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PRELIMINARY COMMUNICATION

Ultra-slow director rotation in nematic side-group polymers detected by N.M.R.

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A novel N.M.R. method is described in which very high values of the rotational viscosity in nematic liquid crystals are measured with an improved accuracy of several orders of magnitude as compared to conventional N.M.R. methods. It consists of monitoring the deuteron line splitting while rotating the sample in a magnetic field. The rotation speed of the sample container is chosen such that the director orientation follows the container orientation, albeit with a certain phase lag. By synchronizing the data acquisition with the container orientation the phase lag is monitored for several hours. A simple relation, derived from the Ericksen–Leslie–Parodi equations, holds between the rotational viscosity and the phase lag. *Frequencies* as low as 10^{-6} Hz can be measured precisely.

When a magnetic field is applied to a nematic mesophase the director tends to align parallel to it provided the magnetic anisotropy is positive. In order to measure the visco-elastic properties the nematic sample is placed in a cylindrical container which is rotated about an axis perpendicular to the field. Two N.M.R. methods of this kind can be distinguished. The first is the application of a sudden finite rotation angle to the container. The response of the sample is recorded by monitoring the N.M.R. spectrum from which a number of viscosity coefficients and the ratio k_{33}/k_{11} of the bend to splay Frank elastic constants can be evaluated [1]. The second method consists of continuously rotating the container while at the same time monitoring the N.M.R. or E.S.R. spectrum [2–4]. To date, this method has been employed without synchronization of the data acquisition with the container orientation. Furthermore, in analysing the experimental results in terms of the continuum theory [5], it was inherently assumed that the elastic constants were negligible. Although the value of the line splitting still probes the average distribution of the director and thus contains information on the rotational viscosity γ_1, the fact that after a period of time the initially uniformly aligned director has changed to a non-uniform distribution, implies that the elastic constants may play a role in this type of experiment.

Here we describe an N.M.R. experiment in which a nematic side-group polymer is subject to continuous sample rotation. The measurements were carried out in a Bruker CXP-300 spectrometer. The crucial difference with the previous experiment is that we have synchronized the data acquisition with the sample rotation which enables us to monitor the phase difference between the average director orientation and the container orientation. The material studied is a polysiloxane with phenylbenzoate as

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the mesogenic unit and with a spacer of six methylene groups, deuteriated at the phenylbenzoate side group. The same system has been studied by Casagrande *et al.* [6] and by Bock *et al.* [7]. It appeared that, whereas the elastic constants k_{11} and k_{33} were of the same magnitude as in the conventional low molecular weight liquid crystals, γ_1 was found to be several orders of magnitude larger. These very high values of γ_1 are thought to be associated with the main-chain reorientation [8].

We use the Ericksen–Leslie–Parodi theory [5, 9, 10] to describe the equation of motion of a non-uniform director distribution $\mathbf{n}(\mathbf{r}, t)$ of a sample subjected to a velocity field $v_x = 0, v_y = z\omega_r, v_z = -y\omega_r$, in which ω_r is the angular velocity of the container. Thus

$$\begin{aligned}
&-\gamma_1(\partial\theta/\partial t - \omega_r) - \partial^2\theta/\partial y^2(k_{11}\cos^2\theta + k_{33}\sin^2\theta)\\
&\quad -\partial^2\theta/\partial z^2(k_{11}\sin^2\theta + k_{33}\cos^2\theta)\\
&\quad +(k_{11} - k_{33})[\{\partial^2\theta/\partial y\partial z + \tfrac{1}{2}(\partial\theta/\partial y)^2 - \tfrac{1}{2}(\partial\theta/\partial z)^2\}\sin 2\theta\\
&\quad -(\partial\theta/\partial y)(\partial\theta/\partial z)\cos 2\theta] + \tfrac{1}{2}B^2\chi_a\sin 2\theta = 0,
\end{aligned} \tag{1}$$

