Magnetic field induced alignment of the directors of a smectic-*A* liquid crystal

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Deuterium NMR is used to monitor the magnetic field induced alignment of the directors in the smectic A phase of 4-octyl-4′-cyanobiphenyl. The experiments consist of first preparing the sample as a monodomain by cooling slowly from the nematic phase in the magnetic field of the NMR spectrometer. The tube containing the sample is then rotated quickly through an angle θ_+, and the subsequent field induced alignment process followed by recording deuterium spectra over a period of time. The results obtained show that the magnetic field induced alignment of the directors in a smectic-*A* sample is qualitatively different from that of nematic samples. Results are reported for the pure mesogen containing deuteriums at the α chain position, and these are compared with data obtained on the alignment process by monitoring the deuterium spectrum of a small amount of an added solute, *p*-xylene-d_{10}. [S1063-651X(99)06608-8]

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INTRODUCTION

There have been many investigations of the alignment of nematic liquid crystalline samples by either a magnetic or an electric field. There have also been several studies of the effect of applying two constraints to a nematic sample, such as an electric field and a surface constraint. As a result the basic features of these hydrodynamic processes have been characterized, and theoretical models based on continuum theory have been developed which successfully describe the phenomena [1]. There have been far fewer studies on smectic-*A* (Sm-*A*) phases, and the basic features of the field-induced alignment process for the director have not been elucidated [2–4]. Here we present the results of a study of the effect on a Sm-*A* phase of applying a magnetic field to align the mesophase directors, **n**(**r**). The alignment process has been monitored by deuterium NMR, and the magnetic field was that of the spectrometer. Deuterium NMR spectroscopy is a particularly useful method for monitoring director alignment [5]. A group of equivalent deuterium nuclei in a molecule which is in a uniformly aligned liquid crystalline phase, that is, one described by a single director **n**, gives a quadrupolar doublet in the NMR spectrum whose separation, $\Delta\nu(\theta)$ depends on the angle θ between **n** and **B**, the direction of the magnetic field of the spectrometer. Thus

$$\Delta\nu(\theta) = \Delta\nu(0°)(3\cos^2\theta - 1)/2. \tag{1}$$

If the directors are not uniformly aligned, then a broadening of the two components of the doublet is produced if the spread of the director orientation is small. In the limit of a random distribution of director orientations, the spectrum has a broad, characteristic shape. The spectra, therefore, are able to reveal how the sample is aligned in the magnetic field at various stages in an experiment, provided that they can be recorded in a time which is short compared with the time scale of the alignment process.

The experiments are very simple, but very informative. The sample chosen to demonstrate the methodology, 4-octyl-4′-cyanobiphenyl (8CB), has a nematic and a Sm-*A* phase (T_{NI} 313.8 K and T_{SmAN} 306.8 K) [6], and can be easily deuteriated in the chain α position. It has a positive anisotropy $\Delta\chi$ in the magnetic susceptibility defined relative to the director, so that the directors can first be uniformly aligned in the nematic phase along the magnetic field B_0 in the spectrometer. Cooling into the Sm-*A* phase preserves the alignment, so that a monodomain Sm-*A* is produced. The sample is then turned about an axis perpendicular to B_0, causing the director to adopt a new orientation θ_0, and the deuterium spectrum is used to monitor how the director is aligned back to its original, equilibrium orientation. We will demonstrate that the alignment process can be monitored by recording the spectra of a sample of 8CB which is labeled with deuterium, or via the spectra from a deuteriated probe molecule dissolved at low concentration in 8CB. The results of these experiments reveal that the alignment process in a Sm-*A* phase has some intriguing features, and is qualitatively different from that in nematic samples.

EXPERIMENT

A sample of 8CB deuteriated at the α position in the alkyl chain was prepared by a slight modification of the route proposed in Ref. [7]. In this method, biphenyl is first acetylated with octanyl chloride, using aluminum chloride with hexane as the solvent. The resulting ketone was reduced with lithium aluminum deuteride and aluminum chloride in dry chloroform. The 4-octylbiphenyl-d_2, specifically deuteriated in the α position, was then iodinated with iodine and periodic acid in trifluoroacetic acid. The resulting 4-octyl-4′-iodobiphenyl was cyanated with cuprous nitrile in dimethylformamide. The extent of deuteriation was monitored by proton NMR spectroscopy and determined to be 95%. The transition temperatures of 8CB-d_2 were found to agree with the literature values [6].

The deuterium spectrum of 8CB-d_2 is a doublet, any fine structure from dipolar coupling being unresolved. The probe molecule used was fully deuteriated *p*-xylene which was pur-

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chased from Aldrich. It was dissolved in 8CB to form a 3% solution by weight, whose spectrum contains a quadrupolar doublet from the aromatic deuterons, and a separate doublet from the methyl deuterons, in each case with fine structure from dipolar coupling between the deuterons. The spectra were recorded on a Bruker MSL 200 spectrometer, which has a magnetic field of 4.67 T. The signals were detected with a home built probe, which has a single solenoid coil mounted horizontally. The samples of approximately 10 mm length were contained in 5 mm outside diameter glass tubes, made from standard NMR tubes, and were confined to one end by a teflon vortex plug (Wilmad). The sample tube can be turned through a predetermined angle under the control of the spectrometer's computer by a stepper motor, as described previously [8]. The spectra were recorded using a quadrupolar echo sequence [9], with a 90° pulse width of 4.1 μs, and an interpulse delay of 50 μs. There were no special constraints on recording the spectra of monodomain samples at the start of the experiments, that is, just prior to turning the sample in the magnetic field. These spectra were recorded by acquiring 100 free induction decays (fids) into 8 k of computer memory with a spectral width of 125 kHz, giving a digital resolution of 31 Hz. To monitor the deuterium spectra during the field induced alignment process in as short a time as possible, conducive with an adequate signal-to-noise ratio, it was necessary to reduce the computer memory to 2 k, and to average only 16 fids for each time step. This increased the digital resolution to 250 Hz, but reduced the time to acquire each fid to 2 ms. The delay between the echo sequences was 30 ms, so that the total time taken to acquire the average of 16 fids was 0.5 s.

