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Observations of the break-up of liquid crystalline polymer threads imbedded in an isotropic fluid

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A droplet, a few hundreds of microns, of liquid crystalline hydroxypropylcellulose (HPC) in water is imbedded into a polydimethylsiloxane (PDMS) matrix and subjected to a shear flow. The droplet is deformed into a thread of high aspect ratio. The textures associated with the break-up of the thread once the flow is stopped are observed by optical microscopy. After stopping the flow a banded texture appears. The droplets resulting from the break-up have a bipolar texture with the two opposite poles being along the former thread direction.

1. Introduction

When a small amount of fluid material A is immersed into a fluid material matrix B, material A takes the shape of a spherical drop, due to the action of interfacial tension. When subjected to flow, the drop will deform and will or will not take a stable shape depending on the result of the competition between the viscous stress and the interfacial tension stress [1]. The ratio of these two stresses is usually expressed by a dimensionless parameter *Ca*, called the capillary number, which has the following form for a shear flow:

$$Ca = \frac{\eta_m \dot{\gamma} R_0}{\gamma_{12}} \tag{1}$$

where η_m is the viscosity of the matrix B, $\dot{\gamma}$ is the shear rate, R_0 is the radius of the undeformed droplet of fluid A and γ_{12} is the interfacial tension between materials A and B.

When $Ca < Ca_{cr}$ at a constant shear rate, Ca_{cr} being a certain critical capillary number function of the viscosity ratio of the two materials, the drop adopts a steady nearly ellipsoidal shape. When $Ca > Ca_{cr}$, the drop is unable to maintain a steady shape and consequently undergoes a transient continuous stretching while adopting a thread-like shape nearly parallel to the shear direction. When the thread becomes very elongated, it is unstable with respect to the tendency of the interfacial tension to reduce its area. Small surface perturbations are magnified under the action of the interfacial tension and give rise to sinusoidal distortions (Rayleigh waves) leading to the break-up of the thread into a series of small droplets. The same mechanism is responsible for the break-up of a long thread immersed in a quiescent matrix.

The mathematical description of the break-up of a Newtonian fluid thread A in a quiescent Newtonian matrix B was given by Tomotika [2]. Initially, the thread of radius r_0 is subject to very small sinusoidal distortions of arbitrary wavelengths λ and equal amplitudes. The amplitude α of the distortions which have a wavelength greater than the thread circumference is assumed to grow exponentially with time:

$$\alpha = \alpha_0 \exp(qt) \tag{2}$$

where α_0 is the initial amplitude of the distortions. The growth rate q is given by:

$$q = \frac{\gamma_{12} \Omega(\chi, p)}{2\eta_m r_0} \tag{3}$$

with $\Omega(\chi, p)$ a complex function calculated from the original Tomotika theory, p the viscosity ratio and χ a dimensionless wavenumber defined as $\chi = 2\pi r_0/\lambda$. For a given viscosity ratio, there is one dominant wavelength λ_m at which $\Omega(\chi, p)$ and consequently the growth rate are maximal. Theoretically, this is the wavelength which causes the thread break-up. Nevertheless, if the initial distortions have different amplitudes the break-up can occur for wavelengths other than the theoretical one [3, 4].

Other mechanisms occur during the relaxation of an elongated thread at rest, such as retraction or 'end pinching' [5]. These mechanisms become predominant over Rayleigh instabilities when the aspect ratio of the thread is lower than 15–20.

Such phenomena as deformation and break-up in flow or at rest have been studied for many years for mixtures

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of isotropic polymers, since they are the basic mechanisms for structuring polymer blends (for a review see [6]). Similar structuring occurs also with systems containing liquid crystals. In polymer dispersed liquid crystal (PDLC) films made of a polymer containing liquid crystalline droplets [7] prepared from a polymer solution, the droplets will be elongated and broken during the manufacturing of the film. Similarly, when polymer blends with one component being a thermotropic polymer are prepared, drops are deformed and broken [8]. Despite the fact that a great number of studies have been published concerning the characterisation (in terms of rheological, mechanical or thermal properties) of such anisotropic polymer blends (for a review see [8]), there is no literature describing the basic mechanisms of drop dispersion. In addition, there is no report in the literature on the textures formed inside a deforming droplet. What is known are the different kinds of texture which can be present in quiescent small molecule nematic droplets at equilibrium. The most common one is the bipolar texture, shown schematically in figure 1.

