Orientational processes in liquid-crystalline polymers due to a magnetic field as studied by electron paramagnetic resonance

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A side-chain liquid-crystalline polymer has been investigated by the spin-probe method. It was found that the method detects a transition from the nematic to the isotropic phase, and that the rotational mobility of spin probes is connected with local mode processes of mesogenic groups. The phenomenon of domain orientation in an external magnetic field is also reported.

(Keywords: liquid-crystalline polymers; spin probes; orientation; magnetic field)

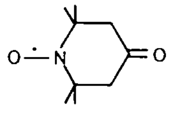
INTRODUCTION

The spin-probe method has been successfully applied in studies of both relaxation and ordering processes occurring in polymers and low-molecular-weight liquid crystals[1,2]. However, to the best of our knowledge, there exist only a few applications of the method in studies of liquid-crystalline polymers (LCP) (i.e. refs. 3 and 4 and references cited therein). Meurisse *et al.*[3] describe molecular ordering and dynamics of main-chain liquid-crystalline polymers, whereas Wassmer *et al.*[4] deal with similar problems for the case of side-chain liquid-crystalline polymers. Many papers have been published on the subject based on the results derived from other experimental techniques[5] (such as, for example, dielectric measurements[6–8], n.m.r. measurements[9–13], etc.).

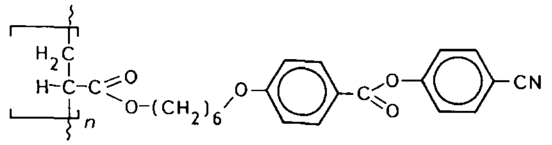
In the present paper we shall instead concentrate on the discussion of some new e.p.r. results on the reorientation of nematic domains as seen by spin probes. The effect of reorientation has already been observed by means of n.m.r. Here, e.p.r. results, as far as we know, are reported in detail for the first time. The preliminary results of our studies have already been presented at the 9th Specialized Ampere Colloque[14].

EXPERIMENTAL

A liquid-crystal polymer sample (Röhm GmbH, Darmstadt, Germany; Laborjournal number 9872/08, $T_{NI} = 122°C$, molecular weight ~11 400) with the structure given below was subjected to e.p.r. measurements:



Spin probe



LCP

These were carried out using a standard X-band spectrometer (Brucker ER 200D-SRC) with a temperature control unit.

The spin-probe samples were obtained by dissolving crystalline 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl in the polymer at a concentration of about 0.01 wt% and a temperature of about 130°C. The prepared samples were put into a 1 mm diameter tube and the e.p.r. spectra were observed in the temperature range from −100 to 150°C.

The results of the temperature measurements were obtained during cooling of the sample, which was stored at a fixed temperature for 10 min before each e.p.r. measurement. Two experimental procedures (A and B) were used to investigate the time evolution of the e.p.r. spectrum. These procedures are illustrated in *Figure 1*. In experiment B, rotation of the sample through an angle θ_0 of about 90° was performed during the decrease of the magnetic field strength.

RESULTS AND DISCUSSION

The obtained e.p.r. spectra correspond to the range of rapid ($T > 100°C$) and slow ($T < 100°C$) rotations of the radicals. The calculation of the correlation times was carried out by assuming rotational isotropy of the probes. We used the known formula[1,2]:

$$\tau_{RR} = K_{m_1,m_2}\,\Delta B(m_2)\left[\left(\frac{I(m_2)}{I(m_1)}\right)^{1/2} - 1\right] \tag{1}$$

$$\tau_{SR} = a(1-S)^b \tag{2}$$

$$f = (2\pi\tau)^{-1} \tag{3}$$

where τ_{RR} and τ_{SR} are correlation times in rapid and slow rotation regions, respectively, I is the line intensity, $\Delta B(m)$ is the linewidth, S is the ratio of the separation between the extremes of the spectrum for a given temperature to its maximum value, f is the rotational frequency, and $m = -1, 0, +1$ is the nuclear magnetic quantum number. We inserted the values $m_1 = -1$, $m_2 = +1$, $K_{-1,+1} = 6.65 \times 10^{-14}$ s T^{-1}, $a = 2.55 \times 10^{-9}$ s and $b = 0.615$.

