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Magnetic field effects in nematic and smectic liquid crystals probed by time resolved observation of orientation relaxation of the spin probe†

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The kinetics of reorientation of the liquid crystal HOPOOB in nematic and smectic phases in the magnetic field was studied by the spin probe technique. The time evolution of the EPR spectrum shape in the course of reorientation in the nematic phase indicates that the mechanism of alignment comprises redistribution between domains of different orientations rather than the turn of the orientation distribution function. A microscopic model of domain structure rearrangement is provided to qualitatively describe the experimental data. In the smectic C phase, partial reorientation is observed upon the action of the magnetic field. A possible mechanism of this process is the reorientation of tilt direction within the smectic layers. It is shown that this process is constrained, and the value of the corresponding elastic constant is estimated.

I. Introduction

Reorientation of liquid crystals in electric and magnetic fields, known as the Fréederiksz effect, is one of the most peculiar features of these materials. Due to the long standing interest in this effect from the point of view of its application in display technology, field-induced reorientation of liquid crystals has been extensively studied both experimentally and theoretically.[1] Usually, the dynamics of reorientation is measured with optical techniques, *i.e.* by measuring birefringence,[2] anisotropy of absorbance[3,4] and Raman scattering.[5,6] These optical techniques are limited to measuring the averaged characteristics of orientation order, namely, the orientation tensor of rank two.

In order to observe more detailed features of the orientation distribution of liquid-crystalline material, magnetic resonance techniques have proven useful,[7–17] including the spin-probe technique. The drawback of these techniques is their relatively low temporal resolution, which makes it difficult to measure transient features of field-induced reorientation on the time-scale of milliseconds to seconds, characteristic of common thermotropic liquid crystals.

In this work, we present a technique for measuring the transient EPR spectra of the spin probe in the liquid crystal in the course of its reorientation in the magnetic field. For this,

one can take advantage of the reversibility of the reorientation process. Instead of fast sweeping the spectrometer field to record a series of spectra, the time dependence of the EPR signal at a fixed value of magnetic field is recorded. By repeating this for various values of magnetic fields, one obtains the time evolution of the EPR spectrum on a millisecond time scale.

We have tested the applicability of the described approach to study the process of magnetic field reorientation of a few liquid-crystalline materials. In the present paper, we report in detail the results obtained for the liquid crystal HOPOOB, as it has been found that this material demonstrates well the characteristic features of the magnetic field re-orientation of nematic and smectic C liquid crystals.

The dynamics of magnetic field reorientation was studied for samples of liquid crystal in EPR tubes with a diameter of 3 mm. It is known that for such samples, the influence of the tube surface on the liquid crystal orientation is negligible,[18] and thus the bulk behaviour of the material can be studied. In additional experiments, a thin homeotropically aligned cell of nematic HOPOOB was used to determine the static properties of the spin probe in the nematic phase, because in such cells, due to strong anchoring of the surface, no magnetic field reorientation is observed.

II. Experimental details

The liquid crystal HOPOOB (Fig. 1a) was used as the liquid-crystalline material. The substance was produced by RIAP (Kiev, Ukraine) and purified by recrystallization from ethyl acetate.

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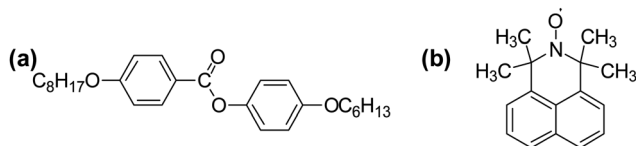
Fig. 1 Chemical structure of the liquid crystal HOPOOB (a) and spin probe A5 (b) used in the present study.

The phase transition temperatures for this substance are: 329.1 K (Cr-SmC), 338.6 K (SmC-N), 362.4 K (N-Iso).[19]

Nitroxide radical A5 (Fig. 1b) was chosen as a spin probe for the present study. It was synthesized and kindly provided by Prof. S. Bottle. Earlier, in our group, it was shown that this radical readily incorporates into liquid-crystalline phases and effectively reflects their orientation order.[20] Due to fast rotation movements, EPR spectra of the spin probe A5 consist of narrow lines, which provide high resolution in orientation measurements.

For sample preparation, a solution of the spin probe in the liquid crystal (0.2 wt%) was prepared in a quartz EPR tube of 3 mm inner diameter. The solution was degassed at 10^{-2} Torr at 363 K for an hour, after which the tube was sealed.

EPR spectra were recorded using an X-band spectrometer Bruker EMX-plus. The temperature of the samples was set in the range 300–370 K using the flow of nitrogen gas. To compensate for systematic errors produced by the temperature control unit of the EPR spectrometer, the temperature of the gas flow was calibrated using an external thermocouple. Thus, the accuracy of temperature setting was about ±0.2 K.

