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G. G. VIOLA and D. G. BAIRD *Polymer Materials and Interfaces Laboratory and Department of Chemical Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061-6496*

Synopsis

An understanding of the flow behavior of liquid crystalline polymers (LCP's) is of immense practical value because of the potential to form high modulus materials from these polymers. These fluids exhibit a high degree of structure even in the quiescent state, as evidenced by their ability to transmit polarized light. In an effort to understand how the structure changes during flow, we have carried out a study on the transient shear flow properties of two thermotropic copolyesters of 60- and 80-mole % para-hydroxybenzoic acid (PHB) and polyethyleneterephthalate (PET) and a lyotropic system of poly-p-phenyleneterephthalamide (PPT) in 100% sulfuric acid. In one of the first theories concerned with the flow behavior of liquid crystalline fluids, which was proposed by Ericksen, the transient flow properties are all predicted to be due to changes in orientation of a director which describes the orientation of packets of rod-like molecules. Stress growth, interrupted stress growth, and stress relaxation experiments are carried out on the three LCP's and at first sight are in qualitative agreement with the predictions of Ericksen's theory. However, wide angle X-ray scattering analysis of quenched samples subjected to shear flow along with annealing experiments on oriented samples indicate that these materials do not orient readily in shear flow. Furthermore, orientation generated during extensional flow relaxes at a rate much faster than is indicated by the interrupted stress growth experiments. It is concluded that the stress growth response of LCP's is due to a disruption of a domain structure which exists within the fluid rather than to orientation changes of the domains of rod-like molecules.

INTRODUCTION

One of the most interesting characteristics of liquid crystalline polymers is that as-spun fibers and as-processed injected molded parts exhibit exceptional physical properties.[1,2] In the case of fiber production, heat treatment leads to better physical proper-

ties, but no further drawing steps are required. In the case of as-injection molded plaques, Jackson and Kuhfuss[2] reported several interesting phenomena. The physical properties of such plaques were seen to be highly anisotropic. The flexural modulus measured along the flow direction into the mold was seen to be up to 10 times greater than that measured transverse to the flow direction. In addition, the value of the flexural modulus measured along the flow direction depended on mold geometry, increasing exponentially with decreasing mold thickness. At values of mold thickness approaching 0.0025m (0.1 inch), a flexural modulus of 1.8×10^{10} Pa (2.6E6 PSI) was measured. This value is approximately one-quarter that of aluminum.

The fact that exceptional physical properties exist in as-processed liquid crystalline materials suggests that some type of structural development may be occurring during flow. Liquid crystalline materials are unique in that they are capable of possessing a high degree of structural ordering in the quiescent state. This is evidenced by the ability of liquid crystalline materials to exhibit birefringence under static conditions. It is generally agreed that such structure is related to the presence of domains in which a high degree of molecular orientation exists. It is reasonable to expect that during deformation such domains may align along the direction of flow, yielding a material with exceptional physical properties. Thus, the rheological properties of liquid crystalline polymers may depend upon some type of rearrangement of structure during flow, possibly that of molecular orientation development.

Other than the measurement of their steady shear properties, few studies of the rheological behavior of liquid crystalline polymers have been performed. The most recent review is given by Wissbrun.[3] His review points out that liquid crystalline polymers apparently may possess very long relaxation times, which may be up to 100 times longer than those of isotropic materials. These materials can also exhibit anomalous phenomena such as negative values of the primary normal stress difference (N_1), negligible or negative die swell, and double stress overshoot peaks upon inception of shear.[4,5,6] Apart from such behavior, however, the steady shear behavior of liquid crystalline polymers seems to resemble closely that of isotropic flexible chain systems.[3] The

significant difference, however, is the ability of liquid crystalline materials to orient under flow conditions. It is believed that the transient flow behavior of polymers is sensitive to changes in structure during flow. Therefore, stress growth and stress relaxation experiments may provide better insight into the differences between isotropic and liquid crystalline polymers and the changes in structure which may take place in liquid crystalline polymers during deformation.

