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Order parameter of side groups of a polysiloxane in liquid crystalline uniaxial phases

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The orientational order of a liquid crystalline side chain polysiloxane has been investigated by means of polarized light spectroscopy and dielectric relaxation measurements. The order parameters $\langle P_2 \rangle$ and $\langle P_4 \rangle$ have been determined as a function of the temperature for the smectic and nematic phases. The orienting properties of the polysiloxane investigated have been compared with those of a polysiloxane with the same mesogenic groups, but a shorter spacer.

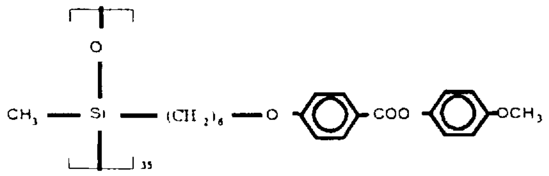
1. Introduction

Thermotropic liquid crystalline side chain polymers have attracted considerable attention during the last decade. From the scientific point of view, these substances are very interesting because of the possibility of combining the properties of low molecular mass liquid crystals and a polymer body in a single specific material [1–3]. The practical interest stems mainly from the prospect of their application in electro-optical display devices and optical data storage [4–6]. Furthermore, polymers with mesogenic side chains can be used as non-linear optical media [7]. In most applications, the liquid crystal molecules must be macroscopically aligned. The side chains of liquid crystalline polymers can be oriented by an external field—mechanical, electric or magnetic, in a similar manner to small liquid crystal molecules. Information about such orientational order in mesomorphic uniaxial phases can be obtained through the estimation of the orientation parameters, $\langle P_2 \rangle$ and $\langle P_4 \rangle$, as well as the molecular distribution function, f.

In this paper we have determined the long range orientational order of a liquid crystalline polysiloxane with mesogenic side chains by using polarized optical spectroscopy methods and dielectric relaxation time measurements. The results of this work have been compared with an earlier study of the orientational order for the polysiloxane with the same mesogenic groups, but with a different length of spacer connecting the polymer backbone and the side chains.

2. Experimental

The liquid crystalline side chain polysiloxane (PS6) having the following structure



was prepared in the Department of Chemistry, Warsaw University of Agriculture (Warsaw, Poland) using commercial poly(methylhydrogensiloxane) with an average degree of polymerization of 35 (Merck, Germany). This polymer was first synthesized by Finkelmann and Rehage [8].

The 4-dimethylamino-4′-nitrostilbene (DANS) used as a fluorescent probe was synthesized and chromatographically purified at the Institute of Dyes, Łódź Technical University (Łódź, Poland). DANS was dissolved in the polymeric host at a concentration of about 1·8 wt %.

The absorption spectra were measured spectrophotometrically using a Specord M-40 (Carl Zeiss Jena), and fluorescence spectra were recorded in Π geometry using a home-made photon counting fluorimeter. The 436 nm line of a high pressure mercury lamp was used to excite the fluorescence. Both in the absorption and the fluorescence measurements, UV polarizers were used. Corrections for the photomultiplier spectra sensitivity and for the response of the device with various directions of polarization were made.

The measurements of the absorption and fluorescence spectra were made as a function of the temperature using oriented samples in 'sandwich' cells of 7 μm thickness. The orientation of the samples was achieved by treatment of the glass surfaces of the cells with polyimide and subsequent rubbing.

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For the dielectric measurements in the frequency range from 10 Hz to 13 MHz, a Hewlett-Packard 4192 A self balancing bridge, controlled by a modified Atari Mega ST II computer, was used. The details of the experiment have been described earlier [9]. The measurements were made, using 'sandwich' cells of 100 μm thickness, as a function of temperature for the nematic and isotropic phases. A magnetic field of 1·2 T was applied to orient the samples.