The process of reorientation of the liquid crystal was monitored after a fast turn of the bulk sample in the EPR cavity. For the fast turn of the sample in the spectrometer, a home-made goniometer setup was built. The sample was fixed in a plain bearing. The turn was accomplished with a stepper motor equipped with a gearbox, which provided a speed of rotation of approximately 3600 degrees s^{-1}. For reorientation measurements, the sample was turned fast by 90°, while the time dependence of the EPR signal at a fixed magnetic field was being recorded. During the turn (0.025 s) and shortly after (ca. 0.2 s), recording the EPR signal was not possible due to detuning of the EPR cavity. Therefore, the first 0.25 s after the sample turn can be regarded as the dead time of the present measurement. After the sample turn, the resonance frequency of the cavity was slightly (by about 0.5 MHz) different from the frequency prior to the turn, which results in the slight shift of the resonance magnetic field. This shift was taken into account during processing of the experimental data. It has been checked that the fast turns of the sample by 180° and 360° were not followed by EPR signal relaxation. Hence, the distortion of LC structure due to hydrodynamic effects during the turn can be considered negligible in our experiments.

In addition to studying the dynamics of the reorientation process, the equilibrium orientation order of nematic HOPOOB was examined in separate experiments. For this purpose, the angular dependence of the EPR spectrum was recorded for aligned samples of HOPOOB in the nematic phase. The recording

of angular dependencies was performed using a goniometer setup with the accuracy of angle setting of ±0.2°. For a nematic liquid crystal, the angular dependence of the EPR spectrum cannot be recoded for the bulk sample, due to fast reorientation of such a sample in the spectrometer magnetic field. Therefore, to study the orientation order in the nematic state, a thin sample of HOPOOB sandwiched between two quartz plates was used. The thickness of the sample was controlled by glass rod spacers (diameter 11 μm). Prior to use, the quartz plates were exposed to dichlorodimethyl-silane vapour for 1 day, to induce homeotropic orientation of the sample. The homogeneity of homeotropic alignment was checked by means of polarization optical microscopy observations. Such sandwiched samples were used for recording of the angular dependence of EPR spectra of the perfectly aligned nematic liquid crystal.

Our optical observation showed that cooling of the thin homeotropically aligned sample of HOPOOB from the nematic to smectic C state does not lead to the perfectly aligned smectic C phase, but rather to a polydomain smectic material.

III. Experimental results

The angular dependence of the EPR spectra of the spin probe A5 in the nematic phase of HOPOOB (T = 350 K), recorded in a thin homeotropically aligned cell, is presented in Fig. 2a. The spectra consist of 3 lines, corresponding to hyperfine splitting on the nitrogen nucleus of the nitroxide moiety. It can be seen that the effective g-factor, hyperfine splitting and linewidth of each hyperfine line are angular dependent due to the alignment of the spin probe in the liquid-crystalline medium.

For the bulk sample of HOPOOB in a quartz tube of 3 mm inner diameter, turning the sample in the magnetic field causes rapid reorientation of the liquid crystal in accordance with the new magnetic field direction. This process is illustrated in Fig. 3, in which the time dependence of the EPR spectrum is displayed for two magnetic fields, which correspond to the maximum of the low-field component of the 90° and 0° spectra (Fig. 3a). It can
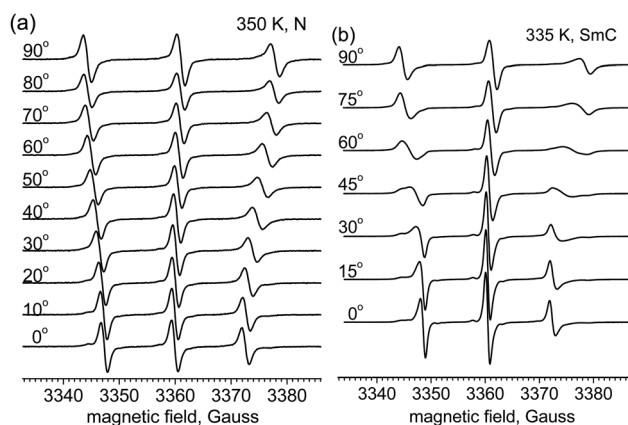

Fig. 2 Angular dependence of EPR spectra of the spin probe A5 in HOPOOB: (a) nematic phase at 350 K, flat aligned cell 11 μm thick, (b) smectic C phase at 335 K, bulk sample ordered by magnetic field in the nematic state.

