Convective director structures upon continuous rotation of nematic side group polymers

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Convective director structures upon continuous rotation of nematic side group polymers

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We present the first study of convective director structures in nematic side group polymers. A thin liquid crystal cell (10–500 μm) was continuously rotated about an axis perpendicular to the field of a 7 T NMR magnet. The director behaviour was followed by deuteron NMR as well as by polarization microscopy. While by optical studies the development of periodic director structures can be directly monitored, the analysis of the NMR lineshape gives detailed information about the director distribution in these structures. The development of the structures depends sensitively on the rotation frequency and is discussed in terms of non-linear amplification of long wavelength director fluctuations due to the coupling between director rotation and viscous flow of the nematic.

1. Introduction

Recently, there has been growing interest in magnetic field induced structures in thin cells of nematic liquid crystals, since they belong to the intensively studied class of non-linear evolving patterns. Static magnetic fields applied perpendicular to the initial director orientation n_o [1–4] as well as rotating magnetic fields [5, 6] have been used to study the formation of periodic director structures in initially uniform nematics. In these experiments the non-linear coupling between director rotation and viscous flow (back-flow) gives rise to convective roll patterns, in which the director varies periodically. In the convection rolls the rotational viscosity γ_1, which describes the uniform director rotation without flow coupling, is replaced by a somewhat smaller effective viscosity, due to the back-flow.

If a nematic liquid crystal with a positive diamagnetic anisotropy χ_a is subjected to an external magnetic field B, the director tends to orient along the field direction. When the sample is continuously rotated about an axis perpendicular to the magnetic field with a frequency $\omega_r > \omega_c = \chi_a B^2/2\gamma_1$, the director is predicted to rotate uniformly with an average frequency [7]

$$\omega_d = (\omega_r^2 - \omega_c^2)^{1/2}, \tag{1}$$

if flow coupling is neglected. However, a number of early ESR and NMR studies of low molar mass liquid crystals [7–10] have already shown that such a uniform director rotation is not stable. Instead a significant broadening of the director distribution was observed in the course of the experiment, but a quantitative analysis turned out to be difficult.

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g 6°C S$_C$ 38°C N 106°C I

g 47°C N 111°C I
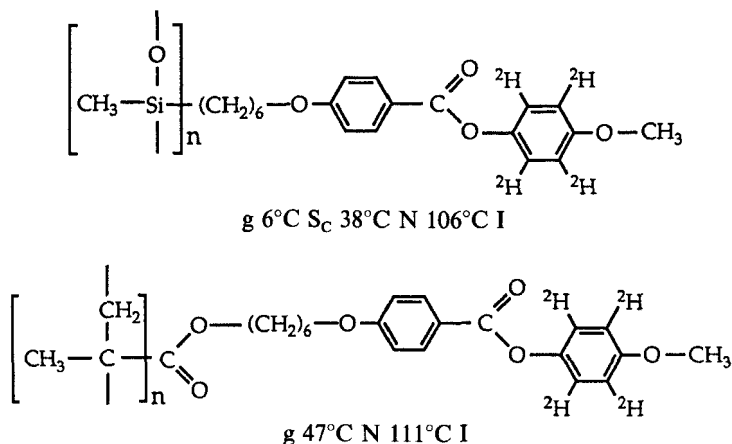
In the present study, the formation of magnetic field induced, convective director structures due to continuous sample rotation is investigated in thin cells of two different nematic side group polymers, namely with a siloxane and a methacrylate main chain and with phenylbenzoate as the mesogenic group. Since deuteron NMR allows site specific determination of the molecular orientation, both polymers have been deuteriated in the mesogenic group, in order to follow selectively the director rotation. Thus by NMR the director distribution and its changes can be measured directly during sample rotation. The director dynamics exhibited by nematic side group polymers [11, 12] is so slow that the director behaviour can be studied under rotations in the millihertz regime, which makes it possible to acquire several NMR spectra within one rotation period. Since the data acquisition is synchronized to the sample cell orientation [13], we are able to measure the angular dependence of the director distribution in real time. Thus rotations of the director according to equation (1) can be distinguished from a broadening of the director distribution due to the non-linear flow coupling.

Apart from the slow director dynamics, we took advantage of a second property specific to liquid-crystalline polymers, namely that the director structure of the mesophase can be frozen in the glassy state. This is in contrast to low molar mass liquid crystals, which often change their microstructure due to crystallization upon cooling. Since it is difficult to study the sample cells inside the magnet by optical microscopy, they were quenched at different stages of the experiment with liquid nitrogen in order to preserve the nematic director structure in the glassy state and afterwards studied under the microscope. Thus the time evolution of director structures as manifested in the optical textures and the director distributions as reflected in the deuteron NMR spectra can directly be related to each other.

2. Experimental

2.1. *Samples*

Liquid-crystalline side group polymers consist of a polymer main chain, which carries rigid side groups (mesogens) via a flexible spacer. The spacer decouples the orientational behaviour of the main chain, which tends to form a random coil, from the mesogens, which tend to align parallel to each other [14]. The investigated side group polymers both have a phenylbenzoate side group and a spacer of six methylene units.

The siloxane chain is known to be very flexible, whereas the methacrylate chain is much more rigid. The phase behaviour of both polymers has been studied by DSC, polarization microscopy and X-ray scattering [15]. The number average molecular weight, determined by GPC, was found to be 27 000 for the polysiloxane and 143 000 for the polymethacrylate.

2.2. *Sample preparation*

In order to combine optical microscopy and NMR studies, liquid crystal cells (without surface treatment) were used for the experiment. The difficulty is that very thin cells are easily studied under the microscope but give only a poor NMR signal, while thicker cells give a better NMR signal, but their transparency is lower. We found that a thickness of 250 μm provides a tolerable compromise. The cells were prepared by melting 1–50 mg (1 mg/10 μm cell thickness) of the liquid-crystalline polymer on a polished glass plate. Afterwards the sample was heated to the isotropic phase and degassed under vacuum for at least 3 days, as described for the preparation of dielectric cells of polymeric liquid crystals [16]. Then spacers made of Mylar-foil were placed on the glass plate and afterwards the whole sample was covered with a second glass plate. In order to adjust the cell thickness to that given by the spacers, the sample was heated again, while slight pressure was applied to the cell. Finally the cell was sealed with epoxy glue.

