# Rheology of liquid crystalline polymers

G. Marrucci

Dipartimento di Ingegneria Chimica, Università di Napoli, Italy

Abstract - Concepts which may be used in interpreting the complex rheology of liquid crystalline polymers are reviewed. Some of them are taken from the nematodynamics of low molecular weight liquid crystals as described by the Leslie-Ericksen theory, others are intrinsic to the viscoelasticity of ordinary polymers. Tentatively, these concepts are used to construct an explanation of the band texture which is frequently observed when liquid crystalline polymers are sheared, and to interpret the complex behavior of normal stresses which exhibit both positive and negative values.

#### INTRODUCTION

The rheology of liquid crystalline polymers appears to be exceptionally complex. The phenomena observed during and/or after flow are extremely diversified and generally different from what is found in either ordinary polymeric liquids or low molecular weight (LMW) liquid crystals. Some understanding of these phenomena seems necessary, however, especially for what concerns molecular orientations. In fact, polymeric articles are manufactured via flow processes and the materials properties in the solid state are strongly influenced by flow induced molecular orientations.

Limiting our attention to nematics only (possibly, to cholesterics), we may expect that in general a flow has the following effects:

1 - The distribution of molecular orientations about the nematic axis (director) is altered.2 - The director itself is affected by the flow.

The first effect is due to the polymeric nature and the consequent (relatively) large values of relaxation times. In LMW liquid crystals, the flow is never strong enough to compete with thermal motions and the equilibrium orientational distribution is preserved. In polymers, conversely, whether liquid crystalline or not, relaxation rates may be smaller than shear rates and the orientational distribution is therefore altered. In ordinary polymeric liquids, this effect (in the sense of deviation from isotropy, of course) is the only one which is present and yet the rheology is already complex. In particular, elastic phenomena are generated such as normal stresses in a simple shear flow. These, however, are always positive in ordinary polymers.

The second effect is the only one that is present in LMW liquid crystals and, by itself, also gives rise to a complex rheology. The interplay between director and velocity gradient generates a viscous stress which is characterized (at the phenomenological level) by five independent viscosities, known as Leslie coefficients. Furthermore, the director is generally non-uniform in space. The spacial distortion of the director generates elastic stresses, named after Frank or Ericksen, which of course bear no relationship with polymer elasticity.

Whenever the director varies considerably throughout the sample, with the possible occurrence of discontinuities (defects or disclinations), we speak of a polydomain structure, a domain being a region where the director is approximately uniform. Polydomains appear to be the rule rather than the exception in polymeric liquid crystals, much more so than in the LMW case. Flow processes are found to alter the structure of polydomains in more than one possible way. There is evidence that the flow may increase the defects or discontinuities (ref. 1) as well as decrease them to form a monodomain (ref. 2). There is also an accumulating evidence about the formation, during or soon after a shear flow, of a peculiar texture made up of bands perpendicular to the shear direction (refs 3-5). The band texture

appears to be linked to the occurrence of another anomalous rheological phenomenon, i.e., of negative normal stresses (ref. 6 & 7).

In what follows, some concepts and results, which are considered relevant toward an understanding of these complex phenomena, are reviewed. The attention is focused in particular on the above mentioned band texture and negative normal stresses. To use the words of Kiss and Porter (ref. 7), "we are very far from unraveling the puzzle", not to mention the possibility of formulating a comprehensive quantitative theory. Thus, concepts will be drawn mainly from what is known for LMW liquid crystals, from theoretical results for rodlike polymers, and from a few experimental results on linear properties recently obtained by Meyer et al.(ref.8).

#### LESLIE COEFFICIENTS IN POLYMERIC NEMATICS

Two of the Leslie coefficients are of special importance in simple shear flow, because they determine whether the director has the tendency to align at a fixed direction or else wants to rotate indefinitely in the shear field. These coefficients are  $\alpha_2$  and  $\alpha_3$ , and their sign determines which alternative will apply. Since  $\alpha_2$  is always negative (with the possible exception of disc-like molecules (ref. 9)), what counts is the sign of  $\alpha_3$ . In most LMW nematics  $\alpha_3$  is also negative. In such a case, the director wants to align at an angle  $\phi_0$  with the shear direction (Fig. 1) given by

$$\cos(2\phi_0) = (\alpha_2 - \alpha_3)/(\alpha_2 + \alpha_3) \tag{1}$$

Usually  $|\alpha_3|$  is much smaller than  $|\alpha_2|$ . Thus, the direction determined by  $\phi_0$  is very close to the shear direction.



