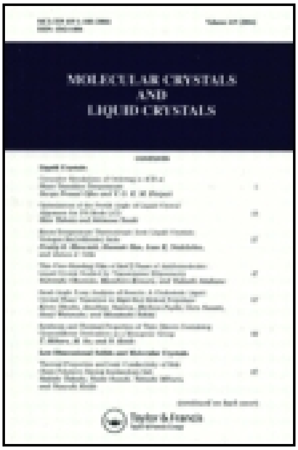

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Some Aspects of the Rheo-Nmr Behavior of the Lyotropic Liquid Crystal Poly(γ-BENZYL-L-GLUTAMATE) in m-Cresol

Catarina Leal [a] [b] , Jacques Klink [c] & Assis Martins [c]

[a] ISEL, R. Conselheiro Emídio Navarro,1, Lisboa, P-1949-014, Portugal

[b] Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Monte de Caparica, P-2825-114, Portugal

[c] Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, Monte de Caparica, P-2825-114, Portugal

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SOME ASPECTS OF THE RHEO-NMR BEHAVIOR OF THE LYOTROPIC LIQUID CRYSTAL POLY(γ-BENZYL-L-GLUTAMATE) IN *m*-CRESOL

*Catarina R. Leal**
ISEL, R. Conselheiro Emídio Navarro,1, P-1949-014 Lisboa, Portugal
and
Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, P-2825-114 Monte de Caparica, Portugal

Jacques van der Klink[†] *and Assis F. Martins*
Departamento de Ciência dos Materiais, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, P-2825-114 Monte de Caparica, Portugal

We report the use of ^2H NMR spectroscopy to study the director orientation in two nematic solutions of poly(γ-benzyl-L-glutamate) (PBLG) in m-cresol during simple shear flow and after its sudden cessation. In the range of applied shear rates ($\dot{\gamma} = 5\ldots150\,\mathrm{s}^{-1}$), a steady-state NMR line shape is reached after a deformation of a few hundred units. Two different line shapes occur that can be related to distinct shear responses in mechanical rheology: the tumbling/wagging and the flow-aligning regimes. The relaxation after cessation of the shear is similar for both cases and essentially follows the "inhomogeneous reorientation" regime known from sudden-rotation NMR experiments. A fit of the relaxation curves indicates that the tumbling parameter λ is (slightly) less than one, as expected for a tumbling system.

Keywords: liquid crystal polymer; PBLG; Rheo-NMR

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[†] Permanent address: FSB, EPFL, CH-1015 Lausanne, Switzerland.

[*] Corresponding author. E-mail: cleal@dem.isel.ipl.pt

INTRODUCTION

The rheology of the lyotropic liquid-crystalline systems formed by solutions of poly(γ-benzyl-L-glutamate) (PBLG) in *m*-cresol has been studied rather extensively, but it continues to yield significant new results [1]. In general, the existence of a range of shear rates, where the first normal stress difference becomes negative and theoretically associated [2] with periodic motions of the director, is well documented for the PBLG system. Direct experimental detection of such director motion, however, is relatively scarce [3].

In this article we explore the information that can be obtained by NMR spectroscopy on such a flowing system. Shear-induced orientation effects on NMR spectra of polymeric liquids have been known for quite some time [4], and several liquid crystals have been studied by Schmidt and colleagues [5] using an NMR viscometer designed for the purpose [6]. We use a simple Couette fixture for shearing without performing viscosity measurements. Its symmetry axis is along the magnetic field, so that there is no suppression of tumbling by the field.

We know from the literature at which ranges of shear rate director tumbling and/or wagging should be expected. The geometry of our Couette cell is such that the NMR spectrum becomes sensitive to out-of-plane motion in the tumbling/wagging regime. The shear aligning at high shearing rates should be strictly in the plane transversal to the magnetic field.

At the moment of cessation of the shear, the director finds itself turned away from the magnetic field over an angle of at least 60 degrees. The return to the equilibrium position could occur either by "homogeneous" or by "inhomogeneous" reorientation [7]. Inhomogeneous reorientation is based on the growth of initially stationary orientation fluctuations. These initial fluctuations are certainly different in the present experiments from those in the "sudden rotation" experiments that we have reported earlier for PBLG/*m*-cresol [8]; however, it has been argued that these differences affect mostly the details of spectral shape, and much less the overall evolution time [9]. This time evolution depends on a number of viscosity parameters, among which is the tumbling parameter λ.

