Shear-history dependent 'equilibrium' states of liquid-crystalline hydroxypropylcellulose solutions detected by rheo-nuclear magnetic resonance

Shear-history dependent 'equilibrium' states of liquid-crystalline hydroxypropylcellulose solutions detected by rheo-nuclear magnetic resonance

M H Godinho[1], J J van der Klink[2] and A F Martins[1]

[1] Departamento de Ciência dos Materiais and CENIMAT, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, P-2825-114 Monte de Caparica, Portugal
[2] Faculté des Sciences de Base, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

E-mail: farinha@cii.fc.ul.pt (A F Martins)

Abstract
The liquid-crystalline polymer system formed by solutions of hydroxypropylcellulose in water has a well known anomaly in the dependence of its mechanical complex modulus on its rheological history. After cessation of an initial rapid shear, the system evolves towards an 'equilibrium' state with a high modulus; after slow shear the 'equilibrium' state has a low modulus. Attempts to distinguish the two states by light scattering, birefringence or x-ray scattering have been unsuccessful. We present the first locally probing experiment, rheo-NMR, that sees a difference between these states. The results show clearly that the low-modulus state is ordered and evolves out of a state that has no macroscopic order (but may be ordered at the mesoscopic level) immediately after cessation of the shear. The high-modulus state is much less ordered, although it evolves from a rather well flow-aligned state immediately after cessation of the shear.

1. Introduction

The rheological behaviour of liquid-crystalline polymer (LCP) systems is technologically relevant as well as scientifically interesting. In the latter respect, poly-benzylglutamate (PBG) and hydroxypropylcellulose (HPC) in different solvents are probably the most widely studied systems [1]. These lyotropics show liquid-crystalline behaviour close to room temperature, which makes them easier to handle than most thermotropics. The hope is that they have at least some characteristics that are common to all LCP systems. Mechanical rheology [2, 3] and rheo-optics [4–7] are frequently adopted experimental techniques; *in situ* x-ray diffraction of systems under shear flow [8, 9] has also been used.

In this work we employ a more recent technique [10], which combines shear flow with NMR spectroscopy (rheo-NMR), to address a question that appears to be specific to

the HPC/water system. It has been found from earlier mechanical rheology experiments that two different 'equilibrium' states may evolve after the cessation of a steady-shear flow, depending on whether this initial shearing was 'slow' or 'rapid'. The two states show markedly different values of the dynamic viscosity η^*, or equivalently of the complex modulus G^*: they are called the low- and high-modulus states. This mechanical characterization has been reproduced by several groups [2, 5], but attempts to distinguish the two states by small-angle light scattering [4, 6], birefringence or x-ray scattering [7, 8] have been unsuccessful. The phenomenon is not general since, in similar mechanical experiments on PBG/*m*-cresol [2, 4], no separate low- and high-modulus states have been found.

We present, for the first time, some rheo-NMR data, taken on the liquid-crystalline system HPC/D_2O, that show a qualitative correlation between the shape of the NMR spectrum and the complex modulus behaviour described in the literature (see, for example, [1, 2]).

1.1. Solvent-NMR in lyotropics

A quiescent LCP system (without external constraints) usually has no macroscopic orientational order, although it is spontaneously ordered at the molecular level [6]. This is loosely ascribed to the existence of mesoscopic domains that are not aligned with each other [11]. An external field (e.g. a magnetic field or a shear field) can, in principle, influence the ordering both at the molecular and the domain levels.

Schematically, a ^2H atom in the HPC/D_2O system can be thought of as being in one of three different environments: the hydroxyl groups of the HPC; water molecules closely associated with a polymer (probably by hydrogen bonding); and relatively free water molecules. In each environment, the 'rigid' value of its tensor interaction between the nuclear quadrupole moment and the gradient of the electric field is averaged to some extent by molecular motion. The free water molecules move isotropically, and their average quadrupole splitting is zero. But the local ordering inside the domains means that the motion of ^2H atoms in hydroxyl groups or in associated water is not isotropic, and their motionally averaged quadrupole splittings, although smaller than the rigid ones, will be non-zero. If the exchange between the three environments is rapid, then only one average type of ^2H atom is actually seen in the NMR spectrum. For the concentrations used here, the fraction of ^2H atoms in the hydroxyl groups is approximately 10^{-2} and it would be hard to detect a separate spectrum. If, furthermore, the fraction of free water molecules happens to be very small, then the ^2H NMR spectrum is representative of the associated water inside the domains. If the exchange of individual ^2H atoms between domains is slow, then the NMR spectrum is a superposition of many individual spectra and, in the limit of an isotropic distribution of domain orientations, a Pake doublet [12] results. Sometimes it is not easy to observe experimentally the spectral details that distinguish the Pake doublet from a simple doublet of lines. In such cases it is helpful to make rotation diagrams, i.e. to observe the spectra after rotation of the sample through several angles (and, in principle, around at least two orthogonal axes). A powder is isotropic, so all spectra in the rotation diagram will be the same. In contrast, the simple doublet has a splitting that varies in a well known way with sample rotation.

