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Online publication date: 06 August 2010

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Preliminary communication

The magnetohydrodynamics of a chiral nematic liquid crystal: the existence of two critical speeds revealed by deuterium NMR

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The magnetohydrodynamics of a chiral nematic liquid crystal made from a mixture of PBLG and deuteriated chloroform was investigated by deuterium NMR. The first critical speed for the sample was determined using a dynamical approach, and the existence of a second critical speed, which is not predicted by theories which take into account only the viscous and magnetic torques, is revealed.

The NMR spectroscopy of spinning nematic liquid crystalline samples has proved to be a valuable method for studying magnetohydrodynamic phenomena [1–5]. In most of these studies the sample was rotated about an axis **R** making an angle $\beta = 90°$ with the magnetic field, $\mathbf{H}_0$, of the spectrometer, and the samples had a positive anisotropy, $\Delta\chi$, in their magnetic susceptibility (see figure 1 for angle definitions). Such samples orient with their directors, **n**, uniformly along the field direction when not spinning. Rotation of the sample with fr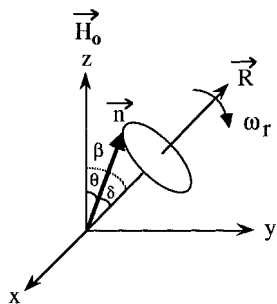equency ω_r produces a torque which tends to move the directors away from the field direction. This is opposed by the magnetic torque, and when $\omega_r < \omega_c$, the critical speed, the directors adopt a new orientation, θ, with respect to $\mathbf{H}_0$. The value of ω_c is predicted to be [6]

$$\omega_c = \left| \frac{\Delta\chi H_0^2}{2\mu_0\gamma_1} \right| \qquad (1)$$

where γ_1 is the twist viscosity coefficient and μ_0 is the magnetic constant. The angle θ is related to ω_r and ω_c by

$$\sin 2\theta = \frac{\omega_r}{\omega_c}. \qquad (2)$$

When ω_r is greater then ω_c, the director is predicted to rotate around **R** with a frequency

$$\omega = (\omega_r^2 - \omega_c^2)^{1/2}. \qquad (3)$$

In practice, equations (2) and (3) are obeyed, except that the directors begin to be distributed over a range of values of θ before ω_c is reached, and they are spread almost uniformly over the plane (*yz*) perpendicular to **R** when $\omega_r > \omega_c$ [3]. Spinning a nematic sample with a positive $\Delta\chi$ at angles other than 90° produces uniform alignment of the directors along **R** when ω_r exceeds a threshold frequency ω_{th} and β is $< 54.7°$, and above this angle the directors are distributed in the plane perpendicular to **R**; the threshold frequency depends on both ω_c and β. A similar behaviour is observed for

Figure 1. Definition of the angles: β, θ, δ are the angles between $\mathbf{H}_0$ and **R**, $\mathbf{H}_0$ and **n**, **n** and **R**, respectively.

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samples with a negative $\Delta\chi$, but now the directors align along **R** for $\beta > 54.7°$, and perpendicular to **R** for $\beta < 54.7°$ [7, 8].

NMR spectroscopy has a unique role in revealing the director distributions produced by spinning samples in a magnetic field. The field is already present in these experiments, and is of sufficient strength to produce alignment of the directors of a nematic sample. We will describe here deuterium NMR experiments on a spinning nematic sample which reveal the existence of a second critical speed, ω_2, which is not predicted by theories which take into account only the viscous and magnetic torques.

The sample studied was a solution of poly-γ-benzyl-L-glutamate (PBLG) dissolved in deuteriated chloroform. The sample was prepared from 400 mg of $CDCl_3$ and 70 mg of PBLG (DP = 1078, MW 236 000 g mol^{-1}) purchased from Sigma Chemical Co. The sample studied therefore contained 15% of PBLG w/w. To ensure a good homogeneity the sample was centrifuged back and forth until an optically homogeneous birefringent phase was obtained. The deuterium spectra were recorded on a Bruker MSL 200 spectrometer.

