6-15-1991

Nematic Director Orientation in a Liquid-Crystal-Dispersed Polymer - A Deuterium NMR Approach

Ralf Stannarius
G. P. Crawford
Liang-Chy Chien
Kent State University - Kent Campus, lchien@kent.edu
J. William Doane
Kent State University - Kent Campus

Follow this and additional works at: https://digitalcommons.kent.edu/cpippubs
Part of the Physics Commons

Recommended Citation

This Article is brought to you for free and open access by the Department of Chemical Physics at Digital Commons @ Kent State University Libraries. It has been accepted for inclusion in Chemical Physics Publications by an authorized administrator of Digital Commons @ Kent State University Libraries. For more information, please contact digitalcommons@kent.edu.
Nematic director orientation in a liquid-crystal-dispersed polymer: 
A deuterium nuclear-magnetic-resonance approach

R. Stannarius, G. P. Crawford, L. C. Chien, and J. W. Doane
Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44242-0001

(Received 13 December 1990; accepted for publication 29 March 1991)

The nuclear-magnetic-resonance (NMR) technique is employed to liquid-crystal-dispersed-polymer (LCDP) systems. Deuterium NMR is used to determine director distributions in LCDP cells in the presence of a magnetic field. The samples consist of a nematic liquid crystal mixed with small percentages of a monomer that is polymerized under different conditions after dissolving it in the liquid crystal. NMR spectra of the deuterated liquid-crystal molecules give information on orientation and order in such systems. The orientation of the polymer skeleton formed during the polymerization is found to be stable. It determines the orientation of the nematic director even in the presence of a strong external magnetic field. Simple models for the director field are presented.

I. INTRODUCTION

A widespread application of liquid crystals are optical displays, where the contrast between on and off states of the display cell is achieved by switching the liquid crystal (LC) director with an external electric field. The phase and amplitude of transmitted polarized light depend upon the director orientation in the display. Most frequently, twisted nematic phases are used with varying twist and surface tilt angles. In recent years, polymer-dispersed liquid crystals (PDLCs) have been employed as light shutters and displays where light scattering is controlled by switching the nematic director. Such systems consist of nematic droplets embedded in a polymer matrix. If the materials are chosen such that the ordinary refractive index \( n_0 \) of the nematic matches the refractive index of the polymer, these PDLC cells can be switched from an opaque to a transparent mode by reorienting the director field in the droplets with an external electric field.

A variation to this approach is the solution of a small amount of polymer-forming material in a nematic matrix to form a liquid-crystal-dispersed polymer (LCDP). In these systems, no droplets are observed but a polymer framework forms in the mixture. Its orientation is determined by the conditions during polymerization, and it reflects the state of order of the nematic matrix. Although these systems can still be influenced by external electric or magnetic fields, and the scattering characteristics can be switched by such fields, their behavior is very different from that of ordinary nematics.

We prepared cells with several concentrations of polymer, applying different curing conditions and measured the state of orientation of the nematic molecules by deuterium nuclear magnetic resonance (NMR). These first NMR experiments on LCDP show that deuterium NMR provides a unique tool in determining the director distribution in such systems. The study of the director field orientation has been accessible by no other experimental technique to date. Additional microscopic studies on these samples were performed to test their optical characteristics.

II. EXPERIMENT

The samples were contained in sandwich cells made from indium-tin-oxide (ITO)-coated glass separated by Mylar spacers. The glass surfaces were cleaned but not further surface treated. The cell thickness of 350 \( \mu \)m is a compromise between a reasonable amount of sample necessary for the NMR experiment and a distance small enough for orientation of the sample by an electric field and penetration of the ultraviolet (uv) irradiation. The sample cells are 25 mm long and 4 mm wide, containing about 40 mg of LCDP mixture and fit the dimensions of conventional NMR sample containers.

The NMR instrument used in the experiments is a superconducting 4.7-T coherently pulsed Fourier-transform deuterium NMR spectrometer running at 30.1 MHz. The temperature in the sample is controlled with a stability and homogeneity greater than \( \pm 0.05 \) K. The samples can be turned by a stepper motor around an axis perpendicular to the magnetic field to arbitrary angles \( \theta_h \) between the sample symmetry axis (glass plate normal) and the static magnetic field \( B_0 \). Since the amount of deuterated substance was very small, 2000–20 000 free-induction decays (FID) were averaged for each spectrum.