The structural development which seems to occur to a much higher degree during flow and processing for LCP's than for ordinary flexible chain polymers suggests that it may be necessary to develop constitutive equations which reflect this structure. There have been several attempts to develop equations for fluids which exhibit significant structure even before flow occurs. Without going into great detail, we note the work of Ericksen,[7] Hand,[21] Leslie and Ericksen,[18] and Doi.[22] Each of these theories contains an equation which relates the structure to the flow and an equation which allows one to calculate the stress as a function of structure and deformation. There have been no thorough evaluations of these theories for polymeric liquid crystals. The purpose of the present paper is twofold. First, we want to determine whether the transient shear flow properties of liquid crystalline polymers are due to orientation changes of the rigid molecules or some other structural changes. Second, we would like to know whether the theories of Ericksen and even Leslie and Ericksen can at least qualitatively account for the transient behavior of LCP's. In this paper we present studies on the steady and transient shear flow properties of a thermotropic copolyester of 60- and 80-mole % PHB/PET and a lyotropic system of PPT in 100% H_2SO_4. We compare these results with the predictions of Ericksen's transversely isotropic fluid theory.

EXPERIMENTAL

Materials

The polymers used in this study consisted of copolymers of 60-mole % and 80-mole % parahydroxybenzoic acid (PHB) and polyethyleneterephthalate (PET). These polymers are difficult to

characterize due to their limited solubility. The details of their preparation are discussed elsewhere.[2] These materials were supplied by the Tennessee Eastman Company.

Further tests were conducted using an anisotropic solution of 12 weight % poly-p-phenyleneterephthalamide (Kevlar®) in 100% sulfuric acid. Solutions were prepared by first chopping lengths of Kevlar fiber into half-inch segments which were cleaned by extraction with acetone in a Soxlet Extractor. The fibers were dried in a vacuum oven at 60°C for several hours and then mixed with 100% sulfuric acid in a Helicone mixer for seven hours at a constant temperature of 70°C.

Rheological Measurements

Rheological measurements were conducted using a Rheometrics Mechanical Spectrometer (Model 605) using both cone-and-plate and parallel plate geometries. In all cases, 50-mm diameter fixtures were used in order to increase the magnitude of the signals sent to the normal force and torque transducers. Due to the low values of viscosity exhibited by the PHB/PET copolymers, a baffle was used on the lower plate in order to keep the sample from seeping out of the gap. For the Kevlar solutions, a baffle was also used. In this case, however, the baffle served to hold a layer of oil which retarded the coagulation of the outer edge as moisture reacted with H_2SO_4. Transient shear measurements were performed on both the PHB/PET copolyesters and the PPT solutions. The Rheometrics Mechanical Spectrometer was used for these measurements. In all tests, a cone-and-plate fixture with a 50 mm diameter and either a 0.04 or a 0.1 radian-cone angle was used. The signals from the transducer were captured on a Gould digital storage oscilloscope and then fed to a strip chart recorder. In this way, stress measurements could be accurately measured for times as short as 0.6 sec.

Sample Preparation

Sheared disks and extended ribbons of the PHB/PET copolyester were prepared in order to determine the effects of shear and extensional flow fields on molecular orientation. Sheared disks

were prepared by first spraying the parallel plate geometry of a Rheometrics Mechanical Spectrometer with a mold release agent. Pellets of the 60-mole % PHB/PET copolyester were then placed on the lower plate and heated to the desired temperature (275°C). After the melt temperature had been reached, the gap was set and the samples sheared at the desired shear rates for a period of time long enough to establish steady state stress levels. The shearing was then stopped, and the fixtures removed from the RMS. Compressed air was blown over the fixtures in order to cool the samples as rapidly as possible.

Ribbons subjected to elongational flow were prepared in the following manner. A slit die was attached to an Instron Capillary Rheometer (Model 3211). At approximately 23 cms, (5 inches) below the die exit, the extruded film was taken up on a set of rolls. The extension rate was varied by changing the roll speed. These experiments were not designed to provide quantitative measurements of extensional flow behavior but only qualitative behavior. Further details of this work are given elsewhere.[20]

Annealing of Samples

In order to determine the extent to which molecular orientation remained in the melt state, oriented samples of the 60-mole % PHB/PET copolymer were annealed for various times at the melt temperature (275°C). The heating oven of the RMS was used for this purpose. The oriented samples were placed on a piece of teflon on the lower plate of a parallel plate geometry. After annealing for various times ranging from 30 seconds to 5 minutes, the samples were removed and quenched.

Wide Angle X-Ray Scattering Analysis

Wide angle x-ray scattering (WAXS) analysis was used to qualitatively determine the degree of molecular orientation present in the PHB/PET samples prepared using the procedures described above. These studies were conducted using a Phillips PW 1720 table top x-ray generator equipped with a Warhus (Stratton) camera. Scattering patterns were recorded photographically using sample to film distances of 5.5 cm.

