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## Liquid Crystals

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## NMR study of the long time, defect-controlled, magnetic reorientation of a nematic polymer liquid crystal

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The magnetic field reorientation of an initially aligned sample of a nematic polymer liquid crystal was followed by proton NMR. Evolution to a metastable (banded) state was considered using a Rheo-NMR technique developed previously. Late stage reorientation was studied by taking into account the dynamics of defects following the formation of splay-bend walls. NMR spectra simulation allowed us to obtain the wall density as a function of time. This result, together with a defect-controlled wall dissolution model proposed by Rey [1], was used to complement the Rheo-NMR technique of measuring the viscoelastic parameters of nematic polymer liquid crystals.

### 1. Introduction

In recent years a novel NMR technique for the measurement of four independent Leslie viscosity coefficients and two Frank elastic constants has been developed [2] and applied to thermotropic main chain [2, 3] and lyotropic [4] nematic polymer liquid crystals (PLC). The principle of this technique is based on the line shape analysis, as a function of time, of the proton NMR spectra following the magnetic reorientation of a previously aligned nematic sample, as described by appropriate hydrodynamic equations. In the above materials, following the rotation of the NMR sample by an angle  $\simeq 90^\circ$  with respect to the strong [5] magnetic field  $\mathbf{H}$  of the spectrometer, the reorientation of the nematic director occurs via a periodic transient pattern driven by a pure bend distortion (optical observations show stripes perpendicular to  $\mathbf{n}_0$ ). The corresponding Leslie equation for the director, neglecting the inertial term, is the following:

$$\gamma_{\text{eff}}(\theta) \frac{\partial \theta}{\partial t} - \frac{1}{2} \chi_a H^2 \sin 2\theta - K(\theta) = 0, \quad (1)$$

where  $\theta(z, t)$  is the reorientation angle of the local directors  $\mathbf{n}(\mathbf{r}, t)$  within the sample, defined in the plane  $(\mathbf{n}_0, \mathbf{H})$ . In equation (1)  $\chi_a$  is the anisotropy of the magnetic susceptibility, the effective viscosity  $\gamma_{\text{eff}}(\theta)$  is a function of  $\gamma_1, \eta_{\text{bend}}, \alpha_1$  and  $\alpha_2$ , and  $K(\theta)$  is

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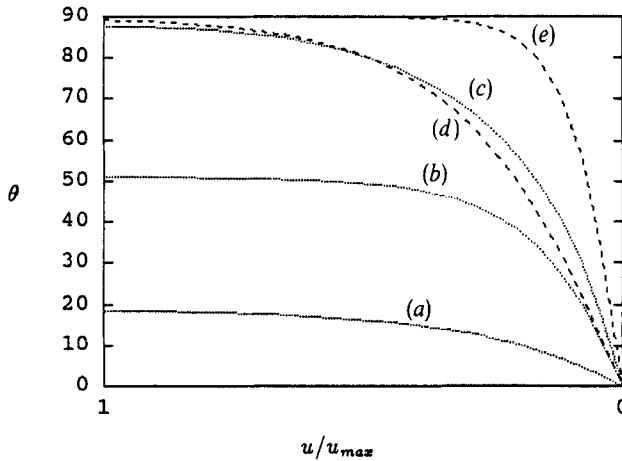


Figure 1. Director distribution  $\theta(u)$  for one quarter of the wavelength of the distortion, calculated for the parameters of AZA9, the PLC of [3]. Curves *a*, *b*, and *c*: solution of equation (1) with  $t = 30$  s (*a*),  $t = 100$  s (*b*) and  $t = 1800$  s (*c*). Curves *d* and *e*: splay–bend wall given by equation (3) with  $u_{\max} = 5$  (*d*) and  $u_{\max} = 15$  (*e*). This figure depicts the time evolution of the distortion of the director field: equation (1) governs the fast reorientation regime leading to a system of splay–bend walls (banded structure, curve *c*). Wall annihilation governs the slow regime (curves *d* and *e*), driving the system from the banded structure to equilibrium (square distribution).

a function of the Frank elastic constants  $K_1$  and  $K_3$ . Equation (1) includes the effect of backflow through the substitution of  $\gamma_1$  by  $\gamma_{\text{eff}}(\theta)$  in the first term and the effect of director field distortions (for example, banded structure) through the form of  $K(\theta)$ , as shown in [2].