The nematic liquid crystal is a mixture of 50% 5CB (4-n-pentyl-4'-cyanobiphenyl) and 50% 5OCB-\( \alpha d_2 \) (4-n-pentyloxy-4'-cyanobiphenyl) deuterated in the first chain segment counting from the aromatic core of the molecule. In this system, we dissolved (1) 1.28, (2) 2.16, and (3) 3.00 wt %, respectively, of the monomer BAB(4,4'-bis-acryloylbiphenyl),

\[ \text{CH}_2 = \text{CH-CH}_2-\text{O-O-CH}_2-\text{CH} = \text{CH}_2, \]
and 0.5 wt % photoinitiator BME (benzoin methyl ether). Each sample was polymerized by irradiation with uv light from a high-pressure mercury lamp for approximately 20 min. During uv exposure, the monomer molecules are activated and linked together to form a polymer skeleton in the sample. We distinguish between three different polymerization conditions.

A: the sample is exposed to uv in the isotropic state of the liquid crystal;
B: the sample is irradiated in the nematic nonoriented state, no external field is applied, and the directors are randomly distributed in the cell;
C: the director field is oriented normal to the surface plates by means of an external electric ac field of 200–400 V during uv irradiation. All samples were studied by optical microscopy before and after curing to determine their textures and phase-transition temperatures. In the following we refer to the samples by a number 1–3, denoting the mixture ratio and a letter A–C indicating the curing conditions.

The complete temperature dependence of NMR spectra was recorded for the pure 5CB/50CB mixture and for the LCDP systems before and after uv exposure. Furthermore, the angular dependence of the spectra was measured for all samples at room temperature in the nematic phase. The deuterium NMR line shape is determined by the quadrupolar splitting. The quadrupolar coupling constant in a rigid molecule due to interaction of the $^2$H nuclear quadrupole moment with the electric-field gradient tensor $V$ is $v_Q = (eQZ^2/\hbar) = 175$ kHz for chain deuterons; its asymmetry parameter $V = (V_{xx} - V_{yy})/V_{zz}$ is negligible and the symmetry axis $z$ is parallel to the CD bond. This quadrupolar interaction is averaged by fast molecular motions in the nematic state. The symmetry of the averaged field gradient tensor is uniaxial, and its principal axis coincides with the molecular long axis. The averaged quadrupolar coupling constant $(v_Q)$ is proportional to the nematic-order parameter $S$. Using the angles $120^\circ$ for the COC bond, $109.4^\circ$ for the OCD bond, and assuming the molecular long axis parallel to the ring para axis, the proportionality factor is given by

$$\langle v_Q \rangle = 72 \text{ kHz s.} \quad (1)$$

This value was assumed for the scaling of the order parameter measurements.

The observed resonance frequency in the nematic phase depends upon the angle $\theta$ between the local nematic director $n$ and the spectrometer field $B_0$ by

$$v_{\pm}(\theta) = \pm P_2(\cos \theta) v_0, \quad (2)$$

where $v_0 = \frac{1}{2}(\langle v_Q \rangle)$ is the frequency splitting for $\theta = 0^\circ$, $P_2(\cos \theta) = (3 \cos^2 \theta - 1)/2$ is the second Legendre polynomial, and $\theta$ is the angle between the local director orientation and $B_0$. Thus, the NMR spectrum yields information about the order parameter and the orientation of the molecules with respect to the $B_0$ field, and the director field can be monitored. In an oriented sample with the director aligned to $B_0$, the spectrum consists of single lines at positions $\pm v_0$. If the director is in an orientation perpendicular to the field, $\theta = 90^\circ$, then sharp lines appear at $\pm v_0/2$. If the director orientations are randomly distributed, the corresponding line shape is a powder pattern [see in Fig. 10(d)]. For an arbitrary distribution density $n(\theta)$ of the directors with respect to $B_0$, the line shape $F(v)$ can be calculated by

$$F(v) = \int_{-\infty}^{\infty} \sum_{\theta(\nu')} \frac{d\theta(\nu')}{d\nu'} |n[\theta(\nu')]G(v - \nu')d\nu', \quad (3)$$

where the sum is over all angles $\theta$ that satisfy Eq. (2) for a given frequency $v$. The convolution function $G(v)$ accounts for contributions from dipolar interactions, field inhomogeneities, and other relaxation factors. It can be determined from an oriented spectrum in the nematic phase, where $\theta = 0^\circ$. In our experiments, we have used a Gaussian function with a half-width of 1.5 kHz. A computer program was written that allows the calculation of the deuterium line shape from a given distribution density $n(\theta)$ of the director field.