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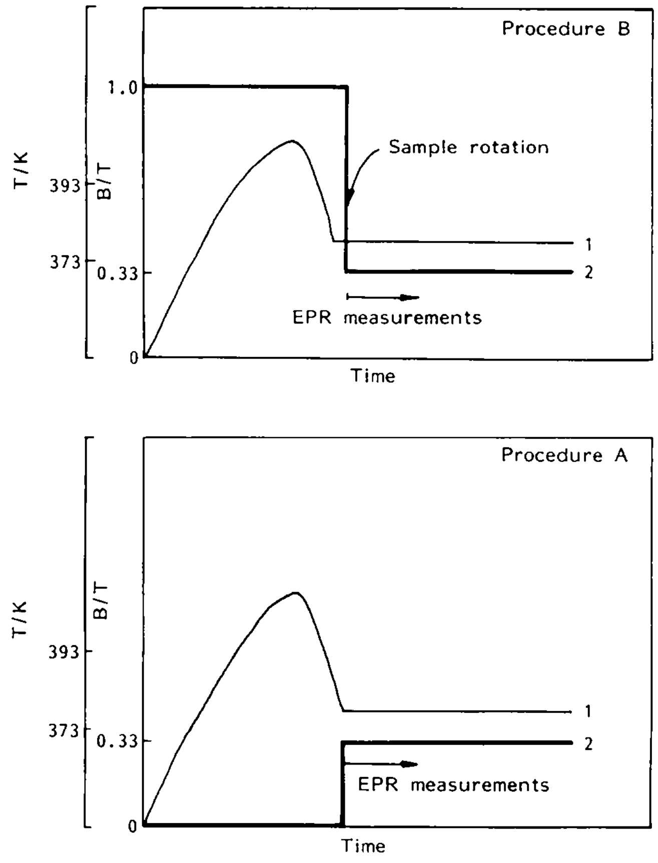

Figure 1 Schematic representation of the two measurement procedures (A and B): (1) temperature; (2) magnetic field strength

Additionally, in the range of rapid rotations we have measured the position of the e.p.r. line in a magnetic field and calculated the anisotropy parameter ε:

$$\varepsilon=\frac{[I(0)/I(+1)]^{1/2}-1}{[I(0)/I(-1)]^{1/2}-1} \qquad (4)$$

characterizing the degree of rotational anisotropy.

The temperature dependence of the above parameters is presented in *Figure 2*. As seen from this figure, the dependence of f vs. $1/T$ can be described, in the whole region, by the Arrhenius equation. This means that the transition from the isotropic state to the nematic state does not reveal itself in the approximation of isotropic rotations. A sudden jump in the position of the e.p.r. line corresponds to this transition. Similar changes in the linewidth and anisotropy parameters are observed as well. In particular, the change of the ε parameter from the value 0.2 to the value 0.4 means, as implied from the analysis presented in ref. 1, that a transition from isotropic rotations (isotropic phase of LCP) to strongly anisotropic rotations takes place. The value of the ratio of the rotational frequencies calculated along the longer axis to that along the shorter axis can be estimated to be at least 10. More precise analysis needs a computer simulation of the spectrum and has not yet been carried out. So, the observed changes in the above-mentioned parameters can be interpreted in terms of a preference for one radical axis due to the appearance of nematic ordering. In order to find out to which relaxational process the rotational mobility of the probes may be related, the e.p.r. results were correlated with data derived from dielectric and n.m.r. measurements[6,7], which is presented in the relaxation diagram in *Figure 3*.

The α relaxation presented here was assigned to processes in which segments of the main chain and/or the same segments coupled via a spacer with mesogenic groups become mobile[6]. Data from dielectric measurements for the β relaxation available for a similar LCP[6] correlate very well with the e.p.r. data presented on the relaxation diagram. This particular relaxation was explained in terms of the rotations of the *p*-cyanophenyl group along its longer axis. This conclusion is in agreement with previous reports[1,3,4] that short chain sequences (local mode relaxations) are responsible for the mobility of small probes. In this case these short chain sequences are very similar to the probe as far as both their dimensions and their structure are concerned. Furthermore, the β process has been detected in mechanical measurements at the temperature determined by the extrapolation of the e.p.r. data[15].