In all the experiments, the measuring cells were filled with the pure polymer or the polymer–DANS mixture in the isotropic phase. Then the samples were cooled very slowly under the influence of the orienting forces (surface interaction or magnetic field) to produce the mesomorphic phase. The procedure gave very good orientation of the mesogenic groups in the thin layers. The quality of orientation of the samples and the temperature ranges of the mesophases were checked by polarizing microscopy in conjunction with a heating stage.

3. Theoretical background

In liquid crystalline side chain polymers, the orientational order depends upon the mesogenic groups [1]. Doping the polymer with a fluorescent dye and utilizing the guest–host effect [10], the orientational order in uniaxial phases may be evaluated using classical methods of optical spectroscopy: polarized absorption and fluorescence measurements. In principle, these methods determine only the degree of order for the guest molecules. However, by choosing a probe with a molecular structure similar in size and shape to that of the mesogenic groups of the 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 well satisfied.

On the basis of the optical absorption anisotropy, one can calculate the average of the second Legendre polynomial, $\langle P_2 \rangle$ using the following formula [11]:

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

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances of the light polarized parallel and perpendicular to the orientation axis of the sample, respectively.

The Legendre polynomial averages, $\langle P_L \rangle$ constitute a set of order parameters for the anisotropic matrix and are defined as follows:

$$\langle P_L \rangle = \frac{\int_0^{\pi} P_L(\cos\beta) f(\beta) \sin\beta \, d\beta}{\int_0^{\pi} f(\beta) \sin\beta \, d\beta}, \tag{2}$$

where the angle β denotes the mean deviation of a molecular axis with respect to the director. The director is the symmetry axis of the orientational molecular distribution function $f(\beta)$.

From the fluorescence measurements, the emission anisotropies, R_1 and R_2 for excitation with light polarized, respectively, parallel and perpendicular to the orientation axis can be calculated from the following formula:

$$R_{1,2} = \frac{J_{\parallel} - J_{\perp}}{J_{\parallel} + 2J_{\perp}}, \tag{3}$$

where $J_{\parallel}$ and $J_{\perp}$ are the intensities of emission polarized parallel and perpendicular to the orientation axis, respectively, measured in the parallel geometry. They require correction for instrumental, concentration and volume factors.

If we assume that the rotational diffusion time, τ_R is much longer than the lifetime τ_F of the excited state of the fluorescent molecule, then R_1 and R_2 can be related with $\langle P_2 \rangle$ and $\langle P_4 \rangle$ as follows [12].

$$R_1 = \frac{\left[\frac{2}{5} + \frac{11}{7}\langle P_2 \rangle + \frac{36}{35}\langle P_4 \rangle\right] P_2(\cos\delta)}{1 + 2\langle P_2 \rangle}, \tag{4}$$

$$R_2 = \frac{\left[\langle P_2 \rangle - \frac{2}{5} - \frac{21}{35}\langle P_4 \rangle\right] P_2(\cos\delta)}{1 - \langle P_2 \rangle + 2\left[\frac{1}{5} - \frac{2}{7}\langle P_2 \rangle + \frac{3}{35}\langle P_4 \rangle\right] P_2(\cos\delta)}, \tag{5}$$

where δ is the angle between the absorption and emission oscillators.

Equations (1), (4) and (5) are valid if the angle between the vector of the absorption transition moment and the long axis of a dye molecule is equal to 0°. For the dye probe DANS, the absorption transition of the longest wavelength is polarized almost parallel to the long axis of the molecule [13, 14].

The simplest form of the undisturbed orientational distribution function of the molecules, $f(\beta)$ is the following [15, 16]:

$$f(\beta) = C \exp\left[-\frac{q}{kT}\sin^2\beta\right], \tag{6}$$

where q is the height of the nematic potential barrier, k is Boltzmann's constant and T is the absolute temperature.

