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Shear Flow Rheology of Liquid Crystalline Polymers

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The rheological behavior of liquid crystalline polymers in shear flows is reviewed with the aim of pointing out the most important features which characterize tumbling. The latter expression refers to the fact that, in some nematics, the director (i.e., the average molecular orientation) is not stable in shear flows unless some other stabilizing field prevails. Many liquid crystalline polymers seem to be tumbling nematics, so that the molecular orientation achieved in a shear flow may be difficult to control.

KEY WORDS Liquid crystalline polymers (LCPs), tumbling nematics, shear flows

INTRODUCTION

One of the attractive features of liquid crystalline polymers (LCPs) is their potential ability to easily become oriented in a flow process, a property which can be exploited to fabricate articles with exceptional properties. The easy orientability is related to the fact that molecular orientation is a collective or cooperative property in a liquid crystalline nematic phase so that the applied field is not counteracted by thermal motion. The average molecular orientation at a material point is a macroscopic quantity described by a unit vector \mathbf{n} called the director.

Good control of the molecular orientation can remain a problem, however, for at least two reasons. One of them is the presence of defects, or disclinations, of the liquid crystalline structure, which are particularly long lived and difficult to eliminate in polymeric systems. Because of these defects, the director field is usually very complex, and the LCP sample is called a polydomain. The second reason is the tumbling nature of many LCPs in shear flows. It should be recalled that a nematic phase behaves in one of two ways when subjected to shear. In so-called flow-orienting nematics, the director sets itself at a stable orientation in the shear plane, forming a small angle (the Leslie angle) with the shear direction. Flow-orienting nematics are the most common occurrence in small molecule nematics. On the contrary, polymeric nematics seem to be tumbling nematics more often than not. In such a case, no "spontaneous" stable orientation of the director exists; as long as no other counteraction arises, the director keeps tumbling indefinitely in the shear field.

This paper briefly reviews some of the ways by which LCPs can be characterized rheologically, with special emphasis on how tumbling can be recognized. We will also discuss why tumbling is likely to generate many defects, and how the defect density is expected to vary with shear rate. Although the problem of predicting molecular orientations in LCPs remains open, some tentative conclusions will be drawn.

NEGATIVE NORMAL STRESSES

The negative normal stress effect is, historically at least, the most important rheological effect which characterizes tumbling LCPs. The experimental evidence was first collected by Kiss and Porter [1] and, subsequently, by many others on a variety of systems (a recent review can be found, for example, in reference 2). The effect consists of the following: If the shear rate $\dot{\gamma}$ is progressively increased starting from low shear rates, the first normal stress difference N_1 (under steady-state conditions) is first found to be positive (meaning that the confining platens of the shear device are being pushed apart), and to increase with increasing $\dot{\gamma}$. N_1 then goes through a maximum and drops toward a negative minimum (meaning that the platens are now pulled one toward the other). Finally, N_1 rises again to positive values, and keeps increasing thereafter. Such a complex behavior is drastically different from that of ordinary polymers, for which N_1 is positive without exceptions, and always grows with increasing $\dot{\gamma}$.

The explanation of the negative normal stress effect was found [3, 4, 5] much after its discovery, and it demonstrated that LCPs showing this effect must be tumbling nematics. The explanation is as follows; First, consider an isotropic phase of rod-like polymers (e.g., a dilute solution). The orientational distribution of these rods, which is isotropic at equilibrium (it can be visualized as a sphere), becomes modified by the shear flow in such a way that orientations which project in the shear plane between 0° and 45° from the shear direction are favored over the others. (More precisely we should say that the tensor of the second order moments of the distribution, which can be represented by a sphere under equilibrium conditions, now becomes an ellipsoid whose major axis lays between 0° and 45° in the shear plane.) The entropic (or viscoelastic) stress is directly related to this orientational "deformation," that is, to the "difference" between the existing ellipsoid and the equilibrium sphere. In particular, N_1 is representative of such a difference along the shear and the gradient directions. From the geometrical representation just recalled, it is apparent that N_1 must always be positive; in particular, because the angle moves from 45° toward 0° as the shear rate increases, N_1 keeps growing monotonically with increasing $\dot{\gamma}$ (the ellipsoid becomes more and more elongated), to saturate when all rods become virtually aligned to the shear direction.