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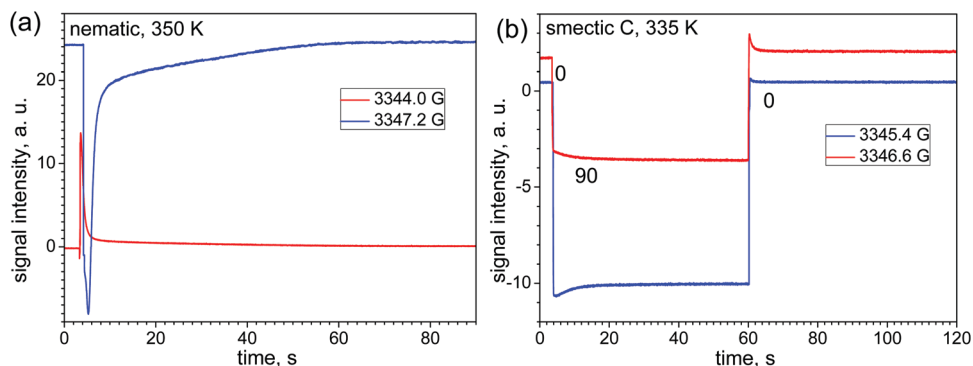*Phys. Chem. Chem. Phys.*, 2018, **20**, 18340–18347 | **18341**

Fig. 3 The time dependence of the EPR signal of A5 in HOPOOB in nematic (a) and smectic C (b) phases upon turning the sample by 90 degrees in the magnetic field.

be seen that before the sample turn, the EPR signal corresponds to the intensity of the spectrum for the 0° spectrum, since the liquid crystal director is parallel to the magnetic field. Immediately after the turn of the sample, the signal changes fast to the value corresponding to the 90° spectrum. Then, the relaxation process returning the EPR signal intensity to the original value is observed. This corresponds to the relaxation of the nematic liquid crystal orientation towards the new magnetic field direction. It should be noted that such behaviour is characteristic of nematic liquid crystals and has been observed in our experiment with other nematic substances (5CB, 8CB, MBBA etc.).

By putting together the time dependent signals recorded for different magnetic field values, one obtains the time evolution of the EPR spectrum. This time evolution for the nematic state of HOPOOB is presented in Fig. 4a. The spectrum immediately after the turn (Fig. 4a, 0.3 s) is close to the 90° spectrum of the angular dependence, and the finishing spectrum (Fig. 4a, 90 s) is close to the 0° spectrum of the angular dependence (cf. Fig. 2a). The characteristic feature of this time evolution is the shape of the transient spectra. Qualitatively, they are similar to the mixture of 0° and 90° spectra of the spin probe, where the fraction of 90° spectrum decreases, and the fraction of the 0° spectrum increases with time. This experimental result rules out the possibility of reorientation of nematic HOPOOB via the turn of orientation distribution function, because in this case, the time evolution of the EPR spectrum would follow along the spectra of angular dependence, such as in Fig. 2a.

The same approach was applied to the liquid crystal HOPOOB in its smectic C state. Cooling the bulk sample of HOPOOB from the nematic to smectic C phase in the magnetic field produces the sample of the aligned smectic C. The angular dependence of the EPR spectrum recorded for this aligned sample is presented in Fig. 2b. It can be seen that the EPR line shapes differ from those in the nematic phase due to the different rotation mobility and orientation order of the spin probe molecules in the two phases. According to our experiments (see below), the turn of the sample in the EPR spectrometer magnetic field leads to partial reorientation of the smectic material. Therefore, each spectrum of the angular dependence shown in Fig. 2b corresponds to the orientation
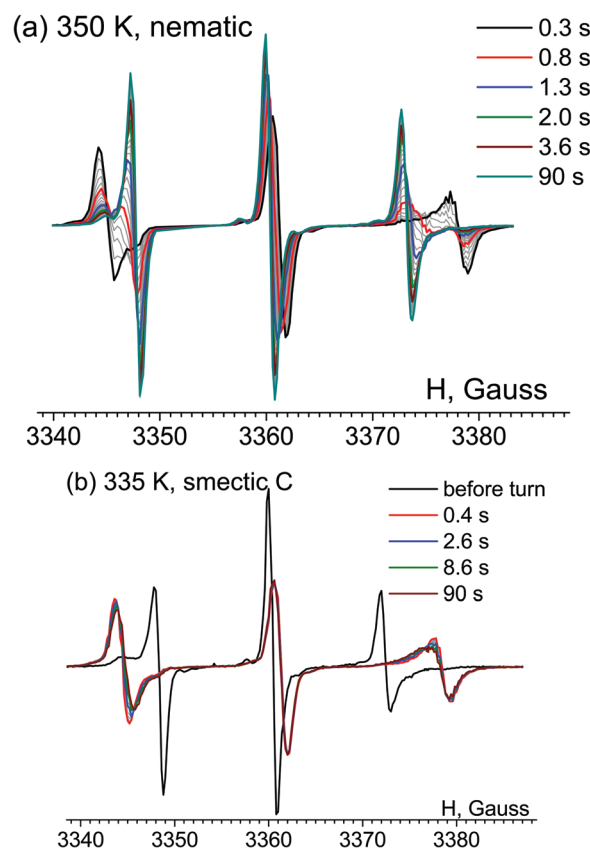