In figure 1 (curve *c*) we show the numerical solution of equation (1) for very long times with the parameters of the PLC studied in [3]. In the limit  $t \rightarrow \infty$  this equation does not lead to a uniform director pattern ( $\theta(z, t = \infty) \simeq 90^\circ$ ) but, instead, to a pattern of splay–bend inversion walls corresponding to a banded texture with a wavelength  $\lambda = 4\xi f(\theta_{\max})$ , where  $f(\theta_{\max})$  is a function of the maximum distortion angle  $\theta_{\max}$  and  $\xi^2 = \bar{K}/\chi_a H^2$  is the magnetic coherence length, with  $\bar{K} = (K_1 + K_2)/2$  an average elastic constant. From this result we can see that the bigger (smaller) the ratio of the elastic to the magnetic energy the bigger (smaller) the magnetic coherence length and hence the wavelength of the final pattern. When the twist elastic constant  $K_2$  is sufficiently smaller than  $\bar{K}$  [1], which is true for most nematic PLCs, this pattern is unstable for out of plane perturbations. A mechanism for the disappearance of inversion walls has been recently proposed by Rey [1], where the collapse of inversion wall segments occurs via the production and displacement of disclination line pairs. It is the purpose of this work to study by NMR the evolution of our system from the metastable state (banded texture) to the true equilibrium state (homogeneous texture). We will first show that the wall disappearance process is observable by NMR. Then we will present our experimental results. After data analysis following the method described in [3], we will discuss these results in terms of the defect-controlled wall dissolution model proposed by Rey.

**2. Wall dissolution as an NMR observable**

The proton NMR line shape of a nematic sample is strongly affected by the director spatial pattern [3]. For a given director distribution  $\theta(z, t)$  we can get the corresponding spectrum  $f(v, t)$  from the spectrum of the aligned nematic monodomain  $f_0(v)$  using

$$f(v, t) = \frac{1}{u_{\max}(t)} \int_0^{u_{\max}(t)} \frac{1}{P_2(\cos \alpha)} f_0\left(\frac{v}{P_2(\cos \alpha)}\right) du, \tag{2}$$

where  $P_2(\cos \alpha)$  is the second Legendre polynomial and  $\alpha = \pi/2 - \theta(u)$  [3]. Here  $u$  is a reduced distance (for example,  $u = qz$  for a sinusoidal distortion) and  $\theta$  is the angle between the local director  $\mathbf{n}(\mathbf{r})$  and the initial orientation. Note that in expression (2) the connection between  $\mathbf{n}_0$  and the molecular geometry is already included in  $f_0(v)$ , which is the experimental NMR spectrum recorded at equilibrium (which we use in digitalized form for the calculation of  $f(v, t)$  in equation (2)). The scaling of  $f_0(v)$  by  $P_2(\cos \alpha)$  assumes that the spectrum is dominated by dipolar interactions. For one splay-bend inversion wall we can write

$$\theta(u) = 2 \arctan(e^u) - \frac{\pi}{2}, \tag{3}$$

where  $u = z/\xi$  and  $\xi$  is the magnetic coherence length [6]. For the banded structure the distance between adjacent walls is given by  $\lambda/2 \simeq 2\xi u_{\max}(t)$  where  $u_{\max}(t)$  is the value of  $u$  for  $z = \lambda/4$ . The density of inversion walls in the sample is related to the upper limit in expression (2): an increase in  $u_{\max}$  corresponds to a decrease in the wall density, and we define the volume fraction of walls  $X_w = 1/u_{\max}$ . The parameter  $u_{\max}$  can be obtained by spectra simulation: it is the upper limit in equation (2) that gives the best fit (line shape simulation). Defining the fit quality function by

$$Q_F = 1 - 2 \frac{\int |f_{\text{exp}} - f_{\text{sim}}| dv}{\int f_0 dv} \tag{4}$$

then  $u_{\max}$  corresponds to the maximum of  $Q_F$ .