ERICKSEN'S TRANSVERSELY ISOTROPIC
FLUID THEORY

The Leslie-Ericksen theory linearized in the rate of deformation tensor is believed to describe the dynamic properties of low molecular weight liquid crystals (LC).[18] However, it is not completely clear from a review of the literature on the rheology of LC's whether this theory has been fully and thoroughly investigated. At the same time, however, the theory is believed to hold for LC's, and LCP's have been found to exhibit the same type of mesophasic structures.[19] Therefore, it is worthwhile to at least make a qualitative comparison between Ericksen's anisotropic fluid theory and the transient flow behavior of LCP's. Although we may not expect a quantitative comparison between the results and theory, there are at least a few ideas in the theory which should be evaluated as they could be applied to the development of more rigorous theories. In particular, we note the idea that the transient flow properties of LCP's are predicted to be determined by changes in the orientation of the director. Furthermore, from a practical point of view, these ideas of flow-induced orientation are attractive since it is believed that the exceptional physical properties found in these materials in the solid state come from this orientation. Hence, an evaluation of Ericksen's transversely isotropic fluid theory is warranted based on the fact there has been no thorough evaluation of the theory for liquid crystalline polymers and because of the potential to better understand the relation between flow and structure for these complex systems.

In this section, the basic concepts behind Ericksen's anisotropic fluid theory will be reviewed. Ericksen has chosen to model fluid anisotropy through the use of a vector, $\underset{\sim}{n}$, called the director. The director always points along the direction of preferred orientation of the fluid particles which are assumed to be rigid rods for LCP's of the nematic type. Whereas for LC's the stress tensor is linearized and the coefficients are taken as constants, we keep all the nonlinear terms for LCP's and write the stress tensor as follows:

$$\underset{\approx}{\tau} = -P\underset{\approx}{\delta} + \alpha_1\underset{\sim}{nn} + \alpha_2\underset{\approx}{\dot{\gamma}} + \alpha_3\underset{\approx}{\dot{\gamma}}^2 +$$
$$\alpha_4(\underset{\sim}{n} \cdot \underset{\approx}{n\dot{\gamma}} + \underset{\approx}{\dot{\gamma}n} \cdot \underset{\sim}{n}) + \alpha_5(\underset{\sim}{nn} \cdot \underset{\approx}{\dot{\gamma}}^2 + \underset{\approx}{\dot{\gamma}}^2 \cdot \underset{\sim}{nn}) \qquad (1)$$

Here $\underset{\approx}{\tau}$ is the total stress tensor, with $\tau_{ii} > 0$ taken as a tensile stress, P is the isotropic pressure, $\underset{\approx}{\delta}$ is the unit tensor, and $\underset{\approx}{\dot{\gamma}}$ is the rate-of-deformation tensor. This expression is obtained by expanding the stress tensor, which is believed to be given as:

$$\underset{\approx}{\tau} = \underset{\approx}{\tau}(\underset{\approx}{\dot{\gamma}}, \underset{\sim}{n}\underset{\sim}{n}). \tag{2}$$

in a polynomial series and then using the Cayley-Hamilton theorem to reduce the higher order terms for shear flow. Just as in the case of the Criminale-Ericksen-Filbey equation, the coefficients (α_i) are taken as functions of the invariants involving $\underset{\approx}{\dot{\gamma}}$, $\underset{\sim}{n}\underset{\sim}{n}$, and combinations of these two tensors as given below:

$$tr\underset{\approx}{\dot{\gamma}}, \ tr\underset{\approx}{\dot{\gamma}}^2, \ tr\underset{\approx}{\dot{\gamma}}^3, \ tr\underset{\sim}{n}\underset{\sim}{n}, \ tr(\underset{\sim}{n}\underset{\sim}{n} \cdot \underset{\approx}{\dot{\gamma}}), \ tr(\underset{\sim}{n}\underset{\sim}{n} \cdot \underset{\approx}{\dot{\gamma}} \cdot \underset{\approx}{\dot{\gamma}}) \tag{3}$$

In order to completely specify all of the unknowns in the system, Ericksen wrote an additional equation for determining the state of the director:

$$\frac{D\underset{\sim}{n}}{Dt} = \frac{d\underset{\sim}{n}}{dt} - \underset{\approx}{w} \cdot \underset{\sim}{n} = \beta_1\underset{\sim}{n} + \beta_2\underset{\approx}{\dot{\gamma}} \cdot \underset{\sim}{n} + \beta_3\underset{\approx}{\dot{\gamma}} \cdot \underset{\approx}{\dot{\gamma}} \cdot \underset{\sim}{n} \tag{4}$$

where D/Dt is the Jauman derivative, d/dt is the material derivative, and w is the vorticity tensor. The β's are also taken as functions of the same invariants as described above.