Formally, the exact director distribution $n(\theta)$ is three dimensional and therefore includes a volume element $\sin \theta$. This introduces a singular point at $\theta = 0^\circ$ resulting in $n(\theta=0^\circ)=0$. In practice, however, it is not necessary to write $n(\theta) = f(\theta)\sin \theta$ where $f(\theta)$ is a non-negative distribution function because there is no rotational symmetry of the director orientation around the magnetic-field direction when $B_0$ is not parallel to the cell normal. Inclusion of the volume element results in a small gap close to $\theta = 0^\circ$ that cannot be detected by the deuterium NMR experiment and therefore is neglected. In practice, the functions $n(\theta)$ were approximated by polygons with 30 discrete adjustable parameters $n_i = n(\theta_i)$ and linear interpolation. The angles $\theta_i$ were chosen such that $P_2(\cos \theta_i)$ are equidistant.

In principle, it is possible to determine any director distribution by fitting the NMR line shape. There are, however, a few restrictions to this procedure.

(i) The function $P_2(\cos \theta)$ is almost constant in the vicinity of $\theta = 0^\circ$ and $90^\circ$. The line shape is very insensitive to small distributions around these angles.

(ii) The phase correction of the NMR spectra has to be performed very carefully. Phase misadjustments influence the correct determination of $n(\theta)$.

(iii) The line shape is ambiguous in a certain range because the two branches of the deuterium spectrum may overlap. However, the function $n(\theta)$ can be determined correctly at $\theta < 35.3^\circ$ and $\theta = 90^\circ$, and the choice of the “smoothest” completion of $n(\theta)$, should yield the correct solution.

(iv) It is not possible to distinguish different azimuthal angles of the director orientation. This problem can be overcome partially by measurement of the angular dependence of the spectra when the sample is rotated in the field.

(v) The NMR line shape is insensitive to the singular point at $\theta = 0^\circ$ that occurs when the volume element $\sin \theta$ is included in the director distribution and therefore is restricted to the plane defined by the field direction and cell normal.

The angular dependence of the NMR spectra is measured by rotating the cell in the spectrometer about an axis perpendicular to \( B_0 \). The experimental geometry and definition of \( \theta_h \) are given in Fig. 1. The director orientation with respect to the cell is described by the angles \( \theta_d \) and \( \Phi_d \) relation. From symmetry considerations we can assume that the angles \( \Phi_d \) are randomly distributed as long as \( \theta_h = 0^\circ \). The relation between \( \theta_d, \Phi_d, \theta_h, \) and \( \theta \) is

\[
\cos \theta = \cos \theta_d \cos \theta_h + \sin \theta_d \sin \theta_h \cos \Phi_d. \tag{4}
\]

In the limit of a completely ordered and a completely disordered sample, the calculation of the NMR spectrum is particularly easy. A random distribution of \( \theta_d \) and \( \Phi_d \) will result in the distribution density \( n(\theta) = \sin \theta \) for the angles \( \theta \), and the corresponding NMR line shape is a powder pattern independent of \( \theta_h \). In a completely oriented sample with the directors aligned to \( \theta_d = 0^\circ \), Eq. (4) leads to \( \theta = \theta_h \) and the spectrum consists of two narrow lines at the positions \( \pm \nu_0 (\cos^2 \theta_h - \frac{1}{2}) \) that depend upon the rotation angle of the cell.

**III. RESULTS AND DISCUSSION**

Microscopic investigations on samples with different amounts of polymer show that the nematic textures and phase transitions are not changed noticeably by the addition of a few percent of monomer and photoinitiator as long as the samples are not uv irradiated. The maximum concentration of monomer that could be dissolved homogeneously in the LC was approximately 5%. At higher concentrations, undissolved small crystals of the additive remained in the mixture. After uv exposure, the physical properties of the systems change drastically. The fluidity vanishes, and a bulk sample will maintain its shape. The conditions during the polymerization influence the optical appearance. The cells cured in the oriented state (type C) remain partially transparent even at 350 \( \mu \)m cell thickness, although more scattering than ordinary nematics. The cells cured in the liquid phase form a highly scattering state in the nematic region; they are transparent only in the isotropic phase of the liquid crystal.