2.3. *NMR and microscopical measurements*

The experiments were carried out by means of a special NMR probe [13], which allows the continuous rotation of the sample about an axis perpendicular to the field of the NMR magnet (see figure 1 (*a*)). Before starting the rotation a planar oriented monodomain was generated by placing the liquid crystal cell with its plane along the magnetic field, heating it into the isotropic phase and then annealing it at a temperature just below the nematic–isotropic transition. Since liquid-crystalline polymers exhibit very high viscosities, the process of monodomain formation took several hours. Following the orientation process by NMR, the development of the doublet spectrum of an oriented nematic sample (see later) indicates that the major part of the sample was oriented within several minutes. However, observing the sample at that time by optical microscopy showed that it still exhibits many defect lines. Since they contribute only a fraction to the entire volume of the sample, they are not detected by NMR. The dynamics of the annihilation of the defects is so slow, that it took about 5 hours before they have vanished and monodomain formation was completed. The orientation of the monodomain is specified by a unit vector n_o.

After checking by optical microscopy that the nematic was homogeneously aligned, the sample was continuously rotated for several hours. During the continuous rotation, NMR spectra were acquired in synchronization with the sample cell orientation as described in [13]. Thus, for every NMR spectrum the actual angle Ψ between the magnetic field and the sample fixed orientation of the initial director n_o (see figure 1 (*b*)) was known, and so the angular dependence of the director distribution could be determined.

Additionally, the sample was quenched every hour at a known sample orientation, typically with $n_o \perp B$, and studied under the optical microscope. The experiments with the siloxane were performed at two different temperatures, 325 K and 350 K. The rotation frequency ω_r was chosen such that the ratio ω_r/ω_c was sufficiently larger than unity (about 2·6) at both temperatures, in order to ensure that the whole director was
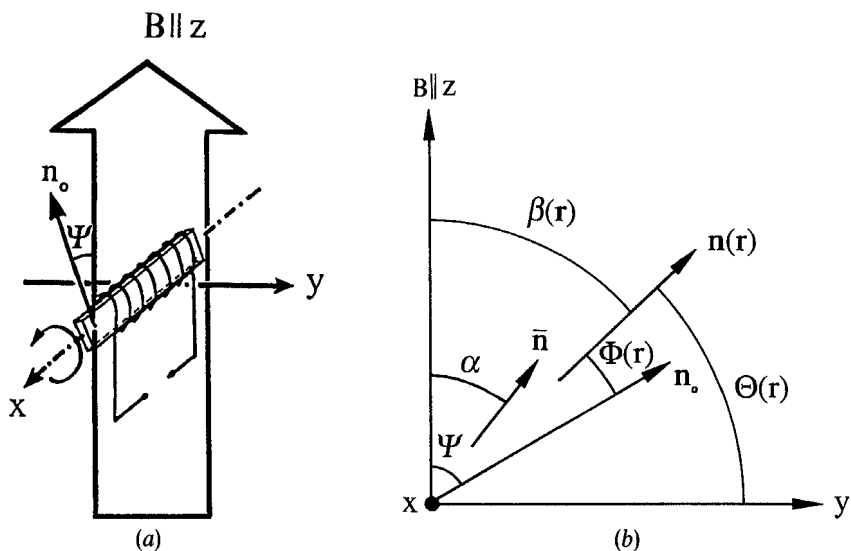
Figure 1.   (a) Experimental set-up for rotating the sample cell about an axis perpendicular to the
magnetic field. (b) Definition of the angles used to describe the director behaviour. At the
beginning of the experiment the director rotation is described by equation (1), which
predicts the orientation $\omega_{d}t = \alpha$ of the actual director $\bar{n}$ to differ from the orientation
$\omega_{r}t = \Psi$ of the sample cell. Upon further revolving the sample a spatial variation of the
director develops in the yz plane ($n_{x} = 0$). The optical properties of this director field are
most conveniently discussed in terms of a sample fixed frame, where the local deviation of
the director from the sample fixed orientation n_{o} is given by the angle $\Phi(r)$ [1, 4]. NMR, on
the other hand, measures the local director orientation $\beta(r) = 90° - \Theta(r)$ with respect to the
magnetic field (laboratory frame). In order to relate both frames to each other the sample
has been quenched, typically with $n_{o} \perp B$ ($\Psi = 90°$) so that the deformation angles $\Phi(r)$, as
detected by optical microscopy, are equivalent to the orientation angles $\Theta(r)$ measured by
NMR.

forced into rotation. Based on the values for ω_{c} known from earlier measurements [13],
ω_{r} was chosen as $3\cdot33 \times 10^{-3}$ Hz at 325 K and $0\cdot125$ Hz at 350 K. For comparison,
experiments with the polymethacrylate were conducted with $\omega_{r} = 3\cdot33 \times 10^{-3}$ Hz at
365 K.

3.   Deuteron NMR

Deuteron NMR is an important method of studying molecular order and dynamics
in both low molar mass and polymeric liquid crystals [17, 18]. The basic relationship
between the deuteron NMR frequency and the molecular orientation is given by

$$\omega = \delta/2(3\cos^2 \vartheta - 1), \tag{2}$$

where δ is the quadrupolar coupling constant and ϑ is the angle between the main axis
of an uniaxial electric field gradient tensor of a C–^{2}H bond and the direction of the
magnetic field. In the nematic phase, the deuteriated phenyl ring rotates rapidly about
its 1,4-axis. This motion gives rise to an averaged field gradient tensor, whose main axis
lies along the molecular long axis and also causes an averaged quadrupolar coupling
constant $\bar{\delta}$. Since the mesogens are aligned on average parallel to the director, the
resonance frequency ω is a direct measure for the director orientation β

$$\omega = \bar{\delta}/2(3\cos^2 \beta - 1). \tag{3}$$

Here $\bar{\delta}$ already includes the Maier–Saupe order parameter of the nematic, being of the order of 0·6 in these systems [15]. In the polysiloxane $\bar{\delta}$ is 7 kHz at 350 K and 9 kHz at 325 K leading to maximum quadrupolar splittings of 14 kHz and 18 kHz, respectively. The polymethacrylate spectra have a maximum splitting of 16 kHz at 365 K. The angular dependence of the resonance frequency ω, given in equation (3) can now be used in order to measure changes in the director distribution, due to continuous sample rotation.