The objective of this paper is to report depolarised optical observations of the break-up of a drop of a liquid crystalline solution of hydroxypropylcellulose (HPC) in water immersed in a matrix of an isotropic polymer, polydimethylsiloxane (PDMS).

2. Materials and techniques

The liquid crystalline solution was prepared using HPC from Aqualon (Klucel L) with a molecular weight of 150 000. The HPC powder, which was dried *in vacuo* at 70°C overnight prior to use, was mixed thoroughly with distilled water at room temperature to yield a solution of concentration 50% w/w HPC. The solution was then centrifuged at 5000 rpm for 5 hours to remove air bubbles. This solution is cholesteric at rest [9]. The HPC solution is a shear thinning material presenting a Newtonian plateau ($\eta = 1180$ Pa s) over a very limited shear rate range (lower than $9 \times 10^{-3}\,s^{-1}$) and a pseudo-Newtonian plateau in the range $0{\cdot}06$–$0{\cdot}2\,s^{-1}$. The existence of a second plateau is usual for lyotropic polymers. The first plateau was also found by Sigillio and Grizzuti [10] for a similar HPC solution.

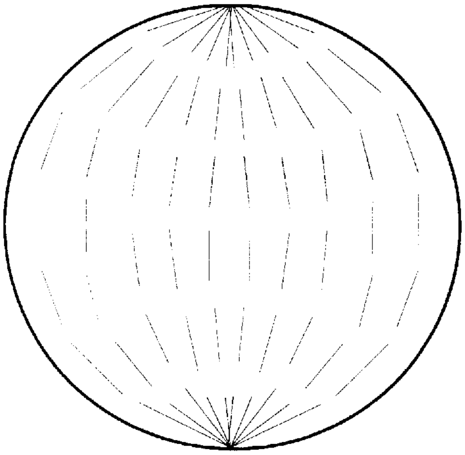


Figure 1. Schematic drawing of the director organisation in a bipolar nematic sphere.

The PDMS sample was a Rhodorsil silicone oil (type 47v600000) kindly provided by Rhône-Poulenc. It has a Newtonian viscosity of 570 Pa.s up to shear rates of about $1\,s^{-1}$.

The interfacial tension between the 50% HPC solution and the PDMS was measured in the rheo-optical system described below using the thread break-up method and was found to be $12{\cdot}2\,mN\,m^{-1}$ [11]. This method is based on the Tomotika theory and was successfully used for the measurement of the interfacial tension of polymer pairs [12].

The experiments were conducted in a rheo-optical system composed of three main parts:

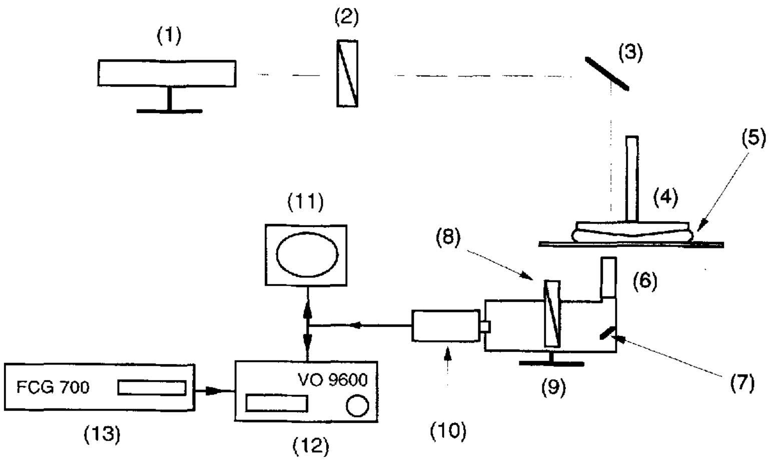
(1) an Instron 3250 constant shear rate rheometer;
(2) an optical system composed of transparent cone and plate tools through which the flow is visualised, and microscopy facilities including a lighting system, an optical train and an optical microscope;
(3) a video data acquisition system to record the optical microscopy images as a function of time.

A detailed description of the rheo-optical system can be found in [13]. A schematic representation is given in figure 2. All the observations in this study were performed using crossed polarizers. The optical axes of the polarizer and the analyser were parallel and perpendicular to the shear direction, respectively.