A remaining birefringence in the isotropic phase is observed after the polymerization, revealed by optical microscopy with crossed polarizers. This was already reported for a similar system by Hikmet. In the type-B and even type-A systems (not oriented during exposure) certain textures remain, and we will show later that this birefringence pattern is caused by the anisotropic optical properties of the polymer. The clearing point is recognized by a texture change in the microscopic picture. More evident, however, is the vanishing response to external electric fields above \( T_{NI} \). The type-C cells (exposed in the oriented nematic state) appear dark in the isotropic phase if the cell surface is normal to the transmitting light. Obviously, the polymer skeleton formed in these cells is oriented homeotropically.

A simple explanation for these optical effects that is supported by the following NMR investigations is that the polymer skeleton is aligned during its formation by the nematic director field. After polymerization, its orientation is fixed and influences the nematic director in turn. The director field is pinned to the polymer skeleton, and in a tension-free state it aligns completely to the oriented polymer. An applied external field of sufficient strength, i.e.,

\[
\varepsilon_{mag} = \sqrt{K_\pi \mu_0/(\chi_\mu B_0^2)}, \quad \varepsilon_{el} = \sqrt{K_\pi \mu_0/(\epsilon_{rel} F_0^2)} < \frac{1}{2} \text{ smaller than the average distance between the polymer strings, may distort the director field in the cavities between the polymer threads but does not influence the polymer skeleton. The light scattering in the nematic phase of type-A cells is caused by a large number of defects in the director field due to the random orientation of the polymer network.}

We found that the orientation of the polymer skeleton is destroyed, however, if the samples crystallize and are reheated into the nematic phase again. The clearing points of all mixtures are noticeably shifted to lower temperatures after polymerization, depending on the polymer concentration. The measured phase-transition shifts are 0.75, 1.55, and 2.2 K for concentrations 1, 2, and 3, respectively.

The determination of the order parameter \( S \) can be performed easily from the deuterium NMR spectra, using Eq. (1). Figure 2 shows the temperature dependence of the quadrupolar splitting \( 2\nu_0 \) of the pure 5CB/50CB mixture (circles, lower scale). The order parameter at the right-hand side corresponds to a calculated averaged quadrupolar coupling constant \( (\nu_0) = 72 \text{ kHz} \). The temperature dependence of the quadrupolar splitting for the cured mixtures 1–3 is not shown here, it is equivalent to that of the pure nematic. The second curve in Fig. 2 represents a typical example of the NMR line splitting after uv exposure (crosses, upper scale for sample 3C, with 3.00% polymer). Except for a shift towards lower temperatures, the curve fits exactly the temperature dependence \( S(T) \) for the pure nematic mixture. The curves of samples 1C and 2C can be matched to the general-order parameter temperature dependence as well by a shift of the temperature scale of 1.55 and 0.75 K respectively. A small coexistence range of the nematic and isotropic phases, increasing from 0.4 K

**FIG. 1. Sample geometry and definition of the angles \( \theta_d, \Phi_d, \theta_h, \) and \( \theta \).**
for the pure system to about 1 K for the cured sample 3C, is observed.

Although some properties of polymerized LCDP samples are very different from those of the uncured mixtures, as fluidity, director reorientation, or birefringence in the isotropic phase, the order parameter measurements show that the principal order properties of the liquid-crystal component remain unchanged. Therefore, we will still refer to the phases of LCDP as nematic and isotropic, depending upon the state of the liquid-crystalline component.

From the spectra in the isotropic phase, we get more information on the molecular order in LCDP. Figure 3 shows a typical isotropic spectrum, on a different frequency scale. A single Gaussian line is observed. The remaining line width above $T_{ni}$ of less than 140 Hz is completely caused by magnetic-field inhomogeneity. A remaining order of the 50CB molecules in the isotropic phase that might have been induced by interaction with the large amount of polymer “surface” in the system can be excluded even in the vicinity of $T_{ni}$. An average-order parameter $\langle S \rangle$ as small as $10^{-3}$ would double the linewidth. Therefore, the optical birefringence observed in the isotropic phase cannot be attributed to the liquid-crystal molecules. It is caused by the anisotropic polymer structure.