Fig. 4 Time evolution of EPR spectrum of A5 in HOPOOB in the course of liquid crystal reorientation in the nematic (a) and smectic C (b) phase. The moment of the sample turn corresponds to 0 s. The legends indicate the time elapsed after the sample turn in seconds.

order distorted by the magnetic field, and this distortion is different for each spectrum. Thus, the presented angular dependence does not correspond to a single orientation distribution.

Fig. 3b illustrates the changes of EPR signal after the turn of the sample by 90 degrees in the magnetic field. Turning the sample from the orientation parallel (0°) to perpendicular (90°) to the initial director causes the sharp change of the EPR signal, followed by partial relaxation on the timescale of a few seconds. This relaxation process indicates that the change of the

magnetic field with respect to the sample director is followed by distortion of the orientation structure of the smectic phase of HOPOOB. Turning the sample back to the original orientation (at time 60 s in Fig. 3b) leads to a change of EPR signal. Again, it can be seen that the sharp change of EPR signal followed by relaxation to the original value takes place. It should be noted that relaxation after the sample turn in the magnetic field was not observed for all tested smectic liquid crystals. In our experiments, we have not found the relaxation for the substances 8CB ($4'$-n-octyl-4-cyanobiphenyl, SmA phase), H59 ((p-decycloxybenzylidene)-p-toluidine, SmA) and HOBDOB (4-n-hexyloxyphenyl-$4'$-n-decyloxybenzoate, SmA and SmC phases). Thus, such behaviour should be considered as a specific property of some smectic C liquid crystals, that is demonstrated by the liquid crystal HOPOOB.

By combining the time dependences of the EPR signal recorded for different magnetic field values, the time evolution of EPR spectra in the course of the relaxation process was determined. The obtained spectra are presented in Fig. 4b. Before the sample turn, the spectrum corresponds to the $0°$ orientation. Immediately after the sample turn, the spectrum has the shape corresponding to the $90°$ orientation. Then, a small change in the spectrum shape is observed in time, namely, a slight decrease of the effective hyperfine splitting and increase of the linewidth of the spectrum. The possible mechanisms of the observed features will be discussed below in Section V.

IV. Mechanism of nematic reorientation

The phenomenological theory of the Fréedericksz transition of nematics states that the external field exerts macroscopic torque on the director of the liquid crystal, which is the sum of the torques exerted on individual molecules. This torque is supposed to reorient the director, so that it turns towards the new magnetic field direction (in the case of positive diamagnetic anisotropy of the liquid crystal molecules), thus the dynamics of nematic reorientation consists in the turn of the orientation distribution, with the invariance of the value of the order parameter. The experimental data obtained for HOPOOB in the nematic phase are in contradiction with this view. The turn of orientation distribution function would manifest itself in the smooth movement of the spectrum lines, according to the positions of lines in the spectrum angular dependence (*cf.* Fig. 2a). Instead, what is experimentally observed is the diminishing of the fraction of molecules oriented perpendicular and the growth of those oriented parallel to the magnetic field direction.

The probable explanation of the observed evolution of EPR spectra is as follows. It is known that even in the aligned liquid crystal, there is a certain equilibrium amount of defects, disclinations and director fluctuations. In the presence of the magnetic field directed differently from the preferential alignment of liquid crystal molecules, these defects and fluctuations

play the role of nuclei for the growth of domains with favourable orientations, *i.e.* those with the least free energy in the external field. Thus, the reorientation occurs by rearrangement of the microscopic structure of the material, wherein the more stable domains grow at the expense of the less stable ones.