The intermolecular forces, leading to the potential barrier, give rise to the orientation of the mesogenic molecules. It is clear that when the degree of order increases, the rotation of the permanent electric dipole around the molecular short axis becomes more and more hindered, which means that the dielectric relaxation frequency connected with this rotation (occurring in the parallel components of the electric permittivity) shifts to lower frequencies.

Meier and Saupe [16] and Martin *et al.* [17], extended the Debye theory of dielectric relaxation in liquids to nematic liquid crystals and showed that the relaxation time, τ in the presence of the nematic potential is larger than the relaxation time, τ_0 for $q = 0$ (no nematic potential) by a factor

$$g = \frac{\tau(q \neq 0)}{\tau_0(q = 0)} \tag{7}$$

called the retardation factor.

τ_0 can be identified with the relaxation time, τ_{iso} in the isotropic state for compounds having a Debye-type relaxation spectrum in this phase. The polymer used in our study satisfies this requirement in the first approximation [18]. In our experiments, we have determined τ_0 by extrapolation from measurements of the dielectric constant, ε_{iso} for the isotropic phase.

Knowing τ_0 and determining τ from the relaxation process observed in the parallel component of the electric permittivity, we have calculated the retardation factor, g and the height of the potential barrier, q, using the plots given by Martin *et al.* [17]. Next the distribution function, $f(\beta)$ and the order parameter, $\langle P_2 \rangle$ have been obtained from equations (6) and (2), respectively.

4. Results

The microscope observations show that both the pure polymer PS6 and the mixture of PS6 with DANS are in the nematic phase from about 320 K. At lower temperatures, the texture observed suggests the existence of the smectic A phase. The nematic–isotropic phase transition occurs at $T_{\text{NI}} = 380$ K for pure PS6 and this temperature decreases in the presence of DANS to $T_{\text{NI}} = 378$ K. Similar decreases in T_{NI} for liquid crystalline side chain polymers after dye addition have been observed previously [19, 20].

Figure 1 shows the order parameter, $\langle P_2 \rangle$ obtained from the polarized absorption and fluorescence spectra, as well as on the basis of the dielectric measurements, as a function of the reduced temperature T^*. $T^* = T/T_{\text{NI}}$, where T_{NI} is the clearing temperature either for pure PS6 or for the PS6–DANS mixture and T is the temperature of the measurement (in K). The dashed line in figure 1 depicts the theoretical results obtained from the Maier–Saupe theory [15] of nematics.

In the table, the time of the electric dipole relaxation around the molecular short axis of the mesogenic groups (δ-relaxation process [18]), τ, the retardation factor, g and the height of the potential barrier, q, are gathered together. For more convenient comparisons of the results obtained here with others from the literature, the values of q are given in two different units.

Figure 2 presents the order parameters determined both from the polarized absorption ($\langle P_2 \rangle$—squares) and fluorescence ($\langle P_2 \rangle$—circles, $\langle P_4 \rangle$—triangles) spectra. Additionally in this figure, the values of $\langle P_2 \rangle$ and $\langle P_4 \rangle$, obtained using the same methods, for the polysiloxane with the same mesogenic groups, but having a shorter spacer connecting the backbone with the side chains (PS3) [21] are shown for comparison. It is seen that the length of the spacer does not affect significantly the long range orientational order.

For calculations of $\langle P_2 \rangle$ from the absorption and fluorescence measurements, the values of the absorbances and the fluorescence intensities were taken at the wavelength corresponding to the maximum of the absorption ($\lambda_{\text{A}}^{\text{max}} = 450$ nm) and emission ($\lambda_{\text{F}}^{\text{max}} = 600$ nm) bands, respectively. The angle δ between the absorption and emission oscillators of the DANS molecule, which is needed to obtain the order parameters from equations (4) and (5), was estimated on the basis of the absorption and fluorescence measurements of DANS in PS6 at room temperature. The probe is then in the smectic phase and the viscosity of the mixture is high. This allowed us to suppose that at this temperature the thermal molecular motions are strongly hindered and have a negligibly small effect on the emission anisotropy. By knowing $\langle P_2 \rangle$ from absorption measurement (equation 1), $\langle P_4 \rangle$ and $\cos \delta$ were determined by solving equation (4) and (5). We found δ to be 13°, which is in good agreement with the value $\delta = 9°$ obtained by us for DANS dissolved in an acrylate liquid crystalline polymer [20] and with $\delta = 17°$ calculated by Chapoy *et al.* [22], for DANS in the low molar mass liquid crystal MBBA. The angle $\delta = 13°$ was assumed to be constant in