EXPERIMENTAL

We prepared two solutions of PBLG (Mw = 296100 g/mol; Sigma Chemical,) in *m*-cresol, with polymer weight fractions of 12.54 and 14.02%. Deuterated benzene, C_6D_6, was added in a weight fraction of 1% to provide a suitable quadrupolar nucleus for NMR detection [10]. For brevity, these samples are designated PBLG-12 and PBLG-14 hereafter.

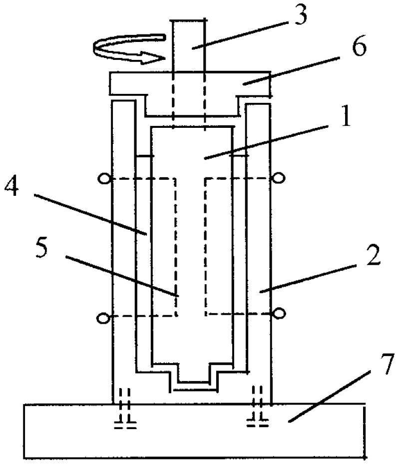


FIGURE 1 Sketch of the Couette flow cell. The main parts are: 1. rotating inner cylinder, outer diameter 8 mm; 2. fixed outer cylinder, inner diameter 9 mm; 3. connection rod to motor; 4. sample space; 5. NMR saddle coil; 6. top cover; and 7. standard probe–insert base.

Rheological data for solutions with the same weight fractions but with Mw = 238000 g/mol and without added deuterobenzene are available in the literature [11]. The NMR equipment is the same as used before [8,12] and consists of a Bruker MSL 300 (7 T field) spectrometer with a special insert for the Bruker BB 300 solids probe. The essential element of that insert is a Couette flow cell, sketched in Figure 1. Its rotating cylinder is driven by a pulse-programmer–controlled stepper motor at the top of the magnet. The insert is compatible with the standard Bruker temperature regulation. The experiments were performed at 303 K. At constant shear rate $\dot{\gamma} = 1, 5, 10, 20, 40, 80, 100$, and $150\,\mathrm{s}^{-1}$, spectra were taken after 0, 100, 300, and 400 units of deformation. Next the shearing was stopped and spectra were taken periodically during recovery, for about 30 min.

RESULTS AND DISCUSSION

The range of shear rates $\dot{\gamma}$ for the main rheological regimes [2] can be found from the literature data [11]. For PBLG-12 the limits are, approximately; tumbling up to $\dot{\gamma} \approx 20\,\mathrm{s}^{-1}$, then wagging up to $\dot{\gamma} \approx 60\,\mathrm{s}^{-1}$, followed by shear aligning at higher $\dot{\gamma}$. The corresponding limits for PBLG-14 are $\dot{\gamma} \approx 40\,\mathrm{s}^{-1}$ and $\dot{\gamma} \approx 150\,\mathrm{s}^{-1}$.

From the line splitting in the spectra after 100, 300, and 400 units of deformation, examples of which are shown in Figure 2, the (average) angle