In a uniformly aligned nematic phase the director has the same orientation throughout the entire sample. Such a monodomain shows a well-resolved doublet in the NMR spectrum [17], in which the splitting is dependent on the director orientation angle β. If the director distribution is non-uniform, a broadening of the NMR lines is observed, since there are now various orientations β, which are contributing at different positions ω to the spectrum. The NMR lineshape $S(\omega)$ observed is a superposition of the subspectra $S_\beta(\omega)$ corresponding to different director orientations β, weighted with the distribution function $P(\beta)$, which gives the probability density of finding a director orientation between β and $\beta + d\beta$

$$S(\omega) = \int_0^{\pi/2} S_\beta(\omega) P(\beta) \, d\beta. \tag{4}$$

If $S(\omega)$ and the $S_\beta(\omega)$ are known, this relation may be used to determine the director distribution function $P(\beta)$ by a lineshape simulation.

According to equation (3), the NMR frequency can only discriminate β values in the interval $0° \leqslant \beta \leqslant 90°$. The distributions $P(\beta)$ presented later are thus contracted to that interval despite the fact that the director angle during continuous rotation also adopts values larger than 90°. It should also be noted that equation (3) is valid only if the motional averaging, which reduces the quadrupolar splitting, is in the fast exchange limit [18, 19]. For liquid-crystalline polymers this is often not the case [18] and the actual $S_\beta(\omega)$ may differ from the simple doublets predicted by equation (3). Nevertheless, equation (4) remains valid and can be used in the lineshape analysis, provided experimentally determined $S_\beta(\omega)$ are available. Therefore, these have been recorded at 325 K as well as at 350 K after rapidly flipping a uniformly oriented bulk sample away from its original orientation by the angle $\beta = \Psi$ [20]. By using a bulk sample rather than a thin cell, the data acquisition time can be reduced and this enables us to acquire a certain subspectrum prior to any director reorientation. If the motional narrowing is rapid with correlation times $\tau_c \lesssim \delta^{-1}$, the main effect is an angular-dependent effective transverse relaxation time T_2^*, which leads to angular-dependent signal reduction in the solid-echo used to record the deuteron NMR spectra [18, 19]. At 325 K the signal decreases smoothly from $\beta = 0°$ to 90° by a factor of two, whereas at 350 K the T_2^* effect is much less pronounced ($\tau_c \ll \delta^{-1}$) and thus the signal intensities for all subspectra are approximately equal.

4. Results

4.1. *Structure formation in NMR and optical microscopy*

In figure 2 the optical and NMR results of the experiments with a 250 μm cell of the polysiloxane are summarized. Polarization microscopy shows that in the course of the experiment from an originally homogeneous sample (see figure 2(a)) at both temperatures a structure of concentric rings (see figures 2(c) and (d)) develops. Since this texture does not change upon further revolving the sample it represents the equilibrium structure of the director field under sample continuous rotation. For
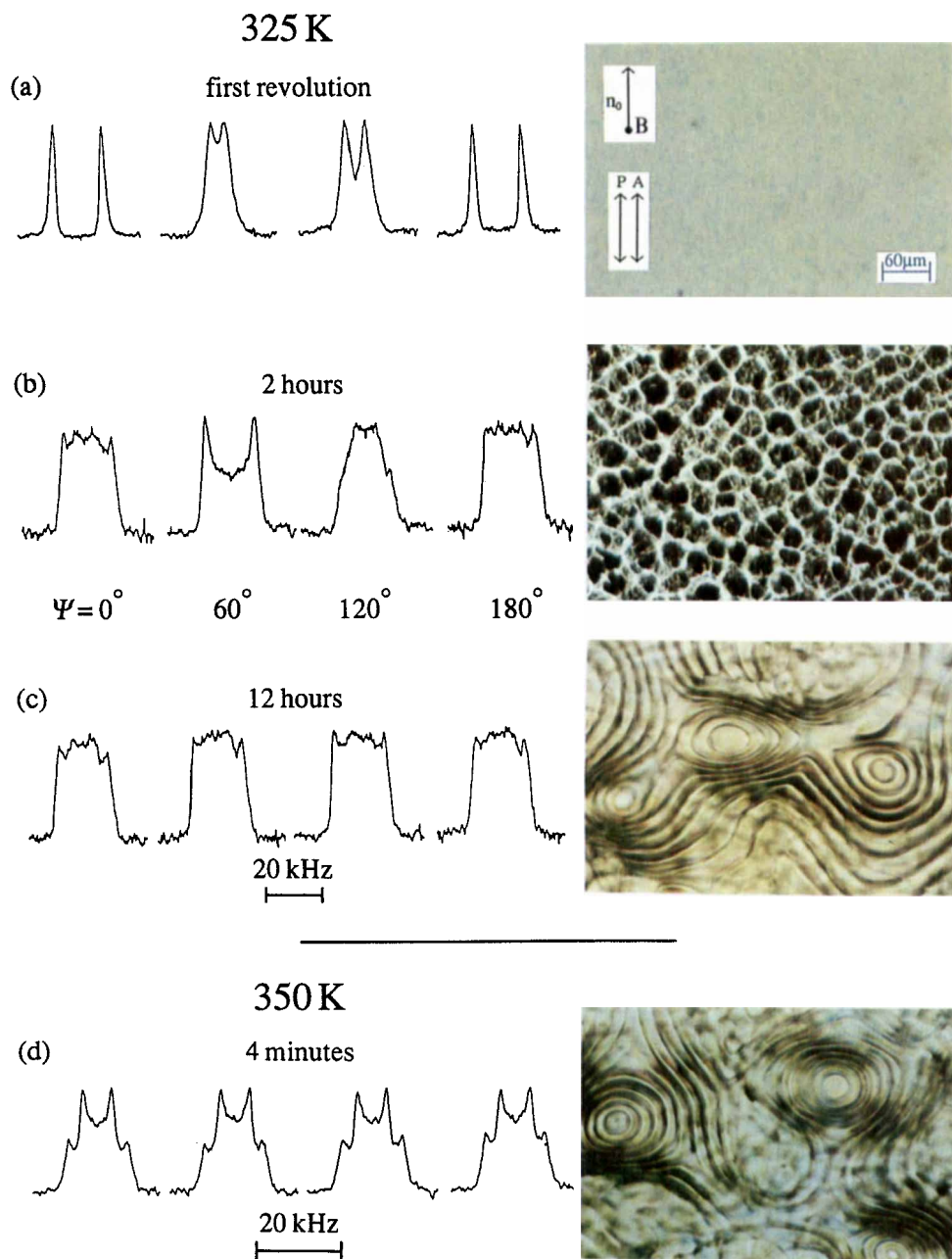
325 K