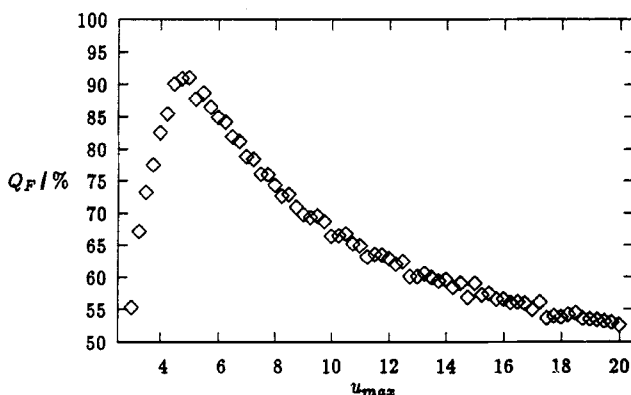


Figure 2. The quality function  $Q_F$  (from equation (4)) versus  $u_{\max}$  for the spectrum of AZA9 taken at  $t = 1150$  s. The best fit corresponds to the curve maximum ( $Q_F = 91\%$ ) and gives  $u_{\max} = 5$ .

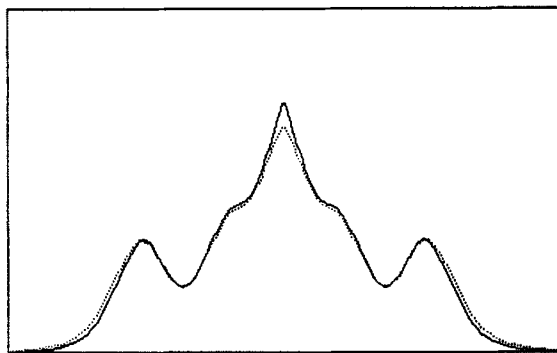


Figure 3. Experimental (—) and simulated (·····) spectra of AZA9 at  $t = 1150$  s, for  $u_{\max} = 5$  (from figure 2).

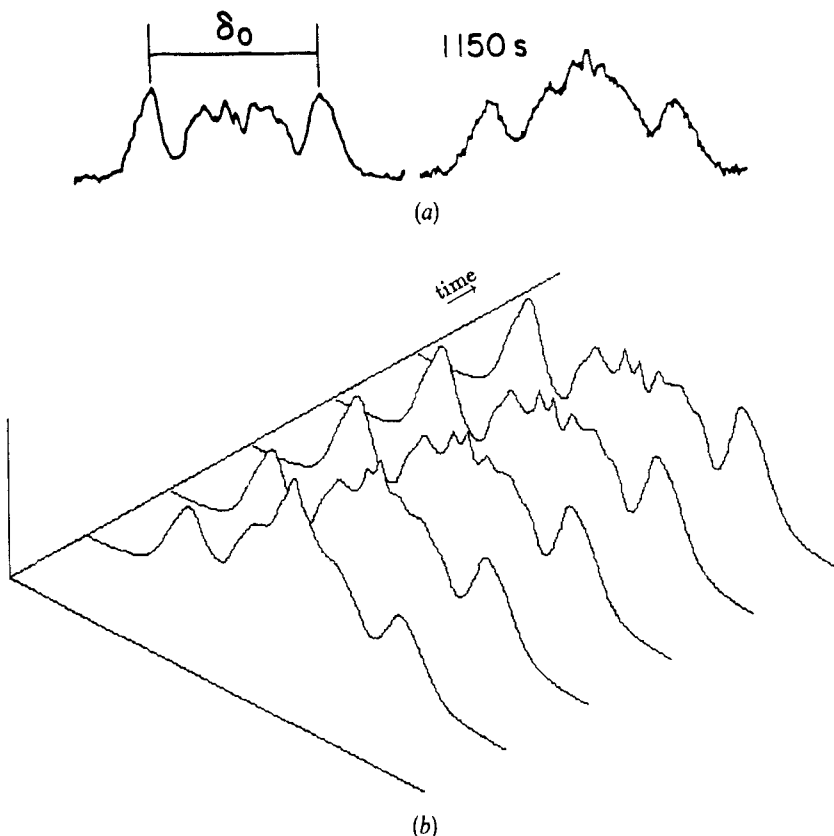


Figure 4. (a) Experimental spectra of AZA9 in equilibrium and 1150 s after the initial sample rotation by  $\alpha = 90^\circ$ . (b) Simulation of the time evolution of the NMR spectrum from the banded texture to the homogeneous texture, assuming an exponential law for the kinetics of wall dissolution.