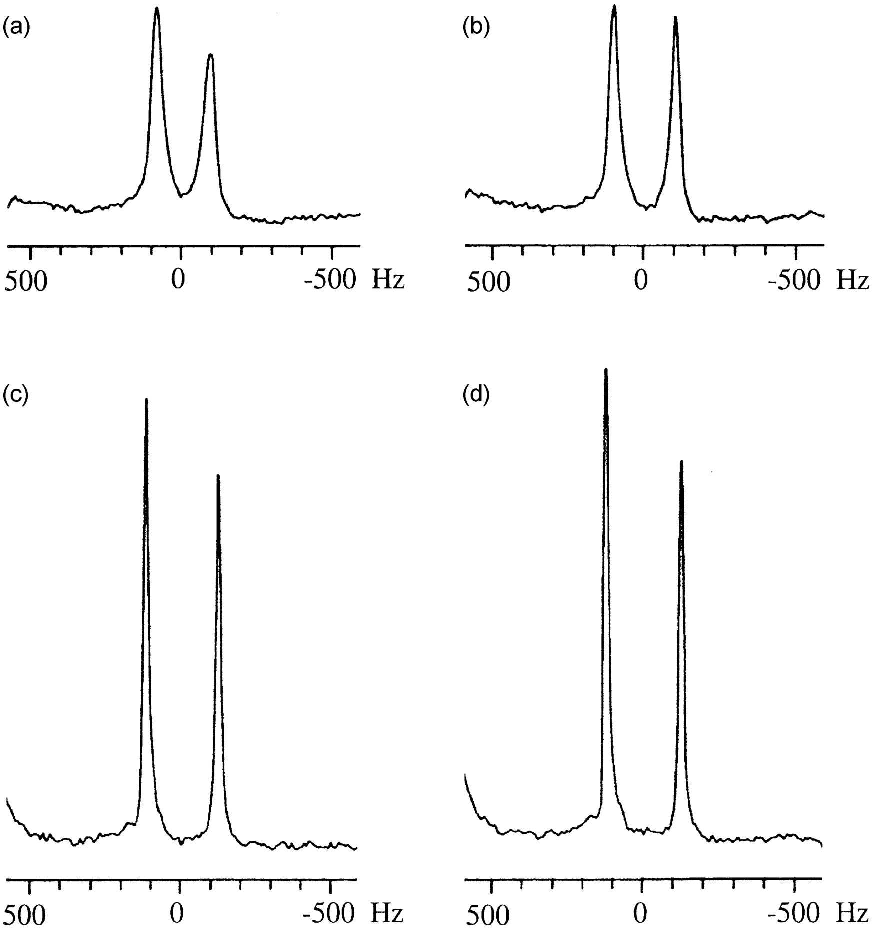
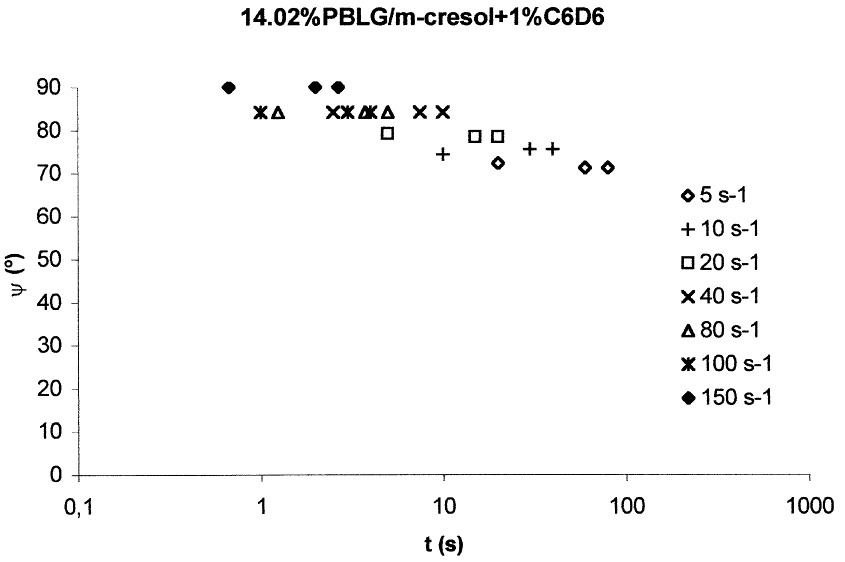


FIGURE 2 ^{2}H NMR spectra of the deuterobenzene in sample PBLG-14. The shearing has just been stopped after 400 units of deformation. The previous shearing rates $\dot{\gamma}$ were (a) 5, (b) 10, (c) 40, and (d) 150 s^{-1}. The first two spectra have roughly the same line splittings and line widths, and similar for the second pair.

between the director and the magnetic field can be calculated. The results for both samples and for all values of $\dot{\gamma}$ studied are shown in Figure 3. Already after 100 units of deformation a (close to) steady state is reached. It is seen that an orientation (nearly) in the flow/flow-gradient plane ($\psi = 90°$) is attained for $\dot{\gamma} \approx 40\,s^{-1}$ in the case of PBLG-12 and for $150\,s^{-1}$ for PBLG-14.