Much different is the situation in a nematic phase (e.g., in a concentrated solution of rod-like polymers). Because the tendency of concentrated rods to align parallel to each other prevails over thermal randomization, the orientational distribution already is anisotropic at equilibrium. The second-moment tensor of the equilibrium orientational distribution is a prolate ellipsoid, axially, symmetric

about the director \mathbf{n} . To describe the effect of a shear flow, we must now distinguish flow-aligning nematics from tumbling ones. In the former case, the primary effect of flow is that of aligning \mathbf{n} (and the whole orientational ellipsoid with it) at a small angle to the shear direction. At large enough shear rates, a second effect of the flow is that the ellipsoid becomes even more prolate than at equilibrium, as the rod-like molecules align more and more to the shear direction. It is apparent that the difference between the existing ellipsoid and the equilibrium one determines a positive value of N_1 also in this case.

Finally consider a tumbling nematic. In such a case, the director \mathbf{n} (together with the associated ellipsoid) keeps rotating in the shear field indefinitely. At a sufficiently large shear rate, the ellipsoid gets deformed here too but, because of the rotational motion, the deformation is in the direction of making the ellipsoid "less" prolate than at equilibrium. In other words, a sufficiently fast tumbling motion randomizes the rod-like molecules, which therefore approach a spherically symmetric distribution. The difference with respect to the equilibrium ellipsoid now is in the opposite direction than in the cases previously considered; there follows that N_1 is negative in these conditions. Notice how unique is the situation of tumbling nematics. In normal cases, flow has an orienting effect on polymer molecules, that is, it works toward a higher degree of order. On the contrary, flow generates less orientational order in this case.

Description of the tumbling case is not concluded here, however. Indeed, we know from experiments that, at even higher shear rates, N_1 becomes positive again. This will occur when the strength of the flow has become so large that tumbling is suppressed altogether, and the molecules increasingly align in the shear direction. In other words, at some critical value of the shear rate, a transition takes place between tumbling behavior and flow-aligning. The detailed calculations [3, 4, 5] show that this dynamic transition occurs, roughly midway, in the range of shear rates where N_1 is negative. After the transition, the ellipsoid of the molecular orientations becomes stationary in time; right at the transition, its shape still is blunter than the equilibrium shape (hence the negative N_1), then becomes more elongated as $\dot{\gamma}$ increases, eventually crossing the equilibrium shape ($N_1 = 0$), and finally elongates more than at equilibrium for even higher shear rates (N_1 positive thereafter).

The synthetic conclusion is that negative values of N_1 unequivocally imply that the nematic is of the tumbling type. The range of shear rates where N_1 is negative marks the dynamic transition from tumbling (at low and moderately-high shear rates) to flow-aligning (at very-high shear rates). It is worth noting that the opposite evidence, that is, the absence of negative values of N_1 in the range of shear rates accessible to measurement does not imply that the LCP under scrutiny is of the flow-aligning category and tumbling is excluded. Unfortunately, the range of shear rates where normal stresses can be measured (in rotational cone-and-plate devices) is much more limited than that for viscosity measurement (for which capillary instruments are used in the high shear rate range). Thus the absence of negative normal stresses in the accessible range does not exclude their occurrence at higher shear rates. In some systems, also in one thermotropic case, [6] the indirect evidence points in this direction.

TIME-DEPENDENT BEHAVIOR

A different way of recognizing the tumbling character of LCPs is through their time-dependent rheological response. A peculiar time-dependent behavior of LCPs is revealed through step changes in shear rate, either step-up or step-down, [7] or flow-reversal [8] experiments. A typical response in all these cases is a sequence of damped oscillations, in both the shear stress and the normal stresses, before the new steady state is achieved. Because these experiments can only be made in a rotational apparatus, the available range of shear rates is limited to relatively low values of $\dot{\gamma}$.

An interpretation of these results was offered by Burghardt and Fuller [9] who developed a calculation based on Leslie-Ericksen theory of nematodynamics (compare, for example, reference 10), a theory originally proposed for small molecule nematics and thus perhaps appropriate also for LCPs at low enough shear rates. The theory embodies both the anisotropy of the dissipation (i.e., the viscosity depends on the director orientation with respect to the velocity gradient) and the Frank elasticity. The latter accounts for orientational distortions (spatial gradients of \mathbf{n}) of the three basic types (splay, twist, bend). By applying this theory to a shear start-up, Burghardt and Fuller [9] were able to show that for a flow-aligning nematic the transient response would not contain oscillations whereas a sequence of damped oscillations is characteristic of the tumbling case. These oscillations correspond to the fact that, because of the tumbling nature of the nematic, the director field "winds up" in space (in the direction of the velocity gradient). Winding up generates an elastic torque on the director which opposes tumbling so that, eventually, tumbling is arrested and the system reaches a steady state. For future reference, Burghardt and Fuller [9] find good agreement with the experiments if in the calculations not the sample thickness is used, but rather a much smaller (and shear-rate dependent) quantity. We shall return to this aspect when discussing defects.