where the angle $\theta(y, z, t)$ specifies the instantaneous local director orientation relative to the magnetic field $\mathbf{B}(0, 0, B)$, i.e. $n_x = 0, n_y = \sin\theta(y, z, t), n_z = \cos\theta(y, z, t)$, χ_a is the anisotropy of the magnetic susceptibility. As is usually done we have neglected the molecular inertia of the system. From equation (1) it can be inferred that a steady state solution of the director distribution may be obtained in terms of γ_1 and the splay and bend elastic constants k_{11} and k_{33}. Indeed, such a non-uniform distribution has been observed experimentally in conventional low molecular weight nematic liquid crystals [3], where after some period of time the initial time dependence in the E.S.R. spectrum gradually disappears, while at the same time the lines broaden. In the experiment on the polymeric sample described here a final steady state was reached in almost all cases of interest, the exceptions being at low temperatures and low rotation speeds. The time needed to reach the steady state ranged typically from a few seconds at the highest temperatures to approximately 48 hours at lower temperatures. However, an analysis of the N.M.R. spectra in terms of the elastic constants is beyond the scope of this preliminary communication and will be presented in a forthcoming publication. Here we reflect on the time dependence of the N.M.R. spectra and more specifically on the time dependence of the deuteron line splitting.

Groups of n spectra, taken 10 min apart, were recorded at angles $\psi = n\pi/4$, $n = 0, 1, \ldots, 7$, in which ψ is the angle the cylinder has rotated from its initial position, modulo 2π. Figure 1 shows a selection of rotation synchronized deuteron spectra taken at $T = 325\,\mathrm{K}$ and $\omega_r/2\pi = 3{\cdot}33 \times 10^{-3}\,\mathrm{Hz}$. For an infinitely high rotational viscosity the dependence of the spectra on the angle ψ should be independent of time. Instead, a phase lag is observed, i.e. the average director orientation lags behind the container orientation. Figure 2 represents the phase shift at the same temperature as a function of time for two different rotation speeds. When we confine ourselves to the time dependence of the deuteron line shape splitting in the initial stage of the experiment, i.e. when the lines are still relatively narrow, figures 1 and 2 may be analysed using equation (1) but neglecting k_{11} and k_{33}, i.e.

$$-\gamma_1(d\theta/dt - \omega_r) + \tfrac{1}{2}B^2\chi_a\sin 2\theta = 0. \tag{2}$$

Below the critical angular velocity ω_c, equation (2) has the familiar steady state solution $\sin 2\theta_\infty = \omega_r/\omega_c$, where $\omega_c = -\chi_a B^2/2\gamma_1$. In this case, the director makes a

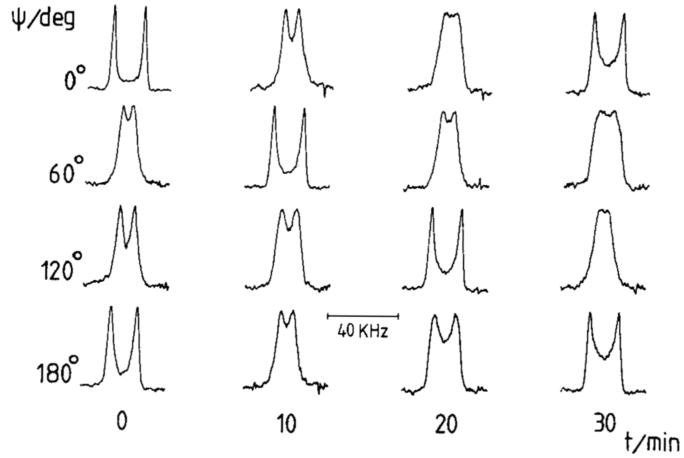

Figure 1. Deuteron N.M.R. spectra recorded at 10 min intervals for half a revolution of the sample container each at values of $\psi = 0°, 60°, 120°$, and $180°$.

