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Rotation relaxation in a side chain liquid crystal polymer in the vicinity of the nematic–isotropic transition temperature

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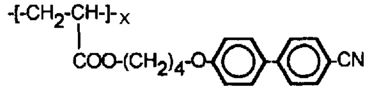
The electric birefringence of three fractions of a comb-shaped nematic polymer with different molecular masses, and having cyanobiphenyl mesogenic groups, in the vicinity of the nematic–isotropic transition temperature has been studied. It was established that two types of relaxation process exist in the vicinity of the nematic–isotropic transition temperature. The Landau–de Gennes model is adequate for a description of the pretransitional electro-optic properties of all the polymer fractions. At the same time, a comparison of some kinetic electro-optical parameters of low molar mass and polymer liquid crystals of similar molecular structure has revealed essential differences in their values that probably are explained by the hindered rotation of mesogenic groups in the polymer samples.

1. Introduction

A transformation of a nematic phase into the isotropic state is characterized by a first order transition. However, due to the small value of the transition heat, there are pronounced pretransitional phenomena in the immediate vicinity of the transition which arise owing to orientational order fluctuations. One of the most efficient methods of studying such phenomena is the electric birefringence (EB) (the so called Kerr effect [1, 2]), permitting studies of equilibrium and relaxation processes.

It was established that two types of relaxation process are typical for kinetic phenomena in liquid crystals near the temperature of the transition to the nematic phase. The first [3–6] is due to the relaxation of the dipole orientation of molecules and is observed in radio-frequency electric fields. Another [7–13] is associated with co-operative relaxation processes and determines (in the isotropic phase) a rotational mobility of dielectrically anisotropic, fluctuating nuclei of the mesophase. Considerable attention has been given to studies of the relation between the structural organization and physical properties of low molecular mass thermotropic nematics below and above the phase transition. It has also been demonstrated that the Landau–de Gennes model may be used for a quantitative description of pretransitional equilibrium electro-optic properties of nematics [14], as well as of their dynamical behaviour above and below the isotropic liquid–nematic phase transition [15–17].

During the last few years there appeared the first publications where studies of pretransitional phenomena in thermotropic LC polymers were reported [18–20]. The present paper deals with further studies of such phenomena. In particular, experimental investigations of the relation between the rotational viscosity of a comb-like LC polymer in the nematic phase and cooperative relaxation processes in the isotropic state in the pretransitional temperature range have been made for the first time. For this purpose, fractions of an acrylic polymer of various molecular masses with cyanobiphenyl side groups have been used.



Glass→N→I

2. Experimental

2.1. *Polymer samples*

The polymer studied was synthesized according to the procedure described in [21]. The polymer was fractionated by fractional precipitation and the molecular masses of the polymer fractions were determined by viscometry. Three fractions, I, II and III, with degrees of polymerization equal to 560, 830 and 2530, respectively, were chosen for the electro-optical investigations. The clearing temperature (T_c) and enthalpy of the nematic–isotropic transition (ΔH) of all these fractions were determined

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by DSC as already described [22], and these values are listed in the table. Values of the rotational viscosity coefficients γ_1 were determined using broad line ^{1}H NMR spectroscopy [22].

2.2. *Physical measurements*

It is well known that the viscosity of LC polymers is usually several orders higher than that of low molecular mass liquid crystals. Therefore, we have used a Kerr cell which could be assembled [20] and allow measurements to be performed with small amounts (less than 40 mg) of high viscosity liquids. Rectangular aluminum electrodes were placed on each side of the cell with the help of flat steel springs. The interelectrode distance of 0·02 cm was fixed using quartz spacers sandwiched between the electrodes. The optical path length was 0·3 cm. The light input to the cell and the light emerging from the cell passed through thin glass platelets which were held in place merely by capillary forces. Sample preparation started with the formation of a polymer film on one of the electrodes by melting the sample in a vacuum. Heating the sample in conjunction with pumping off the air was performed repeatedly in order to remove air bubbles from the polymer sample. Then the cell was assembled and heated in a vacuum; the springs brought the electrodes closer together to a separation determined by the quartz spacer interposed between them. The heating and pumping processes were repeated.