Now we turn to the main chain nematic thermotropic polymer studied in [3], a polyester labelled AZA9, and consider the last experimental NMR spectrum well-simulated with the hydrodynamic model in equation (1), corresponding to  $t = 1150$  s after rotating the sample. Figure 2 shows  $Q_F$  versus  $u_{\max}$  for this spectrum, and figure 3 shows the line shape simulation for  $u_{\max} = 5$  corresponding to the maximum of  $Q_F$ . Figure 4 pictures the simulation of the time evolution of the spectra from the banded texture to the homogeneous texture, assuming an exponential law for inversion wall dissolution. This shows that the process of inversion wall destruction is observable by NMR. It is also seen that the wall dissolution mechanism does not alter significantly the main doublet splitting  $\delta(t)$ , but has a drastic effect on the line shape in the central region of the proton spectra.  $\delta(t)$  is mainly determined by the hydrodynamic regime, while the time evolution of the line shape is dominated at earlier times by the hydrodynamic regime and at late times by the wall dissolution mechanism.

### 3. Experimental

The material considered in this work is a main chain thermotropic polymer: poly(4,4'-dioxy-2,2'-dimethyl azoxybenzenedodecanediyl), a linear polyester usually labelled DDA9, showing a nematic phase between 97 and 136°C ( $M_n \approx 4300$ ). The proton NMR spectra were taken at 60 MHz ( $H \approx 14$  kG) and the sample temperature was kept at 101°C. We followed the experimental procedure described in [2, 3]. The equilibrium spectrum (see figure 5(a)) shows a central line with some structure and a symmetric doublet. The strong central peak is due to the contribution of isotropic droplets remaining in the nematic phase due to polymer dispersion and partial degradation (the actual system is a biphasic N + I). The separation  $\delta_0$  of the main doublet lines in the spectrum is proportional to the molecular degree of order of the (macroscopically) aligned phase. Details on the other features of the spectrum may be seen in [7].

The experiment comprises two phases:

- (i) Magnetic reorientation after initial sample rotation by  $\alpha \approx 20^\circ$ : the reorientation process in this case ( $\alpha < \pi/4$ ) preserves the homogeneity of the director field in the sample (no backflow) and the corresponding equation of motion, a simplified form of equation (1) with  $\gamma_{\text{eff}} = \gamma_1$  and  $K(\theta) = 0$ , gives the characteristic reorientation time  $\tau_0 = \gamma_1 / \chi_a H^2$  [2, 3]. The fit of the time evolution of the main dipolar splitting  $\delta(t)$  to the simplified form of equation (1) ( $\gamma_{\text{eff}} = \gamma_1$  and  $K(\theta) = 0$ ), using  $\delta(t) = \delta_0 P_2(\cos(\alpha - \theta(t)))$ , gives  $\tau_0 \approx 150$  s. For  $\chi_a \sim 10^{-7}$  (cgs), we get  $\gamma_1 \approx 3000$  P.
- (ii) Magnetic reorientation after initial sample rotation by  $\alpha \approx 90^\circ$ : the experimental spectra following a rotation of  $\alpha \approx 90^\circ$  are shown in figure 5(b). The fit of  $\delta(t)$  to equation (1) is shown in figure 6 and the resulting set of Leslie viscosity coefficients, in poise, is  $2600 \leq \gamma_1 \leq 3250$ ,  $22 \leq \eta_{\text{bend}} \leq 25$ ,  $-4020 \leq \alpha_1 \leq -2620$ ,  $-3280 \leq \alpha_2 \leq -2780$ . Concerning the elastic parameters, the spectra simulation technique extensively discussed in [3] gives a better estimation than the fit of  $\delta(t)$  and is presented next.

