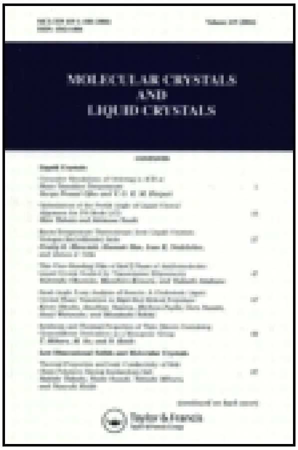

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Molecular Orientation in Liquid Crystalline Side Chain Polymers Doped with Dichroic Dye as Studied by Optical Spectroscopy Methods

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Molecular Orientation in Liquid Crystalline Side Chain Polymers Doped with Dichroic Dye as Studied by Optical Spectroscopy Methods

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The polarized absorption and emission spectra of fluorescent stilbene dye dissolved in two side chain liquid crystalline polysiloxanes have been recorded as a function of temperature in the mesomorphic and glassy phases. From these spectra the order parameters $<P_2>$ and $<P_4>$ as well as the orientational distribution function of the side mesogenic groups have been estimated. The results have been compared with the data obtained for low molecular weight liquid crystal by using the same optical methods.

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

INTRODUCTION

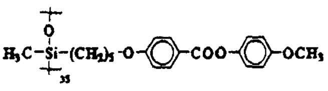
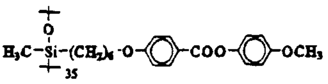
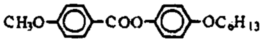
Side chain liquid crystalline polymers combine the unique physical properties of low molecular weight liquid crystals with viscoelastic properties of polymers in a single material[1–4]. Therefore, they have gained great interest both from scientific and technological point of view. The basic study of this type of polymers gives better understanding of specific features and orienting processes in both polymers and liquid crystals. In practice the liquid crystalline polymers can be used in display or optical memory devices, waveguides in optical communications, selective optical filters and reflectors, as well as in non-linear optics. For many applications a macroscopically oriented domain over a large area is required. The bulk alignment of the mesogenic side chains of polymers can be achieved, similarly as for low molecular liquid crystals, using electric or magnetic field or by treating the substrate surfaces by surfactant molecules.

In this paper we have determined the long-range orientational order of two siloxane side chain polymers in uniaxial liquid crystalline phases by means of optical spectroscopy methods. On the basis of the measurements of the polarized absorption and fluorescence spectra of the dichroic stilbene dye dissolved in the polymeric matrix (guest-host system) we have calculated the order parameters $<P_2>$ and $<P_4>$ and have estimated the statistical molecular distribution function of the mesogenic groups in the polysiloxanes-dye mixtures investigated. The results are compared with the data obtained for the low molecular weight liquid crystal having molecular structure very similar to that of the side groups of polymers.

EXPERIMENTAL

The liquid crystalline side chain polysiloxanes given in Table 1 (LCP **1** and LCP **2**) were prepared in the Institute of Chemistry at the University of Agriculture in Warsaw, and the low molecular liquid crystal (LC **1**) was synthesized in the Institute of Chemistry at the Military University of Technology in Warsaw. The molecular structure of these substances and the mesophase ranges, estimated by means of a polarized light microscopy, are given in Table 1.

TABLE 1. Molecular structure and mesophase ranges of substances investigated.

Substance	Molecular structure	Transition temperature/K		
LCP 1		G - N 350		N - I 382
LCP 2		G - S 278	S - N 320	N - I 380
LC 1		Cr - N 326		N - I 351

The dye 4-dimethylamino-4'-nitrostilbene (DANS) was used as a fluorescent probe. It was dissolved in the liquid crystalline matrices at a concentration of 0.3% wt. It was found that addition of such amount of the dye causes a decrease of the nematic-isotropic phase transition temperature, T_{NI} of LCPs of about 2 K, and T_{NI} of LC 1 of about 1 K.

The absorption spectra were recorded by means of a double beam spectrophotometer SPECORD M40 (Carl Zeiss Jena), whereas the polarized components of the fluorescence spectra were obtained using a home-made photon-counting fluorimeter. Experimental details have been reported elsewhere[5]. The measurements were carried out as a function of temperature using "sandwich" cells of 10 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 verified with a polarizing microscope. The temperature of the cells was controlled with an accuracy of ±0.1 K.