Fig. 1. The orientation of the director in a shear flow ( $\alpha_q < 0$ )

Words such as "wants" or "has the tendency" are used because the effect of flow may be effectively counteracted by the Frank elasticity which arises from distortions of the director field. Strong anchoring conditions of the director at the walls and/or defects oppose the aligning tendency due to shear. A compromise is therefore reached which, however, is more displaced toward alignment as the shear rate increases.

A completely different situation is present in nematics which have a positive  $\alpha_3$ . This case, though less frequently, is also encountered in LMW nematics. A fixed direction toward which the director wants to move no longer exists: aside from effects due to Frank elasticity (see next section), the director keeps tumbling indefinitely. By ignoring elasticity, the tumbling frequency may be linked to the shear rate in a simple way. Calling  $\Phi$  the rotation angle as depicted in Fig. 2, the condition of zero torque gives the equation

$$d\Phi/dt = \gamma \left( |\alpha_2| \cos^2 \Phi + \alpha_3 \sin^2 \Phi \right) / (|\alpha_2| + \alpha_3)$$
 (2)

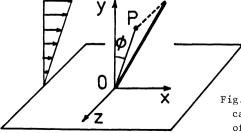


Fig. 2. Definition of  $\Phi$  in the tumbling case ( $\alpha_3 > 0$ ). OP is the projection of the director in the x,y plane.

where  $\gamma$  is the shear rate. By taking  $\Phi = 0$  at t = 0, Eq. 2 is integrated as

$$(\alpha_3/|\alpha_2|)^{1/2} \tan \Phi = \tan \left\{ \frac{\gamma t}{(|\alpha_2|/\alpha_3)^{1/2} + (\alpha_3/|\alpha_2|)^{1/2}} \right\}$$
 (3)

The tumbling period T is given by

$$\gamma T = \pi \{ (|\alpha_2|/\alpha_3)^{1/2} + (\alpha_3/|\alpha_2|)^{1/2} \} \cong \pi (|\alpha_2|/\alpha_3)^{1/2}$$
 (4)

where the latter equality holds in the case  $\alpha_3 << |\alpha_2|$ .

It should be noted that indefinite tumbling of the director does not imply that the shear flow has no orientational effect. If the inequality  $\alpha_3 << |\alpha_2|$  holds true, Eq. 3 shows that the time spent by the director at values of  $\Phi$  close to  $\pi/2$  constitutes the <u>largest part</u> of the rotation period. Thus, the shear orients the nematic axis along some direction of the <u>shear plane</u> (the x,z plane in Fig. 2), though periodically the director "jumps off" that plane and rapidly performs a 180° rotation to "settle down" again in the plane of shear.

Notice that the shear plane rather than the shear direction has been mentioned above because, in fact, the other polar angle of the director remains undetermined. Figure 3 shows possible trajectories of the director over the unit sphere in a representation used by Carlsson (ref. 10). The trajectories are closed curves over the sphere, parametric in the magnitude of the angle (called  $\theta_0$ ) that the director makes with the shear direction when crossing the plane of shear. The flow per se has no influence on  $\theta_0$ , which is therefore maintained indefinitely.

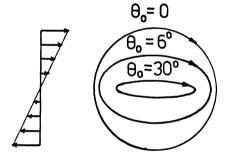


Fig. 3. Unit sphere representation of director trajectories.  $\alpha_3/|\alpha_2| = 0.01$ 

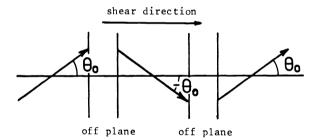


Fig. 4. Schematic of the tumbling process as observed perpendicularly to shear planes.

Figure 4 depicts schematically what would be observed by looking perpendicularly to the plane of shear. Moving along the shear direction, the director maintains the angle  $\theta_0$  while staying close to the plane of shear; it then jumps off the plane, makes half a turn and returns to the plane of shear with the orientation  $-\theta_0$ . At the next jump, it goes back to  $\theta_0$ , and so on indefinitely.