For liquid crystals without aromatic rings, the anisotropy of the diamagnetic susceptibility is usually two orders of magnitude smaller than in the canonical nematics *p*-azoxyanisole (PAA) or *N*-(*p*-methoxybenzylidene)-*p*-butylaniline (MBBA) (see [13, p 288]). Certain chiral polyesters, which probably have cholesteric mesophases, are not appreciably oriented in fields of up to 16 T [14]. No magnetic-alignment data are available for HPC, but structured ^2H NMR spectra have been observed for HPC/D_2O with polymer weight fractions of $\phi_p > 0.5$ [15, 16]. Whether the structure is closer to a Pake doublet (a powder of randomly oriented domains)

than to a simple doublet (a nematic mono-domain aligned in the magnetic field) has not been discussed by these authors, but the $\phi_p = 0.6$ spectrum in figure 3 of [15] in particular has a clear Pake doublet contribution.

2. Experimental details

A batch (lot number FP10 12454) of HPC Klucel EF, with a molecular weight indicated by the supplier (Aqualon) to be $M \approx 10^5$ g mol^{-1}, was used. An aqueous solution of $\phi_p = 0.5$ was prepared according to the following procedure: the powder was dried under vacuum for two days at room temperature and mixed with deuterium oxide (Sigma, 99.9% ^{2}H). The jars containing the solution were sealed, covered with paper to avoid light damage and excessive air incorporation, and stirred. Complete dissolution took place in about two weeks.

In the NMR experiments, the standard Bruker MSL solids probe was used at 46.07 MHz, with three different inserts: the regular Bruker saddle-coil; a single-axis goniometer with a solenoid coil; and a Couette-flow fixture with a saddle coil. The goniometer axis is perpendicular to the magnetic field; the symmetry axis of the Couette is parallel to it. The mechanical motion in both special inserts is derived from a pulse-programmer-controlled stepper motor on top of the magnet. Unless stated otherwise, all NMR data have been taken at a controlled temperature of 303 K. The Couette has an outer cylinder with an inner diameter of 9 mm and a rotating inner cylinder with a diameter of 8 mm. The useful sample height is 20 mm. In the Couette experiments the shearing protocol uses a fixed maximum deformation, $\dot{\gamma}t$, usually 200 units, except for a few cases where it is 1000. A deformation cycle goes from zero to maximum positive deformation, reverses direction to go to maximum negative deformation and reverses again to go back to zero deformation. The number of such cycles is usually chosen to be two or three.

For a qualitative study of the two 'equilibrium' states, the following experiment was performed without temperature control. A simple concentric-cylinder sample holder was made from a 6.5 mm inner diameter NMR sample tube (suitable for the goniometer) and a piece of 5 mm outer diameter plastic rod. No attempt at rigorous control of concentricity was made. The sample in the annular space between the tube and the rod could be sheared by turning the rod manually with respect to the tube. Afterwards the sample holder was put in an NMR probe and in the magnet. Two probe inserts were used: one where the magnetic field is parallel to the cylindrical axis (standard saddle-coil insert) and another where it is perpendicular (the goniometer insert). The manual shearing is of course far from uniform, but we found that it was possible to represent both slow and rapid shearing. The spectra in the goniometer were taken at two orientations that were different by 90°.