(a)   first revolution

(b)   2 hours

$\Psi = 0^\circ$ 60° 120° 180°

(c)   12 hours

20 kHz

350 K

(d)   4 minutes

20 kHz

Figure 2.   Deuteron NMR spectra at $\Psi = 0^\circ$, 60°, 120° and 180° (left) and optical textures after quenching the sample with $\mathbf{n_o} \perp B$ (right) of the polysiloxane at 325 K and $\omega_r = 3{\cdot}33 \times 10^{-3}$ Hz: (a) first revolution, (b) 2 hours, (c) 12 hours (steady state lineshape). At 350 K and $\omega_r = 0{\cdot}125$ Hz: (d) 4 min (steady state lineshape).

intermediate times a texture of regular lines at oblique angles to $\mathbf{n}_o$ is observed (see figure 2(b)), very similar to transient textures evolving in the dynamic of the splay Freedericks transition, which will be reported elsewhere [20]. The process of the structure formation is associated with a significant broadening of the NMR lines. The deuteron NMR spectra finally cover the whole spectral range $-\delta \leqslant \omega \leqslant \delta$ and do not change upon further revolving the sample. Thus, NMR and optical microscopy both imply that under continuous rotation the director field reaches an equilibrium state, in which the NMR lineshape as well as the topology of the texture become independent of the rotation angle Ψ. At 325 K a box-like steady state NMR lineshape is reached after about 12 hours. At 350 K the director dynamics are much faster and the steady state NMR lineshape exhibiting four singularities is already obtained after four minutes. In an earlier NMR study [9] of continuous director rotation in low molar mass liquid crystals very similar lineshapes have been found and were attributed to planar director distributions there. If we perform the experiment with cells of only $10\,\mu$m thickness, except for a few inversion lines, the sample remains homogeneous (see figure 3). Obviously the structure formation is suppressed in thin cells.

4.1.1. *Textures*

In order to compare easily the optical properties of the sample cell with the NMR measurements, the sample was quenched with $\mathbf{n}_o \perp B$ ($\Psi = 90°$) at different stages of the experiment. In this case the sample fixed system is identical to the laboratory system (see figure 1(b)) and the results of the texture analysis can be directly related to the director distributions $P(\beta)$ determined by lineshape analysis. The textures shown in figure 2 are all observed between parallel polarizers along $\mathbf{n}_o$. Starting with a monodomain there is no optical contrast at the beginning of the experiment (see figure 2(a)). After about two hours a structure of regular lines at oblique angles to $\mathbf{n}_o$ has developed (see figure 2(b)), which transforms upon further rotation into a pattern of concentric rings (see figure 2(c)). The bright lines in the textures are due to light being
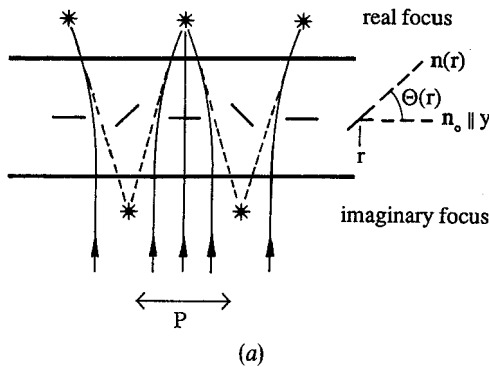

Figure 5. Optical properties of a spatially periodic director field illuminated from below with light polarized (P) along $\mathbf{n}_o$. (a) The periodic variation of the director gives rise to light focusing with a real and an imaginary focus. (b) If the sample is quenched successively with (I) $\mathbf{n}_o \| B$ and (II) $\mathbf{n}_o \perp B$, we observe an inversion of the focusing planes at a given point and thus a spatial shift of the focusing lines in a given focusing plane by half of the periodic length. As an example, the shift of the real focus is illustrated by the optical textures on the right, which represent a top view of the director field shown on the left. This indicates that the director locally rotates in the microscopically detected structures.
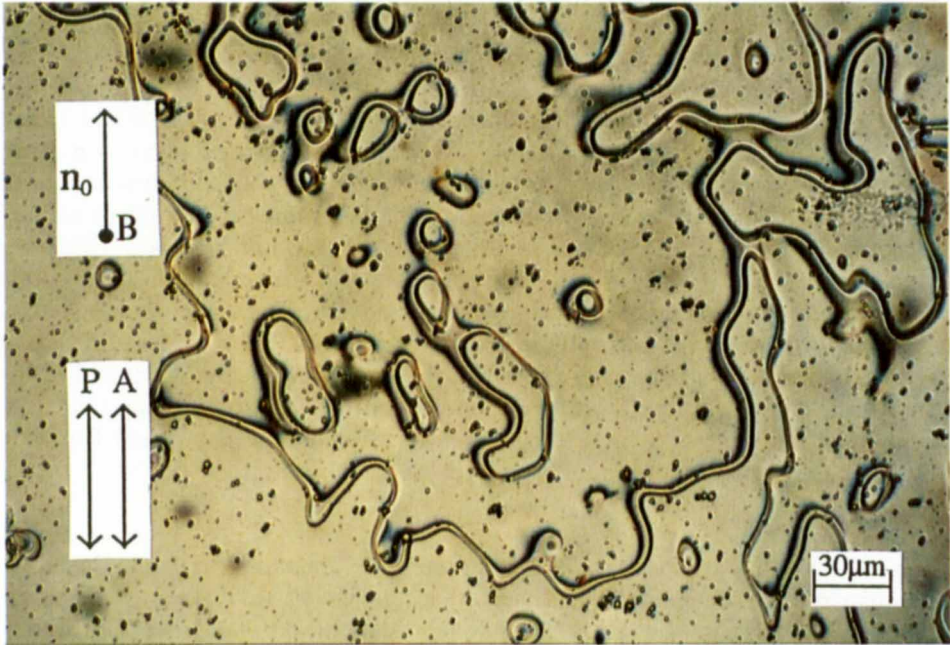
Figure 3.   In a continuously rotated cell of 10 μm thickness the structure formation is suppressed and only some inversion lines are visible.