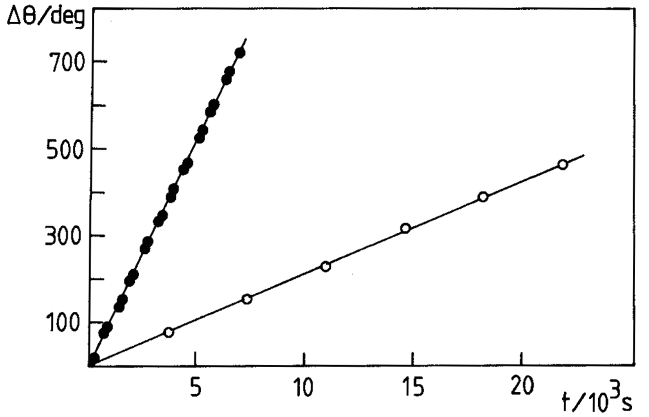

Figure 2. The phase shift $\Delta\theta(t) = \psi(t) - \theta(t)$ between container orientation $\psi(t)$ and director orientation $\theta(t)$ as a function of time at $\omega_r/2\pi = 3{\cdot}33 \times 10^{-3}$ Hz and $16{\cdot}67 \times 10^{-3}$ Hz, represented by the filled and open circles, respectively.

constant angle θ ($\theta < \pi/4$) with the magnetic field. From this steady state the rotational viscosity can be determined, as is shown in, for example, the torsion experiments of Bock *et al.* [7, 11]. They determined γ_1 as a function of temperature in the same polymer system as was used in our investigation (cf. figure 3). In the experiment described here, ω_r was always greater than ω_c in which case a solution of equation (2) is

$$\tan\theta(t) = \frac{\omega_d}{\omega_r}\tan\{\omega_d(t - t_0)\} - \frac{\omega_c}{\omega_r}, \tag{3}$$

where t_0 is an arbitrary constant. The angular velocity ω_d of the director is given by

$$\omega_d = (\omega_r^2 - \omega_c^2)^{1/2}, \tag{4}$$

therefore

$$\gamma_1 = -\frac{\chi_a B^2}{2(\omega_r^2 - \omega_d^2)^{1/2}}. \tag{5}$$

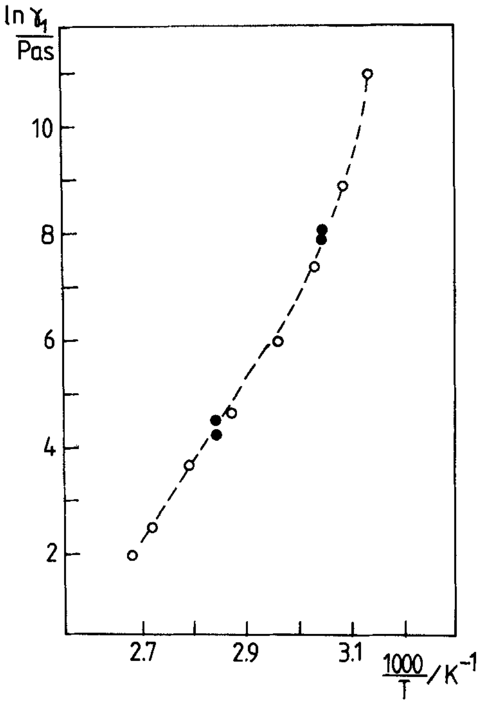

Figure 3. The rotational viscosity γ_1 obtained in this experiment (filled symbols) and the values reported in [7] (open symbols).