A similar situation was described in our prior work[21] concerned with the photo-induced orientation of azobenzene-containing liquid-crystalline material. By analogy with this work, we formulate a simple mathematical model of field-induced liquid crystal reorientation based on the described mechanism. This model is based on the following assumptions:

1. the material consists of domains, *i.e.* relatively large areas with orientations defined by Euler angles Ω, the number density of domains with various orientations is uniform, and the material anisotropy originates from the angular distribution of mean domain sizes;

2. for each orientation Ω, one can define the value of the mean domain radius $R(\Omega)$, such that the total volume of domains with orientation Ω is given by $\frac{4}{3}\pi R^3(\Omega)$, and the surface area of such domains is $4\pi R^2(\Omega)$ (*i.e.* approximation of spherical domains);

3. domain boundaries are distributed statistically; that is, the fraction of contact area between the domains with orientations Ω and Ω', in the whole surface area of domains with orientation Ω, is equal to the total fraction of surface area of domains with orientation Ω' in the total surface area of all domains;

4. reorientation takes place only on the domain boundary, and the velocity of the domain boundary motion is proportional to the difference in free energies of adjacent domains.

With these assumptions, the dynamics of the mean domain radius is given by the equation:[21]

$$\frac{dR(\Omega)}{dt} = M\frac{\int (g(\Omega) - g(\Omega'))R^2(\Omega')d\Omega'}{\int R^2(\Omega')d\Omega'} \qquad (1.1)$$

where $g(\Omega) = -\cos^2(\vec{\mathbf{H}},\vec{\mathbf{n}})$ is the dimensionless free energy of domains with orientation Ω, M is the coefficient equal to the rate of motion of the domain boundary between two adjacent domains with unit free energy difference.

For axial domains, domain orientation is defined by two polar angles $\Omega = (\theta, \varphi)$ of the director in the sample reference frame, in which the magnetic field is directed along the z-axis. Then,

$$g(\theta,\varphi) = -\cos^2 \theta \qquad (1.2)$$

By multiplying both sides of eqn (1.1) by $4\pi R^2(\Omega)$ and integrating over all orientations Ω, one can see that for the evolution given by eqn (1.1), the total domain volume is invariable and can be used for normalization:

$$\int \frac{4}{3}\pi R^3(\theta, \varphi)\sin\,\theta\,d\theta d\varphi = \frac{4}{3}\pi R_0{}^3 \qquad (1.3)$$

By substituting the expression (1.2) for the free energy into eqn (1.1) and using the dimensionless domain radius

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$r = R(\theta,\varphi)/R_0$ and dimensionless time $\tau = M \cdot t/R_0$, the following equation is obtained:

$$\frac{dr(\theta,\varphi)}{d\tau} = \frac{\int (\cos^2 \theta - \cos^2 \theta') r^2(\theta',\varphi') \sin \theta' d\theta' d\varphi'}{\int r^2(\theta',\varphi') \sin \theta' d\theta' d\varphi'} \quad (1.4)$$

The eqn (1.4) is dimensionless and has no model parameters. However, its solution depends on the initial domain size distribution $R(\theta,\varphi)|_{t=0}$. This distribution can be calculated from the orientation distribution function $\rho_D(\theta,\varphi)$ of liquid crystal domains:

$$R(\theta,\varphi) = R_0[\rho_D(\theta,\varphi)]^{1/3} \quad (1.5)$$

By combining eqn (1.4) and (1.5), one obtains the equation for the evolution of the orientation distribution function of domains:

$$\frac{d\rho(\theta,\varphi)}{d\tau} = 3 \frac{\int (\cos^2 \theta - \cos^2 \theta') \rho^{2/3}(\theta,\varphi) \rho^{2/3}(\theta',\varphi') \sin \theta' d\theta' d\varphi'}{\int \rho^{2/3}(\theta',\varphi') \sin \theta' d\theta' d\varphi'}$$
$$(1.6)$$

The initial orientation distribution function can be estimated on the basis of the EPR spectrum angular dependence shown in Fig. 2a. It should be noted that in the developed model, the sample of liquid crystal is assumed to have a hierarchical orientation organization. There is the "internal" orientation order, which relates to uniformly aligned areas of liquid-crystalline material (domains), and the "external" orientation order, caused by the non-uniform angular distribution of domain directors. This "external" orientation distribution of domain directors is present even in the aligned sample of liquid crystal, due to equilibrium director fluctuations, defects and disclinations of the material. This situation is similar to the model of the slowly relaxing local structure described in ref. 22 and 23. The experimentally observed angular dependence of the EPR spectrum is due to the convolution of both orientation effects. The problem of the independent determination of "internal" and "external" orientation distribution functions is mentioned in the literature,[24,25] but it has not been considered in detail, and it is still unclear whether such independent determination is possible only on the basis of EPR spectra. In the present work, for obtaining the orientation distribution of domain directors $\rho_D(\theta,\varphi)$ of HOPOOB, the simulation of EPR spectra in Fig. 2a was carried out in the following way. The "internal" orientation order was simulated by the mean-field potential approach developed by Freed et al.[8,26] with a rather high value of mean-field potential amplitude, $u_0 = 14k_BT$ (k_B stands for Boltzmann constant). The "external" orientation distribution function $\rho_D(\theta,\varphi)$ of the aligned sample was determined by nonlinear least-squares simulation of the experimental spectra. Then, the obtained orientation distribution function $\rho_D(\theta,\varphi)$ was used as the initial orientation distribution of director domains for simulation of magnetic reorientation by eqn (1.6). It should be noted that despite the fact that the value of mean-field potential amplitude u_0 for these simulations has been chosen arbitrarily, it has been checked that different values of potential give qualitatively the same simulation results.