From an experimental point of view, the following procedure was used. A blend composed of the PDMS containing a few large drops (diameter about 1 mm) of HPC solution was introduced between the cone and the plate and subjected to a shear. Under the action of the shear, the large HPC drops were deformed in elongated threads. The flow was stopped when an isolated liquid thread of uniform diameter was obtained. The diameter of the thread depended on the diameter of the initial spherical drop, the shear rate and the total shear strain until the cessation of the flow [11]. Typically, we studied threads of diameter between 10 and 100 µm. The break-up of the thread was then recorded and analysed.

3. Results and discussion

At rest, before starting the flow, the HPC droplets are large, i.e. several hundred microns. Their texture is not well defined and many different defect arrangements can be found inside droplets.



(1) Light source, (2) Polariser, (3) Mirror, (4) Transparent Cone and Plate,
(5) Sample, (6) Objective lens, (7) Mirror, (8) Analyser, (9) Optical Microscope,
(10) Video Camera, (11) Monitor, (12) Video Tape Recorder,
(13) Frame Code Generator.

Figure 2. Schematic representation of the rheo-optical set-up.

Upon starting the flow, the HPC drop starts to elongate and adopt a thread-like shape of which the diameter decreases continuously with time. This continuous stretching is due to the shear rates used in this study (between 0·1 and $4\,s^{-1}$) and the large sizes of the initial drops which make the capillary number always greater than the critical value. It was found that keeping all the relevant parameters (viscosities of the matrix and the drop, interfacial tension) approximately the same, there is no difference between the deformation kinetics of the drop if it is isotropic (isotropic solution of HPC) or anisotropic [11]. After some time, and while the diameter of the thread is still uniform (before the development of Rayleigh instabilities during the flow), the flow is stopped. Very soon, if the previous shear rate exceeds $0{\cdot}5$–$0{\cdot}6\,s^{-1}$, a banded texture begins to develop. This is a sequence of dark and bright bands perpendicular to the thread direction (figure 3(*a*)). Such a texture is well known and appears after cessation of shear for most nematic and cholesteric liquid crystalline polymers [14]. It has also been reported to occur in LC polymer fibres. It is not surprising therefore to find it here. The spacing of the texture is about 6 µm. It does not depend on the thread diameter. This spacing is similar to the spacing that would appear after stopping a shear in a solution of HPC of the same concentration and molecular weight. Such a result, showing that the spacing of a banded texture is independent of the type of flow (shear or elongation) which induced it, was reported by Peuvrel and Navard some years ago [15].

As for the case of thin isotropic threads, surface instabilities develop (figures 3(*b–i*)). There is no major influence of the anisotropic character of the thread or the presence of the band texture. The instabilities develop as if the system was isotropic. The amplitude of the distortions grows exponentially with time as predicted by Tomotika theory for Newtonian isotropic fluids. The distortions which lead to the break-up can have various wavelengths in different threads or in different places for the same thread, which do not always correspond to theoretical. Nevertheless, this phenomenon can occur for isotropic threads as well [3, 4] and is not necessarily due to the anisotropic character of the thread. What is different however is the way the texture will evolve.

The first stage of the Rayleigh instability is the diminishing of the thread diameter close to the location of the wave minimum. It can be seen that this occurs by the dark bands 'flowing' into the thick parts of the thread (wave maxima). When the diameter of the thinning part begins to be smaller than about 70% of the initial diameter, no band texture can be seen there (figure 3(*c*)). At the same time this region becomes darker and darker, an indication that the liquid crystal becomes well oriented in the thread direction. These phenomena occur nearly at the same time that the thinner zone becomes flat and the distortion is no longer sinusoidal. This deviation from the Tomotika theory has often been reported in the literature and is mainly due to the viscoelastic character of the threads [16]. However, it seems that it begins to occur particularly early in our system compared with other isotropic threads [11]. The band texture persists only in the thicker zones. When the thick parts begin to adopt a more 'spherical' shape, their appearance changes and the banded texture slowly disappears, staying only in the thickest parts, near the centre (figures 3(*e–g*)).