A related result is the change of NMR line width at constant deformation as function of $\dot{\gamma}$, which can be seen in Figure 2. The spectra after the



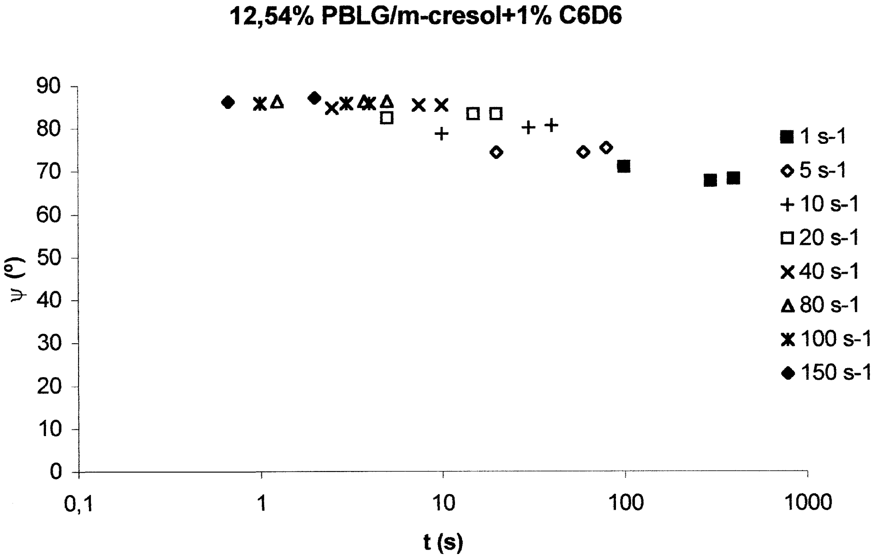


FIGURE 3 The angle ψ between the director and the magnetic field, calculated from the line splittings in spectra as in Figure 2, as a function of total deformation. The parameter is the shear rate $\dot{\gamma}$ during the deformation. Top, sample PBLG-14; bottom, sample PBLG-12.

higher shear rates have practically the same line width as the equilibrium spectra (compare with the lower traces in Figure 4), mainly due to field inhomogeneities. At the lower shear rates, not only is the average director orientation out of the flow/flow-gradient plane, but there is also an additional line broadening, probably due to a spread of several degrees in the angle between the director and the magnetic field. The monodomain that the magnetic field induces in the system at rest is broken up by the shear; individual domains tumble with possibly the same period but not with the same phase. The NMR acquisition is rapid on the tumbling timescale and provides a snapshot average over the director orientation in all domains, which leads to line broadening.

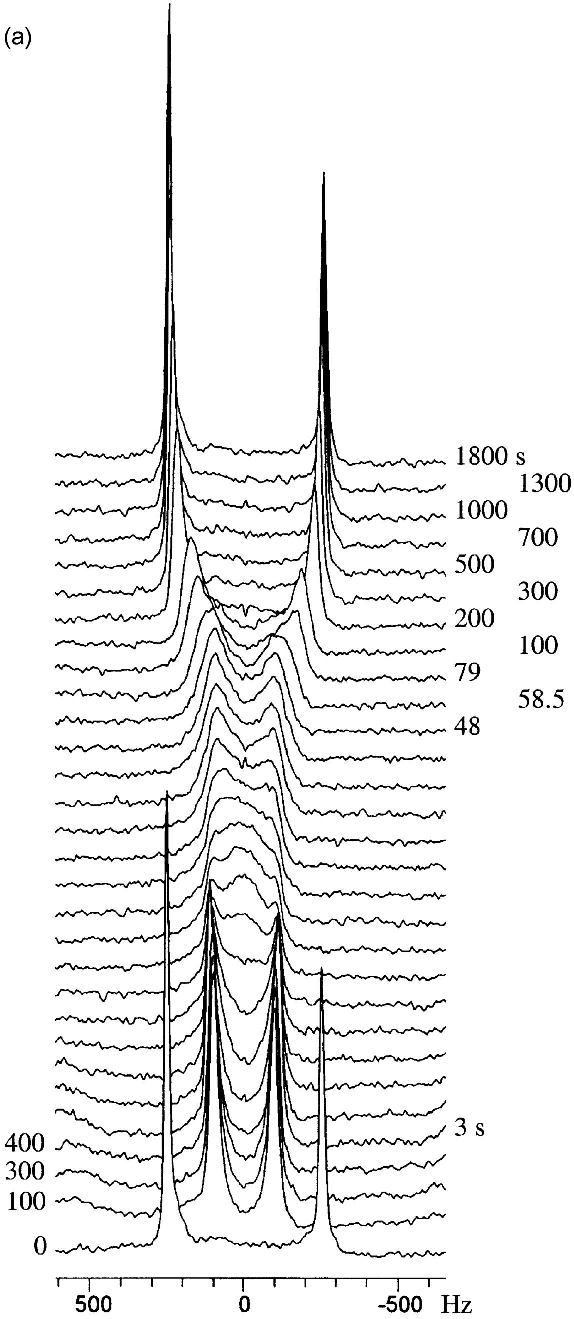
The experimental results suggest (compare Figure 2c with the $\dot{\gamma} = 40\,\mathrm{s}^{-1}$ points in the upper part of Figure 3) that the line narrows before the full flow alignment occurs; tentatively this might be interpreted as saying that the range of angles that a director sees during wagging is smaller than the range during tumbling.