Which alternative applies to polymeric nematics, orientation along  $\phi_0$  (as given by Eq. 1) or tumbling? An answer to this question may be found, at least temporarily, in the theories developed for rodlike polymers. Following an approach suggested by Doi (ref. 11) and using a decoupling approximation, Marrucci (ref. 12) calculated the Leslie coefficients, obtaining in particular:  $\alpha_2$  < 0 ,  $\alpha_3$  < 0 ,  $|\alpha_3|$  <<  $|\alpha_2|$  . Later, however, Semenov (ref. 13) and Kuzuu and Doi (ref. 14) succeeded in removing the decoupling approximation and, though confirming the previous result for most  $\alpha_i$ 's, obtained instead:  $\alpha_3 > 0$  ,  $\alpha_3 << |\alpha_2|$ . Thus, as regards nematics of rodlike polymers, the answer seems to be that they are of the tumbling type. Experiments on a racemic mixture of PBG, a semi-rigid polymer, indicate the results (in poise)  $|\alpha_2|$  = 34.8 ,  $|\alpha_3|$  = 0.16 (ref. 8). Although  $\alpha_3$  appears to be negative in this case, its magnitude is so much smaller than  $|lpha_2|$  that it is not unreasonable to expect that even a weak departure from linearity might induce tumbling in this system as well. On the other hand, it is well known that ordinary polymers always rotate in a shear field. In the following discussion, the assumption will be made that tumbling is the most likely occurrence in liquid crystalline polymers. Whether this is indeed the case cannot be assessed at this time.

## THE INFLUENCE OF FRANK ELASTICITY

The discussion in the previous section did not include the effect of elasticity arising from distortions. As is well known (see, e.g., ref. 15), whenever the director  $\underline{n}$  is non-uniform in space, an elastic energy is present, given by

$$E = \frac{1}{2} K_1 (\operatorname{div} n)^2 + \frac{1}{2} K_2 (n \cdot \operatorname{curl} n)^2 + \frac{1}{2} K_3 (n \times \operatorname{curl} n)^2$$
 (5)

where  $K_1$  ,  $K_2$  ,  $K_3$  are constants having the dimension of a force.

In the absence of defects, the combined effects of flow and elasticity in LMW nematics is described by the Leslie-Ericksen theory. Solutions of the equations are found in some simple cases. For example, in the shear flow of a negative- $\alpha_3$  nematic, it is found that, at large shear stresses  $\sigma$ , the director is everywhere aligned along  $\phi_0$  except in a boundary layer close to the walls, the thickness of this layer being

$$\delta = (\kappa/\sigma)^{1/2} \tag{6}$$

where K is some appropriate combination of the elastic constants.

The same problem in the case of a positive  $\alpha_3$  is already much more complex. Under certain conditions, a stationary solution may exist (no tumbling). This solution was studied in detail by Carlsson (ref. 16), and its stability by Högfors (ref. 17). They also discuss previous results by Pieransky and Guyon (ref. 18) and by Cladis and Torza (ref. 19). In the stationary solution, the director does not rotate in time because of a balance between the torque due to shear and that due to Frank elasticity. Rather, the director varies along the direction perpendicular to the shear planes, sometimes performing several turns. With increasing  $\gamma$ , the number of "windings" of the director increases discontinuously.

These solutions of the Leslie-Ericksen equations, though very important in interpreting the results of carefully performed experiments in LMW nematics, appear to be of limited use in the case at hand. For one thing, because the presence of defects makes the director field extremely complex from the very start. Secondly, because the defect dynamics in a flow field is unknown, even in principle. Finally, because the polymeric nature per se might add effects not included in a linear theory.

As regards the second point, i.e., the effect of flow on defects, it is generally observed that flow drags disclination lines as if they were elastic strings. Although the elasticity of these strings can again be related, at least approximately, to Frank elasticity (ref. 15), other features remain unknown. For example, we do not know whether the fluid goes through the defects or around them, or both. One may guess that the local viscosity is in any event much larger than that of the surrounding fluid because of the discontinuity in molecular orientation, which makes the defect core similar to a region of isotropy and, therefore, of reduced mobility. Thus, the fluid should preferably go around, rather than through, defects as if they were solid. An exchange of material between defective regions and surrounding fluid must nevertheless take place because defect lines are elongated by the flow (ref. 15) thus drawing material from the surroundings. Furthermore, defects are created (ref. 1) and possibly annihilated. For the case of semi-rigid polymers, one further envisages the possibility that different strands of the same macromolecule may belong to different domains, macromolecules of the border regions going across domain borders and/or defects and disclinations.

