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Kerr effect in the isotropic phase of a side-chain polymeric liquid crystal

V. Reys (1), Y. Dormoy (1), D. Collin (1), P. Keller (2) and P. Martinoty (1)

(1) Laboratoire d’Ultrasons et de Dynamique des Fluides Complexes (*), Université Louis Pasteur, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France
(2) Laboratoire Léon Brillouin, C.E.N. Saclay, 91191 Gif-sur-Yvette Cedex, France

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1. Introduction.

Side-chain liquid crystal polymers are composed of a principal chain onto the sides of which mesogenic groups have been grafted, by means of a spacer. These new compounds are presently the object of intense research, since they have special properties associated with competition between the tendency to order, imposed by the mesogenic elements, and the tendency to disorder, imposed by the polymer skeleton [1]. We have recently studied the isotropic phase of a polyacrylate, poly[(acryloxy-6-hexyloxy)-4-cyano-4’-biphenyl], abbreviated to PA60CB, with molecular mass \( M_w \) of 62 000, and

(* Unité de Recherche Associée au CNRS n 851.
polydispersity of 3.38 [2]. This study has shown that the static properties of the local orientational order are comparable to those of pentylycyanobiphenyl (PCB), which is a low molecular weight liquid crystal (LMWLC) with a formula similar to that of the mesogenic elements of the polymer. However, the dynamic properties of the local orientational order are very different from those of PCB. This difference is apparent on the relaxation time of the orientational order parameter, which is about 500 times greater than that of PCB, and which diverges with an exponent of the order of 1.5 rather than 1.

In order to check whether these are general effects, we have studied another side-chain polymer. The compound in question was a polysiloxane characterised by a degree of polymerisation and mesogenic groups which are different from those of PA60CB. The results obtained confirm the abnormal value of the dynamic exponent and the conventional value of the static exponent. They also reveal competition between the dipolar moments induced by the electric field and the permanent moments of the mesogenic molecules. Before presenting and discussing our results (Sect. 4), we shall first of all describe the polymer studied and the technique used (Sect. 2), and then briefly review the Landau-de Gennes theory of the isotropic phase of low molecular weight liquid crystals (Sect. 3).

2. Materials and methods.

The formula and phase diagram of the polysiloxane studied are shown in figure 1. Its molecular mass $M_W$ is 31 000, and its polydispersity is 1.1. It shall subsequently be referred to as $P_{60}^6$, where 6 and 80 represent the number of methylene groups in the spacer, and the degree of polymerisation, respectively. In order to ascertain the influence of the chain on the local orientational order, we have also studied 4-methoxyphenyl 4'-((5-hexenyl) oxy) benzoate, which is a liquid crystal of low molecular weight, with a formula (cf. Fig. 1) identical to that of the mesogenic elements of $P_{80}^6$. This compound shall be referred to as MPHOB.

$$P_{60}^6$$

$$\text{CH}_3$$

$$|$$

$$(\text{CH}_3)_3\text{Si-O-[Si-O]}_{60}\text{Si-}(\text{CH}_3)_3$$

$$|$$

$$(\text{CH}_2)_6\text{O-φ-CO}_2\text{-φ-O-CH}_3$$

$T_N = 108°C$  $T_{N^1} = 46°C$  $T_g^1 = 3°C$

**MPHOB**

$$\text{CH}_2=\text{CH-}(\text{CH}_2)_4\text{-O-φ-CO}_2\text{-φ-O-CH}_3$$

$T_N = 59°C$

Fig. 1. — Chemical formulas and transition temperatures for $P_{60}^6$ and MPHOB.
The birefringence induced by a pulsed electric field was used to simultaneously determine the intensity and the characteristic time of the local orientational order, which appears in the vicinity of the Nematic-Isotropic transition. The birefringence was measured at 6328 Å, with a 5 mW He-Ne laser as a light-source, and a 10 mm long Kerr cell with an inter-electrode length of 2.2 mm, the cell-temperature being kept constant to within ± 0.05 °C. The electrical pulses were rectangular in shape, with a maximum amplitude of 500 V, and for each temperature, their duration was adjusted in such a way as to ensure stationary birefringence. The rise and decay times of the electric field were less than 0.2 μs. This is much less than the relaxation time of the local orientational order of the polymer, which could therefore be determined. The induced birefringence in the P60 is very weak (approximately 100 times weaker than in PA60CB), and only the measurements taken in the first 8 degrees above the nematic-isotropic transition have a good signal-to-noise ratio. The variation of Δn with E² was found to be linear for all the electric fields used.