After discussion of the order parameter, we will now refer to the orientation of LCDP. Figure 4 shows spectra of a 3.00% LCDP in the nematic phase contained in a 350-$\mu$m sandwich cell before irradiation. Spectra were recorded at different $\theta_h$. The experimental line shapes are equivalent at all orientations, as we expect for ordinary nematic phases. The LC molecules with positive diamagnetic susceptibility anisotropy $\chi_2$ are aligned by the large magnetic field $B_0$. The coherence length $\xi_{mag}$ of the order of 2 $\mu$m is much smaller than sample dimensions; therefore, we can neglect the influence of the glass surfaces. The peaks in the spectra remain sharp, their positions correspond to the director orientation $\theta = 0^\circ$ independent of sample rotations ($\Phi_d = 0, \theta_d = \theta_h$). Only the $0^\circ$ and $90^\circ$ spectra are shown, for example.

To make sure that the uv irradiation does not affect the nematic molecules, we have also measured spectra of the pure nematic before and after uv exposure. As expected no changes in the order parameter or in the angular depen-
The angular dependence of the NMR lines is found. After the polymerization, the angular dependence of the line shape is completely changed. It is depicted in Fig. 5 for samples 1C, 2C, and 3C. The oriented nematic director field during the uv exposure has aligned the polymer skeleton. After that the polymer remains in fixed orientation relative to the sample cell and aligns the nematic molecules even after removal of the orienting electric field. In the angular-dependent spectra, the directors in the sample remain aligned parallel to the spectrometer field only at $\theta = 0^\circ$. The lines are narrow as those in Fig. 4, and their splitting is only determined by the nematic-order parameter. If the sample is turned with respect to $B_0$, the director orientations follow the sample rotation as in a smectic A phase. Even the 4.7-T magnetic field of the spectrometer cannot completely reorient the nematic, which is remarkable because the polymer component only represents less than 1/3 of the sample weight.

The resonance frequencies $\pm v(\theta)$ corresponding to angles $22.5^\circ$, $45^\circ$, and $67.5^\circ$ are $0.78v_0$, $0.25v_0$, and $-0.28v_0$, respectively. Peaks that are observed near these positions, in particular for the 3C sample, show that a large amount of the nematic remains in its original orientation fixed by the polymer orientation normal to the sample plane. The reason for the broadening of the peaks at intermediate angles is the incomplete sample alignment. Although the electric field used for orientation was above 200 V, the director field in the 350-µm cells may diverge by several degrees. Such small deviations $\Delta \theta$ of the orientation cause a line broadening of approximately

$$\Delta v = |dv/d\theta| \Delta \theta = \frac{1}{2} \sin 2\theta$$

which has its maximum at $\theta = 45^\circ$ and is negligible at $0^\circ$ and $90^\circ$. A second reason for the line broadening is that the torque of the $B_0$ field that forces the reorientation of the nematic directors out of their original orientation towards $B_0$ is also proportional to $\sin 2\theta$, and is maximum in the $45^\circ$ spectra.

In order to achieve a quantitative picture of the director distribution, we have simulated deuterium NMR line shapes according to Eq. (3) by varying the distribution $n(\theta)$ and $v_0$ and $G(v)$ determined from the $\theta = 0^\circ$ spectra. The computed line shapes that provide the best approximation to the experimental spectra are shown in Fig. 6, together with the corresponding director distribution functions $n(\theta)$ in Fig. 7. For sample 3C we find that almost the complete sample remains fixed to its original orientation. The half-width of the director distribution is about $12^\circ$; that means also that the distribution of $\theta_d$ is about $12^\circ$. These spectra are reminiscent of the orientational behavior of $S_A$ phases, although the mechanisms are completely different in the LCDP samples. For rigidly aligned directors at $\theta_d = 0^\circ$, the maximum of $n(\theta)$ should appear at $\theta = \theta_h$. Actually, it is asymmetrical and shifted towards lower $\theta$ (more parallel to $B_0$) at intermediate $\theta_h$.

We have to remember at this point that the distribu-
tion of \( \theta \) around \( \theta_h \) is not strictly equivalent to the distribution of \( \theta_h \) around \( 0' \) because we cannot distinguish between different azimuthal angles \( \Phi_d \). The distribution function \( n(\theta) \) is always an integral of the distribution density \( n(\theta, \Phi_d) \) over all orientations \( \theta_h, \Phi_d \) that satisfy Eq. (4) for a given \( \theta \). Symmetry considerations suggest that after the curing procedure the azimuthal angles \( \Phi_d \) are equally distributed and that a sufficiently strong external magnetic field at angles \( 0' < \theta_h < 90' \) tends to align the azimuthal angles towards \( \Phi_d = 0' \). The determination of the sample alignment by this NMR method is a good qualitative measure but does not give a complete qualitative description without further theoretical assumptions.

