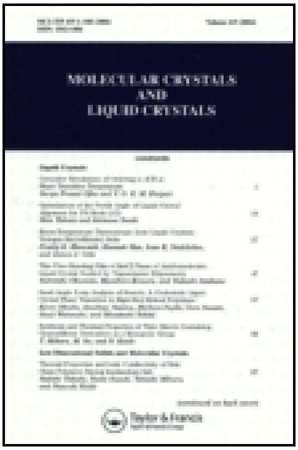

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NMR Study of Flow and Viscoelastic Properties of PBLG/m-Cresol Lyotropic Liquid Crystal

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Director distortion patterns and backflow effects in transient flows of nematic solutions of PBLG/m-cresol are studied by deuteron NMR. The simulation of the observed NMR spectra as a function of time allows to characterise the director field pattern and to evaluate most of the viscoelastic properties of the system. A good agreement with classical rheometry is observed.

Keywords: Liquid Crystal Polymer; PBLG; Rheo-NMR; Viscoelasticity

INTRODUCTION

The hydrodynamic properties of nematic liquid crystals are described by the well-known Ericksen-Leslie equations[1] which involve five viscosities and three elastic constants. It is the purpose of this paper to determine most of these viscoelastic coefficients for a lyotropic main-chain liquid crystal. The method used is based on the observation, by deuteron NMR, of the director reorientation process, in a static magnetic field, of a nematic monodomain

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suddenly rotated through an angle α from its equilibrium position[2]. When $\alpha = \pi/2$, the director field exhibits a transient, spatially periodic, distortion[3] which strongly affects the shape of the NMR spectra.

We have investigated this inhomogeneous reorientation process for a solution of poly(γ-benzyl-L-glutamate) in m-cresol (PBLG/m-Cresol) using deuterated benzene as NMR probe. The simulations of the time-dependent NMR spectra allow to evaluate the four viscosities α_1, α_2, γ_1, η_{bend}, and the ratio of the two elastic constants K_{11} and K_{33}, using a method proposed by Martins et al[2]. The fifth Leslie's viscosity is obtained from classical rheometry.

EXPERIMENTAL

The study was performed on a solution of 17 % of poly(γ-benzyl-L-glutamate) (whose molecular structure is shown in Figure 1) in m-cresol at T = 302K. We used a sample of PBLG with a molecular weight M_w = 280 000 g/mol. The NMR measurements were performed on 1% of deuterated benzene added to the solution.

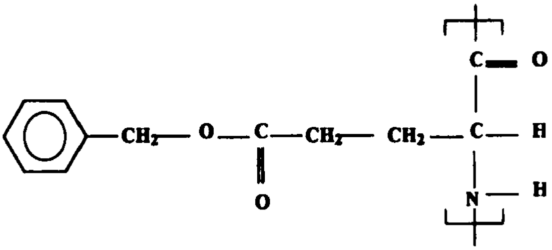

FIGURE 1 Repeating unit of PBLG.

After enough time, the sample, placed in the strong magnetic field of the NMR spectrometer, reaches an equilibrium state (nematic monodomain) where the director is aligned parallel to the magnetic field. Then, the tube containing the sample is suddenly rotated through an angle $\alpha \approx \pi/2$ about an axis perpendicular to the magnetic field direction. This non-equilibrium state entails the relaxation of the director back to equilibrium. The reorientation process is followed up by recording, as a function of time, the NMR spectrum of deuterium, whose doublet splitting (Figure 2) is orientation dependent.

ANALYSIS OF THE EXPERIMENTAL SPECTRA

The equilibrium NMR spectrum of the fully deuteriated benzene molecule, recorded prior to the rotation of the sample, is shown in Figure 2. It is composed by a single doublet with a quadrupolar splitting $\Delta\nu_{eq} = 724\,Hz$.

FIGURE 2 D-NMR spectrum of C_6D_6 in 17% PBLG/m-cresol at 302 K. The line splitting is $\Delta\nu_{eq} = 724\,Hz$.

The spectrum recorded immediately after the 90° rotation of the sample displays a doublet with a splitting $\Delta\nu_{90} = \Delta\nu_{eq}/2$ as expected (See the spectrum at t = 0.1 s in Figure 3). For t > 0, the spectrum evolves as shown in Figure 3: Each sharp line of the initial doublet gives rise to an emerging broad line. After several seconds the two well-defined broad lines converge towards the centre of the doublet, cross each other and move, narrowing, towards their equilibrium positions.

This time evolution of the NMR spectrum results from the reorientation of the director towards the equilibrium direction, parallel to the magnetic field. During this transient process, a spatially periodic distortion of the director field develops, i.e. the angle θ made by the director with its initial direction becomes spatially (and time) dependent[2]. This dependence may be Fourier developed as $\theta(t, z) = \theta_0(t)$ [sin (qz) + ...] but in the kind of problems considered here only one[2] or a few[4] of these Fourier components are necessary (see below).