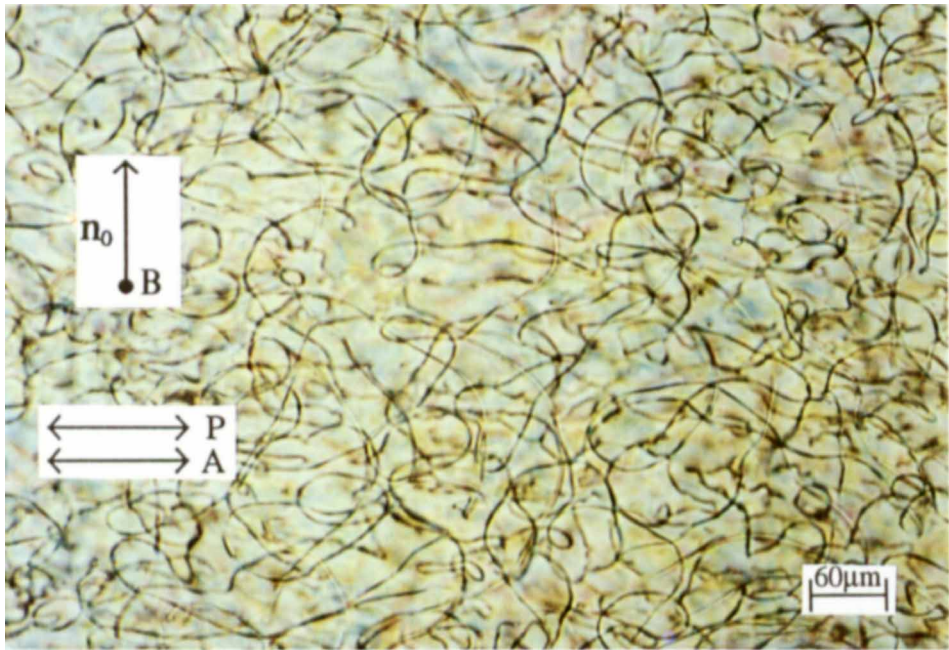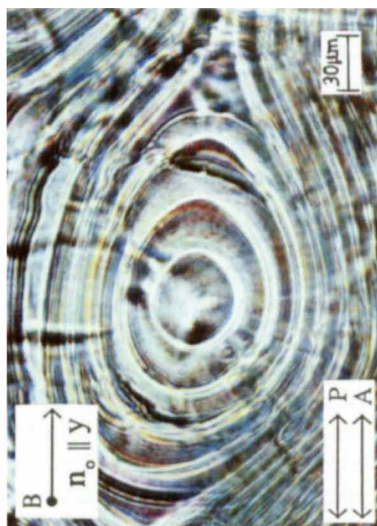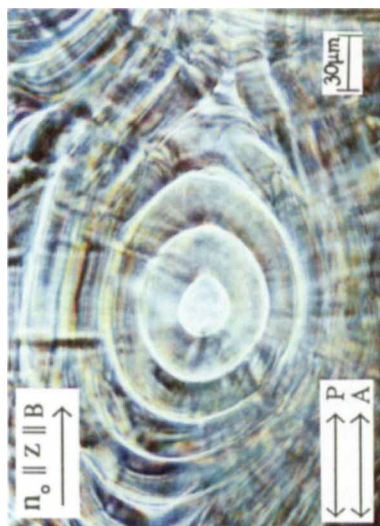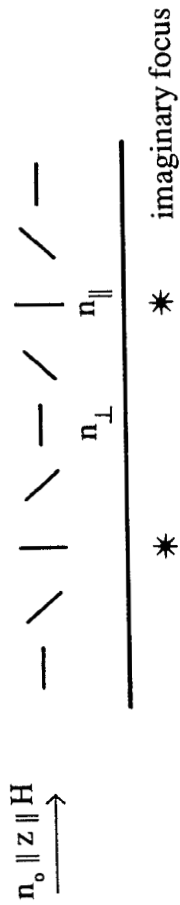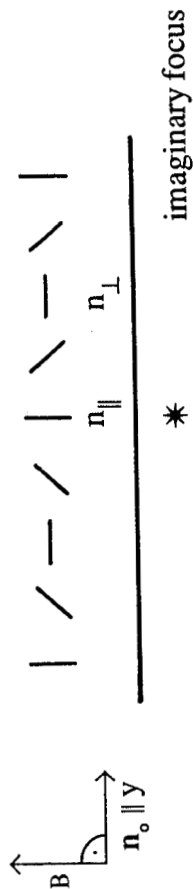Figure 4.   When the sample is placed under the microscope with n_o perpendicular to the polarization direction the periodic director structure is not visible and inversion lines close to the glass surfaces can be detected.

Figure 5.

focused from areas with low refractive index to those with higher refractive index (see figure 5 (*a*)). The maximum value of the refractive index ($n = n_\parallel$) is found in areas where the director is aligned along the initial orientation $\mathbf{n}_o$. In areas where the director is tilted in the *yz* plane away from $\mathbf{n}_o$, the refractive index is smaller and depends on the tilt angle $\Phi = \Theta$ (see figure 1 (*b*))

$$n = n_\parallel \cos^2 \Theta + n_\perp \sin^2 \Theta$$

[21], where $n_\parallel$ and $n_\perp$ are the refractive indices parallel and perpendicular to the director. Thus, the periodic variation of the refractive index is caused by a periodic deformation of the director field, which is therefore directly monitored by optical microscopy.

Since the textures are visible even without polarizers the deformation amplitude Θ_0 is expected to be large. If we rotate the sample by 90° under the microscope, so that n_0 is perpendicular to the plane of the polarizers (P), the texture vanishes, indicating that the refractive index for light polarized perpendicular to $\mathbf{n}_0$ is constant all over the sample. This implies that during the whole experiment the director remains in the plane spanned by $\mathbf{n}_0$ and *B* (*yz* plane) and therefore has no components along the rotation axis ($n_x = 0$). In this sample orientation inversion lines close to the glass surface can be detected (see figure 4). Since they are restricted to the boundary layers they involve only a fraction of the whole sample. Thus they are hardly visible when $\mathbf{n}_0$ is oriented parallel to the polarizers, because in this case the strong light focusing due to the periodic director variation in the bulk of the cell dominates the optical properties of the sample.

Another remarkable feature of the textures is that they show two focusing planes. Similar to the case of Williams domains [21], they represent the real and imaginary focus of the periodic director field [22, 23] (see figure 5 (*a*)). Note that certain areas in the textures of figures 2 (*c*) and (*d*) can be identified by their typical topology, which does not change upon further rotation. This allows us always to study the same area of the steady state texture under the microscope after quenching the sample at different times. If the sample is quenched successively with $\mathbf{n}_0$ parallel and perpendicular to the magnetic field, we observe an inversion of the focusing planes in a certain area (see figure 5 (*b*)). Thus, the focusing lines are shifted by half of the periodic length. This clearly indicates that the director is rotating even in the periodic structure. In areas which are half of the periodic length apart, the director rotates with a phase shift of 90°. Thus, microscopy gives information concerning the morphology of the director structures as well as the director dynamics in these structures.