Lacking a comprehensive theory, an "educated guess" can perhaps be made on how this complex system might behave under the influence of shear. The guess is based on the relative magnitude of the parameters involved and is inspired, of course, by what has been experimentally demonstrated so far. In the following,  $\eta$  will indicate a viscosity, somehow related to the Leslie coefficients of the nematics, K is a characteristic elastic constant, collectively representative of the three constants in Eq. 5,  $\tau$  is a molecular relaxation time, a is some characteristic average dimension of the domains, whose value in the rest state is  $a_0$ .

At sufficiently low shear rates, such that  $\gamma \tau << 1$ , molecular relaxation processes are virtually at equilibrium, and the parameter  $\tau$  may be ignored. Domains are acted upon by the

shear and tend to tumble. In the previous section it was shown that, in the absence of other effects, tumbling has some regularities. It occurs with a definite period and maintains the director in the plane of shear (at some  $\theta_0$  or  $-\theta_0$ ) for most of the time. No regularity can be achieved, however, as long as neighboring domains are out of phase and have different  $\theta_0$  values. On the other hand, bringing domains into register from an initial random distribution implies overcoming forces due to Frank elasticity, which are especially strong in the vicinity of defects. This process will hardly occur as long as viscous forces are weak, i.e., as long as

$$\sigma = \eta \gamma < K/a_0^2$$
 (7)

Thus, in the regime corresponding to the above inequality, domains and defects are expected to tumble irregularly with no special pattern emerging.

By increasing  $\sigma$  beyond the range of inequality (7), viscous forces are strong enough for two effects to become possible: i) reduction of the original domain size  $a_0$  to a smaller value, a, such that the following equality is satisfied in an order-of-magnitude sense (Eq. 8 may be thought of as the equivalent of Eq. 6 in the polydomain case)

$$a = (K/\sigma)^{1/2} \tag{8}$$

and, simultaneously, ii) a tendency of neighboring domains to fall into register in their tumbling motion. The latter effect implies that, for example, two domains such as those in Fig. 5, with both their directors resting temporarily in the plane of shear but at different  $\theta_0$ , will tend to assume a common  $\theta_0$ -value. The driving force for domain coalescence is Frank elasticity which, in this case (domains side by side with respect to the shear direction, and tumbling together), does not work against shear forces.

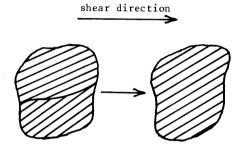


Fig. 5. Coalescence of domains having different  $\theta_0$ -values

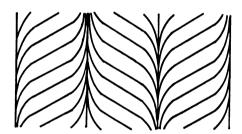


Fig. 6. Director field in tumbling bands observed perpendicularly to shear planes

It is tentatively suggested that the formation of a band texture is a consequence of this mechanism, i.e., of an ordering of neighboring domains along the direction perpendicular to both the shear and the gradient directions. Coherent tumbling of these structures would give rise to a molecular orientation pattern such as that depicted in Fig. 6, where orientations at  $\theta_0$  and  $-\theta_0$  in the shearing planes alternate regularly along the shear direction, separated from one another by a short tumbling region.

The experimental observation whereby the bands are sometimes observed during flow whereas in other cases they are present only after shearing is not in contrast with the above suggestion. In the latter case, one may assume that the process of falling into register of the tumbling units could not be completely achieved during flow. The orientational distribution of the director field created by the shear is however such (i.e., close enough) that, in the rest state, Frank elasticity alone temporarily creates the regular structure before the latter slowly vanishes again into randomness.

### **NEGATIVE NORMAL STRESSES**

The suggestion by Kiss and Porter (ref. 3) that the band structure and negative normal stress differences are related phenomena may be reinforced by considering explicitly the stresses

arising from Frank elasticity. Cartesian components of the Ericksen stress tensor are given by (ref. 15)

$$\sigma_{ij} = -\pi_{ik} \partial_{ik} n \tag{9}$$

where  $\vartheta_{j}n_{k}$  are derivatives of the director components (i.e., components of the director gradient) and tensor  $\pi_{ik}$  is defined as

$$\pi_{ik} = \frac{\delta E}{\delta(\partial_i n_k)}$$
 (10)

E being the distortion energy given in Eq. 5.