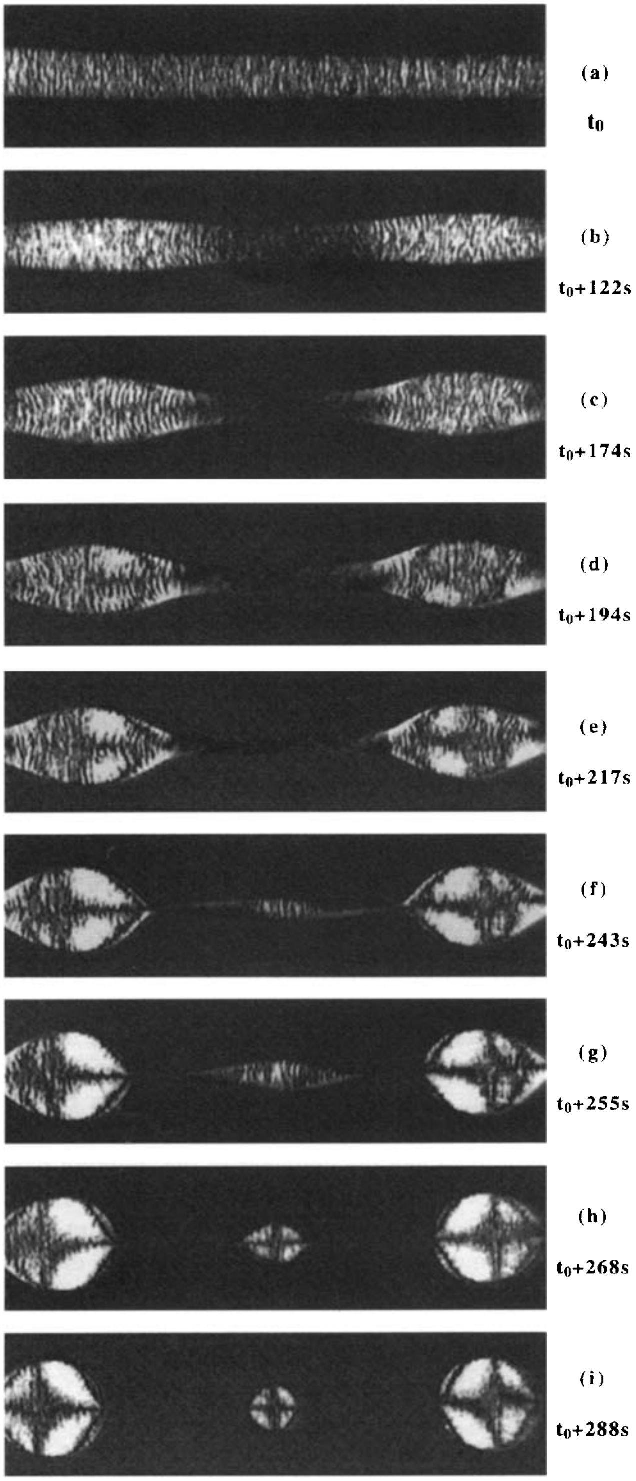


Figure 3. Break-up with time of a thread of a 50% HPC aqueous solution in a PDMS matrix at rest as observed between crossed polarisers. The polarisers are parallel and perpendicular to the thread direction; the initial diameter of the thread is 50 μm.

The thin zone will then break at its two extremities (figure 3(*g*)). Just before and after, the texture in the thick zones (now slightly elongated drops) is very clear, with three dark lines at each extremity, where a few remnants of a banded texture can be seen. The thin zone then retracts (figures 3(*g*–*i*)), and a banded texture appears again very clearly. It quickly becomes a sphere, called a satellite drop, under the action of the interfacial tension (figure 3(*i*)). The thick elongated drops then assume a spherical shape. The texture of the main and satellite drops is the same, i.e. bipolar. The two poles are in the direction of the previous thread. There is thus a continuity between the director arrangement in the thread (banded texture) and in the drops (bipolar texture). It is interesting to note that a bipolar structure is also obtained in the drops resulting from the 'end pinching' mechanism (pinch-off of the rounded ends of the thread).