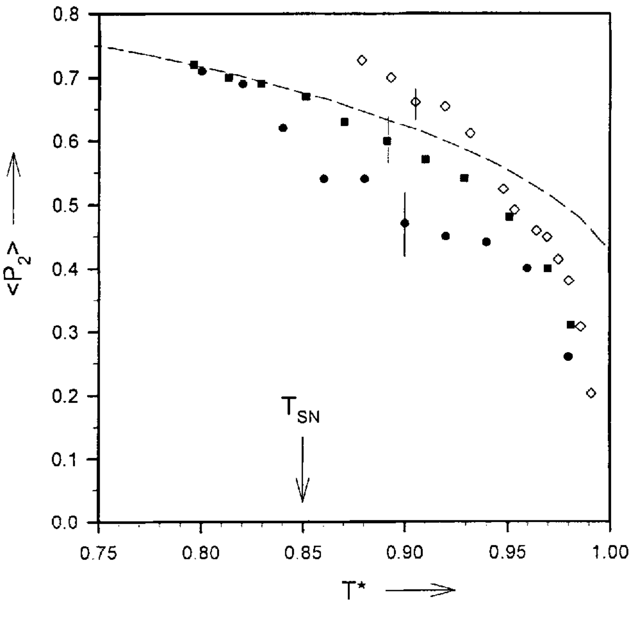

Figure 1. Order parameter, $\langle P_2 \rangle$ versus reduced temperature for PS6 doped with DANS obtained from dielectric (diamonds), absorption (squares) and fluorescence (circles) measurements. Dashed line: Maier–Saupe theory [15]. Arrow indicates approximate value of the smectic–nematic transition temperature.

Relaxation time τ, retardation factor g and height of potential barrier q (and $q_{\mathrm{mol}} = N_{\mathrm{A}}q$) for rotation around the short axis of the mesogenic group of PS6. Error of τ was less than 5 per cent.

T^*	$\tau \times 10^6$/s	g	q/eV	q_{mol}/kJ mol^{-1}
0·920	810	15·5	0·15	14·5
0·932	376	10·6	0·13	12·5
0·948	125	6·3	0·11	10·6
0·954	87·7	5·5	0·10	9·6
0·970	40·2	4·5	0·09	8·7
0·980	20·0	3·2	0·08	7·7
0·991	8·0	1·8	0·04	3·9