4.1.2. *Deuteron NMR lineshape*

In order to relate the observed NMR lineshape to the different stages of the structure formation, angular dependent deuteron NMR spectra have been recorded for a full revolution $0° \leqslant \Psi \leqslant 360°$ prior to each quench. Representative examples for $\Psi = 0°$, 60°, 120° and 180° are shown in figure 2. During the second half of the revolution the angular dependence repeats itself such that the spectra at Ψ_0 and $\Psi_0 + 180°$ are identical. However, upon revolving the sample for several hours the NMR lineshape and its angular dependence significantly change. This shows that the rotor-synchronized data acquisition allows the discrimination of the angle dependence of the NMR lineshape from its time dependence.

Let us first consider the time evolution of the director distribution at 325 K. In the first stage of the experiment (see figure 2 (*a*)), we observe the typical angular dependence of the quadrupolar splitting, reflecting a uniformly rotating director. In the course of

the experiment the NMR lines become significantly broader, which indicates a spreading of the director distribution. At intermediate times the lineshape is still angularly dependent (see figure 2 (*b*)) which implies that the director distribution varies in the laboratory frame upon revolving the sample. This angular dependence is damped as the sample rotation is continued, until finally a box-like steady state lineshape is obtained (see figure 2 (*c*)) which is no longer angularly dependent and represents the equilibrium structure of the director field.

In order to quantify these considerations the director distribution $P(\beta)$ is determined by a lineshape simulation according to equation (4). For the simulation of the spectra recorded during the first revolution, a uniform director distribution with a certain tilt angle $\beta(\mathbf{r}) = \alpha$ is assumed (see figure 1 (*b*)). The broadening of the director distribution upon further rotating the sample is related to the development of a periodic structure, in which the director varies mainly in two directions at oblique angles to $\mathbf{n_o}$ (see figure 2 (*b*)). The local orientation of the director in the laboratory frame is given by the angle $\beta(\mathbf{r}) = 90° - \Theta(\mathbf{r})$ (see figure 1 (*b*)) [1,4]. Thus the corresponding spectra have been simulated by adjusting the amplitude Θ_o and the deformation parameter a [4] of a two dimensional trial function, in which the spatially periodic variation of the director is described by the two wavevectors k_ξ and k_ζ (see figure 6)

$$n_z(\xi, \zeta) = \sin \Theta(\xi, \zeta) = \sin \Theta_o \sin^a k_\xi \xi \sin^a k_\zeta \zeta. \tag{5}$$

Since the optical studies have shown that the director remains in the *yz* plane during the whole experiment, in equation (5) only the n_z component is allowed to vary along the directions ξ and ζ. The deformation parameter $0 \leqslant a \leqslant 1$ determines the shape of the sinusoidal director deformation. For $a = 1$ a harmonic deformation results, whereas for
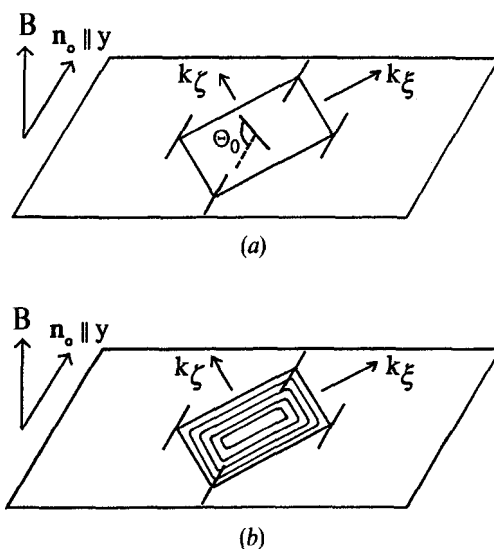
(*a*)

(*b*)

Figure 6. (*a*) Representation of the two dimensional trial function (see equation (5)) used in the lineshape analysis. (*b*) The integration is carried out along the lines of constant deformation angle Θ.
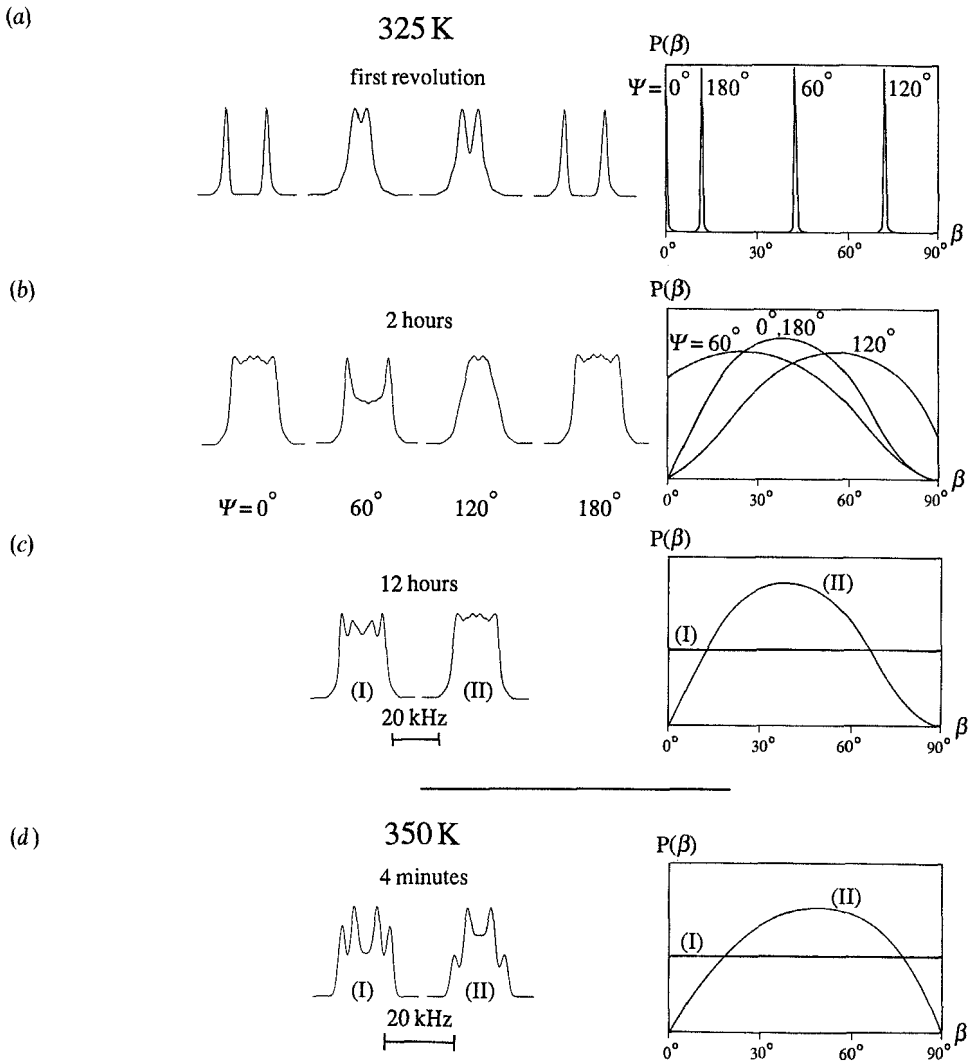
Figure 7. Simulated spectra for $\Psi = 0°$, $60°$, $120°$ and $180°$ (left) and director distribution functions $P(\beta)$ (right) as extracted from the lineshape analysis. The parameters used in equation (5) for the presented simulations (from left ($0°$) to right ($180°$)) are: (a) $\alpha = \beta = 0°$, $42°$, $105°$, $168°$; (b) $\Theta_o = 90°/a = 0.22$, $\Theta_o = 90°/a = 0.15$, $\Theta_o = 90°/a = 0.56$, $\Theta_o = 90°/a = 0.22$; (c) (I): $P(\beta) = $ constant, (II): $\Theta_o = 90°/a = 0.22$; (d) (I): $P(\beta) = $ constant, (II): $\Theta_o = 90°/a = 0.43$.