Apart from the effects described above, we observed another effect as yet unknown for low-molecular-weight liquid crystals. This effect reveals itself in the form of time changes in the e.p.r. line position. It is present only for the nematic phase and constitutes yet more evidence for the orientational influence of the molecules forming this phase on the spin probes. Therefore, we have also

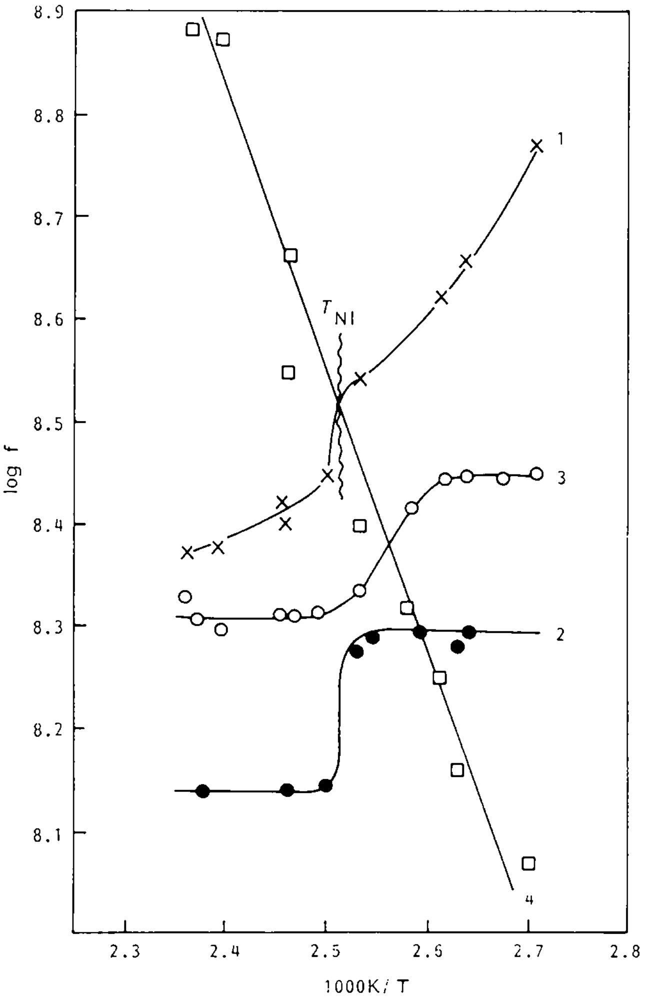

Figure 2 Temperature dependence of the e.p.r. parameters (curves 1–3) and the relaxation diagram for the LCP in the fast rotation region (curve 4): (1, 2) the linewidth and line position (in arbitrary units); (3) the anisotropy parameter ε (in arbitrary units)

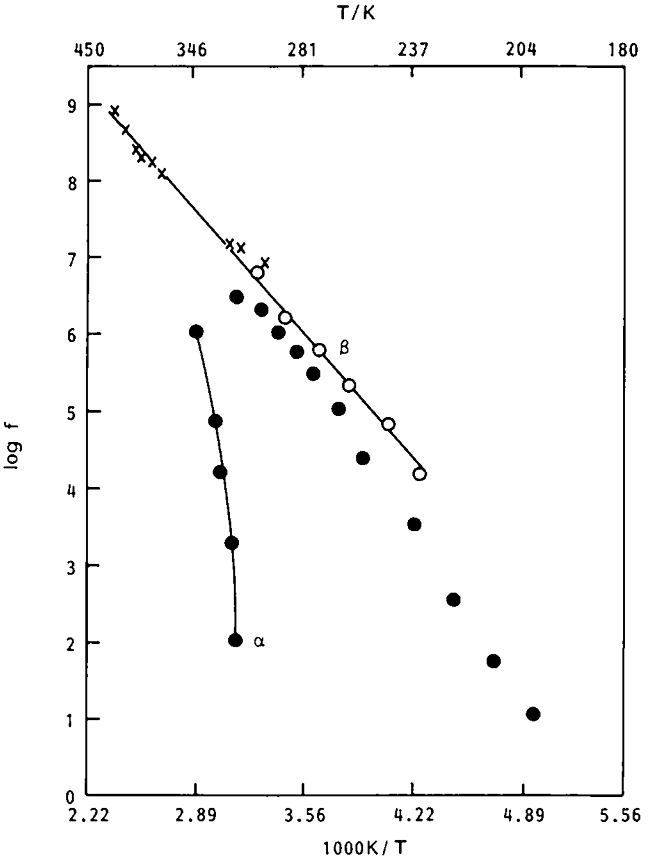

Figure 3 The relaxation diagram for LCP: (●) dielectric data[6–8]; (○) n.m.r. data[6]; (×) e.p.r. data from the present work

undertaken the investigation using two different procedures, A and B. One may expect that procedure A should lead to the creation of a polydomain structure of the sample, whereas procedure B should lead to a monodomain structure (see discussion in ref. 10).