3. Results

During rapid shearing (5 s^{-1} $\leqslant$ $\dot{\gamma}$ $\leqslant$ 126 s^{-1}) the splitting in the spectrum increases continuously with shear rate from about 235 to about 410 Hz. Two examples are shown in the lower left-hand part of figure 1, where the intermediate rate $\dot{\gamma} = 1.34$ s^{-1} gives a splitting of about 110 Hz. At low $\dot{\gamma}$ the splittings fall below 2 ppm and are difficult to measure. After shear rates of 0.3 or 0.5 s^{-1}, the final spectrum is a rather nice doublet, with a quasi-history-independent splitting of about 200 Hz (three spectra, top right-hand part of figure 1). Shear rates of $\dot{\gamma} = 5$, 6, 50 or 126 s^{-1} result in a final state where the spectrum is a broad line with a flattened top with a full width at half maximum (FWHM) of about 250 Hz. The value $\dot{\gamma} = 1.34$ s^{-1} leads to an intermediate spectral shape. On a scale of days, the flat-topped
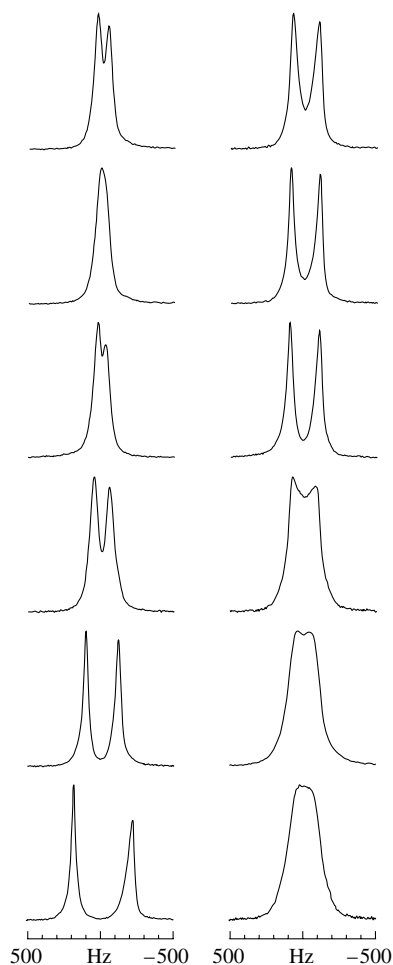
Figure 1. ^{2}H NMR spectra of D_2O in the HPC/water system after different protocols of *in situ* shearing in a Couette geometry, with its symmetry axis parallel to the magnetic field. The horizontal axis is 1000 Hz (roughly 22 ppm) in all cases. Left-hand column: spectra taken immediately after the deformation cycle. Right-hand column: spectra taken a long time afterwards. Top row: shearing rate $\dot{\gamma} = 0.3$ s^{-1}, three cycles of a maximum deformation of 200 units; waiting time before taking the right-hand spectrum, 3 h. Second row: $\dot{\gamma} = 0.5$ s^{-1}; two cycles of 200 units; waiting time 3 h. Third row: $\dot{\gamma} = 0.5$ s^{-1}; two cycles of 1000 units; waiting time 4 h. Fourth row: $\dot{\gamma} = 1.34$ s^{-1}; two cycles of 200 units; waiting time 4 h. Fifth row: $\dot{\gamma} = 5$ s^{-1}; two cycles of 200 units; waiting time 4 h. Sixth row: $\dot{\gamma} = 126$ s^{-1}; three cycles of 200 units; waiting time 30 min. All spectra shown in the right-hand column slowly evolve further over a period of days, but they do not reach a common shape.

line will evolve further, acquiring some structure. Over such an interval of time, the two-line spectrum loses some of its sharpness. However, both types of shape remain distinct.

The evolution of the spectra in figure 2 depends on whether the splitting during the shear (not shown, but similar to the left-hand column in figure 1) is larger or smaller than the 200 Hz in the top right-hand part of figure 1. If it is smaller, then during relaxation the splitting grows continuously without much change in line-widths, as in the left-hand column of figure 2. In the opposite case, during relaxation the splittings diminish and the lines merge into a single rather
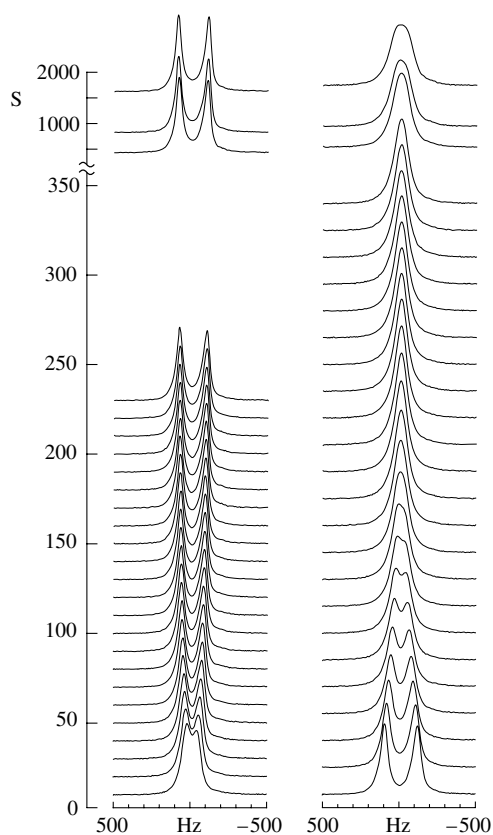
Figure 2. The evolution in time (from bottom to top) of the ^{2}H NMR spectra after the cessation of shearing. Left-hand column: slow shearing, corresponding to the second row of figure 1. Right-hand column: rapid shearing, corresponding to the fifth row of figure 1. The lower left-hand part of the figure shows spectra taken at 10 s intervals; the lower right-hand part shows spectra taken at 15 s intervals. Note the break in the time scale, shown on the left, for the upper three spectra in each column.