In order to simplify the mathematics, use is made of the theoretical result for rodlike polymers (ref. 20) whereby the bend elastic constant  $K_3$  is predicted to be much larger than both  $K_1$  and  $K_2$ . Equation 5 can then be written in the simpler form

$$E \cong \frac{1}{2} K_3 \left( \underbrace{n}_{i} \times \text{curl } \underbrace{n}_{i} \right)^2 = \frac{1}{2} K_3 \underbrace{n}_{i} \underbrace{n}_{i} \underbrace{n}_{i} \underbrace{n}_{k} \underbrace{n}_{i} \underbrace{n}_{k}$$
(11)

When the band structure is developed, derivatives along the band direction are zero. If, as in Fig. 2, x, y, z, are coordinates along the shear, the gradient and the band directions, respectively, one finds

$$(\sigma_{xx} - \sigma_{zz})/K_3 = -n_x^2 \{(\partial_{xx}^n)^2 + (\partial_{xy}^n)^2 + (\partial_{xz}^n)^2\}$$
 (12)

$$(\sigma_{xx} - \sigma_{yy})/K_3 = -n^2 \{(\partial_{x} n_x)^2 + (\partial_{x} n_y)^2 + (\partial_{x} n_z)^2\} + \{(\partial_{y} n_x)^2 + (\partial_{y} n_y)^2 + (\partial_{y} n_z)^2\} n^2$$
(13)

The normal stress difference in Eq. 12 is thus shown to be always <u>negative</u> in a band structure. Lacking sufficient information on the director field, the sign of the difference in Eq. 13 is uncertain; yet a negative result is not only possible but perhaps even likely. In the band structure,  $n_{\rm X}$  is larger than  $n_{\rm Y}$  most of the time, and where this does not occur (in the tumbling zone) it is not implausible that derivatives along x are larger than those along y. It is further noted that the sign result of Eq. 12 (perhaps also that of Eq.13) does not depend crucially on having neglected  $K_1$  and  $K_2$ . In the opposite extreme assumption, i.e., in the case where all three constants are taken to be equal, a similar result is obtained. This indicates that a negative normal stress difference due to Frank elasticity is intrinsic to the band structure (at least as regards  $\sigma_{\rm XX}$  -  $\sigma_{\rm ZZ}$ ).

Of course, the Ericksen stress considered in this section is not the total stress. Contributions other than that arising from distortions may be significant. These are discussed in the next section.

# **EFFECT OF MOLECULAR RELAXATIONS**

If  $\tau\gamma$  is of order unity or larger, molecular relaxation phenomena are to be taken into account. In a shear flow of ordinary polymers, relaxation effects reveal themselves through positive normal stress differences due to stretching of molecules in the shear direction (both  $\sigma_{xx}$  -  $\sigma_{yy}$  and  $\sigma_{xx}$  -  $\sigma_{zz}$  are positive), and by the companion phenomenon of a non-Newtonian viscosity, decreasing with increasing shear rate.

One may perhaps expect that a similar stretching of semi-rigid polymers occurs in the tumbling domain situation considered here. Especially at the border between domains, where orientation of the director changes abruptly and the mobility is presumably reduced, molecules belonging to both domains do not have the time to diffuse freely from one domain to the next and get stretched accordingly. A situation similar to that of "tie molecules" in semi-crystal line polymers is envisaged, where neighboring crystalline regions are mechanically linked by polymer molecules belonging to both.

Considering in particular the band structure depicted in Fig. 6, one expects that in the border regions between orientations  $\theta_0$  and  $-\theta_0$  "tie molecules" exist which link consecutive domains. It is possible that the value of  $\theta_0$  in any given case results from a balance between Frank elasticity and polymer elasticity. Since the former arises from distortions of the director field, its effect is in the direction of minimizing the distortion energy. In the

tumbling case, there exists a single orientation of the director which minimizes distortion energy, i.e., the direction orthogonal to both the shear and the gradient. Thus, as a consequence of Frank elasticity,  $\theta_0$  would tend to become  $\pi/2$ . On the contrary, polymer elasticity wants to align the molecules in the shear direction, i.e., toward  $\theta_0$  = 0.