The sample was first heated into the nematic phase and left for about 30 min, which ensures a complete alignment of the directors along the magnetic field. A cooling rate of about 1 °C/min was used to bring the sample to the desired temperature in the Sm-A phase. The sample was turned by issuing a series of n pulses from the Aspect 3000 computer of the spectrometer to a stepper motor in a total time which was typically 50–100 ms. The stepper motor had a step size of 1.8°, and care was taken to ensure that the gears connecting the drive shaft to the NMR sample tube were fully engaged at the start of the experiment. This helps to minimize the difference between the angle θ, through which the director turns, and θ', calculated as 1.8n. The value of θ was determined using Eq. (1) and the splittings immediately before ($\Delta \nu_0$) and after turning ($\Delta \nu_+$) with a precision of $\pm 0.2°$. After turning, acquisition was triggered following a delay t, and the averaged fid stored by buffered acquisition in the memory of the Aspect 3000. The delay t was incremented and another averaged fid stored; this process was repeated for as long as necessary in order to characterize the alignment process.

RESULTS AND DISCUSSION

Pure 8CB-d_2

A monodomain sample of the Sm-A phase was prepared by first allowing the sample to achieve a uniform alignment of the directors in the nematic phase before cooling into the Sm-A phase to 294 K. At this temperature the spectrum was a doublet with a splitting $\Delta \nu_0 = 65\,582 \pm 60$ Hz, and with a
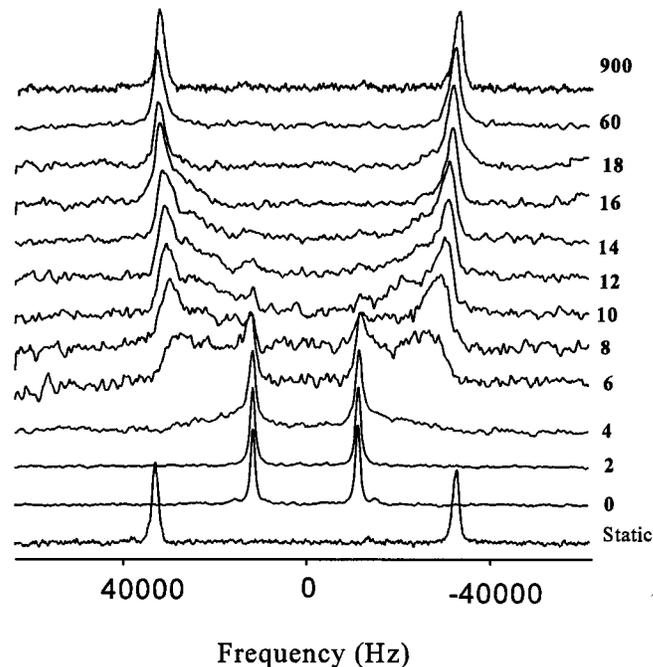

FIG. 1. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 which was prepared as a monodomain in the Sm-A phase at 296 K, and was then turned through 41°. The spectra were recorded at the intervals in time shown alongside each trace in minutes. The spectrum labeled ''static'' was taken immediately prior to turning the sample.

width at half height Δ_0 of 1900 ± 30 Hz. The sample tube was rotated in 50 ms through 23 steps, and the splitting $\Delta \nu_+$ at time t_+, immediately after turning, was $22\,950 \pm 250$ Hz, which corresponds to an orientation θ_+ of $41.2° \pm 0.2°$.

The linewidths before and after (Δ_+) turning will have contributions from unresolved dipolar coupling Δ_{D0} and Δ_{D+} from spin-spin relaxation rates Δ_{R0} and Δ_{R+}, and from misalignment of the directors Δ_{n0} and Δ_{n+}. The observed value of Δ_+ was 1220 Hz, and to estimate how much of this could arise from director misalignment we assume that $\Delta_{R0} = \Delta_{R+} = \Delta_{n0} = 0$. In this case $\Delta_{D+} = 1900(\Delta \nu_+/\Delta \nu_0) = 665$ Hz, and $\Delta_{n+} = 555$ Hz. This corresponds to a misalignment of the directors of only 0.2°, which can be taken to be a reasonable estimate of the actual, and hence negligible deviation from a monodomain.

The spectra were recorded at intervals of time for 1 h and selections from this data set are shown in Fig. 1. The spectrum consists of a single doublet for the first 2 min, but there is a loss of intensity, and a broadening of the lines as shown in Fig. 2. After this initial period the directors begin to align to the field direction, as revealed by the appearance of resonances corresponding to larger quadrupolar splittings. In fact, a broad range of resonances is observed which is consistent with a spread in the director orientations of approximately between 41° and 10°. This shows that in the alignment process the directors do not remain parallel, but move at different rates toward the field direction. Note in particular that a part of the sample remains at θ_+ for up to 12 min. After 1 h the splitting was $64\,940 \pm 250$ Hz, which corresponds to $\theta = 4.6° \pm 1°$, and Δ was 2400 Hz, suggesting a spread in director orientation which is greater than at the start of the experiment. However, the sensitivity of the spectrum
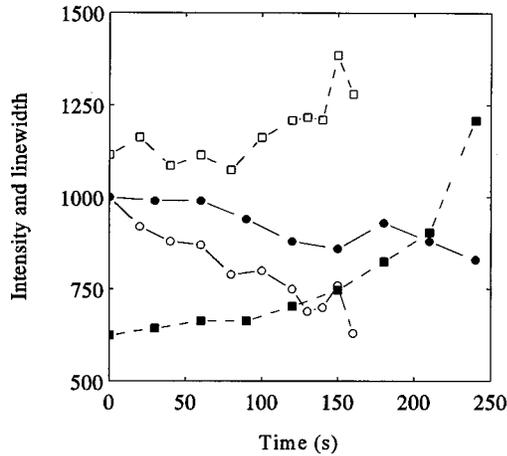
FIG. 2. The time dependence of the intensity (circles, normalized to 1000) and average linewidths (squares) of the components of the doublet in the deuterium spectrum of 8CB-d_2 in the pure (open symbols), and including 3% of p-xylene-d_{10} (filled symbols) after the sample was prepared as a monodomain in the smectic-A phase and subsequently turned through 41°.

to a spread in the director orientations is least when θ is close to zero, and so the values of $\Delta\nu$ and Δ alone close to this orientation do not reveal the nature of the distribution with great accuracy. To determine more accurately how the directors are distributed at long times after turning the sample, the following experiment was performed. The sample was prepared as a monodomain by cooling from the nematic phase, and then turned to 41.1°, as determined from the relative values of $\Delta\nu_0$ and $\Delta\nu_+$, and then left for 15 h. After this time the initial splitting had been recovered to within the experimental error of ±250 Hz. The sample was now turned again through 23 steps, and the spectra shown in Fig. 3 obtained. At time t_+ the spectrum is consistent with most of the directors being at 42.7° with a narrow distribution, whilst the rest are distributed around 50° with a broader distribution. Fitting the line shape, approximately, to four Gaussian broadened lines gives intensities of 70% for the lines corresponding to 42.7°, and 30% for those at 50°. The simplest interpretation of this result is that the director distribution before the second rotation was bimodal and peaked at approximately $\theta=0°$ (70%) and 7° (30%).