### 4. Line shape analysis

Following [3], we simulated the line shape of the NMR spectra as a function of time using the solution  $\theta(z, t)$  of equation (1). As a first approximation we neglected the

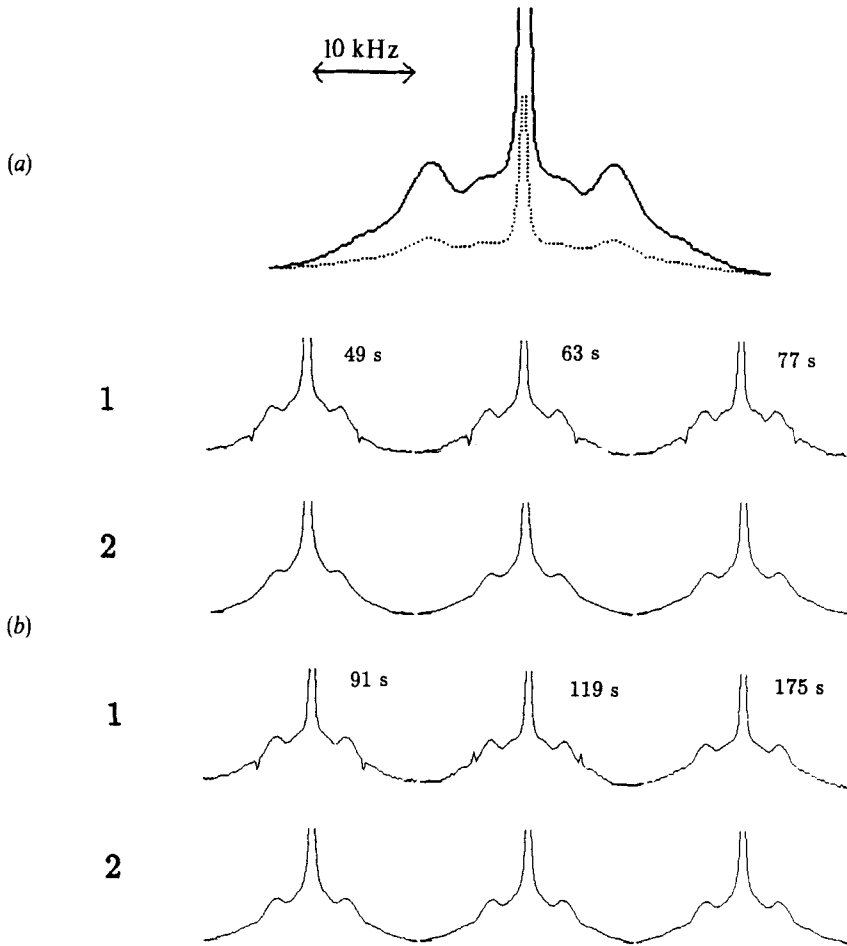


Figure 5. (a) Equilibrium NMR spectrum. The dotted curve represents the whole spectrum (see text); in the upper curve we have rescaled the spectrum and cleared most of the central peak, corresponding to the (irrelevant) isotropic part of the sample. (b) Time evolution of the NMR spectrum after the initial sample rotation by  $\alpha \approx 90^\circ$ : (1) experimental spectra; (2) simulated spectra using equation (2) with contributions from both the hydrodynamic reorientation model in equation (1) and the static inversion wall model in equation (3).

influence on the line shape of the thermal fluctuations of the director field quantified by the static order parameter  $S_{\text{stat}}$  [3, 8] which are not averaged out on the NMR time scale. From this simulation we got  $K_1 q^2 \approx 0.3 \text{ dyne cm}^{-2}$  and  $K_3/K_1 \approx 0.5$ . In this approximation we were not able to simulate the spectra around the magic angle, where the effect of  $S_{\text{stat}}$  is most important [8]. This is a source of error for the determination of some of the viscoelastic parameters, but does not affect our main conclusions. Our last step in the lineshape analysis was to consider contributions from wall disappearance to the time evolution of the line shape. These contributions show up on the central part of the spectra, as shown by simulation in figure 4 for the polymer of [3]. In the present case the analysis was made harder by the presence of the strong isotropic peak in the NMR spectra of our polymer. The results of this analysis are shown in figure 5.