$a = 0$ the angle Θ is spatially independent. The director distribution $P(\beta) = P(90° - \Theta)$ $= \tilde{P}(\Theta)$ is obtained from equation (5) by integrating over half a period of k_ξ and k_ζ for $\Theta = $ constant

$$\tilde{P}(\Theta) = \int_0^{\pi/k_\xi} \int_0^{\pi/k_\zeta} \delta[\Theta - \Theta(\xi, \zeta)] \, d\zeta \, d\xi. \qquad (6)$$

This equation describes the performance of the numerical integration in order to obtain the director distribution function. Note that variation of the deformation parameter a may change the position of the maximum of the distribution function $P(\beta)$. The agreement of the simulated lineshapes shown in figures 7 (a)–(d) and the experimental

ones in figures 2 (*a*)–(*d*) is very good indeed. At the beginning of the experiment the director distribution is very narrow and indicates a uniformly rotating director. The deviation of the actual director angle α from the rotation angle Ψ can be explained in terms of equation (1).

After about two hours, the director distribution reaches its maximum width ($\Theta_o = 90°$) as suggested by the strong optical contrast of the evolving microscopical textures. The director rotation in the periodic structure is associated with a change in the shape of the periodic director distortion in equation (5), which thus shifts the position of the maximum of $P(\beta)$. The fact that the director distribution is angularly dependent at that time implies that the mechanical torque still dominates the director behaviour. As the rotation is continued the angular dependence of the director distribution is damped until an equilibrium distribution corresponding to a texture of concentric rings is reached after about 12 hours. Although this director structure is somewhat different from that given by equation (5), the associated steady state director distribution can still be described by the trial function. This implies that the assumed two dimensional periodic director variation in the form of a square is a good approximation to the circular director variation observed. In this director structure the mechanical torque is balanced by the magnetic, viscous and elastic torques, so that the director distribution becomes stationary in the laboratory system.

The steady state deuteron NMR lineshapes at 325 K and 350 K are rather different despite the fact that the textures are alike at both temperatures (see figures 2 (*c*) and (*d*)). Indeed the director distributions extracted by a lineshape analysis from both spectra are virtually identical (see figures 7 (*c*) and (*d*)). The differences in the experimental lineshape merely reflect the angular dependence of the transverse relaxation times T_2^* as discussed in section 3. Since experimental subspectra rather than theoretical ones are used in our analysis, the director distributions $P(\beta)$ extracted from the lineshapes are not affected by this.

At 350 K the deuteron NMR spectrum exhibits the four singularities characteristic for the lineshape of a planar distribution, independent of β [9, 18, 19], since these T_2^* effects are less pronounced at higher temperatures. Thus for comparison in figures 7 (*c*) and (*d*) we also show the lineshape corresponding to such a planar isotropic distribution. Although this simulation reflects at both temperatures the main features of the steady state lineshape, the agreement with the experimental spectra is less satisfactory than for the planar distributions based on equation (5).

5. Discussion

The analysis of both textures and deuteron NMR lineshapes thus shows that a periodic deformation of the director field develops upon continuous rotation of the director. This may be attributed to the non-linear amplification of long wavelength director fluctuations whenever the director is close to the bistable orientations $\alpha = 90°$ and 270° [2]. At these rotation angles the magnetic torque has opposite direction in regions separated by half of the wavelength of the fluctuation. The associated gradients of the director rotation rate give rise to a flow in the plane of the director (*yz* plane), which exerts an additional torque on the director and further amplifies the fluctuation amplitude. This non-linear feedback between the spatial gradient of the director rotation rate and viscous flow (back-flow) leads to the formation of convection rolls (see figure 8) in which the viscosity associated with the director rotation is reduced at some cost in elastic energy. While the minimization of the elastic energy favours long
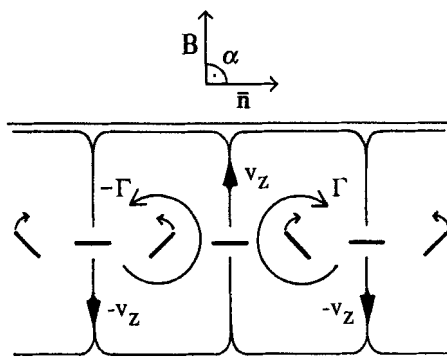
Figure 8.   Convection rolls evolving due to the non-linear coupling between director rotation
and viscous flow v. At rotation angle $\alpha = 90°$ and $270°$ the magnetic torque Γ has opposite
sign in areas which are half of the periodic length apart.

wavelengths of the director deformation, the reduction of the viscosity by flow coupling
is most efficient when the wavelength is small, and thus the associated director
gradients are large [2, 3]. The length scale of the observed periodicity represents a
compromise between these contributions. In the concentric convection rolls of the
steady state the torques acting on the director are balanced in such a way that the
director distribution becomes stationary in the laboratory frame. Since optical
microscopy has shown on the other hand that the director locally rotates in the
convection rolls, this indicates a dynamic equilibrium situation in which the number of
directors rotating out of a certain angular element $d\beta$ is equal to the number entering it.
Since the director distribution of the steady state is not isotropic, this condition can
only be fulfilled if the director rotation rate is dependent on angle, and thus on space
(because the director angle varies periodically in space). One might emphasize here that
the balance of torques is not a local property but concerns the sample as a whole. The
existence of spatial gradients of the rotation rate explains why even the steady state can
have a convective structure. The flow, on the other hand, stabilizes the periodic director
profile. Thus flow and gradients of the director rotation rate are mutually dependent.
Additional coupling between director rotation and the polymer chain may also give
rise to flow effects, but is not considered in this study.