RESULTS AND DISCUSSION

Determination of the viscoelastic coefficients

The NMR spectra were simulated in order to determine the time evolution of the director distribution[4]. Hence, the viscoelastic parameters can be evaluated following a method proposed by Martins et al[2] which involves the numerical integration of the director equation

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

where χ_a is the anisotropy of the magnetic susceptibility of the polymer, $\gamma_{eff}(\theta)$ an effective viscosity and $K(\theta)$ an elastic term due to the distortion of the director field during the reorientation. We have[2]:

$$\gamma_{eff}(\theta)=\gamma_1-\frac{(\alpha_2-\gamma_2\sin^2\theta)^2}{(\alpha_1\cos^2\theta+\gamma_2)\sin^2\theta+\eta_c} \qquad (2)$$

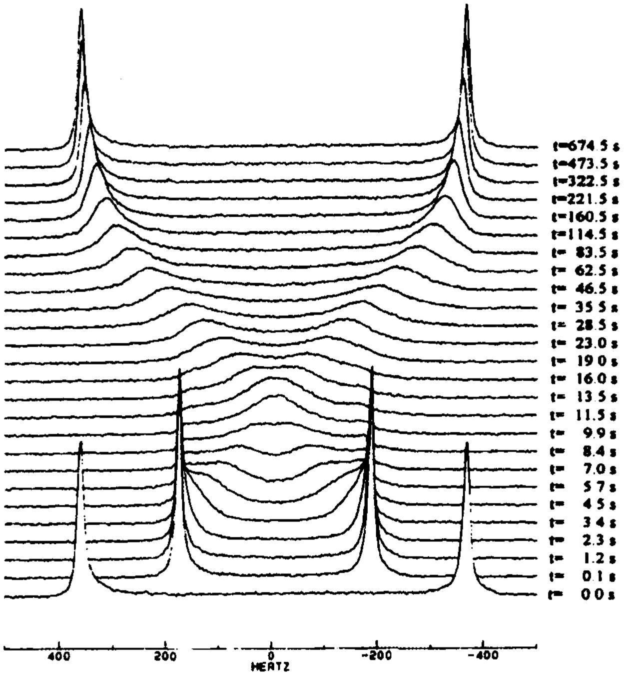

FIGURE 3 Time evolution of the deuterium NMR spectrum following a sudden rotation of the sample trough an angle $\alpha = \pi/2$.

$$K(\theta) = f(\theta)\frac{\partial^2\theta}{\partial z^2} + \frac{1}{2}\left[\frac{\partial f(\theta)}{\partial\theta}\right]\left[\frac{\partial\theta}{\partial z}\right]^2 \text{ with} \tag{3}$$

$$f(\theta) = K_{11} - (K_{11} - K_{33})\cos^2\theta \tag{4}$$

The numerical resolution of the differential equation (1) was performed with $\theta(t,z) = \theta_0(t)\sin(qz)$. The excellent result displayed in Figure 4 was obtained with the following values of the viscoelastic parameters:

$$\begin{aligned} \alpha_1 &= -1.21\times10^3 Pa.s, & \gamma_1 &= 1.33\times10^3 Pa.s, & & \\ \alpha_2 &= -1.33\times10^3 Pa.s, & \eta_{bend} &= 0.7 Pa.s, & K_{11}/K_{33} &\approx 10^{-2}, \end{aligned} \tag{5}$$

where $\eta_{bend} = \gamma_1 - \alpha_2^2/\eta_c$ is the fitted parameter, instead of η_C, for it is easily obtained with a good accuracy ($\pm 0.5\, Pa.s$). The two parameters α_1 and α_2 are very well defined ($\pm 0.02\times10^3\, Pa.s$) once the viscosity γ_1 is known. In this case γ_1 was very difficult to evaluate because equivalent fits were obtained for γ_1 in the range 10^3 Pa.s $\leq \gamma_1 \leq$ 10^5 Pa.s. The reported value of γ_1 in (5) results from the comparison with classical rheometry, as discussed below.

Comparison with classical rheometry

Now, our purpose is to relate the NMR results with the measurements of the classical rheological functions. In order to do that, we use the constitutive equations for nematic liquid crystal polymers recently proposed by Martins[5]. In this theory the first $N_1(\dot\gamma)$ and second $N_2(\dot\gamma)$ normal-stress differences as functions of the shear rate $\dot\gamma$ are expressed as[5] :

$$\begin{aligned} N_1(\dot\gamma) &= N_{10} + (\dot\gamma/\delta)\left(a + c\tau\dot\gamma + \varepsilon(b-\varepsilon a)\tau^2\dot\gamma^2\right) \\ N_2(\dot\gamma) &= N_{20} - \tfrac{1}{2}(1-\varepsilon)\left[N_1(\dot\gamma) - N_{10}\right] + \beta\dot\gamma \end{aligned} \tag{6}$$

where $\delta = 1 + (1-\varepsilon^2)\tau^2\dot\gamma^2$, $\beta = \tfrac{1}{2}(b-\varepsilon a)$, N_{10} and N_{20} are Ericksen stresses, τ is the relaxation time of the polymer memory function and $-1 \leq \varepsilon \leq 1$. The coefficients a, b, c are known functions of the Leslie's viscosities α_i (i = 1…6) and of the two non zero components n_1, n_2 of the director when aligned in a simple shear flow:

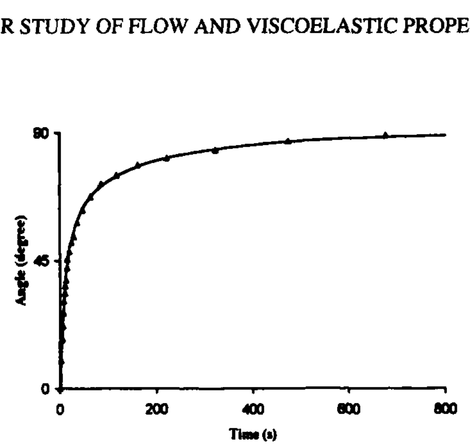

FIGURE 4 Best fit of θ_0 values obtained from the NMR spectra simulation (▲) found by integrating Equation 1 (—).

$$\begin{aligned} a &= n_1 n_2 \left[\alpha_1 (n_1^2 - n_2^2) + \alpha_5 - \alpha_6\right] \\ b &= n_1 n_2 (\alpha_1 + \alpha_5 + \alpha_6) \\ c &= 2 n_1^2 n_2^2 \alpha_1 + \alpha_4 + n_2^2 \alpha_5 + n_1^2 \alpha_6 \end{aligned} \tag{7}$$

Moreover, we define a parameter d, which is zero for an aligned polymer, by

$$d = \alpha_2 - n_1^2 (\gamma_1 + 2\alpha_2). \tag{8}$$

Although relations (7) and (8) are defined for a shear-aligned polymer, we may conserve them in the case of tumbling assuming an *effective* alignment angle Θ ($n_1 = \cos\Theta$), and treating d as a free parameter, since the tumbling motion is strongly non-uniform, i.e. the molecules align, most of the time, about Θ.

A fit of the theory[5] to the experimental data for $N_1(\dot{\gamma})$ was performed for a 14% solution of PBLG/m-cresol and yield the values of the parameters a, b and c[6]. Then, the inversion of the formulae (7) and (8) yields all the Leslie's viscosities as functions of γ_1, Θ and d. To make the comparison with NMR, we consider one value of γ_1 in the range given above and the associated values of α_1, α_2 and η_{bend}. Based to these values, we can decide whether the system is shear aligning or not. In the first case d is zero and the relation (8) determines Θ. No parameter has to be adjusted and the comparison is direct. In the case of tumbling, we first choose a value for Θ which, then, determine d through the relation (8), in such a way that just one parameter has to be adjusted. This procedure has been performed for different values of γ_1. An important result is that a very good agreement is obtained for a value of γ_1 consistent with homogeneous reorientation. Table 1 presents this result.

TABLE 1 Comparison between Rheo-NMR and classical Rheometry

Viscosity Coefficients	Rheo-NMR (Pa.s)	Conventional rheometry $\Theta_{eff} = 1.4°$ $d = -5.2$ (Pa.s)
γ_1	1.332×10^3 ⟶	1.332×10^3
α_1	-1.212×10^3	-1.216×10^3
α_2	-1.328×10^3	-1.328×10^3
α_3	4.000×10^0	4.410×10^0
α_4	0.825×10^2 *	1.134×10^2
α_5	1.239×10^3 *	1.207×10^3
α_6	-0.85×10^2 *	-1.164×10^2
η_{bend}	0.740×10^0	0.720×10^0

* Evaluated from a combination of $N_2(\dot{\gamma} \to 0)$ and NMR data

In order to complete the set of Leslie's viscosities, we have estimated the viscosity α_6 from the *slope*, in the vicinity of zero shear rate, of the second normal stress difference $N_2(\dot{\gamma})$, given by $n_1 n_2(\alpha_1 n_2^2 + \alpha_6)$ from the Martins' theory; then, α_4 and α_5 become calculable from the viscosities measured by NMR.

CONCLUSION

The time evolution of the director field distortion of PBLG in m-cresol during the inhomogeneous reorientation following a 90° rotation of the initially homogeneous sample in a strong magnetic field has been observed by deuteron NMR of a benzene-d_6 probe. The numerical simulation of the reorientation process has provided the four Leslie's viscosities γ_1, α_1, α_2 and η_{bend}, as well as the elastic constants ratio K_{11}/K_{33}. Data from classical rheometry provided the fifth independent Leslie's viscosity and simultaneously suppressed some uncertainty on γ_1. To our knowledge, this is the first time that the complete set of Leslie's viscosities for a liquid crystalline polymer has been obtained. Very good agreement was found between classical rheometry and rheo-NMR data. Moreover, a negative value was found for the ratio α_2/α_3, suggesting that PBLG should be classified in the group of shear tumbling polymers.

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