Scattered-light intensity measurements were also carried out on the same set-up. For practical reasons, these measurements were only taken for one observation angle, chosen so as to correspond to 90° to the incident beam.

Δn/E², τ and I were measured simultaneously on the same sample, which had been degassed prior to the experiments, and the measurements taken under an inert atmosphere.

3. Review of the Landau-de Gennes model [3].

For a uniaxial nematic, the order parameter is a symmetrical tensor of zero trace which can be written as:

\[ Q_{\alpha\beta} = \frac{1}{2} S (3n_\alpha n_\beta - \delta_{\alpha\beta}) \] (1)

where \( n_\alpha, n_\beta \) are the components of a unit vector (the director) which indicates the direction of the optical axis, and \( S \) is a scalar which fixes the molecular orientational rate in relation to the optical axis.

In the isotropic phase, the free energy per unit volume can be expressed as a function of a development of \( Q_{\alpha\beta} \) in the following way:

\[ F = F_0 + \frac{1}{2} A Q_{\alpha\beta} Q_{\beta\alpha} - \frac{1}{3} B Q_{\alpha\beta} Q_{\beta\gamma} Q_{\gamma\alpha} + \frac{1}{4} C (Q_{\alpha\beta} Q_{\beta\alpha})^2 + \] (2)

which, using (1), can also be written as:

\[ F = F_0 + \frac{3}{4} A S^2 - \frac{1}{4} B S^3 + \frac{9}{16} C S^4 + \] (3)

If coefficient \( B \) were zero, then the system would involve a second-order Nematic-Isotropic transition at temperature \( T_\ast \). That this is not the case indicates that the transition is of the first order, and occurs at temperature \( T_c > T_\ast \). The Landau model assumes that \( A = a (T - T_\ast) \), and that coefficients \( B \) and \( C \) are only very slightly dependent on temperature. This development of the free energy enables us to show that the scattered-light intensity \( I \) (proportional to \( \langle Q^2 \rangle \)) scales as:

\[ I \sim \frac{T}{T - T_\ast} \] (4)

which shows that \( I \) diverges when \( T \to T_\ast \).
In the presence of a dc electric field $E$, the term $-(1/2) \varepsilon_0 \varepsilon_{a\beta}^{dc} E_a E_\beta$ must be added to (2) where $\varepsilon_0$ is the vacuum permittivity, and $\varepsilon_{a\beta}^{dc}$ the dc dielectric tensor. $\varepsilon_{a\beta}^{dc}$ is linked to the $Q_{a\beta}$ order parameter by the relation:

$$(\varepsilon_{a\beta})^{dc} = (\bar{\varepsilon})^{dc} \delta_{a\beta} + \frac{2}{3} (\Delta \varepsilon_{\text{max}})^{dc} Q_{a\beta} \quad (5)$$

where $\Delta \varepsilon_{\text{max}} = \varepsilon_1 - \varepsilon_\perp$ represents the anisotropy of $\varepsilon$ for a perfectly oriented nematic, and $\bar{\varepsilon} = (1/3)(2 \varepsilon_\perp + \varepsilon_1)$. The order produced by the electric field $E$ can be calculated by minimizing the free energy. With $E$ along Oz, we find:

$$S = \frac{2 \varepsilon_0 (\Delta \varepsilon)^{dc}_{\text{max}}}{9 a(T - T_c^*)} E^2 \quad (6)$$

This leads to an electrically induced birefringence given by

$$\Delta n = \Delta n_{\text{max}} S = \frac{2 \varepsilon_0 \Delta n_{\text{max}} (\Delta \varepsilon)^{dc}_{\text{max}}}{9 a(T - T_c^*)} E^2 \quad (7)$$

where $\Delta n = (\varepsilon_{ee})^{1/2} - (\varepsilon_{\alpha\alpha})^{1/2}$, and $\Delta n_{\text{max}}$ is the anisotropy of the refractive index in the oriented nematic phase ($S = 1$).