   The mechanism described implies that the characteristic time for the flow-coupled
director reorientation τ_{eff} is of the same order as the revolution time of the sample cell.
This ensures that close to the angles $\alpha = 90°$ and $270°$ there is enough time for the
amplification of fluctuation amplitudes by director reorientation. The reorientation
time of the director without flow coupling, as obtained from the solution of the Leslie–
Ericksen equations [24], is $\tau = 2/\omega_c$. The time τ is comparable to the time for a full
revolution $T = 2\pi/\omega_r$ if ω_r is of the order of ω_c. This condition indeed is fulfilled in both
of our experiments where $\omega_r = 2\cdot6\,\omega_c$.

   For further testing the applicability of the assumed mechanism, the speed of sample
rotation at 325 K has been increased by a factor of 10 to $\omega_r = 26\,\omega_c$. Even after 48 hours
no structure formation could be observed. This is in accord with the prediction that the
structure formation only occurs when the rotation speed is on the time scale of the
director reorientation rate. The structure formation is apparently based on a balance of
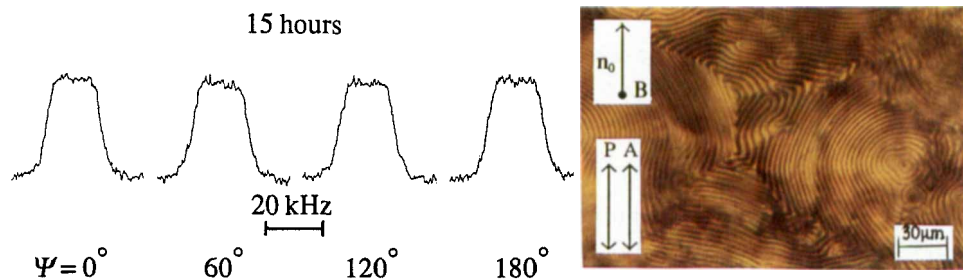the mechanical torque $(\sim\omega_r)$ and the magnetic torque $(\sim\omega_c)$ which induces the

15 hours

20 kHz

$\Psi = 0°$ $60°$ $120°$ $180°$

Figure 9. Deuteron NMR spectra at $\Psi = 0°$, $60°$, $120°$ and $180°$ (left) and optical texture (right) after reaching the steady state of the polymethacrylate at 365 K and $\omega_r = 3·33 \times 10^{-3}$ Hz.

reorientation of the director. If the magnetic torque dominates ($\omega_r < \omega_c$) the director is fixed under a certain angle by the magnetic field and does not rotate at all [7]. If the mechanic torque completely dominates ($\omega_r \gg \omega_c$), the structure formation is suppressed, since the fast rotation does not provide enough time for the amplification of spatial director gradients in the bistable orientations. Thus only in an intermediate range does the structure formation occur.

As we have noted (see figure 3) in very thin cells, independent of the rotation speed, no structure formation is observed. The critical magnetic field $B_{c_i} = \pi/d\,(k_{ii}/\chi_a)^{1/2}$, necessary to induce one of the three basic director deformations [25] (where k_{ii} are the elastic constants for the splay ($i = 1$), twist ($i = 2$) and bend ($i = 3$) deformation), is inversely related to the cell thickness d. Thus, we might expect the critical field in such thin cells to be larger than the applied field strength, so that no director deformation occurs. The critical field for a splay deformation, at $\alpha = 90°$ is estimated as 1·5 T by using the value of the splay elastic constant k_{11} given in [11]. Since this value is significantly smaller than the applied field strength of 7 T this cannot explain the suppression of the structure formation in thin cells. Here we should remember that the length scale of the observed periodicity is a compromise between elastic and viscous forces. In thin cells the elastic coupling to the wall may dominate the process of wavelength selection and overcome the viscous energy contributions. Thus, the selected wavelength becomes infinitely long and the homogeneous rotation of the director is stabilized, since periodic deformations of the director field are damped by elastic restoring forces.

In order to examine whether convective director structures can also be observed upon continuous rotation of other nematic side group polymers, an experiment with a 250 μm thick cell of the polymethacrylate was performed. Since this sample has a higher molecular weight and a more rigid backbone than the siloxane, it exhibits a much higher viscosity. This explains why the experimental temperature had to be raised to 365 K at a rotation frequency of $3·33 \times 10^{-3}$ Hz in order to retain a ratio ω_r/ω_c of about 2·6. The spectra in figure 9 show that the methacrylate also reaches a steady state in which the director distribution is stationary in the laboratory frame. The similarity of the lineshape with the box-like steady state lineshape of the siloxane indicates, furthermore, that the molecular motion of the deuteriated phenyl ring is on the same time scale in both polymers, as long as their viscosities are comparable. The analysis of the microscopic texture provides results equivalent to the siloxane. It shows that also in the methacrylate the steady state exhibits a convective structure, in which the director varies periodically in the *yz* plane.

6. Conclusion

The formation of periodic director structures upon continuous sample rotation is observed in two systems which are very different in molecular weight and chain mobility. Thus, it can be anticipated that this is a typical effect in nematic side group polymers. The strong spatial variation of the director rotation rate found in the experiments is associated with the formation of convection rolls. The developing director structures can be monitored directly by microscopy, while the amplitude and shape of the director deformation are determined by NMR. The structure formation is suppressed in thin cells and occurs only if ω_r is of the order of ω_c. The similarity of our NMR results with previous studies on low molecular weight nematics [9] implies that these convective director structures might also be generated in common nematics, although at much higher rotation frequencies.

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