The EB was measured in an electric field $E < 3 \times 10^3$ V cm^{-1} in the frequency range from 10^2 to 10^6 Hz. The electric field was applied for a period of time up to 10 ms. Measurements of the EB were performed with a decay period of 1–2 Hz. The EB was measured by the method of compensation of the phase difference between the ordinary and extraordinary beams of light using a rotational elliptical compensator. The Kerr constant K was calculated from the experimental dependence of birefringence on E^2 making use of the calibration constant of the cell obtained by the use of reference liquids.

The authors also investigated the EB-decay curve after switching off the rectangular pulsed field; d.c. pulses of duration up to 5 ms and an amplitude of $< 10^2$ V were used with the decay time $< 0{\cdot}5$ µs. The optical pulse was registered by means of a memory oscilloscope as the dependence of the photocurrent on time $I(t)$. The dependence of the reduced EB on time $\Delta n(t)/\Delta n_0$ was found from photocurrent recordings using the relationship:

$$\Delta n(t)/\Delta n_0 = [I(t)/I_0]^{1/2}$$

Here Δn_0 and I_0 are equilibrium values. The samples were thermostated with an accuracy of up to 0·1 K.

The molecular parameters, phase transitions, electro-optical and viscosity characteristics of LC polymer fractions I, II and III and the liquid crystalline low molecular mass analogue: T^* is the latent phase transition temperature; K_0 is the Kerr constant; τ_2 is the rotational mobility of fluctuating nuclei in the mesophase in the pretransitional temperature region; γ_1 is the rotational viscosity coefficient; ΔH is the enthalpy of the transition from isotropic to liquid crystalline phase.

Sample	Molecular mass (viscosity average)	T_c/K	T^*/K	$K_0(T-T^*) \times 10^7$ /(cm/300 V)^2	$\tau_2\,(T-T^*) \times 10^3$ /s K	γ_1 /Pa s [22]	ΔH /J g^{-1} [22]	Calcd. from equation (2): $\tau_2\,(T-T^*) \times 10^3$/s K
LC polymer								
Fraction I	$1{\cdot}8 \times 10^5$	410·5	409·8	1·6	1·2	250	1·7	6·6
Fraction II	$2{\cdot}6 \times 10^5$	408·7	407·8	1·5	1·3	330	1·8	8·4
Fraction III	$8{\cdot}1 \times 10^5$	409·0	408·6	0·9	0·9	550	2·1	11·8
Low molecular mass sample								
40CB [17]	251	352·6	351·2	2·0	$3{\cdot}2 \times 10^{-4}$	$0{\cdot}9 \times 10^{-2}$	1·7	$4{\cdot}2 \times 10^{-4}$

3. Results and discussion

The EB was proportional to $\mathbf{E}^2$ in the isotropic melts of all fractions in the range of field strengths **E** used (the Kerr law). Kerr constants discussed below were obtained from the slopes of the straight lines representing the dependence of Δn on $\mathbf{E}^2$ (figure 1). Equilibrium Kerr constants K_0 measured using a rectangular, pulsed electric field or low frequency sinusoidal fields ($f < 100$ Hz) increase abruptly as the temperature approaches T_c, corresponding to the isotropic liquid–nematic phase transition, as illustrated in figure 2. The Kerr constant vs. temperature dependence can be approximated to by the Landau–de Gennes relationship

$$K_0^{-1} \sim (T - T^*),$$

where T^* corresponds to the temperature of the latent phase transition ($T^* < T_c$).