$(\Delta \varepsilon)^{dc}_{\text{max}}$ has been calculated by Maier and Meier [4], taking account of the contributions of the induced and permanent dipoles. Based on the Onsager model, this calculation gives:

$$(\Delta \varepsilon)^{dc}_{\text{max}} = 4 \pi N \left[ \Delta \alpha + \frac{F'}{\mu^2} \frac{3 \cos^2 \beta - 1}{2 k_B T} \right] h F' \quad (8)$$

where $N$ is the number of molecules per unit volume, $\Delta \alpha$ the molecular polarisability anisotropy, $\mu$ the permanent dipole, and $\beta$ the mean angle between the permanent dipole and the long axis of the molecule. $F' = 1/(1 - \bar{\alpha} f)$ is the factor which describes the reactive field with $f = 8 \pi N (\bar{\varepsilon} - 1)/3(2 \bar{\varepsilon} + 1)$ and $\bar{\alpha}$ the mean molecular polarisability. $h = 3/(2 \bar{\varepsilon} + 1)$ is a factor which describes the cavity field. In these conditions, $\Delta n/E^2$ is written:

$$\frac{\Delta n}{E^2} = \frac{8 \varepsilon_0 (\Delta n)_{\text{max}} \pi N}{9 a(T - T_c^*)} \left[ \Delta \alpha + \frac{F'}{\mu^2} \frac{3 \cos^2 \beta - 1}{2 k_B T} \right] h F' \quad (9)$$

In the presence of an electrical field, the behavior of the order parameter is governed by the equation:

$$\nu \frac{\partial}{\partial t} Q_{a\beta} + AQ_{a\beta} = \frac{\varepsilon_0 (\Delta \varepsilon)^{dc}_{\text{max}}}{3} E_a E_\beta \quad (10)$$

where $\nu$ is a local friction coefficient. Equation (10) is obtained assuming that there is no flow, i.e. no coupling to gradients of the velocity field.

This equation enables the transient birefringence associated with the switch-on and cut-off of the electrical field to be determined. For a rectangular field, one obtains for the rise-and-decay birefringence:

$$\Delta n_R(t) = \Delta n_0 (1 - e^{-\nu \tau}) \quad (11a)$$

$$\Delta n_D(t) = \Delta n_0 e^{-\nu \tau} \quad (11b)$$

where $\tau = \nu/A$ is the order parameter relaxation time and $\Delta n_0$ the stationary birefringence, given by equation (7).
4. Results and discussion.

4.1. Static investigations. — We shall begin by presenting the stationary electrically-induced birefringence data taken from MPHOB, which will be necessary in order to interpret the results obtained for the polymer. Figure 2 shows that birefringence is negative throughout virtually the whole of the temperature-range studied, and changes sign at a temperature $T_0$ of the order of 80 °C. Such behavior has been encountered in other compounds [5], and reflects the existence of competition between the electrical moment induced by the field and the permanent moment proper to the molecules. It should, indeed, be remembered that birefringence can be written according to equation (9) as:

$$\Delta n = \frac{\Omega}{E^2} \left( \frac{F' \mu^2 (3 \cos^2 \beta - 1)}{2 k_B T} - \Delta \alpha \right)$$

where $F' \mu^2 (3 \cos^2 \beta - 1)/2 k_B T$ and $\Delta \alpha$ are the contributions of the permanent dipoles and the dipoles induced by the field respectively; $\Omega$ is given by

$$\Omega = \frac{8 \hbar F' \varepsilon_0 (\Delta n)_{\text{max}} \pi N}{9 a}$$

If $T_0$ is called the temperature at which birefringence is cancelled out, equation (12) can be rewritten:

$$\frac{\Delta n}{E^2} (T - T_0) = \Omega \Delta \alpha \left( 1 - \frac{T_0}{T} \right)$$

Fig. 2. — Variation of $(\Delta n/E^2)(T - T_0)$ ratio as a function of $1/T$ for MPHOB where $T_0$ is the virtual second order transition temperature and $\Delta n$ the birefringence induced by an electrical field $E$. The results show that $\Delta n$ changes sign at temperature $T_0$. The solid line represents the fit with equation (14) (see text).
where temperature $T_0$ is given by:

$$
T_0 = -\frac{F'(3 \cos^2 \beta - 1)}{2 k_B} \frac{\mu^2}{\Delta \alpha}
$$

(15)

The fact that $T_0$ is positive implies either that $F'(3 \cos^2 \beta - 1) < 0$ and $\Delta \alpha > 0$, or that $F'(3 \cos^2 \beta - 1) > 0$ and $\Delta \alpha < 0$. For elongated nematic molecules, $\Delta \alpha$ is always positive \[5\]; $F'(3 \cos^2 \beta - 1)$ must therefore be negative.