In the case of the threads formed using a very low shear rate (lower than $\approx 0{\cdot}5\,\mathrm{s}^{-1}$) the banded texture does not occur all along the thread after the cessation of the flow. It starts to occur only when the capillary instabilities are sufficiently developed (for example when the distortions have an amplitude similar to that of the thread in figure 3(*b*)) and only at locations close to the wave maxima. According to experiments performed by Maffetone *et al.* with a similar HPC solution [17], a banded texture forms very rapidly in a sheared sample when a second shear, orthogonal to the first, is applied. Even in cases where the first deformation by itself was insufficient to generate the texture, the second deformation effectively produced the band texture. Furthermore, when the authors allowed more time to elapse before starting the second motion, a smaller deformation was required for the appearance of the banded texture. We can assume that there is some equivalence between the band formation in the threads and the case studied in [17]. In our case, the second motion is the one which appears in the growing wave maxima, orthogonal to the former shear direction. The subsequent shape and texture evolution in these threads is otherwise the same as for those previously described.

One possible explanation for the transformation mechanism of the banded texture of the thread to the bipolar texture of the thread to the bipolar texture of the drops is the following. It is known that after a shear, a banded texture originates from a pseudo-sinusoidal distortion of the director along the previous flow direction [9]. To translate this for a thread means that a director arrangement as shown in figure 4(*a*) must be achieved. To render the picture clear, not all the orientations are represented in the figure. The pseudo-sinusoidal arrangement of the director in the banded texture is schematically drawn as a zig-zag pattern. One has to

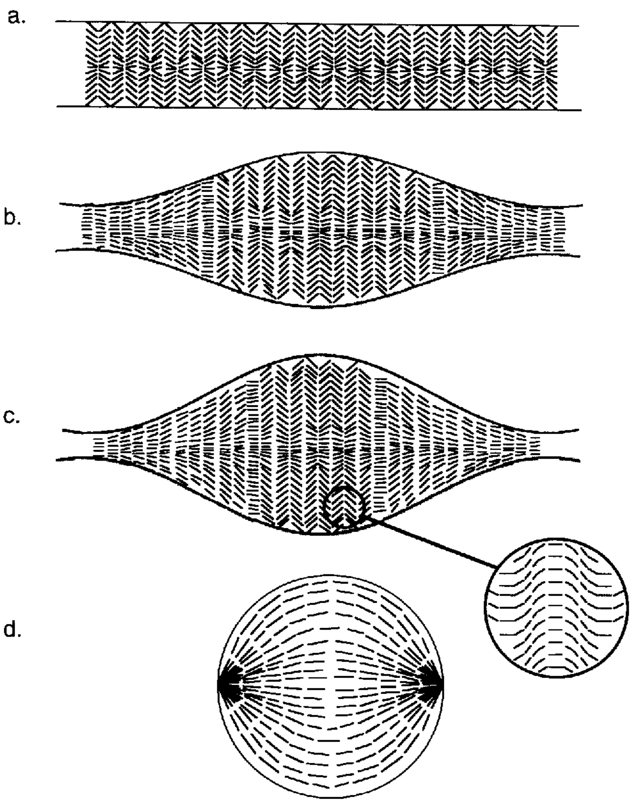


Figure 4. Schematic drawing of a possible mechanism leading to the formation of bipolar structure inside the droplets. The short lines represent the director organisation; the banded texture has a pseudo-sinusoidal path which, for clarity of the picture is schematically represented as a zig-zag.

imagine, however, that the location between two opposite orientations in the zig-zag involves an orientation parallel to the thread axis, as shown in the inset (figure 4(*c*)). The change from a banded texture in the thread to a bipolar texture in the resulting drops is then natural, since it does not require any major director reorganisation, as illustrated in the sequence of figures 4(*b*–*d*). The satellite drop acquires the same structure since a banded texture is formed during the retraction. It must be stated that this is the first reported observation that such a texture can be formed under retraction.

4. Conclusion

This is the first reported observation of the textures formed during and after break-up of a liquid crystalline polymer thread immersed in a quiescent isotropic matrix. A banded texture similar to that observed in neat liquid crystalline polymers occurs during thread break-up. The evolution of this texture depends on the evolving shape of the thread which is driven by the development of the interfacial tension instabilities. The spherical drops created by the break-up have a bipolar texture similar to that observed in small molecule nematic liquids. The transformation of one texture to the other is probably the result of the most energetically favourable director reorganisation. This study adds some insight into the structuring dynamics of liquid crystalline polymer blends. It seems that the main features of the shape evolution of liquid crystalline polymer threads at rest are similar to those of conventional polymer threads. The same conclusion is drawn from a study of the shape evolution of liquid crystalline drops during flow [11].

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