The qualitative difference in line widths under low and high rates of shear (Figure 2) persists after cessation of the shear. An example is provided by the two series of spectra of PBLG-14 in Figure 4. However, these data show also that the overall time scale of the recovery is not much influenced by these differences in microstructure, as can be seen more quantitatively in Figure 5. After the first ten seconds, the recovery becomes independent of the shear history and is similar to that found in “sudden-rotation” experiments [7], such as shown in Figure 4 of Verom et al. [8] for a very similar PBLG system. In a recent numerical simulation of this recovery process (see Martins et al. [9], Equation (19)) it was also remarked that the NMR line shapes are rather sensitive to the initial conditions, while the overall timescale is not. This idea is further supported by Figure 6, which shows for each of the two samples a single fit to all recovery data using the method of Martins et al. [7]. The fit parameters shown in Table 1 are reasonable, and in particular the parameter $\lambda = (-2\alpha_2/\gamma_1) - 1 < 1$, as is expected for a tumbling system.

In conclusion, ^{2}H NMR spectroscopy on PBLG/m-cresol, with the magnetic field along the vorticity axis of a simple shear flow, shows a constant angle between field and director after a few hundred units of strain. The linewidth in this situation is different for low and high shear

▶

FIGURE 4 Two complete sets of ^{2}H NMR spectra of the deuterobenzene in sample PBLG-14. In each set, the lower four spectra are after 0, 100, 300, and 400 units of deformation (the latter have been shown individually in Figures 2b and 2c). Then the shearing is stopped, and every three seconds a spectrum is taken, up to 48 s. Further spectra are labelled with the time after cessation of the shear. The shearing rates $\dot{\gamma}$ are (a) 10 and (b) 40 s^{-1}.


(a)
1800 s
1300
1000
700
500
300
200
100
79
58.5
48
3 s
400
300
100
0
500
0
-500
Hz