The experimental points were analysed with equation (14) which indicates that variation of $(\Delta n/E^2)(T - T_0^*)$ as a function of $1/T$ must be linear, and the results in figure 2 show that this is indeed the case. The parameters corresponding to this analysis are:

$$
T_0^* = 58.93 \pm 0.01 ^\circ C
$$
$$
T_0 = 79.56 \pm 0.02 ^\circ C
$$
$$
\Omega \Delta \alpha = (2758 \pm 16) \times 10^{-20} \text{ m}^2 \text{ V}^{-2} \text{ K}.
$$

Fig. 3. — Same as for figure 2, but for $P_{80}^g$. The data show that the birefringence is positive. The solid line represents the best fit with equation (14). The temperature $T_0$ at which the birefringence changes sign is outside the range of occurrence of the isotropic phase.
It must be noted that the temperature $T_0$ of the $P_{80}^6$ is not identical to that of MPHOB. This also applies to the slope of the straight line representing the variation of $\Delta n/E^2(T - T_c^*)$ with $T^{-1}$. These differences are a reflection of the influence of the polymer skeleton on the ratio of the induced and permanent moments of the mesogenic molecules.

In order to confirm the value of $T_c^*$ in relation to the polymer, we have also taken scattered-light intensity measurements. The results obtained are given in figure 4. They were analyzed using the following law:

$$I = I_0 + \frac{MT}{T - T_c^*}$$  \hspace{1cm} (16)$$

and the fit to the experimental plot, shown as a solid line in this same figure, corresponds to the following parameters:

$$I_0 = 0.648 \pm 0.042 \text{ (a. u.)}$$

$$M = (5.30 \pm 0.63) \times 10^{-3} \text{ (a. u.)}$$

$$T_c^* = 107.86 \pm 0.13 \text{ °C}.$$  

Constant $I_0$ accounts for temperature-independent parasitic effects which could be due to synthesis residues (for example the catalyst). This fit shows that the intensity of the light scattered by the local orientational order diverges as $(T - T_c^*)^{-1}$, which agrees with the theoretical predictions. Note that, to within experimental error, the value of $T_c^*$ is the same as that deduced from analysis of the $\Delta n/E^2$-curve.

![Graph of P80 variation](image)

**Fig. 4.** — Critical variation of the intensity of the light scattered by $P_{80}^6$ as a function of temperature.

4.2. **Dynamic investigations.** — These measurements only concern the polymer, as the characteristic time associated with MPHOB is too short to be determined with the experimental set-up in use.

The recordings obtained for each temperature were analysed using a single-time exponential, as suggested in equations (11a) and (11b). These analyses show that, for each of the
temperatures considered, the characteristic time \( \tau \) associated with the switch-on of the field is similar to that associated with the cut-off. Analysis of these same recordings, using a Gaussian distribution of exponentials, or a stretched exponential, confirms that the transient regime does indeed correspond to a single-time exponential (single-order moment close to zero, or stretching coefficient of the order of one). The values of \( \tau \) shown below correspond to those determined when the field is cut off.

In order to determine the critical behavior of \( \tau^{-1} \), which according to the Landau-de Gennes model is written \( \tau^{-1} \approx A/\nu \), it is necessary to know the variation of \( \nu \) with temperature.