The spectra in Fig. 3 show that after 2 min the directors begin to return to being aligned along the field, but in a more complex way than when the sample had not been rotated previously and was initially a monodomain. This is possibly because the directors with $\theta_+ = 42.7°$ align differently for those with $\theta_+ = 50°$. Such a difference has been found for nematic samples [10], where there is a change in behavior when θ_+ exceeds 45°. Thus, when $\theta_+ < 45°$ for a nematic sample, the directors are pulled towards the field by the magnetic torque, T_{mag},

$$T_{\mathrm{mag}} = -\tfrac{1}{2}\Delta\chi B^2 \mu_0^{-1}\sin 2\theta \qquad (2)$$

which is resisted by the viscous torque T_{vis},

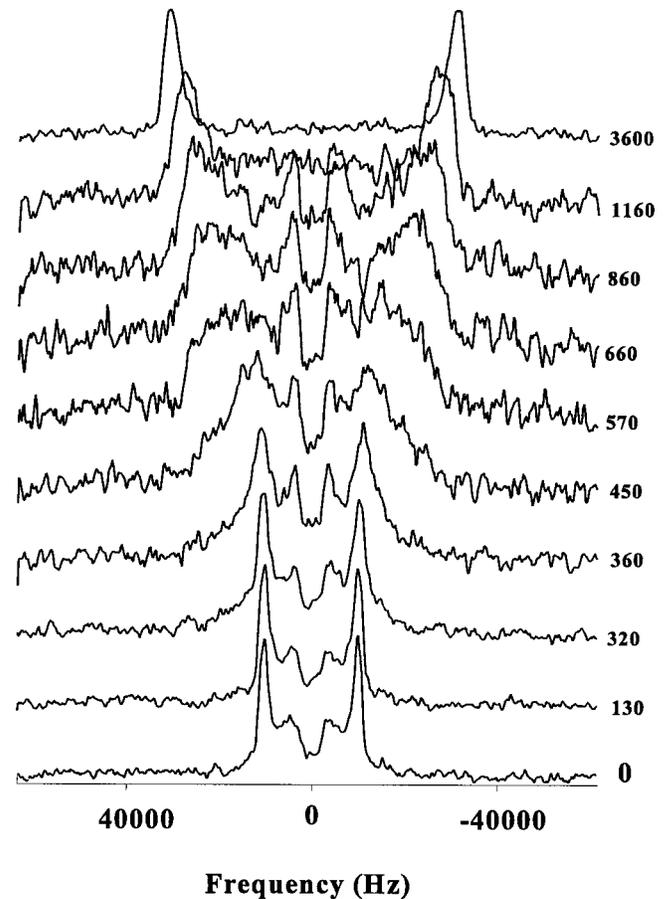$$T_{\mathrm{vis}} = -\gamma_1 d\theta/dt, \qquad (3)$$

FIG. 3. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 which was prepared as a monodomain in the Sm-A phase at 296 K, was then turned through 41°, left to align for 15 h, and then turned again through 41°. The spectra were recorded at the intervals in time shown alongside each trace in seconds.

where γ_1 is a rotational viscosity coefficient. Under the influence of these two torques, the directors should return uniformly to alignment along the magnetic field with a time dependence of θ given by

$$\tan\theta(t) = \tan\theta_+ \exp(-t/\tau), \qquad (4)$$

with the relaxation time

$$\tau = \mu_0 \gamma_1 / \Delta\chi B^2. \qquad (5)$$

Experiments on nematic phases show that Eq. (5) is obeyed to a good approximation [1,8]. For the Sm-A phase of 8CB-d_2, the alignment process is clearly more complex, which is to be expected given its layer structure. The spectrum obtained for the orientation θ_+ in Fig. 1 shows that the sample has rotated as a monodomain, and by implication this means that the smectic layers are still intact, and that they remain so for the 2 min when the spectra are essentially unchanged. After this period the spreading of the directors suggest that the layer structure begins to break down, which allows the directors to rotate more easily. The reason for the initial delay in aligning the directors could be that a monodomain smectic-A sample cannot rotate because there is strong anchoring of the layers at the inner surface of the
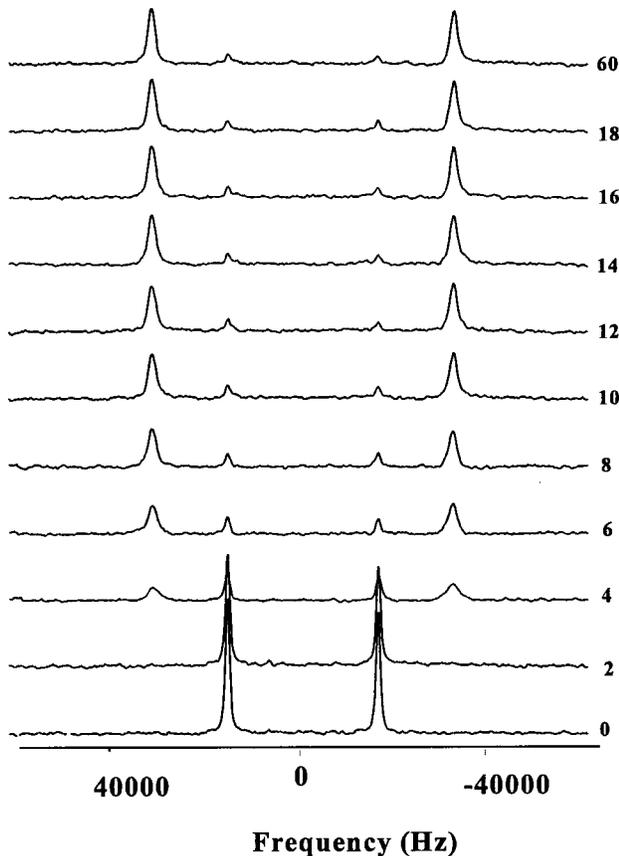
FIG. 4. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 which was prepared as a monodomain in the Sm-A phase at 296 K, and was then turned through 88°. The spectra were recorded at the intervals in time shown alongside each trace in minutes.
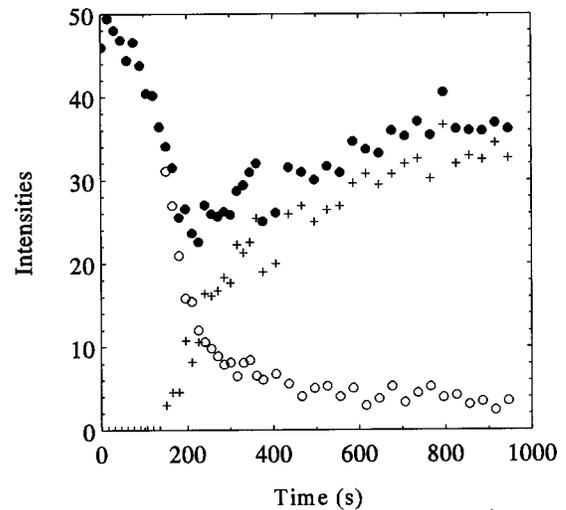