Another rheological experiment in this category is that of strain recovery, determining the shear deformation γ which is elastically recovered when the shear stress σ of a steady flow is suddenly removed. Experiments of this kind on some LCPs show large values of γ ; these appear incompatible with a flow-aligning assumption while they are quite acceptable in the tumbling case [11, 12]. It is the Frank elasticity accumulated in the "windings" of the director field (mentioned above) which would relax in the recovery experiment.

Summing up, LCPs can also be characterized rheologically in time-dependent situations. In particular, tumbling seems to reveal itself through repeated oscillations when the shear rate is changed, and through large values of strain recovery when the shear stress is removed. It is worth emphasizing that, although these experiments again are limited to low or moderate values of $\dot{\gamma}$, here the effects are expected not to be restricted to a specific range (differently from the negative normal stress effect), and are in fact typical of the values of shear rate which can be accessed experimentally. Rather, a limitation may be represented by the fact that reliable measurements of time-dependent responses require a more sophisticated instrumentation.

OPTICAL OBSERVATIONS

Another way of characterizing the rheological behavior of LCPs is through optical observations of a flowing sample. Indeed the new expression "rheo-optics," which became popular some years ago, [13] now includes many different experiments on either flowing or relaxing samples such as polarized microscopy, light scattering, dichroism, conoscopy, and the like. Particularly important in providing a direct evidence of tumbling in LCPs were the experiments of Srinivasarao and Berry, [14] and Burghardt and Fuller, [15] who carefully prepared "monodomain" samples uniformly oriented parallel to the confining plates (quite a painstaking operation), and then observed how the director would start rotating when shear (along the director) was switched on. It was found that \mathbf{n} started rotating "downward," rather than upward to approach the Leslie angle, thus demonstrating the tumbling character of the systems investigated.

With the exception of these special cases, the rheo-optical experiments (just like the rheological ones) are made on polydomain samples where many defects are present. In fact, these experiments aim precisely at investigating the structure of the polydomain, and its evolution as a consequence of either a flow or a relaxation process. Elements of the polydomain structure are: defect density, defect morphology, defect type, as well as enough descriptors of the average molecular orientation, that is, of the \mathbf{n} -field. It is here recalled that the defects of a nematic phase are point- or, more frequently, line-disclinations where the \mathbf{n} -field is singular (i.e., where the director is not defined). The molecular structure of the defect "cores" is not known in detail, but it is expected that the orientational order of the molecules in these cores is less than in the surrounding nematic, that is, that defect cores are closer to isotropy.

On a local basis, a defect cannot be eliminated (nor created) because of the fixed topology of the surrounding \mathbf{n} -field. However, processes occurring on some larger scale can destroy or create defects. For example, defect lines forming loops (as is usually the case) can shrink and vanish; two defects of a different type having complementary topologies can coalesce and disappear, and so forth. Such events are believed (and sometimes observed) to take place in relaxing samples where, in fact, the defect density decreases and the texture becomes more coarse. The reverse process can be envisaged to occur in a flowing sample where, unfortunately, the observation of the elementary mechanisms becomes much more difficult if not impossible. Determination of broader aspects of defect kinetics, such as changes in the defect density (or texture "refining") can, however, be made in flowing samples as well, and have, in fact, been made also in LCPs [16, 17].