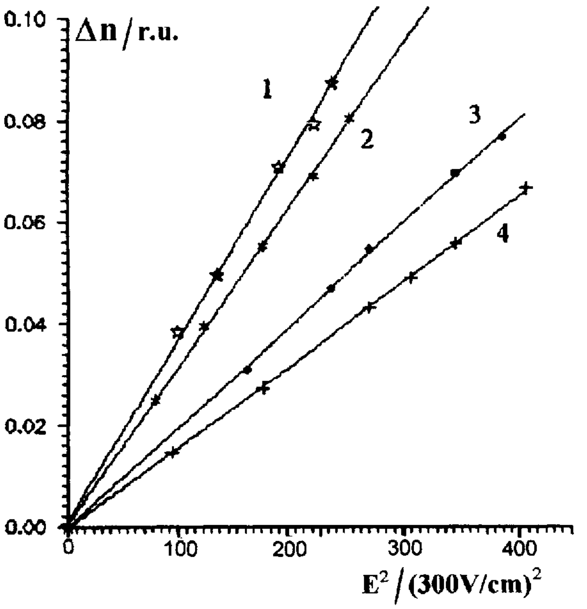

Figure 1. Birefringence Δn as a function of the electric field $\mathbf{E}^2$ in the isotropic phase of polymer fraction II at various temperatures: 376·7 K (1), 378·7 K (2), 380·6 K (3), 384·7 K (4).

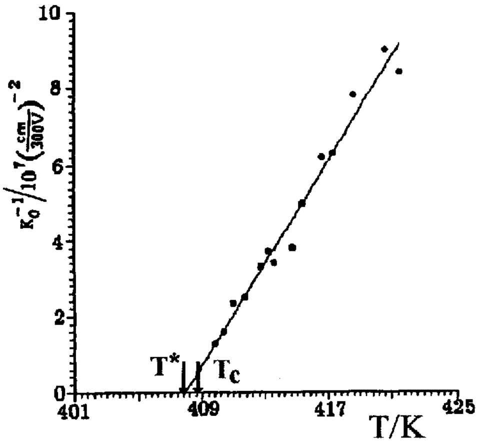

Figure 2. Temperature dependence of the Kerr constant K_0^{-1} for polymer fraction II.

The values of T^* obtained from the dependence of K_0 on temperature are given in the table. They differ from T_c for fractions I–III by less than one degree. The value of $K_0(T\text{–}T^*)$ obtained for all fractions from the corresponding dependence of K_0 on temperature are listed in the table. For comparison, the value of $K_0(T\text{–}T^*)$ for the low molecular mass nematic simulating the side group of the LC polymer is shown in the last column of the table.

As seen from the data listed in the table, not only are the values of the equilibrium EB for the polymer in the isotropic melt much like those for its low molecular analogue, but also the temperature dependences of K_0 are similar. With increasing molecular mass of the fractions, the values $K_0(T\text{–}T^*)$ are even lowered somewhat. This implies that the main chain of the polymer molecule in equilibrium has an insignificant effect on the fluctuations of orientational order as well as on the motion of the polar mesogenic groups of a macromolecule in an electric field. The molecular orientation in the field is realized, evidently, through the motion of polar mesogenic side groups separated from the main chain of a polymer by a flexible methylene spacer. The result provides evidence that the orientational interaction between the mesogenic nuclei of a macromolecule plays a significant role in pretransitional phenomena.

The studies of dispersion and relaxation of the EB in the isotropic phases of the fractions studied also provide important information on the processes of molecular orientation and ordering of mesogenic side groups in polymer liquid crystals. Figure 3 shows the dependences of the Kerr constant of one of the polymer fractions on the frequency of the sinusoidal varying electric field at various temperatures. Similar results were also obtained for other fractions.

A strong dispersion of the Kerr constant K_f was observed for frequencies $f > 10^4$ Hz. With increasing frequency, the effect was reduced to a certain limiting value K_∞ which points to the dipolar nature of the relaxation process. Since the dispersion of K_f is revealed in fractions of different molecular mass in one and the same frequency range, it may be concluded that the dipolar mechanism of the molecular relaxation is weakly dependent on the length of the main chain. This supports the above mentioned conclusion that the motion of polar mesogenic side groups containing cyano groups, which are oriented along the electric field, is of a local (small scale) character. Note that the compensational method of EB measurement employed by us [2] gives