FIG. 5. Time dependencies of the intensities of the deuteron NMR peaks shown in Fig. 4. The intensity of the peaks corresponding to $\theta = 88°$ are shown as $\bigcirc$, those for $\theta = 0°$ are shown as $+$, and the total intensity is denoted by $\bullet$. Only the first 1000 s of the alignment process are displayed.

sample tube. In order to rotate, the layers must first break down into domains having a range of Sm-A layer correlation lengths, whilst still preserving the director alignment at θ_+. As the correlation length within a domain decreases a point is reached when it begins to rotate in the field. At this point the sample is more nematic than smectic like. Finally there is a slow process when the domains with their directors more or less parallel with the field unite to form a monodomain Sm-A structure.

When $\theta_+ > 45°$ for nematic samples the director alignment proceeds by a different mechanism [10]. The simplest case is when $\theta_+ = 90°$, when the directors can return to having $\theta = 0°$ equally probably by rotating clockwise or counterclockwise. This establishes a director flow pattern, and the director alignment dynamics now depends on both viscous and elastic torques, and on the shape and dimensions of the container.

The alignment dynamics of the 8CB-d_2 sample in the Sm-A phase is also qualitatively and quantitatively different when $\theta_+ = 90°$, as shown by the spectra in Fig. 4. In this case the initial quadrupolar splitting $\Delta \nu_0$ was 65 185 $\pm$ 250 Hz, and the average linewidth was 1800 $\pm$ 250 Hz. After turning, $\Delta \nu_+$ was 32 469 $\pm$ 250 Hz, corresponding to $\theta_+ = 88.0° \pm 0.2°$, while the average linewidth, Δ_+, had been reduced by almost the same ratio as the splittings to 950

$\pm$ 250 Hz. There is an initial period of about 2 min when the directors remain at this orientation, and then there is a rapid alignment of a part of the sample to having $\Delta \nu = 65 429 \pm 250$ Hz, which corresponds to θ being close to zero. The alignment is too rapid to be detected by deuterium NMR, which means that it is completed within the time taken to record a single fid, which was 4 ms. As time progresses the fraction, $P(0°)$, of the sample with $\theta = 0°$ grows, while $P(88°)$, the fraction at 88°, decreases as shown in Fig. 5. The alignment process was still incomplete after 1 h in that not all the sample has returned to being aligned along the field. Figure 5 also shows $P = P(0°) + P(88°)$, and this reveals that a significant fraction of the sample is not being detected. This is probably because some of the sample has a very broad distribution of directors, so that the deuterium signal is dispersed approximately evenly over 65 kHz and is too weak to be detected in the time interval necessary to follow the alignment process.

The alignment process for the Sm-A sample with $\theta_+ = 88°$ is similar to that for $\theta_+ \approx 41°$ in that there is an initial period when the spectra do not change. This could again be when the monodomain is breaking up into a number of smaller domains, each with the same director alignment but with different layer correlation lengths. It is not obvious, however, why the alignment of the smaller domains produced should be so much faster than when θ_+ is 40°, but we can conjecture that it is because of a similar involvement of elastic forces as in the case of nematic samples.

One of the most intriguing aspects of the experimental results obtained for the field induced alignment process for monodomain Sm-A samples which were turned through either 41° or 88° is the existence of a period immediately after turning when most of the sample remains at the initial orientation before beginning to be aligned by the field. This delay may occur because alignment by the field requires that first the smectic layer structure has to be disrupted, and that this is facilitated by the presence of defects in the spatial ordering. Some defects will be present before turning the sample,
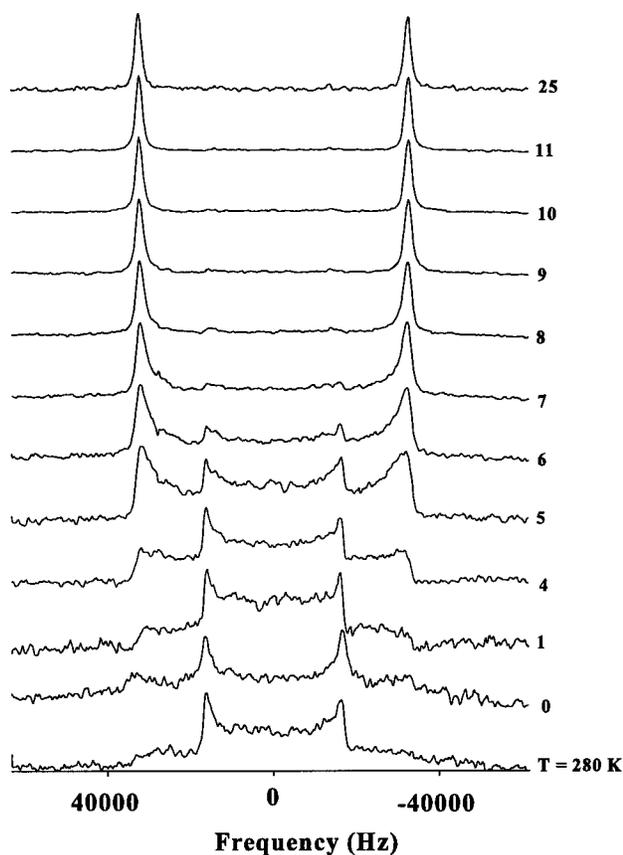
FIG. 6. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 which was prepared with a random distribution of the directors in the Sm-A phase at 77 K, and was then placed in the magnetic field of the spectrometer at 280 K. The sample temperature was raised to 295 K, and spectra were recorded at the intervals in time shown alongside each trace in minutes.