The details of the model simulations are described in the ESI† (Appendix A).

The results of the simulation are illustrated in Fig. 5. The time evolution of the orientation distribution function of the domain directors is presented in Fig. 5a. It can be seen that in the initial moments of reorientation, the domains oriented parallel to the new magnetic field direction start to grow and eventually start to dominate in the orientation distribution. Fig. 5b shows the EPR spectrum evolution predicted by the described model. It can be seen that the theoretical spectra are in qualitative agreement with the experimentally obtained ones (Fig. 4a). Superposition of theoretical and experimental spectra is presented in the ESI† (Fig. D1) to illustrate their agreement. It should be noted that the theoretical spectra were obtained without the use of any fitting parameters, and therefore they do not reproduce the experimental spectra quantitatively, however, the clear qualitative similarity can be observed.

Fig. 5c illustrates the kinetics of EPR signal change at two points in the spectra, which correspond to the maxima of the left components the of 0° and 90° spectra. These kinetics can be compared with the experimental ones (Fig. 3a) to conclude that they demonstrate good agreement.

Thus, a simple geometrical model based on the mechanism of microscopic structure rearrangement of the liquid crystal matrix accounts for the experimental data obtained in the present work. However, it should be noted that this model contains a number of simplifications, the principal ones being:

(1) the assumption of isotropic distribution of the number of domains;

(2) the assumption of a statistical orientation distribution of domain surface areas, which holds all the way through the orientation process.

V. The model for smectic C reorientation

The experimental data obtained for HOPOOB in the smectic C phase indicate that its orientation structure is modified by the magnetic field of the EPR spectrometer (ca. 3300 Gauss). The most important structural features of the smectic C phase are (1) the presence of a layered structure and (2) the tilt of molecular long axes with respect to layer normal. The tilt angle will be denoted here as Ψ. Thus, the reorientation of the smectic C structure in the magnetic field can proceed (a) with the distortion of layer structure, (b) by the change of molecule tilt angle, or (c) by the rotation of tilt direction. Theoretical considerations present in the literature[27-29] as well as the experimental data[7,12] indicate that only the latter case is realized in low magnetic fields such as that in the present work.

Let us consider the possibility of a change of tilt direction in the magnetic field for the situation experimentally considered in Section III. The smectic C sample was obtained by cooling of the nematic phase in the bulk sample under the magnetic field of the EPR spectrometer. In this situation, the polydomain sample should form, in which the normals to the smectic layers
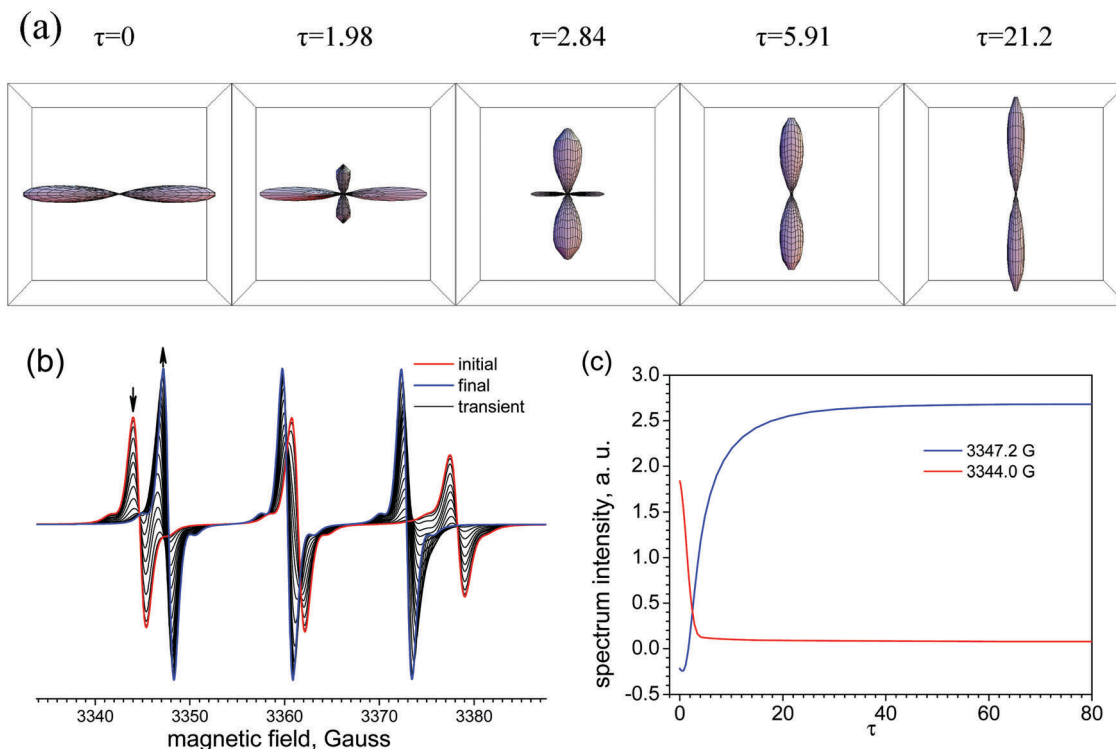
Fig. 5 (a) Evolution of orientation distribution function of the sample in the course of magnetic field reorientation according to eqn (1.6) with the initial orientation distribution obtained from the experimental EPR spectra (see text). (b) The time evolution of EPR spectra predicted by model (1.6) and (c) kinetics of EPR signal change under the fields corresponding to the maxima of the low-field components of the 0° and 90° spectra (at field values of 3347.2 and 3344.0 Gauss).