Different values of  $\theta_0$  seem to have been observed experimentally (usually after the sample has solidified). Kiss and Porter (ref. 3) report a value of 45°. A similar value, ca. 40°, is reported by Zachariades et al. (ref. 5). However Qian (ref. 21) has evidence of a much smaller value, of the order of a few degrees. Finally, the optical results obtained during flow by Asada et al. (ref. 2) indicate  $\theta_0$  = 0 (less than 10° in any event) though the existence of bands was not investigated in their work.

Competition between Frank and polymer elasticities might also explain the transition from negative to positive normal stresses which takes place by increasing the shear rate. The order of magnitude of normal stresses due to Frank elasticity is obtained from Eqs. 12-13 and Eq. 8 as

$$|\sigma_{xx} - \sigma_{yy}|_{Frank} \cong K/a^2 \cong \sigma$$
 (14)

i.e., these normal stresses should grow like the imposed shear stress  $\sigma$ . Conversely, for ordinary polymers at least, it is known that normal stresses due to polymer elasticity grow like

$$\left| \begin{array}{ccc} \sigma & -\sigma & \sigma \\ \sigma & \sigma & \sigma \end{array} \right|_{\text{polymer}} \cong \tau \gamma \sigma$$
 (15)

i.e., they are smaller or larger than the shear stress depending on  $\tau\gamma$ . Thus, a value of  $\tau\gamma$  of order unity should mark the crossover from negative to positive overall normal stresses.

Of course, the opposite transition (from positive to negative values) which occurs at small  $\gamma$  (ref. 6 & 7), cannot be explained in terms of the same competition. As a consequence, the positive normal stresses observed at very low  $\gamma$  should not be interpreted in terms of ordinary polymer elasticity but rather as a manifestation of the liquid crystalline state. The positive to negative transition would occur because disordered domains organize themselves in the band structure, thus generating Ericksen stresses of the form reported in Eq. 12 & 13.

#### **ESTIMATES AND COMPARISONS**

As mentioned previously, not much is available in support of the various conjectures presented so far. The purpose of this section is to show that, at least, no striking contradiction with experiments is found either.

For what concerns domain size in sufficiently strong shear flows, we have the prediction of Eq. 8 which can be regarded as an obvious consequence of dimensional analysis. Actually, if also polymer relaxation effects are important, Eq. 8 should be generalized as

$$a = (K/\sigma)^{1/2} f(TY)$$
 (16)

but we have no inkling on the shape of the function f. Notice, however, that effects due to molecular relaxation might already be accounted for to some extent in the non-Newtonian character of  $\sigma$  in this region. The order of magnitude of K to be used in Eq. 8 seems to be  $10^{-6}$  or  $10^{-5}$  dynes (ref. 8 & 20). In those cases where bands are observed,  $\sigma$  is typically of order  $10^3$  dynes/cm². Then, Eq. 8 correctly predicts a domain size in the micron or sub-micron range. Notice further that a is predicted to decrease with increasing shear rate as is indeed observed (ref. 5). The - 1/2 power law in  $\sigma$  implies a weaker power with respect to  $\gamma$  because the material is usually shear thinning in this region. As mentioned above, the possible influence of  $f(\tau\gamma)$  (beyond shear thinning) is unknown.

As far as the complex behavior of normal stresses is concerned, the experiments of Kiss and Porter (ref. 6 & 7) on PBG and PBZCL solutions show the following features. Normal stresses at very low shear rates undergo a qualitative change when, by increasing polymer concentration the liquid crystalline state sets in. Whereas below the transition normal stresses grow with a power of  $\gamma$  close to 2 (as expected in polymers which are isotropic at rest), the exponent becomes close to 1 after the transition. This behavior is in agreement with the expectation that, in nematics, normal stresses are first order effects (ref. 11). Notice further that

this behavior is preserved, in the very low shear rate range, also for concentrations which give rise to the negative normal stress phenomenon at intermediate  $\gamma$ -values. Thus, the first region of positive normal stresses seems to be linked to the liquid crystalline character of the system, rather than to polymer elasticity, as discussed in the previous section.