and their concentration will depend on the history of the sample, that is, on how good a monodomain sample is produced by cooling from the nematic phase. To test this idea we have investigated the field induced alignment process for a sample prepared in such a way as to have a random distribution of directors and, hence, layer normal orientations. The ideal way to do this would be to start with a sample at thermal equilibrium in the Sm-A phase, and to randomize the director orientations by, for example, mechanical agitation. This was not possible with the probe used to detect the NMR signals, and as a compromise a random distribution was obtained by heating a sample into the isotropic phase outside the spectrometer, and then cooling rapidly by immersing in liquid nitrogen. The cold sample was then transferred into the magnetic field of the spectrometer and allowed to come to thermal equilibrium at 280 K, when it is still a solid. After warming to 295 K, and leaving for a few minutes, the spectrum labeled as being at $t=0$ in Fig. 6 was obtained. This has a shape which shows that the directors are approximately randomly oriented, and the outer shoulders have a splitting of $64\,696\pm250$ Hz, while the splitting of the inner horns is $32\,956\pm250$ Hz, which correspond well with the values expected of $65\,185\pm250$ and $32\,593\pm250$ Hz for a sample at thermal equilibrium at 295 K. The most significant feature of the alignment process shown in Fig. 6 is that it is faster than when starting from a monodomain sample. Thus after 25 min
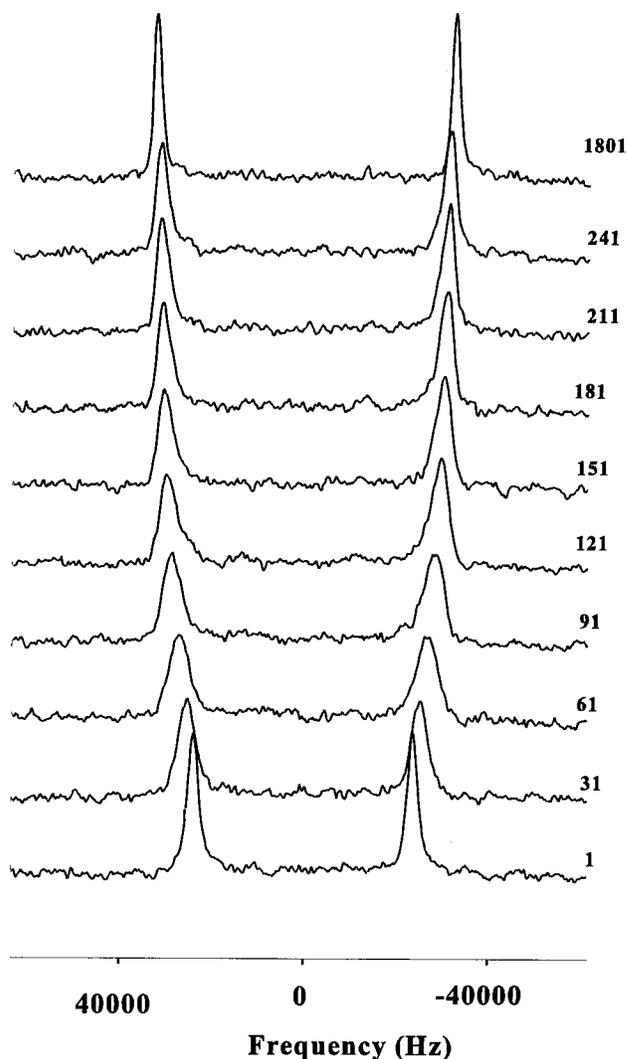

FIG. 7. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 which was aligned from a random distribution of the directors at 295 K, and then turned through 25°. The spectra were recorded at the intervals in time shown alongside each trace in seconds.

the quadrupolar splitting has grown to $\Delta\nu=65\,185$ ±250 Hz, and the linewidths are $\Delta=1900\pm250$ Hz, which indicate that the sample is a monodomain. That this is a well-ordered monodomain is shown by the spectrum (see Fig. 7) obtained by rotating this sample to 25.1° when $\Delta\nu_+=47\,600\pm250$ Hz and $\Delta_+=2400\pm250$ Hz. The spectra obtained as this sample is aligned by the magnetic field are shown in Fig. 7. Note the absence of a significant delay at the start of the alignment process. This is in contrast to the behavior in an experiment when the sample was started from a monodomain produced from cooling from the nematic phase, and then turned through 25°. The difference between these samples, both seeming to be monodomains in terms of director alignment, could be a difference in the degree of ordering of the smectic layers, that is a difference in their correlation lengths.

The sample does move from $\theta=25.1°$ to 0° as a monodomain, but this process does not obey Eq. (4). Figure 8 shows how tan θ varies with time, and it is clearly not a monoexponential decay. The data do, however, fit a biexponential decay:
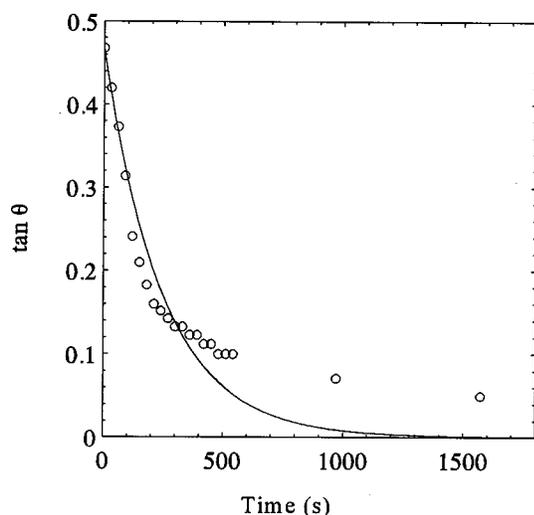
FIG. 8. Decay with time of tan θ, where θ is the angle between the director and the magnetic field. The sample of 8CB-d_2 was prepared first as a random distribution of directors, and then left to align in the magnetic field before turning through 25°. The continuous line is a fit to the data of Eq. (4).

$$\tan \theta = 0.119 \exp(-at) + 0.373 \exp(-bt), \qquad (6)$$

with $a = 0.0005 \, \text{s}^{-1}$ and $b = 0.008 \, \text{s}^{-1}$, which suggests that the process proceeds through an intermediate state.