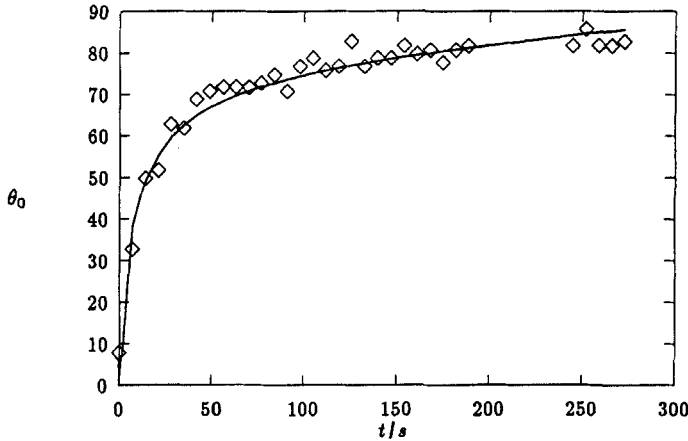


Figure 6. Fit of the time evolution of the main dipolar splitting of the NMR spectrum to equation (1). The corresponding fitting parameters are given in the text.

**5. Analysis of the NMR results in terms of a defect-controlled wall dissolution model**

Rey has proposed [1] a dynamical model of approach to equilibrium mediated by defect interaction and consequent wall dissolution. He first showed that the instability of a splay-bend wall to localized small wavelength fluctuations results in the production of a disclination line pair of strength  $\pm 1/2$  and in the collapse of a splay-bend inversion wall segment. Then he showed that a disclination line embedded in a splay-bend inversion wall is subjected to a pulling force equal to the surface tension of the inversion wall. From this he obtained the growth law governing the wall disappearance. If the initial line separation is larger than a critical length  $L_c$ , the homogeneous texture will replace the banded texture. The growth law governing the kinetics of the process is

$$\int_{L_0}^L \frac{dL}{2v(L)} = \int_0^t dt, \tag{5}$$

where  $L_0$  is the initial line separation, and

$$v(L) = \frac{2K[(1/\pi S) - (\xi/L)S]}{\gamma_1 \xi S \ln(L/r_c)} \tag{6}$$

is the velocity of the travelling disclination line embedded in a director field containing another disclination line and a splay-bend inversion wall. In equation (6),  $K$  is an average elastic constant,  $\xi$  is the magnetic coherence length,  $S$  is the strength of the disclination line pair and  $r_c$  is an integration cut-off length ( $r_c \sim 30 \text{ \AA}$ ). Putting  $v(L=L_c) = 0$  in equation (6) gives the critical length  $L_c = \pi \xi S^2$ . The growth law in equation (5) gives the time required to dissolve a length  $L$  of splay-bend inversion wall of thickness  $2\xi$  by the displacement of the disclination line pair of strength  $\pm S$ .

As seen in § 2, the quantity measured by NMR is  $u_{\max}$  and now we have to relate it to the length  $L$  in expression (5). Assuming the number of defects  $n_L$  to be constant during the process of wall dissolution, and considering a circular section of the NMR sample tube, we have for the total length of dissolved wall  $L_D(t) = n_L L(t)$ , where  $L(t)$  is the length dissolved by one defect during the time  $t$ . If  $L_F(t)$  is the total length of walls in the