RESULTS AND DISCUSSION

Long-range orientational order in the liquid crystalline phases arises because of the tendency of the rod-like molecules to align their long axes along a certain preferred direction, described by the director, **n**. In liquid crystalline side chain polymers the orientational order is related to the mesogenic side groups, neglecting any possible anisotropic orientation of the backbone[1]. Doping the liquid crystal with a fluorescent dye and utilizing the guest-host effect[6], the orientational order in the uniaxial phases may be evaluated from the polarized absorption and fluorescence measurements. In principle, by these methods only the degree of order for the guest molecules can be determined. However, choosing a dye probe with a molecular structure similar in size and shape to that of the molecules of the mesogenic host, no significant difference in the orientational order for the pure mesophase and for the guest dissolved in the anisotropic host is expected and the assumption that the orientation of the guest reflects the orientation of the matrix is justified.

On the basis of the optical absorption anisotropy of the dye dissolved in the liquid crystal matrix it is possible to calculate the average over the second Legendre polynomial, $<P_2>$ using the following formula[7]:

$$<P_2> = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp}, \tag{1}$$

where $A_\parallel$ and $A_\perp$ are the absorbances of the light polarized parallel and perpendicular, respectively, to the director, **n**.

Equation (1) is valid if the angle between the vector of the absorption transition moment and the long axis of the dye molecule is equal to 0°. For the dye probe DANS the absorption transition moment of the longest wavelength is polarized almost parallel to the long axis of the molecule[8].

The averages over Legendre polynomials, $<P_L>$ constitute a set of order parameters for the anisotropic matrix[9] and are defined as follows:

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

θ is the angle between the long molecular axis and the director, **n**.

The method allowing to calculate the order parameters, $<P_2>$ and $<P_4>$ from the polarized fluorescence measurements had been developed on the basis of the theory given by Zannoni[10] and is described in details in[11]. The equations, from which the order parameters can be calculated, are solvable if the angle δ between the absorption and the emission oscillators of the dye is known. We have calculated this angle from the same equations but for the data from the absorption and fluorescence measurements of DANS in LCP 1 at room temperature. The probe was then in the glassy state and one could suppose that no thermal motions reducing the emission anisotropy occur. Therefore, in this case, $\langle P_2 \rangle$ obtained from the fluorescence measurements must be equal to that determined on the basis of the polarized absorption spectra. This condition reduces the number of unknown parameters, and thus, the desired angle can be calculated. We have obtained the value of δ equal to $(12\pm2)^\circ$.

Figure 1 presents the order parameter, $\langle P_2 \rangle$, estimated from the absorption measurements (circles) and $\langle P_2 \rangle$ and $\langle P_4 \rangle$, determined from the fluorescence measurements (crosses) as a function of the reduced temperature, $T^*=T/T_{NI}$ for DANS dissolved in LCP 1 (a), LCP 2 (b) and LC 1 (c). 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}=450 nm) and the emission (λ_F^{max}=610 nm for LCPs and 630 nm for LC 1), respectively.

From the results presented in Fig. 1a it is seen, that the glassy phase cannot be strictly treated as a "frozen" state, because small, but measurable decrease of the order parameter $\langle P_2 \rangle$ is observed. This fact indicates that a small perturbation of the orientational order occurs in this phase. The changes in the transmitted light intensity under polarizing microscope, during temperature rise in the glassy phase, additionally confirm this fact. In the mesophase the temperature dependence of the order parameter of side chain liquid crystalline polymers corresponds to that of the low molecular weight liquid crystal. It is seen, however, that the values of $\langle P_2 \rangle$