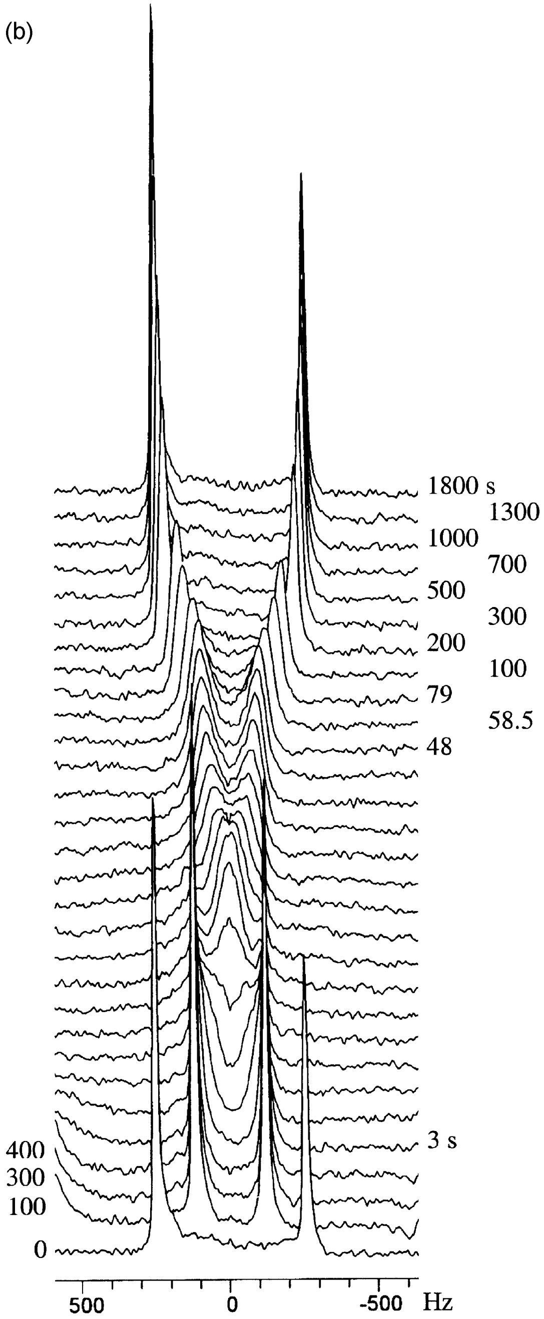
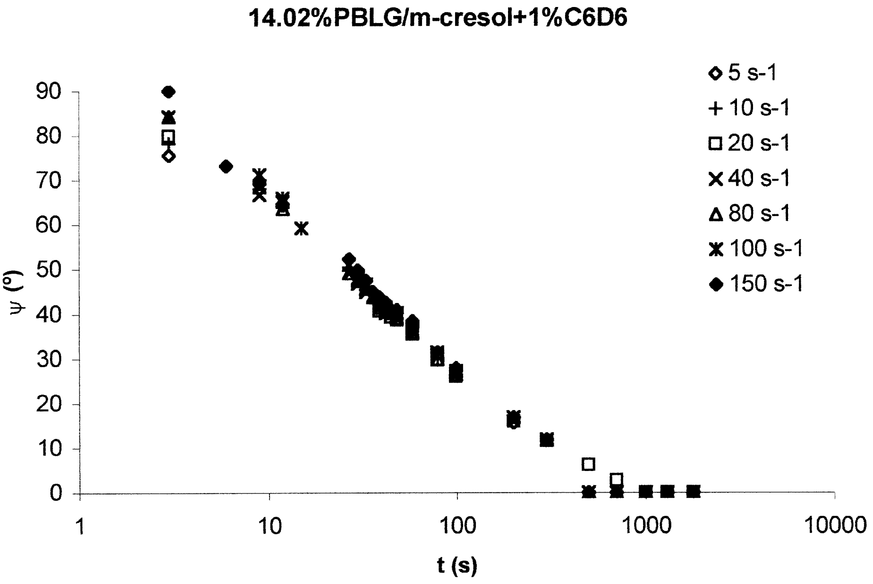


FIGURE 4 Continued.



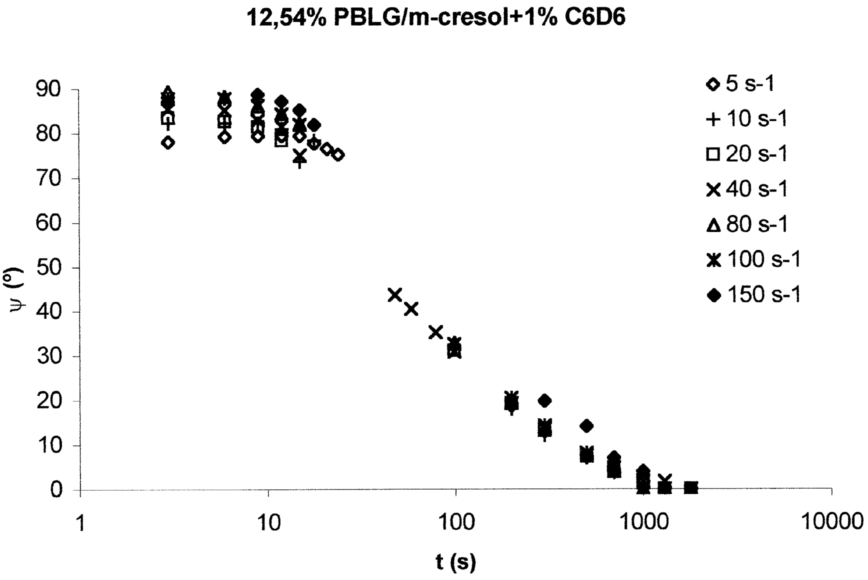


FIGURE 5 The angle ψ between the director and the magnetic field as function of the time t since cessation of the shear, calculated from the line splittings in spectra as in Figure 4. The parameter is the shear rate $\dot{\gamma}$ during the deformation. After the first ten seconds, the recovery is independent of $\dot{\gamma}$. Top, sample PBLG-14; bottom, sample PBLG-12.