The observed shifts of the line could then be connected with the orientation of regions with nematic ordering in the magnetic field during e.p.r. measurements, while the kinetics of the orientational process should be different in both cases. In fact, the results obtained depend on the procedure (*Figure 4*) and the temperature. Similar orientational processes of main-chain LCP in a magnetic field were previously observed using n.m.r. by Moore and Stupp[10] (see also refs. 11–13). They assumed that the monodomain sample can be described by a single orientation angle θ:

$$\tan\theta = \tan\theta_0 \exp(-t/\tau) \qquad (5)$$

The ordering of the postulated polydomain structure was described by assuming that particular domains orient independently of their neighbouring domains and assuming the appropriate distribution function of directors (for the details see ref. 10).

The polydomain sample can then be described by the macroscopic order parameter $\langle S_{zz}^2\rangle$:

$$\langle S_{zz}^2\rangle = \tfrac{1}{2}\langle(3\cos^2\theta - 1)\rangle = \frac{\int_0^\pi \rho(\theta, t_r)(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2})^2 \sin^2\theta \, d\theta}{\int_0^\pi \rho(\theta, t_r)\sin\theta \, d\theta} \qquad (6)$$

where θ is the angle between the direction of packing of the molecules, $t_r = t/\tau$, τ is the relaxation time and $\rho(\theta, t_r)$ is the distribution function of directors.

Unfortunately, the formalism developed by Moore and Stupp[10] cannot be adopted directly in the interpretation of our e.p.r. data because the parameters measured by us cannot simply be related to $\tan\theta$ or the order parameter. Below we propose a simplified (computer simulation would be necessary for a greater precision) method for the interpretation of the observed changes in the e.p.r. spectra.

As well known (see e.g. refs. 1 and 2), the effective parameters describing the hyperfine (A) and Zeeman (g) interactions, determining the e.p.r. line position, have the form:

$$A_{\text{exp}} = (A_\parallel^2 \cos^2\theta + A_\perp^2 \sin^2\theta)^{1/2} \qquad (7)$$

$$g_{\text{exp}} = (g_\parallel^2 \cos^2\theta + g_\perp^2 \sin^2\theta)^{1/2} \qquad (8)$$

where θ is the angle between the direction of the magnetic field and the rotation axis of the radical; and $A_\perp$, g_{-} and $A_\parallel$, $g_{|}$ are correspondingly the values of A and g for perpendicular and parallel orientation of the magnetic field with respect to this axis.

It follows, from these equations, that the position (L) of the extreme ($m = +1, -1$) e.p.r. lines may be satisfactorily calculated from the relation:

$$L^2 \sim A^2 \sim \cos^2\theta \qquad (9)$$

The above relation enables the discussion of our results in terms of the quantities proposed in Moore and Stupp[10], i.e. basically $\langle S_{zz}\rangle$, which is also proportional to $\cos^2\theta$.

First of all, in order to make our results independent of the sample rotation angle θ_0 and to avoid the necessity of calculating the $A_\perp$ and $A_\parallel$ parameters, the amplitude of the line position changes was normalized to unity. In consequence, normalization of equations (5) and (6) is necessary. In particular, equation (5) can be transformed to the form:

$$\cos^2\theta = [1 + \tan^2\theta_0 \exp(-2t/\tau)]^{-1} \qquad (10)$$

which, from the standpoint of an experimentalist, is normalized since $\cos^2\theta \to 1$ for $t \to \infty$, and $\cos^2\theta \to 0$ for $t \to 0$ because $\tan^2\theta_0 \gg 1$.