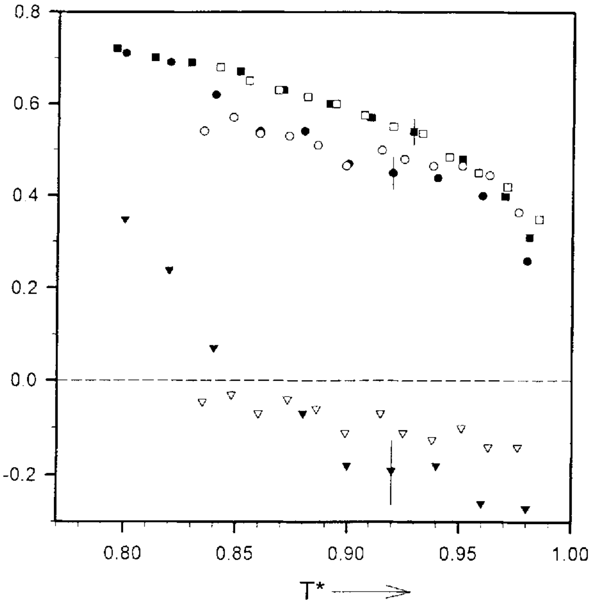

Figure 2. Order parameters, $\langle P_2\rangle$ and $\langle P_4\rangle$ versus reduced temperature for PS6 (number of carbon atoms in spacer $n = 6$) and PS3 ($n = 3$) doped with DANS: squares—$\langle P_2\rangle$ determined from absorption, circles—$\langle P_2\rangle$ and triangles—$\langle P_4\rangle$ determined from fluorescence measurements. Filled symbols: PS6, open symbols: PS3 [21].

our experimental temperature range and the $\langle P_2\rangle$ and $\langle P_4\rangle$ values were determined from the measured fluorescence intensities and equations (4) and (5) using this value of the intermolecular angle.

Knowing the $\langle P_2\rangle$ and $\langle P_4\rangle$ parameters, one can obtain the truncated distribution function $f_4(\beta)$ [22, 23]:

$$f_4(\beta) = \frac{1}{2} + \frac{5}{2}\langle P_2\rangle P_2 + \frac{9}{2}\langle P_4\rangle P_4. \tag{8}$$

In figure 3 the distribution functions $f_4(\beta)$ for PS6 doped with DANS in the smectic ($T^* = 0{\cdot}82$) and nematic ($T^* = 0{\cdot}88$) phases are plotted.

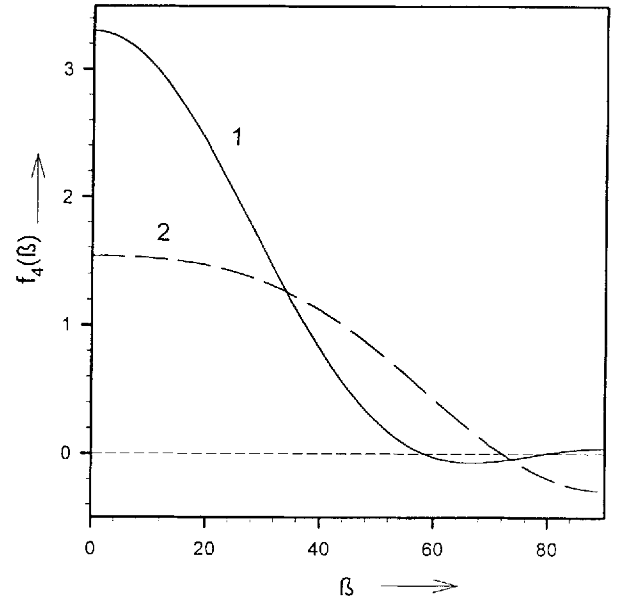

Figure 3. Molecular distribution function $f_4(\beta)$ for PS6 doped with DANS in the smectic (1) and nematic phases (2).

5. Discussion

From figure 1, it is seen that the changes in the order parameter, $\langle P_2\rangle$ with rising temperature for pure PS6 and the mixture of PS6 with DANS are characteristic of those for most low molar mass nematics and are in substantial agreement with theoretical prediction. The differences observed in the vicinity of the clearing point between the experimentally obtained $\langle P_2\rangle$ values and those calculated from the Maier–Saupe theory can arise from the fact that this theory was derived for small molecular nematics. In liquid crystalline polymers, the mesogenic segments are attached to the rigid backbone and therefore their translational and rotational motions are, to some extent, restricted. The resulting formation of 'clusters' with different orientations could lead to the decrease in $\langle P_2\rangle$.