We first of all supposed the thermal variation of \( \nu \) to be Arrhenian in nature, as in the case of conventional liquid crystals [6]. If this were the case, \( \tau \) would be:

\[
\tau = b \, e^{w/k_B T} \left( \frac{T - T_c}{T - T_c^*} \right).
\]  

(17)

Figure 5 shows that it is, indeed, possible to analyze the experimental results using this equation. The fit is obtained with the following parameters

\[
\begin{align*}
b &= (1.04 \pm 0.63) \times 10^{-11} \, \text{S K} \\
w/k_B &= 5652 \pm 223 \, \text{K} \\
T_c &= 108.48 \pm 0.02 \, ^\circ\text{C}.
\end{align*}
\]

It should, however, be pointed out that the value of \( T_c^* \) is incompatible with that determined from the static data (induced birefringence or scattered-light intensity). It is therefore necessary to apply to the fit the value of \( T_c^* \) obtained from the static measurements, but when this is done, it is no longer possible to obtain a good fit, as can be seen from figure 6. Equation (17) is not therefore a satisfactory description, of the divergence of \( \tau \).

Another possibility consists in using the Williams-Landel-Ferry free-volume theory (W.L.F.) [7] which predicts that viscosity will vary as a function of temperature, according to the law:

\[
\nu = \nu_g \exp \left( \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \right)
\]  

(18)

where \( C_1 \) and \( C_2 \) are constants, \( T_g \) the glass transition temperature and \( \nu_g \) the viscosity at \( T_g \). With this thermal variation of \( \nu \), the characteristic time \( \tau \) would be:

\[
\tau = \frac{C_3}{T - T_c^*} \exp \left( \frac{C_1 (T - T_g)}{C_2 + (T - T_g)} \right).
\]  

(19)

The analyses carried out with this equation, in which the values of \( T_c^* \) and \( T_g \) are imposed \((T_c^* = 107.8 \, ^\circ\text{C}, T_g = 3 \, ^\circ\text{C})\), show that it does not account for the critical behavior of \( \tau \), as in the previous case.

Since none of the conventional behaviors of \( \nu \) gives a satisfactory account of our data within the framework of the de Gennes model, we have assumed that \( \tau \) varies according to a power law.

In this eventuality, representing \( \tau \) as a function of \( T - T_c^* \) in logarithmic coordinates should give a straight line, and the results in figure 7 show that this is, indeed, the case. The divergence of \( \tau \) is well accounted for by the law:

\[
\tau = \frac{C}{(T - T_c^*)^\beta}
\]  

(20)
Fig. 5. — Variation of the characteristic time $\tau$ of $P_{80}^6$ as a function of $T - T^*_c$, where $T^*_c$ is the virtual second-order transition temperature. The solid curve represents the fit of the data to equation (17). This adjustment cannot be accepted, as it gives a value of $T^*_c$ which is different from that determined from the static experiments (see text).

Fig. 6. — Same as for figure 5, but with the value of $T^*_c$ fixed at its static value ($T^*_c = 107.8 \degree C$). The disagreement between the experimental plot and the theoretical fit (the solid line) indicates that the characteristic time $\tau$ does not obey equation (17).

Fig. 7. — Variation of the characteristic time $\tau$ of $P_{80}^6$ as a function of $T - T^*_c$. The solid line represents the fit of the data to equation (20). The fit yields $1.49$ for exponent $\beta$ and a value of $T^*_c$ which is in good agreement with that determined by static experiments.
with

\[
\beta = 1.49 \pm 0.15 \\
C = (57.50 \pm 15.8) \times 10^{-6} \text{ S K} \\
T^*_c = 107.87 \pm 0.18 ^\circ \text{C}.
\]

The transition temperature \(T^*_c\) is identical to that determined by the static data, and this makes the analysis credible. The value of exponent \(\beta (=1.5)\) confirms the value found previously for PA60CB, and would thus appear to be intrinsic to side-chain liquid-crystal polymers.

5. Conclusions.

In this article, we have demonstrated that the nematic-isotropic transition of \(P_8^6\) is characterised by a conventional value of the static exponent (1), and an abnormal value of the dynamic exponent (1.5). These results confirm those obtained previously on another side-chain polymer, PA60CB, with different physico-chemical characteristics. They suggest that the static behavior of liquid-crystal polymers is identical to that of low molecular-weight liquid crystals, but that their dynamic behavior is completely different, indicating that the classical dynamic description of low molecular-weight liquid crystals does not apply to them. We have also shown the existence of competition between the dipolar moment induced by the electrical field and the permanent moments of the molecules. This competition does not exist for PA60CB.

References