are statistically distributed over the cone with aperture 2Ψ and axis directed along the magnetic field. After the turn of the magnetic field by 90 degrees with respect to the initial direction, for some domains, it may be energetically favourable to turn the direction of the tilt, so as to minimize the free energy density of the smectic phase in the magnetic field, which is proportional to

$$u = -\mathcal{M}(\mathbf{n} \cdot \mathbf{h})^2 \qquad (1.7)$$

Here, $\mathbf{n}$ is the liquid crystal director and $\mathbf{h}$ is the unit vector directed along the magnetic field, $\mathcal{M}$ is the magnitude of magnetic interaction anisotropy, $\mathcal{M} = \dfrac{1}{2} \dfrac{M}{\rho N_A} \dfrac{\chi_a}{\mu_0} H^2$, where χ_a is the anisotropy of diamagnetic susceptibility, μ_0 is the magnetic constant, ρ is material density, M is molar mass, N_A is the Avogadro constant and H is magnetic field flux density. Just after the turn of the sample, the molecules are preferably oriented at 90° to the magnetic field direction. Then, the relaxation takes place. If all domains are free to change the direction of their tilt in order to minimize the potential (1.7), then after relaxation, there will be a distribution of director orientations. The distribution of the angles ξ between the domain director and magnetic field can be calculated by minimizing the potential of eqn (1.7) for each domain. Details of this calculation are given in the ESI† (Appendix B). The resulting distribution is presented in Fig. 6a (blue histogram). The shape of this distribution depends on the value of the tilt

angle Ψ of the smectic C phase. For the calculations, the value of $\Psi = 27°$ known for the SmC phase of HOPOOB[30] was used. The histogram presented in Fig. 6a indicates that in the case of free rotation of tilt direction, the predicted orientation relaxation is significant, with all domains reorienting from the initial 90° orientation.

The calculated distribution can be used for estimation of the shape of the EPR spectra corresponding to this model. This is illustrated in Fig. 6b. There, the black line corresponds to the spectrum before the turn, and the red line corresponds to the spectrum right after the turn. The blue line depicts the spectrum after relaxation in the model of free rotation of the tilt direction. Details of the spectral simulation are given in the ESI† (Appendix C). By comparison of the theoretical spectra with the experimental ones presented in Fig. 4b, one can conclude that the model of free rotation of tilt direction predicts a much more pronounced change of the spectra than those experimentally observed. To account for this deviation, it should be taken into account that the relaxation of the tilt direction is not free, but hindered by elastic constraints. In this case, the eqn (1.7) can be modified by the elastic term:

$$u = -\mathcal{M}(\mathbf{n} \cdot \mathbf{h})^2 + K\left(\frac{\Delta \alpha}{l}\right)^2 \qquad (1.8)$$

where K is the elastic constant and $\Delta\alpha/l$ is the difference of the azimuth angle of the tilt direction per unit length. In the