Alignment of samples of 8CB containing *p*-xylene-d_{10}

Adding a deuterated solute to a liquid crystal and measuring its deuterium NMR spectrum provides an alternative way of following the magnetic field induced alignment process for the director. However, the use of a probe molecule to monitor a liquid crystalline phenomenon always raises the question of how the presence of the solute affects the properties of the liquid crystal. The presence of a nonmesogenic solute will certainly tend to lower the transition temperatures between the phases, as well as change the viscosities and elastic constants, and these factors can be expected to change the rate at which the field induced alignment occurs at a particular temperature. As we shall see, however, the presence of the *p*-xylene has an unexpected influence on the field induced alignment process of the directors in the Sm-*A* phase of 8CB.

Our first experiments using the deuterium NMR spectrum of the solute to monitor the alignment process were done on mixtures of 3% *p*-xylene-d_{10} dissolved in undeuterated 8CB. The sample had $T_{\text{NI}} = 308 \pm 0.5 \, \text{K}$ and $T_{\text{SmAN}} = 301 \pm 0.5 \, \text{K}$, and the experiments were performed at 298 K. Turning the sample through 22 steps, and recording spectra during the alignment process, gave the series of spectra in Fig. 9. The time taken to record each fid was 0.3 s, and 16 fids were averaged in a total time of 4.8 s to produce each spectrum after Fourier transformation. The values of $\Delta \nu_0$ and $\Delta \nu_+$ for either the aromatic or methyl deuterons can be used to obtain the director alignment immediately after turning, and these both gave $\theta_+ = 38.2° \pm 0.2°$. The overall behavior is similar to that observed for pure 8CB-d_2. First there is an initial period when the splittings do not change,
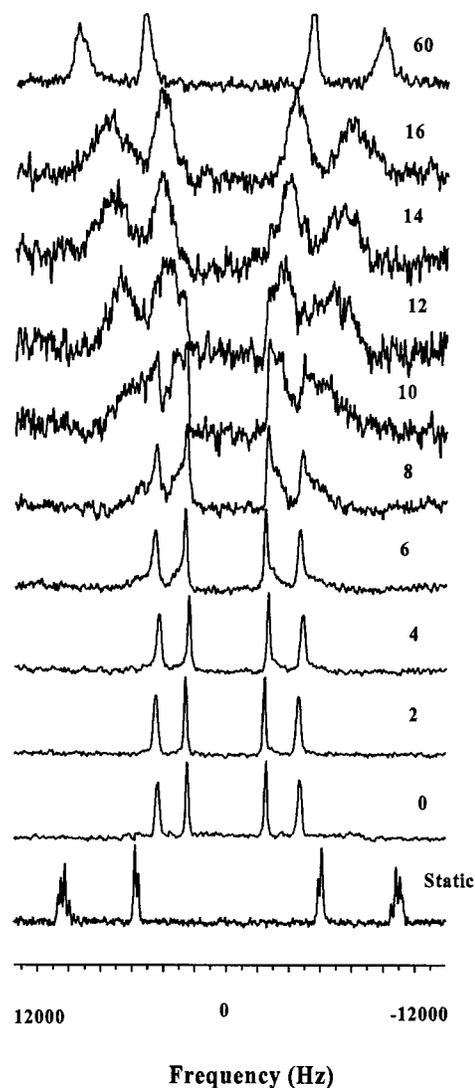

FIG. 9. 30.7 MHz spectra of the deuterons in *p*-xylene-d_{10} dissolved in 8CB. The sample was prepared as a monodomain in the Sm-*A* phase at 298 K, giving the spectrum labeled as ''static,'' and then turned through 38°. The spectra were recorded at the intervals in time shown alongside each trace in minutes.

but there is a loss in intensity, after which it is possible to detect new lines in the spectrum, which correspond to the directors being distributed over a range of angles. After 1 h the lines begin to sharpen, but even after 15 h the spectrum has still not returned to that at time t_0, and the splittings correspond to a director orientation θ of 15°. This is significantly larger than the value of 4.6° obtained for the alignment of the directors in pure 8CB after 15 h following a rotation of 41°. The larger value of θ found after 15 h for the solution indicates a slower return to complete alignment than for the pure 8CB-d_2 sample, even though the temperature is higher for the mixture than for the pure compound, and so the decay rate might be expected to be faster.

These results indicate a difference in behavior between the pure 8CB and 8CB containing the solute. This could be because the solution behaves differently to the pure mesogen under field induced alignment, or more intriguingly that in the solution the solvent and solute behave differently. To resolve this point, an experiment was performed at 296 K on
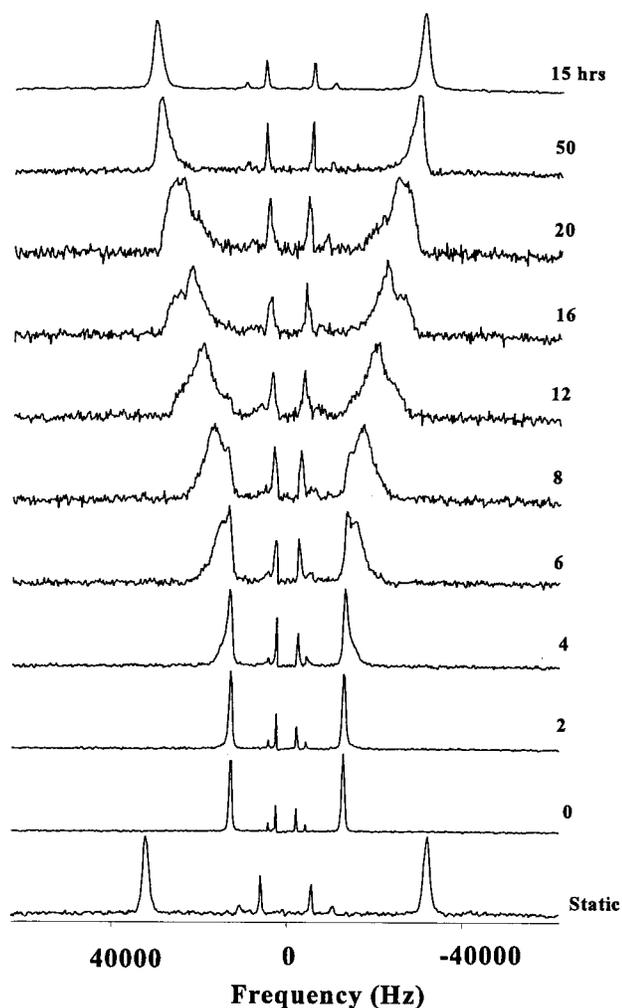
FIG. 10. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 containing 3% by weight of p-xylene-d_{10}. The sample was prepared as a monodomain in the Sm-A phase at 296 K, and was then turned through 39°. The spectra were recorded at the intervals in time shown alongside each trace in minutes. The spectrum labeled static was taken immediately prior to turning the sample, and the top trace after 15 h.