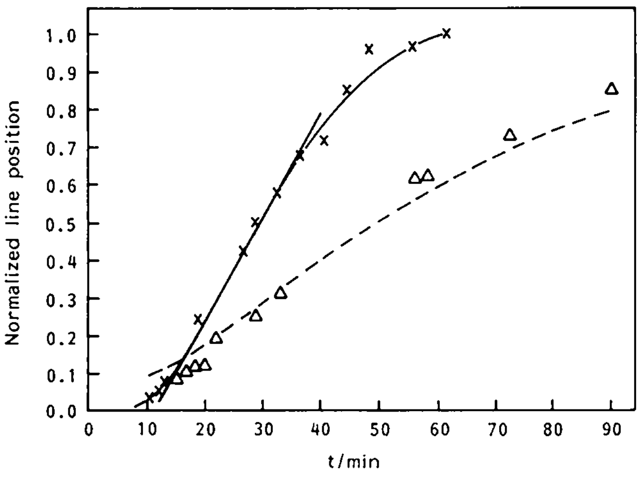

Figure 4 Time dependence of the squared e.p.r. resonance field. (×) Experimental points, procedure B. (——) Theoretical curve according to equation (10); the values of parameters $\tau = 18$ min and $\tan^2\theta_0 = 30$ were obtained from equations (11) and (12) applied to the linear part of the curve. (○) Experimental points, procedure A. (- - -) Fitting of equations (6) and (9) to the experimental points with $\tau = 36$ min

Expanding function (10) into a Taylor series around the inflection point, one can find the following parameters a and b (in the equation of type $y = ax + b$), which describe approximately the function (6) in this region:

$$a = \tfrac{1}{2}\tau \tag{11}$$

$$b = [1 - \ln(\tan \theta_0)]/2 \tag{12}$$

For a polydomain sample the value of $\cos^2 \theta$ was obtained by calculation of S_{zz} (from equation (6)) followed by normalization. The rate of domain orientation for the samples investigated in both versions of the experiment is presented in *Figure 4* together with the results from the discussed simulations. Good agreement between experimental and theoretical results for the monodomain sample is observed. A similar simulation for the assumed polydomain sample does not give such good agreement. This has already been noticed[10] for samples of similar molecular weight. A question emerges whether one can distinguish, based on the shape of the curves presented in *Figure 4*, the monodomain structure from the polydomain one.

As follows from our experience, for angles $\theta_0 \approx 90°$ the curves obtained from equations (6) and (10) do not seem to differ in their shape up to $t_r = 1.5$, and this is seen in those parts of *Figure 4* in which the curves are almost linear. More appreciable differentiation of the dynamics is seen only for $1.5 < t_r < 4$. Moreover, owing to the fact that the first e.p.r. spectrum, taken using procedure B, is measured about 1 2 min after the magnetic field jump, the initial part of the curve is 'cut off'. Therefore, it seems that the experimental solution of the above-mentioned problem is very difficult, if possible at all. On the other hand, *Figure 4* shows the different dynamic behaviour of the orientational processes taking place in both experiments. Our preliminary investigations seem to indicate that the above-mentioned differentiation becomes less pronounced when the temperature increases.

We noticed that the dynamics of the described processes (and the shape of the respective curves) depend, as was stated in ref. 9, on the rotation angle of the sample. Marked differences were found for angles $\theta_0 > \pi/4$ and $\theta_0 < \pi/4$. Taking all these facts into account, it is advisable to extend the measurements to a wider range of angles θ_0 and to probe the samples using radicals with greater anisotropy of tensor A in order to improve the measurement accuracy. We plan to do some of these investigations in the near future.

CONCLUSIONS

The spin-probe method as applied to the side-chain liquid-crystalline polymers discussed here supplies (owing to the spin probe–mesogenic group coupling) valuable information on local mode relaxational processes of mesogenic groups.

Changes in the anisotropy of the probe motion are connected with the formation of a nematic phase. The information obtained for the polymers discussed is similar to that which can be obtained from the spin-probe method for low-molecular-weight liquid crystals.

The possibility of observation of the time evolution of the e.p.r. line position enables one to monitor the domain orientational processes under the influence of a magnetic field.

Information about relaxation processes taking place in liquid-crystalline polymers derived from spin-probe e.p.r. studies is, at least, competitive with that obtained from n.m.r.

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