narrow line. This subsequently broadens considerably without—on a timescale of hours—acquiring structure, as in figure 2, right column.

It has been observed, during mounting and demounting of the Couette fixture, that a slight (unintentional) turning of the axis that drives the inner cylinder of the Couette will destroy the single-line spectrum and create the doublet. Once the axis has been demounted without disturbing the sample, each of the two states remain stable when the probe is taken out of the magnet and put back in. The results obtained in the concentric-tube sample holder after manual shearing are shown in figure 3. The two lower rows of spectra show that, after shearing, the sample has—to a good approximation—cylindrical symmetry. For 'slow' deformation, the left-hand column shows that there is alignment perpendicular to the sample axis—it may be radial or tangential in the cylindrical axes system or (though unlikely) random in the plane. After rapid deformation, the sample is not quite isotropic, but the degree of alignment is less than after slow deformation.

Some Couette rheo-NMR experiments have also been performed on PBG/*m*-cresol using the same protocol as above. It was found that the final state is independent of the initial shear rate. While this result is in line with those of mechanical experiments [2, 4], it is probably strongly influenced by the well known magnetic alignment of PBG/*m*-cresol.
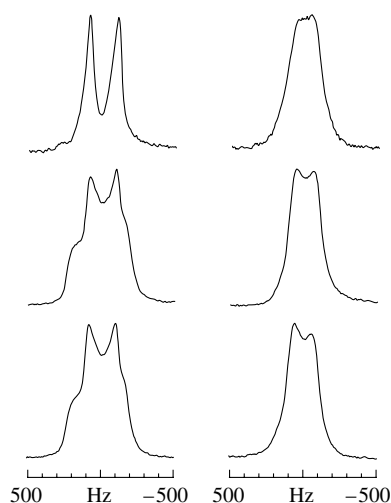
Figure 3. ^{2}H NMR spectra of D$_2$O in a HPC/water sample, in a small concentric-tube sample holder that approximates a Couette geometry. The shearing, performed outside the magnet by manually turning the inner cylinder, is either 'slow' (left-hand column) or 'fast' (right-hand column). The shearing rate is not constant and the cylinders are only approximately collinear, but these spectra can be understood qualitatively. The three rows are for three mutually orthogonal orientations of the Couette axis with respect to the magnetic field: in the top row the axis is parallel to the field (compare with the right-hand column of figure 1). The left-hand column shows that the splitting in the three spectra in the upper right-hand corner of figure 1 is due to alignment perpendicular to the magnetic field. The interpretation of the right-hand column is less precise: the anisotropy of the sample is much less marked after rapid shearing than after slow shearing.

4. Discussion

The NMR sees a qualitative difference between the 'equilibrium states' evolving in this lyotropic system after slow- and after rapid shearing. These are called, on the basis of mechanical measurements, the low-modulus and high-modulus states. At least the low-modulus state is clearly anisotropic (as shown by its quadrupole-split NMR spectrum). This is contrary to what has been concluded from birefringence and light scattering [7, 8]. In agreement with mechanical results (figure 9 of [2]), we find that the high-modulus state is rather fragile, in that a small deformation $\dot{\gamma}t$ at low $\dot{\gamma}$ will transform it into the low-modulus state.

The left-hand column of figure 3 indicates that the low-modulus state is either tangentially or radially aligned in the cylindrical geometry of the Couette cell (while the magnetic field is axial). We have no means of determining experimentally the axis of alignment during shear or relaxation, but it is reasonable to assume that the alignment is tangential (in the direction of the flow) during all stages. This leads to the important conclusion that the evolution of the splitting from left to right in the top three rows of figure 1—an example of which is given by the left-hand column of figure 2—is due to a change in the 'degree of order' in the sample, rather than a reorientation of directors. The low-modulus state evolves by an increasing degree of order after cessation of the flow. But in the evolution towards the high-modulus state, the opposite must happen (at least during the initial stages). We have no evidence for an important degree of alignment of this LCP system on a 24 h timescale in the 7 T field used here.