FIG. 11. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 containing 3% by weight of p-xylene-d_{10}. The sample was prepared as a monodomain in the Sm-A phase at 296 K and turned through 39°, allowed to align in the magnetic field for 15 h, and then turned again through approximately 39°. The spectra were recorded at the intervals in time shown alongside each trace in minutes.

a mixture of 3% by weight p-xylene-d_{10} in 8CB-d_2, so that the deuterium spectra of both solute and solvent can be monitored simultaneously during alignment by the magnetic field. The transition temperatures of this sample were $T_{NI} = 307 \pm 0.5$ K and $T_{SmAN} = 299 \pm 0.5$ K. A monodomain sample in the Sm-A phase at 296 K was prepared by cooling from the nematic phase. The quadrupolar splitting for the 8CB-d_2 deuteriums was $64\,453 \pm 250$ Hz, with an average linewidth of 1300 ± 250 Hz. Note that the linewidth is smaller than that of 1900 ± 250 Hz obtained for the sample of pure 8CB-d_2. It is not possible to decide whether this reduction in linewidth for the mixture results from a reduction in the spin-spin relaxation rate of the deuteriums, or whether there is a smaller spread in the director orientation. Figure 10 shows the spectra taken after this monodomain sample had been turned through 23 steps. One hundred fids were averaged in a total recording time of 3 s to produce the spectra shown for each time interval in Fig. 10. The time to record each fid was 30 ms, which is long enough for the deuterons
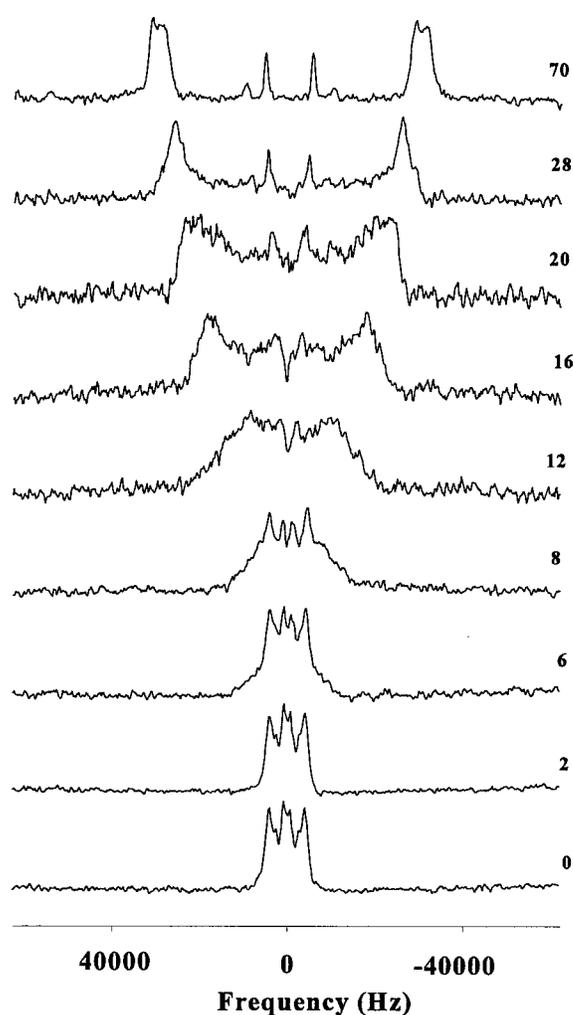
in 8CB to regain their equilibrium spin populations, but too short for this to occur for the deuterons in p-xylene. There is, therefore, a reduction in signal intensity for the deuterons in the solute, which is more severe for the slowly relaxing methyl nuclei, and so their intensity is dramatically reduced. This does not detract from the ability to measure the quadrupolar splittings of the solute and solvent in the mixture. The value of $\Delta\nu_+$ for 8CB-d_2 after turning was $25\,635 \pm 250$ Hz, which gives $\theta_+ = 39.3° \pm 0.2°$. The ratio $\Delta\nu_+/\Delta\nu_0$ is the same for the solvent and the solute, the latter being measured for the aromatic deuterons alone, and this proves that the solvent and solute are described by the same director alignment at time $t = t_+$. The linewidths of 8CB-d_2 reduced on turning to 630 ± 250 Hz, which is consistent with the preservation of a good monodomain sample. The time course of the spectra for this mixture is similar to that in Fig. 9 for p-xylene-d_{10} in 8CB, and, most significantly, after 15 h the splittings for the solvent and solute are in agreement with a value of $\theta = 10° \pm 0.5°$. This shows that
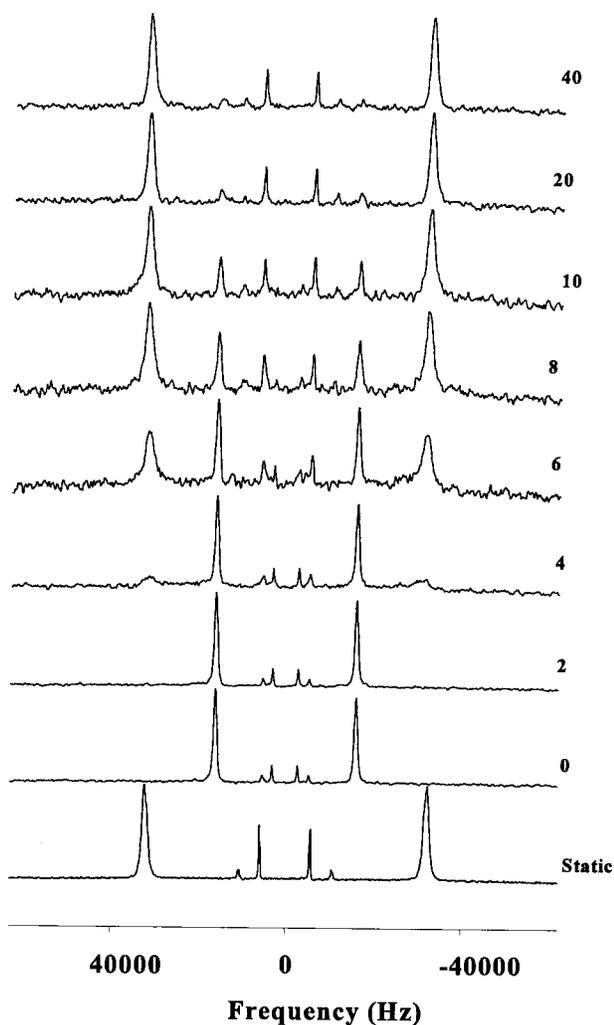
FIG. 12. 30.7 MHz spectra of the deuterons in a sample of 8CB-d_2 containing 3% by weight of p-xylene-d_{10}. The sample was prepared as a monodomain in the Sm-A phase at 296 K, and was then turned through 88°. The spectra were recorded at the intervals in time shown alongside each trace in minutes. The spectrum labeled "static" was taken immediately prior to sample turning.

