular motions are strongly hindered and the rotational relaxation time is much greater than the lifetime of the excited state of the fluorescent guest molecule. Therefore, in this case, $\langle P_2 \rangle$ obtained from the fluorescence measurement must be equal to that determined on the basis of the polarized absorption spectra. We have obtained the value of α being equal to (6±4)°.

Figure 1 presents the order parameter $\langle P_2 \rangle$, estimated from the absorption measurements (circles) and $<P_2>$ and $<P_4>$, determined from the fluorescence measurements (crosses) as a function of the reduced temperature T^* ($T^*=T/T_{NI}$) for the dye dissolved in 6OCB and 8OCB. For calculations of the order parameters, the values of the absorbance and fluorescence intensity have been taken at the wavelengths corresponding to the maxima of the absorption (λ_A^{max}=439 nm) and emission (λ_F^{max}=510 nm), respectively. The squares in these figures represent the values of $<P_2>$ obtained on the basis of the refractive indices measurements by means of the Vuks approximation for 6OCB[7] and from optical birefringence measurements by using the method described in[12] for 8OCB[13].

In principle, from the absorption and fluorescence measurements of the dye dissolved in the liquid crystal, only the order parameters of the guest molecules can be determined, as the guest-host interactions can cause perturbation in the molecular alignment and the order of the host does not need to be the same as that of the guest. From the data presented in figure 1 follows, that the dependence of the order parameter $<P_2>$ on the reduced temperature obtained by using the optical spectroscopy methods for 6OCB and 8OCB doped with the dye is similar to that determined from the anisotropy of the refractive index for pure liquid crystals. The absolute values, however, differ only slightly. This means, that in this case no significant difference in the orientational order for the dichroic dye and for the liquid crystals occurs and the molecular orientation of the guest reflects very well the orientation of the host molecules.

The order parameters $<P_2>$ estimated from the absorption and fluorescence measurements at the same reduced temperatures for 8OCB are equal to each other only to the certain temperature in the smectic A phase. In the vicinity of the smectic-nematic transition the both values begin to differ and this difference increases in the nematic phase, what is also observed for 6OCB. This effect arises in general from the fact that the fluorescent molecule is excited at a certain orientation $\Omega_0(\theta)$ and is observed after a time t at an orientation $\Omega(\theta')$. The nematic phase is in less degree viscous than the smectic A phase and this time is comparable to the relaxation time of the molecule, therefore, the influence of the rotational motion on the fluorescence depolarization cannot be further neglected.

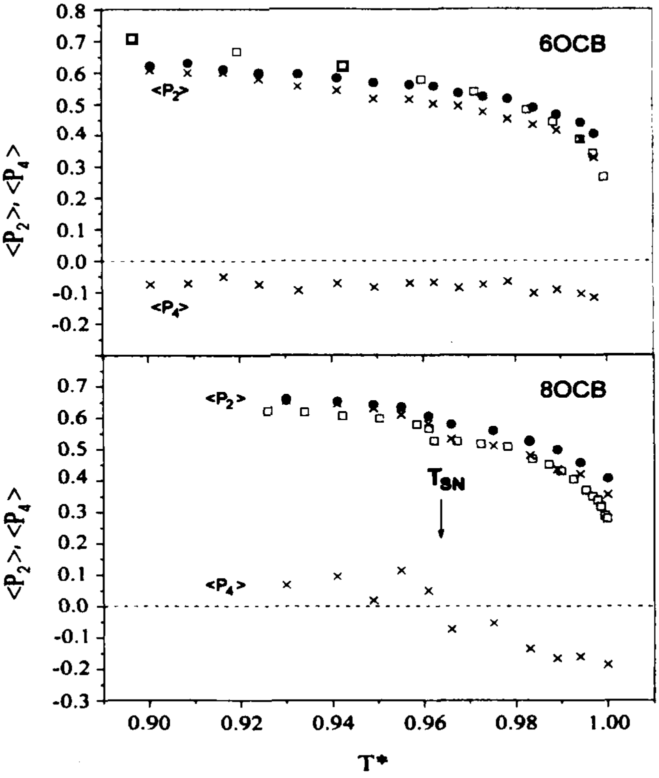


FIGURE 1 Order parameters for dye-liquid crystal mixtures obtained from the absorption (circles) and fluorescence (crosses) measurements. Squares represent $<P_2>$ value determined from the anisotropy of the refractive index.

As regards the order parameter $\langle P_4 \rangle$, it is seen, that it is positive only in the smectic A phase, whereas in the nematic phase is always negative. Such behaviour of $\langle P_4 \rangle$ had been already observed for many dye-liquid crystal mixtures[4,11,14-17], although it is not in agreement with the theoretical predictions[18,19]. One of the possible explanation of the negative $\langle P_4 \rangle$ values for 6OCB and 8OCB seems to be the molecular association caused by the presence of the strong polar terminal - CN group.

Knowing $\langle P_4 \rangle$ it is possible to obtain the truncated distribution function $f(\theta)$[14,15], which fully describes the orientation of the molecules with respect to the director. The examples of this function for the dye-8OCB mixture in the smectic A (T^*=0.941) and nematic (T^*=0.975) phases are presented in figure 2. It is seen, that the low value of $\langle P_4 \rangle$ strongly influences the shape of the distribution function: at the temperature corresponding to the nematic phase $f(\theta)$ is significantly broadened with respect to that determined in the smectic A phase.

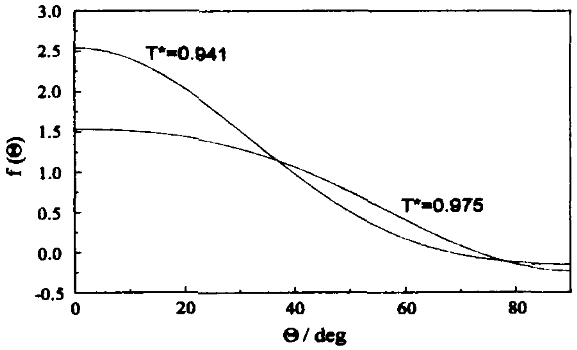


FIGURE 2 Molecular distribution function, $f(\theta)$ in the smectic A (T^*=0.941) and nematic (T^*=0.975) phases for dye-8OCB mixture.

Acknowledgements

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