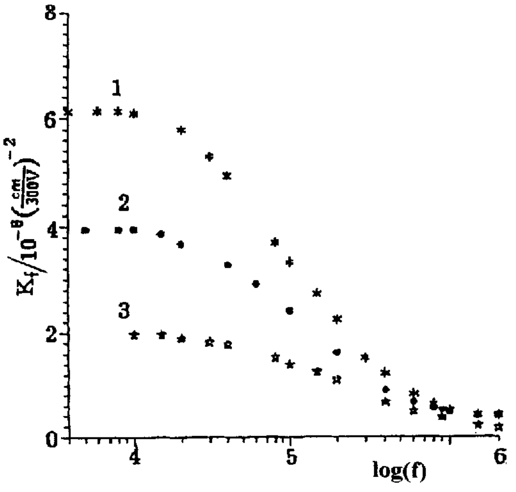

Figure 3. The dependence of the Kerr constant of polymer fraction II versus the electric frequency at different temperatures: 410·4 K (1), 411·7 K (2), 415·3 K (3).

information on the frequency dependence of K_f in relation only to the dipole mechanism of orientation. Hence, for a quantitative analysis of dispersion data and determination of the corresponding relaxation times τ_1, the Debye–Lorentz equation can be employed. It describes the process of dipole relaxation of the Kerr effect:

$$K_f = K_\infty + (K_0 - K_\infty)/(1 + 4\pi^2 f^2 \tau_1^2) \qquad (1)$$

Figure 4 shows the temperature dependences of the relaxation times τ_1 for fraction II. They were obtained with the use of relaxation frequencies for $K = 0{\cdot}5(K_f - K_\infty/(K_0 - K_\infty)$. The data of figure 4 allow determination of the activation energy of the dipole relaxation process which was found to be $E_A = 40 \pm 2\,\mathrm{kcal\,mol^{-1}}$. The value of E_A obtained is more than twice the activation energies of dipole relaxation for low molecular mass nematics [2, 23].

The employment of pulsed rectangular d.c. electric fields made it possible to gain quantitative information on the rotational mobility of fluctuating nuclei in the mesophase in the pretransitional temperature region. For this purpose, the decay of the EB vs. time after excitation was studied. The decay is given by:

$$\Delta n_t = \Delta n_0 \exp(-t/\tau_2) \qquad (2)$$

Figure 5 shows, according to equation 2, the dependence of $\ln \Delta n_t/\Delta n_0$ as a function of time. It should be noted that the molecular dipole dispersion of the EB discussed above and featuring relaxation times of the order 10^{-6} s proceeds much faster than the co-operative relaxation, for which a characteristic time τ_2 is of the order of 10^{-3}. Therefore, the latter process cannot be revealed in the time dependence of the EB represented in figure 5. A linear dependence of $\Delta n_t/\Delta n_0$ on time suggests that the mono-exponential behaviour of the EB decay enables one to obtain the relaxation time τ_2 from the slopes of the corresponding straight lines. The values of τ_2 found in this way are represented for one of the fractions as a function of temperature in figure 6. Similarly to the equilibrium case, the relaxation time τ_2 dramatically increases in magnitude (τ_2 is proportional to $(T - T^*)^{-1}$) as the temperature T_c is approached. Corresponding values of $\tau_2(T - T^*)$ for the fractions investigated are listed in the table. For analysis of the kinetic properties of the isotropic liquid phase and the relative viscosity in the nematic state, a relation between kinetic parameters below and above the phase transitions temperature T_c (in the absence of flow) can be expressed as [24]

$$\gamma_1 = 9\nu Q^2/2 \qquad (3)$$

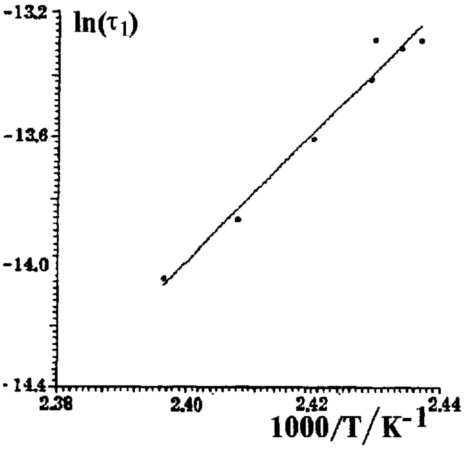

Figure 4. The temperature dependence of relaxation time τ_1 for polymer fraction II.