The PBLG molecule is chiral, and in an unconstrained sample the PBLG forms a chiral nematic phase, N*. However, $\Delta\chi$ is positive for PBLG, and in the applied magnetic field ($H_0 = 4.67$ T) the helical director structure unwinds and the N* phase converts to a normal nematic phase, N. This process has been studied previously [9, 10] for a PBLG/CH_2Cl_2 solution, and the present sample behaves in a similar way. After residing in the magnetic field for a period of about 20 min the initially unordered sample becomes uniformly ordered with the directors, **n**, parallel to H_0; the deuterium spectrum from the $CDCl_3$ is a doublet, separation $\Delta\nu$, as shown in figure 2 (*a*).

Figures 2 (*b*) and (*c*) show the effect on the deuterium spectrum of rotating the sample about an axis at $\beta = 90°$ to H_0 with a stepper motor at speeds of (*b*) 0.175 Hz (*c*) 5 Hz. In each case the spectra are consistent with the director adopting an approximately random distribution in the plane perpendicular to **R**, which is in accord with previous experiments of this nature on both low molar mass [1, 11] and polymeric nematic samples [3] when $\omega_r > \omega_c$.

When the sample rotates at ω_c, the theory predicts that the director is tilted by a 45° angle leading to a quadrupolar doublet reduced by a factor 4 compared with the static sample. Experimentally, this situation was never reached since a powder pattern is observed at a speed of 0.175 Hz, this corresponding to the lowest possible speed with our stepper motor. Consequently, the first critical speed for the sample was determined by tilting the sample quickly using the stepper motor
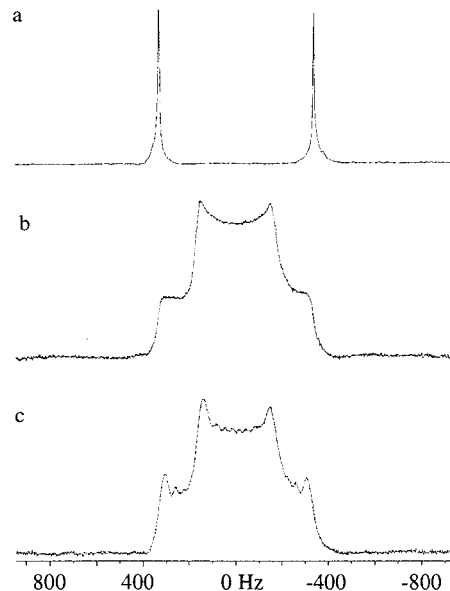

Figure 2. 30.7 MHz ^{2}H spectra of a sample of PBLG dissolved in $CDCl_3$. (*a*) Static sample, and spinning about an axis perpendicular to the magnetic field at (*b*) 0.175 Hz and (*c*) 5 Hz.

controlled by the pulse programmer of the spectrometer [12]. The tilt angle used was 45°. The deuterium spectra as a function of time are shown in figure 3. The quadrupolar splitting depends on time through

$$\Delta\nu_Q(t) = \left[\frac{3\cos^2\theta(t) - 1}{2}\right]\Delta\nu_Q(0) \qquad (4)$$
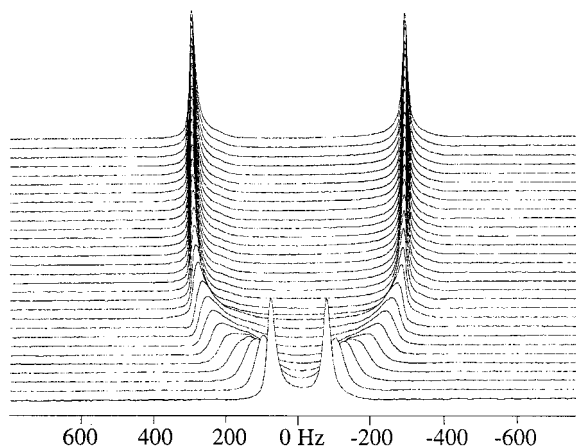
Figure 3. 30.7 MHz ^{2}H spectra of a sample of PBLG dissolved in $CDCl_3$. The sample was turned through 45° and then allowed to relax back to having the directors uniformly oriented along the field. The spectra were recorded at intervals of 30 s, and each spectrum was the result of averaging four free induction decays recorded in 2 k of data points and a spectral width of 2000 Hz. The total time to record each spectrum was 4 s.