The qualitative result is that the director orientation locked in by the polymerized structure in the 3\% sample is only slightly influenced by the relatively strong \( B_0 \) field. The spectra of sample 2C show in principle the same features, although the field influence is more pronounced. If we assume that the quality of alignment in the absence of the external magnetic field is the same for samples 2C and 3C, then the differences between spectra (a)-(h) and (i)-(m) in Figs. 5 and 6 reflect the stronger influence of the \( B_0 \) field. The spectra (a)-(d) in Figs. 5 and 6 for the 1.28\% sample and their corresponding \( n(\theta) \) suggest that this polymer concentration is at the critical lower limit. The field reorients large parts of the director field; the ratio between fixed and realigned parts of the nematic is approximately 1:1. Still, the polymer skeleton retains its memory for the original orientation. After the sample is turned back to \( \theta_h = 0' \), the line shapes are reproducible.

The influence of the magnetic field on the orientation of LCDP samples suggests the assumption of a behavior similar to a Fréedericksz transition. The director orientation is elastically distorted by the \( B_0 \) field but remains fixed at the polymer skeleton. Whereas at low polymer concentrations a given external field can easily align the nematic director field, above a critical concentration the average distance between neighboring polymer strings or clusters becomes smaller than the correlation length corresponding to the field strength. The calculation of the director field in such a LCDP system, using the Frank elastic theory of the nematic phase, a finite anchoring strength at randomly distributed pinning lines or points, and an angular-dependent field interaction term would be an interesting task. From the resulting three-dimensional director field, the distribution function \( n(\theta) \) could be determined and the corresponding NMR spectra could be compared to the experiment. This procedure exceeds the framework of this publication, but we will show a rough first approximation to outline the principal effects of such a model.

We assume that a nematic liquid crystal is confined between two planar surfaces with a spacing \( d \), apply the one-constant approximation \( K_{11} = K_{22} = K_{33} = K \), and minimize the free energy for an infinitely strong planar anchoring. A term accounting for an external magnetic field \( B \) at an angle \( \theta_h \) between the field and the director orientation at the surface is included in the calculation. The linear coordinate normal to the glass plates is \( z \), the angle between the director and the boundary director orientation is denoted by \( \theta_h \), and the angle \( \theta \) between director \( n \) and field \( B \) is given by

\[
\theta(x) = \theta_h - \theta_d(x).
\]

The equation for the free-energy density is

\[
f = f_0 + \frac{1}{2} K \left( \frac{d\theta_d}{dx} \right)^2 + \frac{1}{2} \mu_0 B^2 \cos^2(\theta_d - \theta_h)
\]

with the solution

\[
d\theta_d \sqrt{\cos^2(\theta_m - \theta_h) - \cos^2[\theta_d(x) - \theta_h]} = \frac{B}{B_c} dx
\]

where

\[
x = (\pi/d)z.
\]

The maximum director deformation \( \theta_m \) in the middle between the boundaries is calculated from

\[
\int_0^{\theta_m} d\theta_d \sqrt{\cos^2(\theta_m - \theta_h) - \cos^2[\theta_d(x) - \theta_h]} = \frac{B \pi}{2 B_c}
\]

where

\[
B_c = (\pi/d) \sqrt{K \mu_0 / \chi_a}
\]

Now we know the function \( \theta(x) \) and if we assume a uniform distribution of the molecules along the \( x \) coordinate, we can determine \( n(\theta_d) \sim |d\theta_d/dx| \) immediately from Eq. (7). By inserting the distribution function \( n(\theta) = n(\theta_h - \theta_d) \) into Eq. (3) we can simulate the corresponding
FIG. 8. Angular dependence of simulated spectra from a planar elastic director deformation with strong anchoring for different $B/B_c$. Similar line shapes should be observed if a Fredericksz transition in a planar sandwich cell is studied by NMR. As $B_c$ is related to the distance between the boundaries, it is a measure for the polymer concentration. $B_c$ should increase with increasing concentration. The LCDP system is much more complex, however. First, one has to include a distribution of the angles between the field and the boundary orientation of the director because of incomplete alignment. Figure 8(b) shows the corresponding spectra for a Gaussian distribution of $\theta_h$ with a half-width of $20^\circ$. Some principal features of the experimental spectra are reflected even with this crude approximation, in particular for high polymer concentrations. Further, one has to include at least a two- or even three-dimensional director field $n(r)$, a random distribution of the pinning points, and a finite anchoring strength. For a more detailed theory, it will be necessary to get more information about the polymer structure, e.g., by electron microscopy.