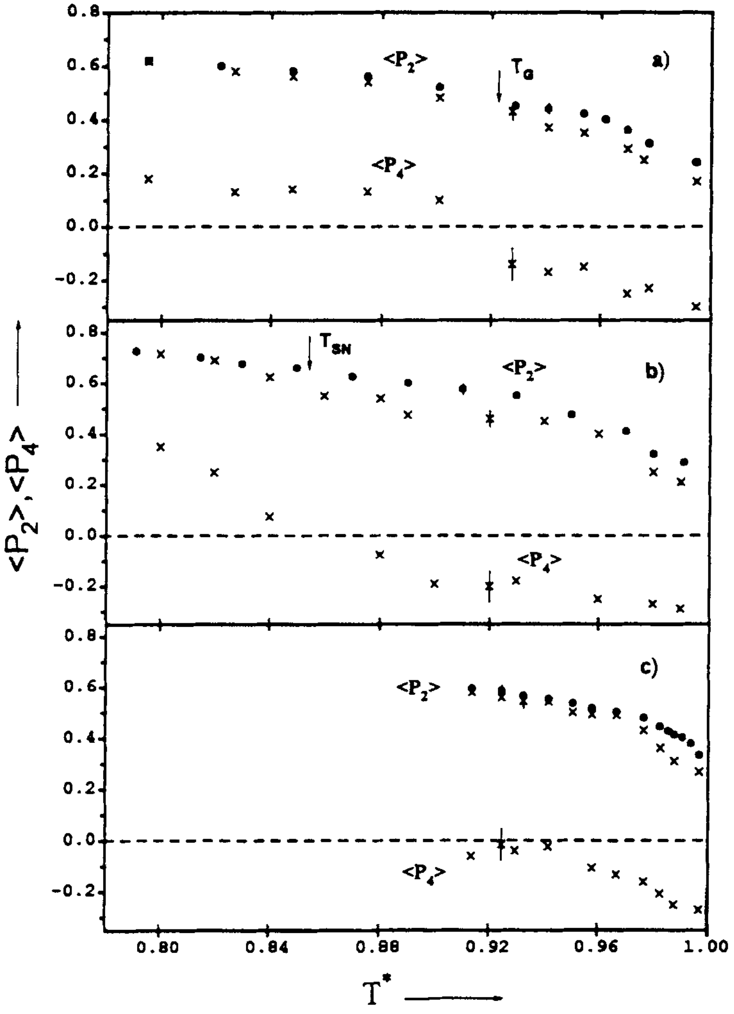


FIGURE 1 Order parameters, $\langle P_2\rangle$ and $\langle P_4\rangle$ *versus* reduced temperature for LCP 1 (a), LCP 2 (b) and LC 1 (c) doped with DANS: circles - $\langle P_2\rangle$ determined from absorption, crosses - $\langle P_2\rangle$ and $\langle P_4\rangle$ determined from fluorescence measurements.

determined from the fluorescence depolarization are always somewhat lower than those obtained from the polarized absorption spectra at the same reduced temperature. This effect is especially remarkable in the nematic phase. It can be due to the rotational motions of the fluorescent molecules during the lifetime in the excited state, which affect the emission anisotropies.

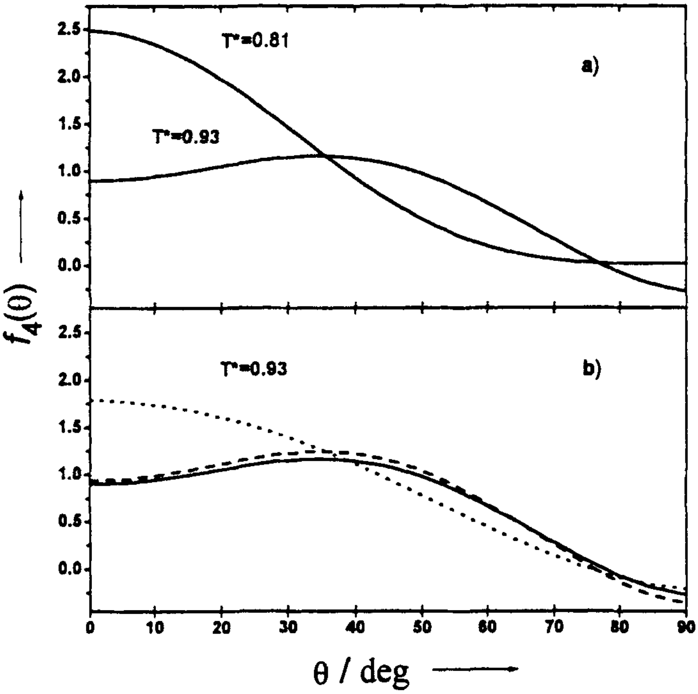


FIGURE 2 Molecular distribution functions, f_4 (θ) for : a) LCP 1 - DANS mixture in the glassy (T^*=0.81) and nematic (T^*=0.93) phases ; b) LCP 1 (solid line), LCP 2 (dashed line) and LC 1 (dotted line) doped with DANS in the nematic phase.

As regards $<P_4>$, it is seen that in the glassy and smectic phases these values are positive, whereas in the nematic one they are negative. Such behavior of $<P_4>$ had been also previously observed [5,12-16], although it is not in agreement with the theory. The negative value of $<P_4>$ influences strongly the breadth of the molecular distribution function [5], $f_4(\theta)$, what can be distinctly seen in Fig.2a.

Fig.2b shows $f_4(\theta)$ for all the substances investigated at $T^*=0.93$ (in the nematic phase). Comparing the shapes of the distribution function, it is seen that the orientational order of the small liquid crystal molecules is more developed than that of the mesogenic groups attached to the rigid polymer backbone, which interferes with the uniform molecular alignment. However the length of the flexible spacer does not cause the significant difference in the long-range orientational order of the polymer side groups in the nematic phase.

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