In the negative normal stress range of PBG solutions, the magnitude of these normal stresses is very close to that of the shear stresses attained in the same range. For PBCZL solutions, the negative normal stresses are somewhat smaller than shear stresses. These results compare favorably with the idea that the quantity which is measured in this range is a difference of the quantities given by Eq. 14 and Eq. 15 when, in the latter equation, TY is already close to unity.

Finally, beyond the negative to positive transition, normal stresses should become larger than shear stresses, according to Eq. 15. Whenever the data extend somewhat beyond the transition, this is indeed what is found (e.g., 14 w% PBG solution, 14.1 w% PBLG solution, 27.6 w% PBCZL solution, etc.).

#### CONCLUSIONS

On the assumption that polymeric nematics are of the tumbling type, the possibility has been discussed that the band texture is a manifestation of ordered tumbling. Once they have gone into register, domains tumble continuously between  $\theta_0$  and  $-\theta_0$ , where  $\theta_0$  is the angle between director and shear direction in the shear plane. It has been shown that Ericksen normal stress differences associated with this structure are likely to be negative. The transition from negative to positive normal stresses which is observed at large shear rates would mark a dominance of polymer elasticity over Frank elasticity. The competition between the two kinds of elasticity might determine the value of  $\theta_0$  in any given system.

Although the proposed interpretation is highly speculative and obviously incomplete, it has the merit of being based on concepts which are expected to play a general role in these systems, quite independently of the particular chemistry. Even if special effects may well exist in some systems which are absent in others, it is not unreasonable to expect that most of the rheological complexity exhibited by liquid crystalline polymers could be explained in general terms by developing a theory which encompasses both LMW nematodynamics and polymer viscoelasticity.

## **ACKNOWLEDGEMENT**

Work supported by the Department of Education, Rome, under the program "Polymer Engineering".

# **REFERENCES**

- 1. D.J. Graziano and M.R. Mackley, Mol. Cryst. Liq. Cryst. 106, 73 (1984).
- 2. T. Asada, S.Onogi and H. Yanase, Polym. Eng. Sci. 24, 355-360 (1984).
- 3. G. Kiss and R.S. Porter, Mol. Cryst. Liq. Cryst. 60, 267-280 (1980).
- 4. A.M. Donald, C. Viney and A.H. Windle, Polymer 24, 155-159 (1983).
- 5. A.E. Zachariades, P. Navard and J.A. Logan, Mol. Cryst. Liq. Cryst. 110, 93-107 (1984).
- 6. G. Kiss and R.S. Porter, J. Polym. Sci. Polym. Symp. 65, 193-211 (1978).
- 7. G. Kiss and R.S. Porter, <u>J. Polym. Sci. Polym. Phys</u>. <u>18</u>, 361-388 (1980).
- 8. R.B. Meyer, F. Lomberg, V. Taratuta, S. Fraden, S.D. Lee and A.J. Hurd, <u>Faraday Disc. 79</u>, Cambridge 1985.
- 9. T. Carlsson, Mol. Cryst. Liq. Cryst. 89, 57-66 (1982).
- 10. T. Carlsson, Ph. D. Thesis Inst. Theor. Phys. Göteborg 1984.
- 11. M. Doi, J. Polym. Sci. Polym. Phys. 19, 229-243 (1981).
- 12. G. Marrucci, Mol. Cryst. Liq. Cryst. 72, 153-161 (1982).
- 13. A.N. Semenov, Zh. Eksp. Teor. Fiz. 85, 549-560 (1983).
- 14. N. Kuzuu and M. Doi, J. Phys. Soc. Japan 53, 1033-1040 (1984).
- 15. P.G. de Gennes, The Physics of Liquid Crystals, Clarendon Press, Oxford (1975).
- 16. T. Carlsson, Mol. Cryst. Liq. Cryst. 104, 307-334 (1984).
- 17. C. Högfors, Proc. IX Int. Congr. Rheol. Vol. 3, p. 317, Univ. Mexico, Mexico (1984).
- 18. P. Pieranski and E. Guyon, Phys. Rev. Lett. 32, 924 (1974).
- 19. P.E. Cladis and S. Torza, Phys. Rev. Lett. 35, 1283 (1975).
- 20. J.P. Straley, Phys. Rev. A 8, 2181-2183 (1973).
- 21. R. Qian, Academia Sinica, Peking, personal communication.