The equations presented thus far comprise the nonlinear version of Ericksen's transversely isotropic fluid theory. In order to further simplify the theory, Ericksen linearized Eqs. (1) and (4) with respect to the rate-of-deformation tensor. For the purposes of this study, the nonlinear stress equations will be conserved, but the linear director equations will be used. Although this may seem to be inconsistent, there are several reasons for this choice. The linearized stress equations are not capable of predicting a shear rate dependent viscosity function.[7] Since it is known that most liquid crystalline polymers exhibit shear-thinning viscosity behavior, the linear theory is not suitable for use with LCP's. With the use of the nonlinear theory, the α's in Eq. (1) can at least be made functions of the shear rate, $\dot{\gamma}$, as shown later. Similarly, the linear director equations exclude the shear rate dependence of the orientation of the director. There is no evidence to support

that such a shear rate dependence of molecular orientation exists
for liquid crystalline materials. Until further data are available,
we will facilitate this initial comparison with experimental data
by using the linear director equation. Even if the nonlinear direc-
tor equation were used, the general results and ideas should not
be changed. Linearization of Eq. (4) with respect to the rate-of-
deformation tensor yields the following equation for determining
the director:

$$\frac{D\underset{\sim}{n}}{Dt} = \frac{d\underset{\sim}{n}}{dt} - \underset{\approx}{w} \cdot \underset{\sim}{n} = \lambda[\underset{\approx}{\dot{\gamma}} \cdot \underset{\sim}{n} - n(\underset{\sim}{n} \cdot \underset{\approx}{\dot{\gamma}} \cdot \underset{\sim}{n})] \qquad (5)$$

where $\lambda = \beta_2$ and is a constant.

With the assumption that $|n| = 1.0$ and the director equation is
linear in $\underset{\approx}{\dot{\gamma}}$, we can show for the case of shear flow that the in-
variants become:

$$tr(\underset{\sim}{n}\underset{\sim}{n} \cdot \underset{\approx}{\dot{\gamma}}) = 2n_1 n_2 \dot{\gamma}_{12}, \ tr(\underset{\sim}{n}\underset{\sim}{n} \cdot \underset{\approx}{\dot{\gamma}} \cdot \underset{\approx}{\dot{\gamma}}) = 2n_1 n_2 \dot{\gamma}_{12},$$

$$tr\underset{\approx}{\dot{\gamma}}^2 = 2\dot{\gamma}_{12}^2. \qquad (6)$$

For shear flow the final orientation of the director depends on the
value of λ. If λ is set equal to one (see Eq. (14)), then for shear flow
the only significant invariant which remains is $2\dot{\gamma}_{12}^2$. For the same
conditions, but for $\lambda > 1$, n_1 and n_2 are constants and the in-
variants become functions of both the shear rate, $\dot{\gamma}$, which is
equal to $\frac{1}{2}tr\dot{\gamma} \cdot \dot{\gamma}$ and $\dot{\gamma}_{12}$. For the equations which follow the α_i's
are taken as functions of γ only.

For simple shear flow along the X1 direction, Eqs. (1) and (5)
yield the following forms for the components of stress tensor and
the director equation:

$$\tau_{11} = -P + \alpha_1 n_1^2 + \frac{\alpha_3 \dot{\gamma}^2}{4} + \alpha_4 n_1 n_2 \dot{\gamma} + \frac{\alpha_5 n_1^2 \dot{\gamma}^2}{2} \qquad (7)$$

$$\tau_{22} = -P + \alpha_1 n_2^2 + \frac{\alpha_3 \dot{\gamma}^2}{4} + \alpha_4 n_1 n_2 \dot{\gamma} + \frac{\alpha_5 n_2^2 \dot{\gamma}^2}{2} \qquad (8)$$

$$\tau_{33} = -P + \alpha_1 n_3^2 \qquad (9)$$

$$\tau_{12} = \alpha_1 n_1 n_2 + \frac{\alpha_2 \dot{\gamma}}{2} + \alpha_4 (n_1^2 + n_2^2) \frac{\dot{\gamma}}{2} + \frac{\alpha_5 n_1 n_2 \dot{\gamma}^2}{2} \qquad (10)$$