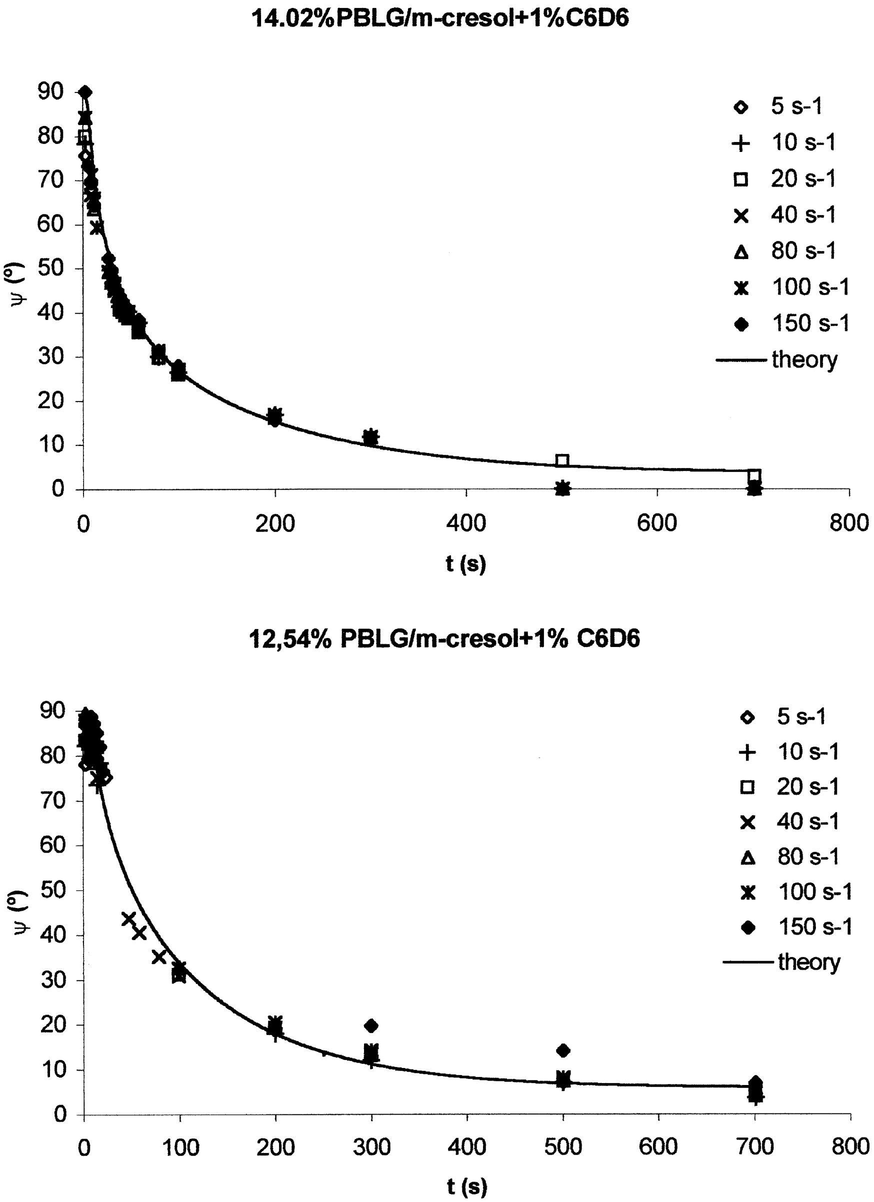


FIGURE 6 Fits of all the data points in Figure 5 for sample PBLG-14 (top) and PBLG-12 (bottom). The fit parameters are given in Table 1.

TABLE I Viscoelastic Parameters for the Fits Shown in Figure 6

Sample	α_1	α_2	η_{bend}	γ_1	η_c	K_1/K_3	χ_a
PBLG-12	−0.17	−0.62	0.0079	0.64	0.61	0.2	106
PBLG-14	−0.48	−0.78	0.0056	0.80	0.77	0.1	113

K_1/K_3 is the ratio of splay and bend elastic constants.
$\gamma_1 = \alpha_3 - \alpha_2; \eta_c = (-\alpha_2 + \alpha_4 + \alpha_5)/2$ and $\eta_{bend} = \gamma_1 - {\alpha_2}^2/\eta_c$.
The α_i are Leslie viscosity coefficients in kPa·s.
The estimated values for the anisotropy of the magnetic susceptibility χ_a are in μemu/cc.

rates, compatible with the idea of tumbling/wagging and shear aligning of the director, respectively. When the shearing is stopped, the director relaxes back towards the direction of the magnetic field. After about ten seconds, this relaxation is essentially independent of the shear history.

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