The values of the order parameter, $\langle P_2\rangle$ determined at the same reduced temperature by using various methods differ from each other. The differences between $\langle P_2\rangle$ estimated from the dielectric measurements and the values obtained from the polarized spectroscopy methods seem to be understandable if one takes into account the fact that in the dielectric relaxation process, the short range interaction plays an important role, whereas the order parameter derived from the optical data reflects only the long range order. However, the lower value of $\langle P_2\rangle$ estimated from the fluorescence studies, with respect to that determined from the absorption measurements, has also been observed for low molar mass liquid crystals [22–25]. This effect arises in general from the fact that the fluorescent molecule is excited at a certain orientation $\Omega_0(\beta)$ and is observed after a time t at an orientation $\Omega(\beta)$.

Let us now consider the possible reasons for the inaccuracy of the depolarization fluorescence method. If all systematic errors are eliminated (as was done in our experiments, using the appropriate geometry and incorporating the optical corrections), then the following principal factors or processes can lead to misinterpretation of the experimental data: (1) the interaction between the dye molecules and the mesogenic groups, which causes the order of the host needs not be the same as that for the guest, (ii) the rotational diffusion time, τ_R is comparable to the fluorescence lifetime, τ_F of the dye probe, (iii) the non-constant value of the angle δ at various temperatures, (iv) the non-rigidity of the fluorescent molecule, (v) fluorescence depolarization due to dye–dye interactions and to the transfer of the excitation energy.

The perturbation of the orientation of the mesogenic groups by the guest molecules should influence the results obtained *both* from the fluorescence and absorption measurements, and therefore it does not seem that this effect could explain the differences between the $\langle P_2 \rangle$ values determined from these two methods. The dye–dye interaction and the excitation energy transfer should also be excluded, because the estimated distance between the dye molecules is relative large, and moreover, any significant changes in the absorption and fluorescence spectra at different concentration were observed.

Information about the rotational motions of the molecules can be obtained from the dielectric relaxation measurements. In liquid crystalline polymers, three relaxation processes: δ, α and β are possible [26]. We have found [18] that any of these processes has a relaxation time comparable to the fluorescence lifetime of DANS, which was estimated to be 2 ns [27]. Indeed, the guest dissolved in the polymer matrix can move independently of the mesogenic groups [18], but the necessary correlation of motions means that the times of rotation about the short and long axes are only somewhat shorter than those of the side groups of the polymeric host. Only the relaxation time due to an internal reorientation inside the dye molecule can be of the same order as the fluorescence lifetime, and therefore our assumption that the fluorescence probe is rigid cannot be true. The change of the angle δ between the absorption and emission oscillators with rise in temperature can be another reason for the error in the fluorescence depolarization method in our case. A solution of these problems is not possible until a time dependent fluorescence depolarization experiment is carried out.

All these factors affecting the emission anisotropy influence, first of all, the order parameter $\langle P_4 \rangle$, because it depends on higher powers of the deviation angle and therefore is more sensitive to molecular fluctuations. It is however not really likely that by introducing corrections for all the additional effects mentioned above, one can obtain positive values of $\langle P_4 \rangle$ for the nematic phase that are consistent with theory [15, 28]. Many authors have observed very low and even negative values of $\langle P_4 \rangle$ using Raman scattering [29–32], which is an instantaneous spectroscopic process. In order to explain the non-typical behaviour of $\langle P_4 \rangle$ in the nematic phase, many attempts have been made [23, 29, 30], but up till now the reason for the discrepancy between experimentally obtained $\langle P_4 \rangle$ values and results derived from theories has not be found. It seems that the low negative values of $\langle P_4 \rangle$ in the nematic phase obtained for the polysiloxanes investigated by us are in great part due to the strong tendency of the mesogenic groups to tip away from the director, an effect which is probably connected with the perturbation of the molecular alignment by the rigid polymer backbone.

The value of $\langle P_4 \rangle$ strongly influences the shape of the molecular distribution function, $f(\beta)$. In figure 3, we can see that $f_4(\beta)$ at the temperature corresponding to the nematic phase is significantly broadened with respect to that determined for the smectic phase.

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