where $\Delta v(0)$ is the splitting for the static sample. If the sample can be regarded as being subject only to the viscous and magnetic torques, then $\theta(t)$ obeys the equation

$$\tan[\theta(t)] = \tan[\theta(t=0)] \exp\left[-\frac{t}{\tau}\right] \qquad (5)$$

with

$$\tau = \frac{1}{2\omega_c}. \qquad (6)$$

This gave $\omega_c = 2.4 \pm 0.2 \times 10^{-3}$ rad s^{-1}, or $3.8 \pm 0.4 \times 10^{-4}$ Hz. In a low molar mass nematic sample, ω_c for $H_0 = 4.7$ T varies typically between 3 and 10 Hz [12]. The very small value measured here shows the large viscosity of the medium.

Figure 4 shows the deuterium spectra produced by spinning the sample by an air turbine using a Bruker VASS probe at $\omega_r = 200$ Hz over a range of angles β between **R** and **H**$_0$. When $\beta = 43.3°$ the quadrupolar splitting has reduced in value by a factor of 0.29, which confirms that the directors are at an angle of $\delta = 0°$ with **R**. This is consistent with the theoretical predictions made by Courtieu *et al.* [7], which are based on the theory of Hornreich [13], which takes into account only the viscous and magnetic torques. Note that there are weak spinning sidebands at $\pm \omega_r$, which reveals that the alignment of the directors along **R** is not perfect, but that they are distributed in a cone. Changing β produces a progressive reduction in Δv by the factor $(3\cos^2 \beta - 1)/2$ as the magic angle is approached, and a growth in the intensity of the sidebands. At the magic angle the sidebands are consistent with the directors being randomly distributed in space, and this is in agreement with the theory of Courtieu *et al.* [7].
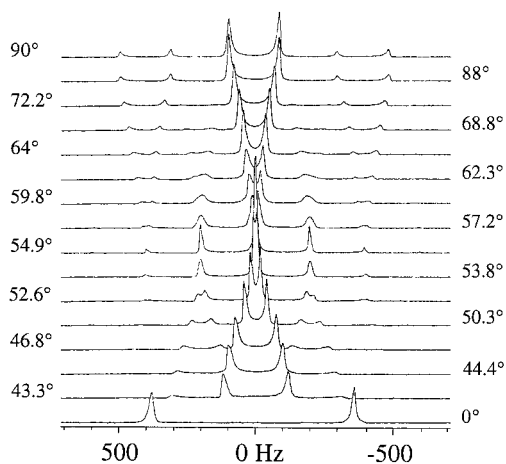
Figure 5 shows the effect of increasing the spinning rate at a constant value of $\beta = 43.3°$. Increasing ω_r at first increases the uniformity of the alignment of the directors along **R**. Thus, the sideband intensities decrease, which is in qualitative agreement with the predictions made by Courtieu *et al.* [7]. They predicted, however, that the uniformity of alignment should be virtually complete when $(\omega_r/\omega_c) > 10$, whereas in the present case the alignment is not complete even when (ω_r/ω_c) is $> 10^5$. A much more dramatic deviation from predicted behaviour occurs when ω_r exceeds 300 Hz, as shown in figure 5. The sharp doublet spectrum changes into a broad distribution corresponding to the directors being distributed with δ ranging from 0° to 90°. The 90° orientation manifests itself as the inner peaks, which increase in magnitude until at $\omega_r = 860$ Hz, the fastest speed achieved with this sample, the distribution of orientations is close to being random. Note that spinning sidebands at $\pm \omega_r$ are present, showing that the directors are still rotating with the spinning rate of the container. The same change in director orientation occurs for all the values of β accessible with the VASS probe, i.e. 43.3° to 90°.