Finally, we have recorded spectra from samples that have been cured in the isotropic phase and simulated the corresponding line shapes with the same procedure as used for the oriented LCDP samples. In this case we know the exact function $\pi(\theta_d,\Phi_d)$; in the absence of external fields it should be a random distribution. We can observe the pure influence of $B_0$ on the sample alignment. The NMR spectra should be independent of the rotation angle $\theta_h$, independent of a two- or even three-dimensional director field $n(r)$, a random distribution of the pinning points, and a finite anchoring strength. For a more detailed theory, it will be necessary to get more information about the polymer structure, e.g., by electron microscopy.

NMR line shape. The results are shown in Fig. 8(a) for different field angles $\theta_h$ and different $B/B_c$. Similar line shapes should be observed if a Fredericksz transition in a planar sandwich cell is studied by NMR. As $B_c$ is related to the distance between the boundaries, it is a measure for the polymer concentration. $B_c$ should increase with increasing concentration. The LCDP system is much more complex, however. First, one has to include a distribution of the angles between the field and the boundary orientation of the director because of incomplete alignment. Figure 8(b) shows the corresponding spectra for a Gaussian distribution of $\theta_h$ with a half-width of $20^\circ$. Some principal features of the experimental spectra are reflected even with this crude approximation, in particular for high polymer concentrations. Further, one has to include at least a two- or even three-dimensional director field $n(r)$, a random distribution of the pinning points, and a finite anchoring strength. For a more detailed theory, it will be necessary to get more information about the polymer structure, e.g., by electron microscopy.

Finally, we have recorded spectra from samples that have been cured in the isotropic phase and simulated the corresponding line shapes with the same procedure as used for the oriented LCDP samples. In this case we know the exact function $\pi(\theta_d,\Phi_d)$; in the absence of external fields it should be a random distribution. We can observe the pure influence of $B_0$ on the sample alignment. The NMR spectra should be independent of the rotation angle $\theta_h$, independent of a two- or even three-dimensional director field $n(r)$, a random distribution of the pinning points, and a finite anchoring strength. For a more detailed theory, it will be necessary to get more information about the polymer structure, e.g., by electron microscopy.

Finally, we have recorded spectra from samples that have been cured in the isotropic phase and simulated the corresponding line shapes with the same procedure as used for the oriented LCDP samples. In this case we know the exact function $\pi(\theta_d,\Phi_d)$; in the absence of external fields it should be a random distribution. We can observe the pure influence of $B_0$ on the sample alignment. The NMR spectra should be independent of the rotation angle $\theta_h$, independent of a two- or even three-dimensional director field $n(r)$, a random distribution of the pinning points, and a finite anchoring strength. For a more detailed theory, it will be necessary to get more information about the polymer structure, e.g., by electron microscopy.
IV. CONCLUSIONS

In this paper we have shown that the deuterium NMR spectra of LCDP provide detailed information about order and orientation of the nematic director in these new materials. We show that small percentages of polymer are sufficient to stabilize the nematic director even in strong external magnetic fields. The LCDP properties are, in particular, induced by the polymerization of the dissolved monomers in the mixture. Polymerization was achieved by uv irradiation of the samples.

The critical amount of polymer skeleton that is necessary to fix the director orientations is about 1%. A good orientation is achieved with approximately 3% polymer component in the system. At low concentrations, the magnetic field distorts the director field, while the polymer structure at least retains an orientation memory. It seems that, although it cannot be proven by our experiments, once the polymer structure is formed in the sample its orientation is no longer influenced by the external field at all. During the polymerization, the nematic director field defines the orientation of the polymer skeleton.
The order parameter of the nematic component in LCDP is not changed from that of the pure nematic phase except for a small temperature depression of the phase-transition temperatures after polymerization of about 0.7 K per 1% additive. The remaining birefringence of the samples above the clearing point is caused by the anisotropic structure of the polymer framework. We could not detect nematic order in the deuterium spectra above $T_{nc}$.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation (NSF) under Solid State Chemistry Grant No. DMR88-17646. The deuterated compound was synthesized by Sandy Keast and Mary Neubert whose work was supported under NSF Solid State Chemistry Grant No. DMR88-18561.