Before touching on some of these results, it is worth mentioning that tumbling in particular is widely believed to be a very effective source of defects. Indeed, it seems unlikely that actual tumbling can occur "in phase" throughout a macroscopic sample; moreover, the winding up of the director will generate so much elastic strain (in the sense of Frank elasticity) that defect nucleation can become energetically convenient. Various indications, both experimental [17] and theoretical [2, 18] point to the conclusion that, in steady shear flows of a tumbling nematic, a well-defined defect density can be associated to any given shear rate. The theoretic-

cal viewpoint is that defect cores act as internal anchoring walls for the director so that tumbling will be arrested if the concentration of such "walls" is large enough. This viewpoint is somewhat supported by the findings of Burghardt and Fuller [9] on the smallness of the characteristic length, and on its dependence on shear rate. The characteristic dimension in the problem would be the distance between neighboring defects, rather than the sample thickness. The characteristic length a based on defect density is expected to decrease with increasing shear rate, [19] in agreement with the experimental observations of texture refining [17]. Recent calculations [2, 18] predict that, although a decreases with increasing $\dot{\gamma}$ in the intermediate range of shear rates, it should become a constant at very small values of $\dot{\gamma}$.

Textures and associated characteristic lengths in the polydomain sample are typically investigated by microscopy or by light scattering. In our laboratory, we have been using very simple experiments of bright-field microscopy, which exploit the scattering property of the defects. If the sample is transparent enough, defects will appear very clearly as dark objects (points or lines) against a bright background. One advantage of this simple technique [20] is that the flowing sample can be scanned not only along its larger dimensions (length and width) but also across the thickness by focusing at different depths. Phenomena can be observed directly either while they occur or can be recorded and later analyzed. In the experiments reported in reference 20, the LCP sample (an aqueous solution of hydroxypropylcellulose 50% by weight) flows in a channel whose thickness is of the order of 1 mm while the rest of the geometry can be easily varied to simulate flow in a mold. Figure 1 shows a typical result of rectangular channel flow. In particular, Figure 1a shows the texture which is observed close to the wall where the shear rate is maximum; a high density of dark lines is apparent, parallel to the shear direction. Figure 1b, however, shows the situation prevailing close to the midplane of the channel where the shear rate is very small; the texture is much coarser, and "grainy" in appearance. The same grainy structure appears at all shear rates which are low enough. The photograph in Figure 2 was obtained in the converging flow upstream of a constriction, where there is a combination of shear and elongation. Here again the dark lines appear to mark the streamlines. Of course, the director field remains unknown and is probably very complex.

Finally, information about the \mathbf{n} -field is typically obtained through techniques which make use of polarized light. Particularly noteworthy in this regard are the works of Hongladarom et al. [21, 22] who use a spectroscopic birefringence technique; the beam enters the sheared sample perpendicular to the confining walls (i.e., along the direction of the velocity gradient) so that the measured birefringence Δn is indicative of the optical anisotropy between the direction of shear and the third (or neutral) direction. Their results show that, throughout the intermediate shear rate range, the value of Δn remains fixed at a value which is roughly 50% of the maximum (the maximum value is measured in a well-oriented monodomain), then rises to a value close to the maximum (but not quite) at very high shear rates. This result is consistent with the theory, previously mentioned, which predicts the dynamic transition from tumbling to flow-aligning at high shear rates. Much more surprising were the results obtained after switching off the flow. In the initial part of the relaxation process, the birefringence was found to increase