Figure 4.   30.7 MHz ^{2}H spectra of a sample of PBLG dissolved in CDCl$_3$ spinning at 200 Hz about an axis β, whose value is given against each spectrum, with the magnetic field.
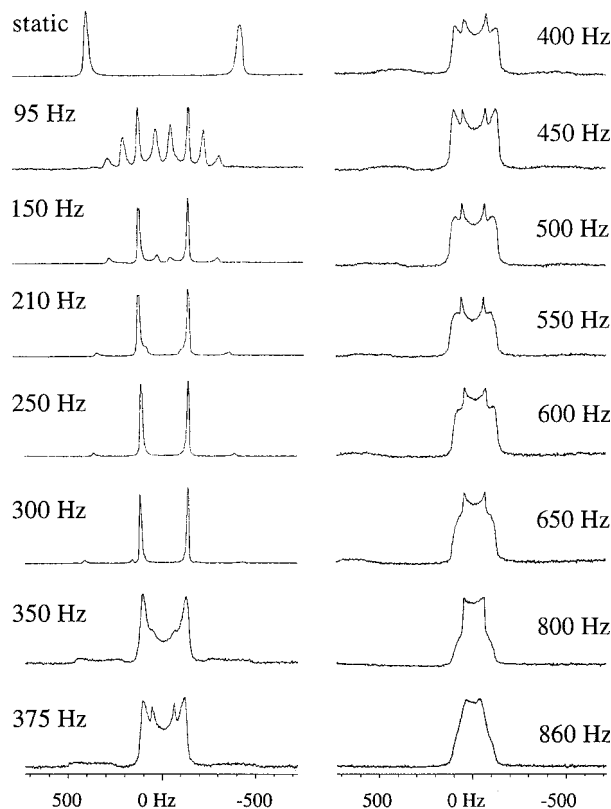

Figure 5.   30.7 MHz ^{2}H spectra of a sample of PBLG dissolved in CDCl$_3$ spinning about an axis inclined at an angle $\beta = 43.4°$ with the magnetic field. Each spectrum was recorded with a different spinning speed, which is given alongside each trace.

Figure 6 shows spectra taken with $\beta = 90°$, and now the change is from the directors being essentially completely aligned in the plane perpendicular to **R** when ω_r is < 350 Hz ($\delta = 90°$ in agreement with the predictions of Courtieu *et al.* [7]) to there being an increasing amount of the orientations down to and including $\delta = 0°$. Thus the spectra broaden and increase in width, the outer wings corresponding to the directors being aligned along **R**. The upper threshold frequency is independent of β, unlike the lower threshold frequency predicted by Courtieu *et al.* [7]. It is a second, upper critical speed, ω_2.