By observing the phase lag $\Delta\theta(t) = \psi(t) - \theta(t)$ between the container and director orientation, ω_d is derived from

$$\omega_d = \omega_r - \Delta\theta/t. \tag{6}$$

The experimental results in figure 2 do indeed obey these simple relations. In order to obtain γ_1 according to equations (4) and (5) the anisotropy of the magnetic susceptibility, χ_a, has to be known. It refers to the director and is related to the anisotropy of the magnetic susceptibility of the mesogen, χ_{am}, according to

$$\chi_a = \langle P_2 \rangle \chi_{am}, \tag{7}$$

where $\langle P_2 \rangle$ is the second rank orientational order parameter. The values for γ_1 given in the table were derived using a calculated value [12, 13] of 1·23 × 10^{-9} m^3/kg for χ_{am} and an order parameter $\langle P_2 \rangle = 0{\cdot}8$, determined from the quadrupole splitting. The uncertainties of the calculated value of χ_{am} are estimated [12, 13] to be ± 10 per cent and do not affect the conclusions drawn in this paper. The values for γ_1 are in excellent agreement with the values reported in [6] and [7] (see figure 3). Furthermore, since γ_1 in nematic side-group polymers is several orders of magnitude larger than in low

The experimental values for the rotational viscosity γ_1 at $T = 325$ K for two different rotation velocities ω_r of the container, obtained using equation (5).

$(\omega_r/2\pi)$/Hz	3·33 × 10^{-3}	16·67 × 10^{-3}
$(\omega_d/2\pi)$/Hz	3·04 × 10^{-3}	16·61 × 10^{-3}
$(\omega_c/2\pi)$/Hz	1·87 × 10^{-6}	1·66 × 10^{-6}
γ_1/Pa s	2828	2762

molecular weight liquid crystals, the angular velocity, ω_c, can be determined down to extremely low values. The magnetic resonance technique can be used to measure time constants such as the spin–lattice relaxation time T_1 which can be as long as several weeks. However, in contrast, the lowest rates accessible to date by the spin–alignment technique [14] are of the order of 10^{-2} Hz. The introduction of rotation synchronization enables us to extend this range and to probe *frequencies* ($\omega_c/2\pi$) of the order of 10^{-6} Hz, which is the domain of, for example, mechanical response experiments.

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References

[1] MARTINS, A. F., ESNAULT, P., and VOLINO, F., 1986, *Phys. Rev. Lett.*, **57**, 1745.
[2] LESLIE, F. M., LUCKHURST, G. R., and SMITH, H. J., 1972, *Chem. Phys. Lett.*, **13**, 368.
[3] CARR, S. G., LUCKHURST, G. R., POUPKO, R., and SMITH, H. J., 1975, *Chem. Phys.*, **7**, 278.
[4] EMSLEY, J. W., KHOO, S. K., LINDON, J. C., and LUCKHURST, G. R., 1981, *Chem. Phys. Lett.*, **77**, 609.
[5] LESLIE, F. M., 1968, *Archs ration. Mech. Analysis*, **228**, 265.
[6] CASAGRANDE, C., VEYSSIE, M., WEILL, C., and FINKELMANN, H., 1983, *Molec. Crystals liq. Crystals*, **92**, 49.
[7] BOCK, F.-J., KNEPPE, H., and SCHNEIDER, F., 1989 (to be published).
[8] FABRE, P., CASAGRANDE, C., VEYSSIE, M., and FINKELMANN, H., 1984, *Phys. Rev. Lett.*, **53**, 993.
[9] ERICKSEN, J. L., 1966, *Physics Fluids*, **9**, 1205.
[10] PARODI, O., 1970, *J. Phys., Paris*, **31**, 581.
[11] BOCK, F.-J., KNEPPE, H., and SCHNEIDER, F., 1988, *Liq. Crystals*, **3**, 217.
[12] FLYGARE, W. H., and BENSON, R. C., 1971, *Molec. Phys.*, **20**, 225.
[13] FLYGARE, W. H., 1974, *Chem. Rev.*, **74**, 653.
[14] SPIESS, H. W., 1980, *J. chem. Phys.*, **72**, 6755.
[15] BÖFFEL, C., 1986, Ph.D. thesis, University of Mainz.