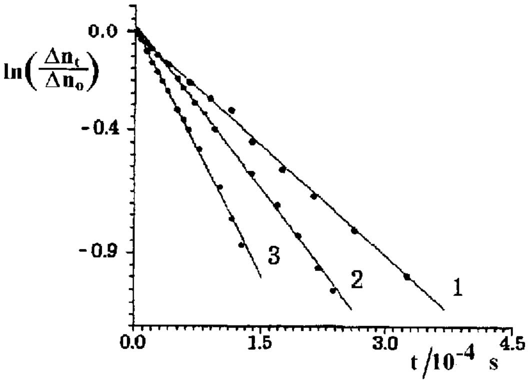

Figure 5. The temperature dependence of $\ln(\Delta n_t/\Delta n_0)$ for polymer fraction II at the temperatures 412·7 K (1), 413·5 K (2), 415·6 K (3).

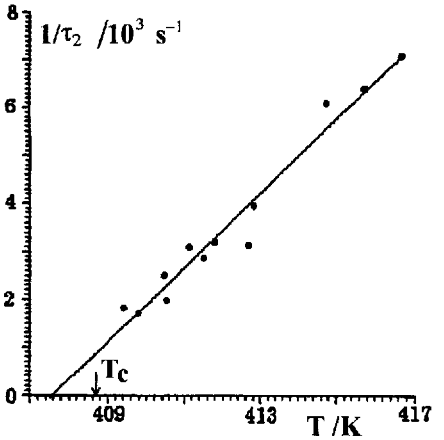

Figure 6. The temperature dependence of the rotational mobility τ_2 of fluctuating nuclei in the mesophase of polymer fraction II.

where v is the viscosity of a substance in the isotropic phase and Q is the order parameter. Taking into account the experimental temperature dependence of the characteristic time

$$\tau_2^{-1} = a(T - T^*)/v, \tag{4}$$

where a is the coefficient in the Landau expansion of the free energy in terms of the order parameter, and making use of the expression for the heat of the phase transition

$$\Delta H = aT_cQ_c^2/2, \tag{5}$$

where Q_c is the order parameter at the phase transition point, it is easy to obtain:

$$\gamma_1 = 9\tau_2(T - T^*)\Delta H/T_c \tag{6}$$

Thus, using the relation (6) and experimental values of the rotational viscosity γ_1 and $\Delta H(T_{N\text{-}I})$, the values of $\tau_2(T\text{–}T^*)$ can be related to the experimental data obtained in the present work.

We note that the validity of the relation (6) was confirmed by studies of the kinetic properties of low molar mass nematic LCs [15–17] which pointed to the similarity between the mechanism responsible for rotational relaxation in nematics and isotropic phases in the pretransitional region. Experimental data on the temperature dependence of the rotation viscosity γ_1 of the polymer fractions investigated here were obtained in [22] where wide line ^{1}H NMR spectroscopy was used.

Corresponding experimental data extrapolated to the temperature T_c are listed in the table; also are listed the values of ΔH which correspond to the enthalpy of the transition from the isotropic phase to the nematic phase for all fractions. Substitution into equation (6) of the values of rotational viscosity γ_1, ΔH and T_c gives the values $\tau_2(T\text{–}T^*)$ shown in the last row of the table. It is seen that experimental and calculated values of $\tau_2(T\text{–}T^*)$ differ by a factor of six or even more: the experimental values of $\tau_2(T\text{–}T^*)$ were lower than the corresponding calculated values.

The experimental facts considered above are likely be a consequence of the more complicated kinetic processes in polymer LCs as compared to low molecular mass nematics in the region of the phase transition from the isotropic to the liquid crystalline state. To understand and describe these results completely, further studies with a wide variety of oligomers with different degrees of polymerization are necessary. Seemingly, the relation between the kinetic parameters of low molecular mass nematics below and above the phase transition (predicted in the de Gennes model) which satisfactorily describes the experimental data should be modified for application to thermotropic side chain LC polymers.

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