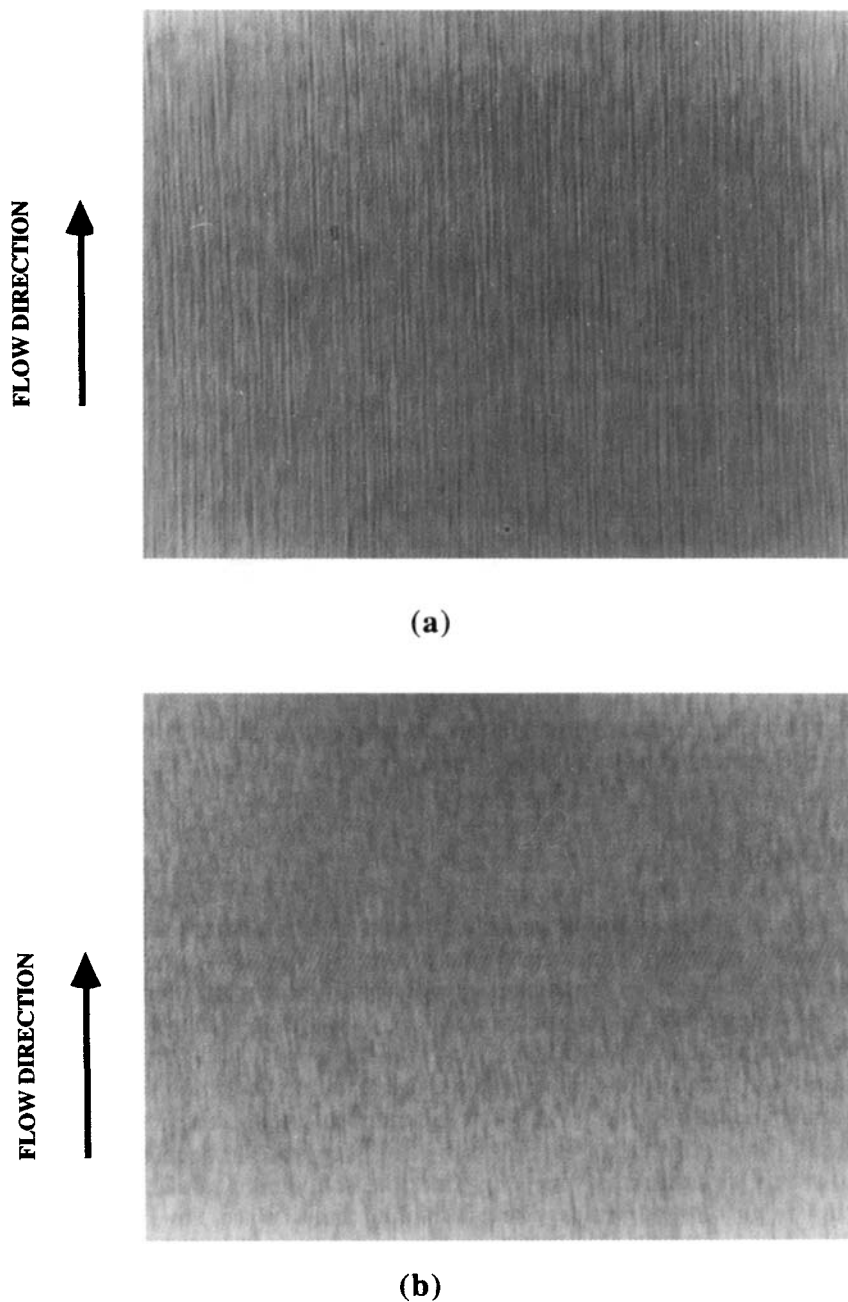


FIGURE 1 Microscopic observations (total magnification $\times 200$) of a lyotropic LCP (hydroxypropylcellulose in water) flowing in a rectangular channel: a) Texture observed by focusing on a plane very close to the confining wall; b) Texture observed close to the midplane, where the shear rate is very small. The arrow in the figure indicates flow direction. Gradient direction is orthogonal to the plate.



FIGURE 2 The same HPC solution as in Figure 1 entering a constriction in the channel. The pattern shown does not exhibit significant changes along the thickness. Flow and gradient directions as in Figure 1.

to the maximum value; only much later the orientation decayed toward the typical overall randomness of a static polydomain.

CONCLUSION

As anticipated in the introduction, our present understanding of LCP rheology is only partly satisfactory. The tumbling nature of many LCPs seems to explain some peculiar effects, yet other important aspects of this complex phenomenology still wait to be interpreted. As regards molecular orientations in steady shear flows, we can tentatively conclude the following:

At very high shear rates, that is, above the dynamic transition from tumbling to flow-aligning behavior, good molecular orientation is expected and, in fact, measured [21]. The orientation is not fully 100%, probably because of “trapped” defects, which would take a very long time to disappear (if at all).

In the range of shear rates where tumbling takes place the situation is more complex, and molecular orientation is certainly incomplete. The data of Hongladarom et al. [21] indicate that the average orientation gives rise to a birefringence which is 50% of the maximum, independently of shear rate. At the same time, we know from both experiments and theory that the domain size a decreases with increasing $\dot{\gamma}$. Putting these two pieces of information together one would conclude that, although the domain size changes, the director field remains self-similar. In other words, the pattern of molecular orientations remains the same by changing the shear rate, though it develops over spatial distances which are shear rate dependent. The details of the molecular orientation field, however,

remain obscure. Theoretical results [2, 23] indicate that the director should vary within the plane formed by the shear and neutral directions, while orientations along the velocity gradients are avoided, the reason being that the viscous torque on the director would be much larger in the latter case. One further indication is that the director field should favor twist distortions over bend and splay which, especially in the polymeric case, are much more energetically expensive. This view is consistent also with recent electron micrographs of a thermotropic LCP sample, quenched immediately after shear [6].

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