There have been earlier observations by NMR of changes in director orientation on spinning nematic samples above ω_{th}, which are similar, but not identical, to the behaviour described here. Thus, Bayle *et al.* [14]
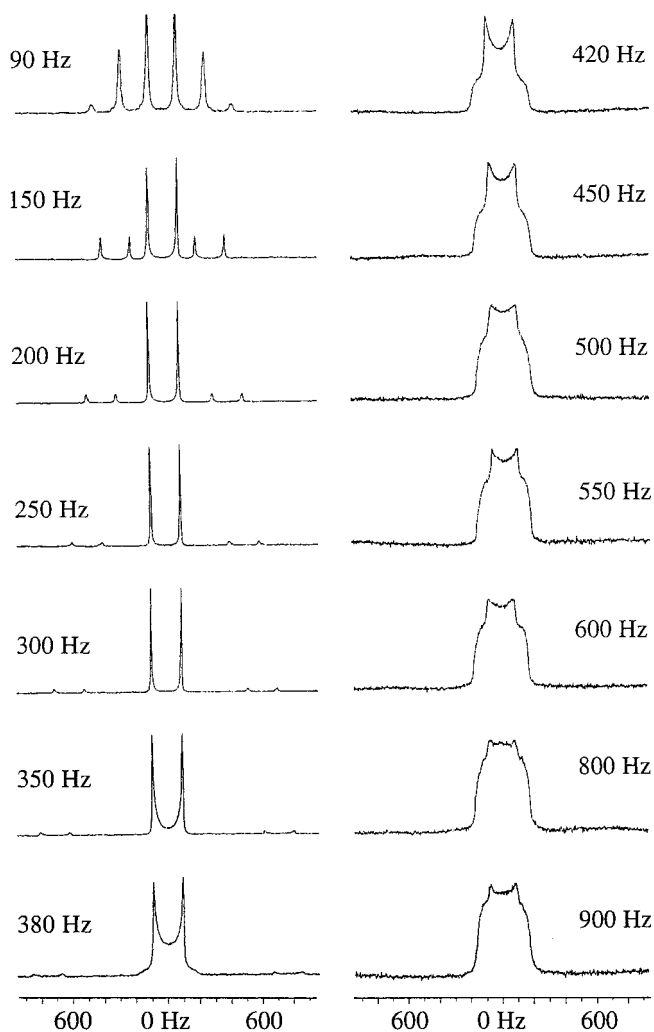
observed the ^{19}F spectrum of CF_2ClCCl_3 dissolved in a mixture of thermotropic liquid crystals which had $\Delta\chi$ negative and close to zero. They observed that at spinning speeds < 60 Hz the sample behaved as expected with directors uniformly aligned along **R** when $\beta > 54.7°$, and perpendicular to **R** when $\beta < 54.7°$. Above 60 Hz the spectra were consistent with the directors being uniformly aligned in the plane perpendicular to **R** for all values of β. Bayle *et al.* [15] observed the same switch in director orientation for the same compound dissolved in a lyotropic system having $\Delta\chi$ negative. Arun-Kumar *et al.* [16] observed the deuterium NMR of $CDCl_3$ dissolved in a mixture of thermotropic liquid crystals which had $\Delta\chi$ positive and close to zero. They found a normal alignment of the directors for a spinning speed of 470 Hz and $\beta = 53°$, that is **n** along **R**. When ω_r was raised to 1200 Hz the directors switched to being perpendicular to **R**. These observations of a change in director orientation with increased spinning speed differ from that found for the PBLG/CDCl$_3$ system in that the change appears to be between uniform alignments of the directors, whereas for PBLG/CDCl$_3$ a distribution of director orientations is produced.

The PBLG molecules are chiral, and in an unconstrained sample (i.e. zero magnetic field, and no rotation) the directors adopt a supramolecular helix. In a magnetic field, this helix is unwound and the sample is a normal nematic phase. It is possible that the second critical speed observed here marks the re-establishment of a supramolecular helix, which would lead to a distribution of directions as observed. However in this case the critical speed might be expected to depend on the angle β, which is not observed experimentally. We conclude that it is not certain at this point in time that the existence of the second critical speed is a general phenomenon for all nematic samples or whether it exists only for those which are formed from chiral molecules. Experiments are in progress to clarify this point.

Figure 6.   30.7 MHz ^{2}H spectra of a sample of PBLG dissolved in CDCl$_3$ spinning about an axis inclined at an angle $\beta = 90°$ with the magnetic field. Each spectrum was recorded with a different spinning speed, which is given alongside each trace.

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