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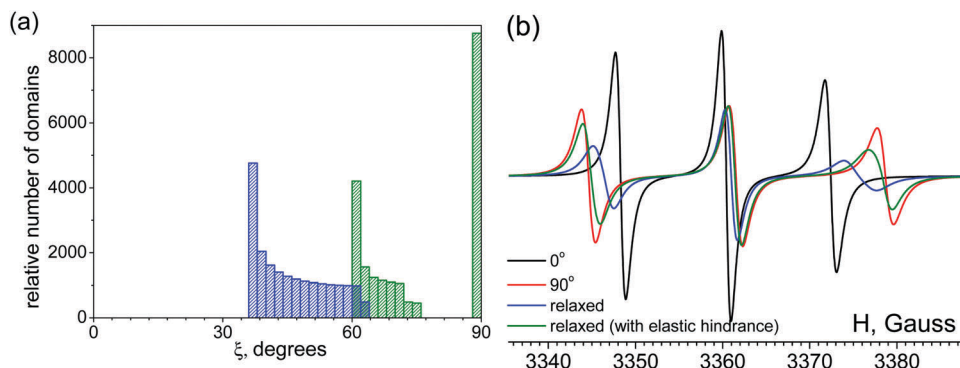
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Fig. 6 (a) The orientation distribution of relaxed directors in the case of free rotation of tilt direction (blue) and with the elastic constraint of tilt direction rotation. (b) Simulated EPR spectra of the smectic C phase before the turn (black), just after the turn (red) and after relaxation without (blue) and with (green) the elastic constraint on the tilt direction (see text).

described system, the difference of the azimuth angle $\Delta\alpha$ corresponds to the adjacent domains with different directions of layer normal. Therefore, distance l has the order of magnitude of the average domain size.

The optimal direction of molecular tilt can be determined by minimization of the corresponding potential (1.8), as described above for the potential (1.7). The resulting distribution of director orientations with respect to the new magnetic field direction depends on the value of the effective constant K/l^2 (of dimension J m^{-3}). Calculations have been carried out for a number of values of the effective constant, and the value $K/l^2 = 0.15 \cdot \mathcal{M}$ has been found to demonstrate the best agreement with the experimental EPR spectra. The corresponding optimum orientation distribution of directors is presented in Fig. 6a (green histogram). It can be seen that, as in the case of the free rotation, some domains change their orientations after the turn of the sample in the magnetic field, whereas a significant fraction of domains stay in the 90° orientation. The comparison of EPR spectra calculated for different models of reorientation can be drawn in Fig. 6b (blue and green lines). One can see that taking into account the elastic constraint leads to better agreement with the experiment (*cf.* Fig. 4b). Superposition of theoretical and experimental spectra is presented in the ESI† (Fig. D1) to illustrate their agreement. It can be seen that the theoretical spectra do not reproduce the experimental ones quantitatively, however, a clear qualitative similarity is observed.

The obtained value of $K/l^2 = 0.15 \cdot \mathcal{M}$ has the following physical meaning. In the case of a very large elastic constant $(K/l^2 \gg \mathcal{M})$, the tilt direction relaxation is absolutely restricted by an elastic constraint. In this case, the spectrum of the sample after the turn is given by the red line in Fig. 6b. For the case when the elastic constraint is in the order of magnitude of the magnetic interaction anisotropy, $K/l^2 \sim \mathcal{M}$ (the case realized in our experiments with HOPOOB), a partial reorientation of tilt direction is observed (green line in Fig. 6b). If the elastic constant becomes smaller, $K/l^2 \ll \mathcal{M}$, the reorientation of tilt direction becomes effectively free, and the resulting EPR spectrum of the sample after turn and subsequent orientation relaxation is given by the blue line in Fig. 6b. One can

hypothesize that upon a further increase of magnetic action with respect to the elastic constraint, the rearrangement of the domains may be observed, accompanied by the growth of domains with favourable orientations (*i.e.* those with the lowest free energy of interaction with the magnetic field) and the diminishing of those with less favourable orientations, which is analogous to the situation described for nematic liquid crystals in Section IV.

VI. Conclusions

In the present work, the evolution of EPR spectra was measured in the course of magnetic field induced reorientation of the liquid crystal HOPOOB in nematic and smectic C mesophases. The experimental data obtained for reorientation in the nematic phase rule out the possibility of reorientation *via* the turning of orientation distribution function and corroborate the mechanism of reorientation by the growth of areas with favourable orientations. A simple model of microscopic structure rearrangement qualitatively agrees with the obtained experimental results.

The orientation relaxation is experimentally demonstrated in the smectic phase of HOPOOB. It is shown that hindered reorientation of the tilt-direction within the smectic layers can explain the experimentally observed EPR spectra.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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