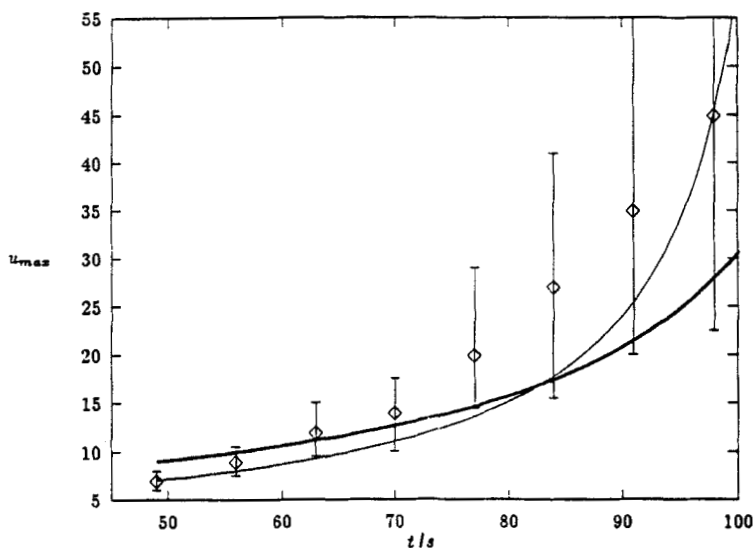


Figure 7. Fit of the wall dissolution equation (7) to  $u_{\max}$  obtained from the simulation shown in figure 5.  $\diamond$ , Experiment; —, fit 1; - - -, fit 2.

sample, then  $L_F(t) = L_1 - L_D(t)$ , where  $L_1$  is the initial length of wall (corresponding to the instant  $t = 0$  when the first defect is created). The volume fraction of walls is given by the ratio of the area covered by walls in a square section of the NMR tube over the total area of the tube section:  $1/u_{\max}(t) = 2\xi L_F(t)/\pi R^2$ , where  $R$  is the tube radius. Combining these expressions we get the following relation between  $u_{\max}$  and  $L$ :

$$\frac{1}{u_{\max}(t)} = \frac{1}{u_0} - \frac{2\xi}{\pi R^2} n_L L(t), \quad (7)$$

where  $u_0 \equiv u_{\max}(t=0) = \pi R^2 / 2\xi L_1$ . Equations (5), after inversion, and (7) allow us to obtain  $u_{\max}$  as a function of time. Figure 7 shows two typical fits of  $u_{\max}(t)$  to the experimental points obtained from the simulation of the NMR spectra. The corresponding fitting parameters are shown in the table.

The ratio  $K_2/K_3$  can be obtained from  $L_0$  in the limit of Rey's threshold instability condition (with the approximation  $\xi^2 = K_3/\chi_a H^2$ )

$$\pi^2(1 - K_2/K_3) = 1 + \frac{\pi^2}{4}(1 + 3K_2/K_3)(\xi/L_0)^2 \quad (8)$$

and is also given in the table.

	$L_c/\mu\text{m}$	$L_0/L_c$	$n_L$	$u_0$	$K_2/K_3$	$\xi/\mu\text{m}$
Fit 1	2.5	1.3	$10^6$	9	0.37	3.1
Fit 2	5.2	3.0	$10^5$	10	0.75	6.6

## 6. Discussion

Fit 1 gives an unrealistic number of defects  $n_L$  (see the table), corresponding to a separation of disclination lines smaller than  $L_c$ , and should be disregarded, while fit 2 gives a separation of the order of  $L_c$ . We will therefore consider only the second set of parameters in the table, corresponding to an initial volume fraction of walls of  $\sim 10$  per cent. The corresponding wave-length of the banded texture is  $\lambda \simeq 4\xi u_0 = 260 \mu\text{m}$ , and from the values  $K_2/K_3 \simeq 0.75$  (in the table) and  $K_1 q^2 = 0.3 \text{ dyne cm}^{-2}$  and  $K_3/K_1 \simeq 0.5$  obtained with the hydrodynamic model in section 4 we can estimate the three Frank elastic constants.

In conclusion, we have demonstrated that the Rheo-NMR technique described in this paper allows us to estimate four independent Leslie viscosity coefficients and the three Frank elastic constants of nematic PLCs. This study also gives support to Rey's model [1] for the process of wall dissolution. The numerical results produced above may however be less accurate than actually allowed by the technique used, due to particular experimental difficulties experienced in this work (low spectrometer performance and partial sample degradation).

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