It seems that, at low shear rates, rapid director tumbling (compared to the inverse of the splitting in the spectrum; of the order of milliseconds) decreases the average degree of order

seen by NMR along the flow direction, leading to an observed splitting close to zero in the three top left-hand spectra in figure 1. (The order seen inside the domains may remain unaffected.) High rates of shear break up the domains, creating a kind of flow-aligned mono-domain whose order increases with increasing shear through stretching of the polymer molecules (the three bottom left-hand spectra in figure 1). After cessation of the slow shear, the tumbling slows down, gently aligning the domains without perturbing them in the three top right-hand spectra of figure 1 (these are not really single crystals, but rather a tangential arrangement of crystallites), as is also shown in some detail in the left-hand column of figure 2. But, after the rapid shear, the re-coiling polymers first destroy the order inside the supposed mono-domain (signalled by the rather narrow single line, obtained less than a minute after cessation of the shear at $\dot{\gamma} = 126\,\mathrm{s}^{-1}$, but only after several minutes in figure 2, right-hand column). Then they break the order up into a polydomain structure with a non-zero order inside each domain, as suggested by the flat-topped curves in the lower right-hand part figure 1 and the axiality shown in the right-hand column of figure 3. The lack of clear splittings may be due to either different degrees of order in different domains that are all aligned along the previous flow direction, or to domains with the same internal order but powder-like alignment. The fragility of the high-modulus structure provides an argument in favour of the latter possibility.

Acknowledgments

References

[1] Burghardt W R 1998 Molecular orientation and rheology in sheared lyotropic liquid crystalline polymers *Macromol. Chem. Phys.* **199** 471–88
[2] Hongladarom K, Secakusuma V and Burghardt W R 1994 Relation between molecular orientation and rheology in lyotropic hydroxypropylcellulose solutions *J. Rheol.* **38** 1505–23
[3] Grizzuti N, Cavella S and Cicarelli P 1990 Transient and steady-state rheology of a liquid crystalline hydroxypropylcellulose solution *J. Rheol.* **34** 1293–310
[4] Takebe T, Hashimoto T, Ernst B, Navard P and Stein R S 1990 Small-angle light scattering of polymer liquid crystals under shear flow *J. Chem. Phys.* **92** 1386–96
[5] Ugaz V M, Cinader D K and Burghardt W R 1997 Origins of region I shear-thinning in model lyotropic liquid crystalline polymers *Macromolecules* **30** 1527–30
[6] Walker L and Wagner N 1994 Rheology of region I flow in a lyotropic liquid-crystal polymer: the effects of defect texture *J. Rheol.* **38** 1525–47
[7] Ernst B and Navard P 1989 Band textures in mesomorphic (hydroxypropyl)cellulose solutions *Macromolecules* **22** 1419–22
[8] Keates P, Mitchell G R, Peuvrel-Disdier E and Navard P 1993 *In situ* x-ray scattering study of anisotropic solutions of hydroxypropylcellulose subjected to shear flow *Polymer* **34** 1316–19
[9] Hongladarom K, Ugaz V M, Cinader D K, Burghardt W R, Quintana J P, Hsiao B S, Dadmun M D, Hamilton W A and Butler P D 1996 Birefringence, x-ray scattering and neutron scattering measurements of molecular orientation in sheared liquid crystal polymer solutions *Macromolecules* **29** 5346–55
[10] Grabowski D and Schmidt C 1994 Simultaneous measurement of shear viscosity and director orientation of a side-chain liquid-crystalline polymer by rheo-NMR *Macromolecules* **27** 2632–4
[11] Marrucci G, Grizzuti N and Buonaurio A 1987 Band formation in sheared HPC solutions: effects of sample thickness *Mol. Cryst. Liq. Cryst.* **153** 263–9

[12] Pake G E 1948 Nuclear resonance absorption in hydrated crystals: fine structure of the proton line *J. Chem. Phys.* **16** 327–36

[13] de Gennes P G 1974 *The Physics of Liquid Crystals* (Oxford: Clarendon)

[14] Maret G and Blumstein A 1982 Orientation of thermotropic liquid-crystalline polyesters in high magnetic fields *Mol. Cryst. Liq. Cryst.* **88** 295–309

[15] Wang B C and Spontak R J 1997 Phase behaviour of aqueous hydroxypropylcellulose mesophase mixtures: molecular weight considerations *Liq. Cryst.* **22** 359–65

[16] Werbowyj R S and Gray D G 1980 Ordered phase formation in concentrated hydroxypropylcellulose solutions *Macromolecules* **13** 69–73