the solute and solvent molecules in the mixtures can be described by the same director alignment, that is, the behavior of the solute faithfully follows the director of the phase.

We will return to a consideration of the spectrum obtained 15 h after turning the sample, but first we note that there is a significant quantitative difference between the behavior of pure 8CB and 8CB containing p-xylene during the period immediately following turning the samples. This is illustrated in Fig. 2, which compares the intensities and linewidths of the quadrupolar doublet given by 8CB-d_2 in both samples in the period up to the appearance of extra resonances from those parts of the sample which are aligning to the field direction. This shows that the peaks from 8CB-d_2 in the mixture are losing intensity and broadening more slowly than for the same peaks in the pure mesogen.

We now return to the spectrum in Fig. 10 which corresponds to $t = 15$ h. The peaks in this spectrum have widths which are considerably broader than those at time t_0, indicating a spread in the directors. This was confirmed by performing a second rotation on this sample through 23 steps,
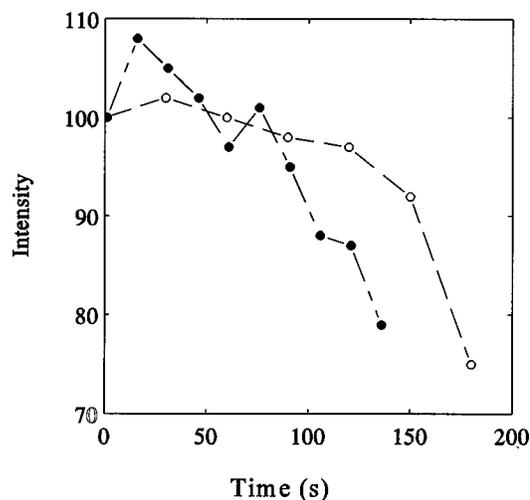

FIG. 13. Intensities of the quadrupolar doublet given by the deuterium nuclei in 8CB-d_2 when a sample of the pure mesogen (filled circles), or one containing 3% by weight of p-xylene-d_{10}, (closed circles) has been turned through 88°, and left to align with the direction of the applied magnetic field.

which produced the spectra shown in Fig. 11. These spectra were recorded as the average of 16 fids. The intensity distribution in the spectrum at time t_+ is attributed to there being at least a bimodal distribution of the directors. The intensity is dominated by that from 8CB-d_2, and the lines in the center correspond to θ_+ being close to 54.7°, while those at the outside correspond to θ_+ being either 49.8° ± 0.2° or 60.0° ± 0.2°, depending on the sign taken for the splitting, which is not available from the experiment. The bimodal distribution persists throughout the alignment process and after 70 min is giving two sets of quadrupolar doublets for 8CB-d_2. We conclude from these experiments on p-xylene-d_{10} in 8CB and in 8CB-d_2 that the alignment process after turning through 40° is changed quantitatively, but not qualitatively, by the addition of the solute. The most significant change being that it becomes more difficult to align the directors completely.

An experiment on the mixed sample of 8CB-d_2 plus p-xylene-d_{10} was also done in which the angle turned through was 88°. The experiment was performed at 296 K, and the quadrupolar splitting before and after turning were 64 636 ± 250 and 32 226 ± 250 Hz, respectively, giving $\theta_+ = 88.2° ± 0.2°$. The linewidth before and after turning were 1500 ± 250 and 800 ± 250 Hz, again demonstrating the preservation of a good monodomain on rotating the sample. Figure 12 shows the evolution of the spectra with time, and it is clear from a comparison with Fig. 4 that adding the solute does not change the general nature of the alignment process after the sample has been turned through 88°, but, as for the case when θ_+ was 40°, it does slow it down. This is readily seen from the intensities of the peaks from 8CB-d_2 in the pure and mixed samples, which are compared in Fig. 13 for the period up to the appearance of peaks corresponding to $\theta = 0°$.

CONCLUSIONS

Our main conclusion is that deuterium NMR spectroscopy can provide a wealth of detailed information on how Sm-A

samples are aligned by a magnetic field. The results reported here are preliminary and our aim has been to demonstrate the general features of the alignment process as revealed by deuterium NMR for just one mesogenic sample, 8CB. There are a number of different kinds of Sm-*A* phases, and it remains to be seen how general the observed phenomena are, but the results described here do suggest that the magnetic field induced alignment of the directors in a smectic-*A* sample are qualitatively different than for nematic samples. The striking features which we highlight here are the presence of a relatively long initial period when the director orientation for the bulk of the sample does not change; a middle period when director alignment proceeds relatively rapidly, but not to completion; and a final, very slow process of producing a fully aligned sample. It is also apparent that the addition of *p*-xylene as a solute has a profound influence on the final stage, and in our experiments a fully aligned sample was not obtained even after 15 h following a rotation of the director to approximately 40°.

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