$$\tau_{13} = \alpha_1 n_1 n_3 + \frac{\alpha_4 n_2 n_3 \dot{\gamma}}{2} + \frac{\alpha_5 n_1 n_3 \dot{\gamma}}{4} \qquad (11)$$

$$\tau_{23} = \alpha_1 n_2 n_3 + \frac{\alpha_4 n_1 n_3 \dot{\gamma}}{2} + \frac{\alpha_5 n_2 n_3 \dot{\gamma}^2}{4} \qquad (12)$$

$$\frac{dn_1}{dt} = \frac{\dot{\gamma} n_2}{2} [\lambda + 1 - 2\lambda n_1^2] \qquad (13)$$

$$\frac{dn_2}{dt} = \frac{\dot{\gamma} n_1}{2} [\lambda - 1 - 2\lambda n_2^2] \qquad (14)$$

$$\frac{dn_3}{dt} = -\dot{\gamma} \lambda n_1 n_2 n_3 \qquad (15)$$

Analysis of the above equations yields several interesting facts concerning the predictions of Ericksen's theory. It can be seen that the viscosity and normal stress differences are functions of the director components as well as the shear rate. Thus, the values of viscosity and normal force predicted by the theory will depend on the orientation of the director. The theory predicts a yield stress value in the shear and normal stresses as evidenced by the α_1 term. It should also be noticed that in order to determine the transient or steady state predictions of the theory, the three coupled differential equations for the director components need to be solved. These three differential equations comprise an initial value problem. Therefore, an initial orientation for the director is needed in order to calculate the predictions of the theory for transient flows. At steady state conditions, however, it is possible to solve for the state of the director by setting the left-hand side of Eqs. (13) through (15) equal to zero. This yields:

$$\tan\theta = n_2/n_1 = [(\lambda - 1)/(\lambda + 1)]^{1/2} \qquad (16)$$

where θ is the angle made between the director and the shear direction and λ is an eigenvalue for the director equations. There are three limiting cases of Eq. (16), depending on the value of λ chosen. For $0 < \lambda < 1$ the director is unstable and tumbles in space.[7] If $\lambda = 1$, then $\theta = 0$ and the director aligns perfectly with the shear direction. Finally, if $\lambda > 1$, then the director assumes an angle to the shear direction determined by Eq. (16). Thus, in shear flow, Ericksen's theory can predict perfect alignment, unstable tumbling, or a constant angle of inclination of the fluid particles to the shear direction.

In order to evaluate Ericksen's theory, an estimate of the relative magnitudes of the material parameters in the theory is nec-

essary. It should be apparent, however, that without simplifying assumptions there is no practical way of determining the material parameters in the theory. There are six unknowns (α_1 through α_5, and λ), and at best one can measure three material parameters in a simple shear flow experiment (η, N_1, N_2). Therefore, the following simplifying assumptions were made, as discussed in greater detail elsewhere,[20] in order to allow for determination of some of the material parameters in Ericksen's theory. It was assumed that $\lambda = 1$, and thus perfect alignment of the fluid particles would be predicted during shear flow and at steady state $n_1 = 1$. These assumptions then make the α_i's functions of $\dot{\gamma}$ only. It was also assumed that α_1 is zero, implying the absence of a yield stress.[3] This seems to be a valid assumption as only a few liquid crystalline polymers seem to exhibit yield stresses,[3] and this behavior may not be due to liquid crystalline effects.[9] With these simplifying assumptions, along with the assumption that $\eta = 3\bar{\eta}$ where $\bar{\eta}$ is the extensional viscosity, expressions for the steady state material functions were found as given elsewhere.[20] The steady state values of η and N_1 were used to reduce the transient material functions, η^+ and N_1^+. In the next section, we compare the transient properties of several LCP's with the predictions of Ericksen's theory as used in this paper.

RESULTS

Predictions of Ericksen's Theory

We first investigate the predictions of Ericksen's theory for stress growth upon inception of shear flow. Numerical methods were used to solve the three coupled differential equations for the director components. Three different initial conditions were investigated corresponding to initial director orientations ($n_1 = 1$, $n_2 = n_3 = 0$, etc.). For all cases, simple shear flow along the X1 direction was assumed and a λ value of 1 was used. Note that for $\lambda = 1$, Eq. (16) predicts that at steady state, perfect alignment of the director with the flow direction will occur and $n_1 = 1$.

For an initial condition of $n_3 = 1$, all three director equations are equal to zero. This is easily seen by substitution of $n_3 = 1$ into Eqs. (13) through (15) and by using the assumption given by Ericksen that $|n| = 1$. For this case, the director is initially lying
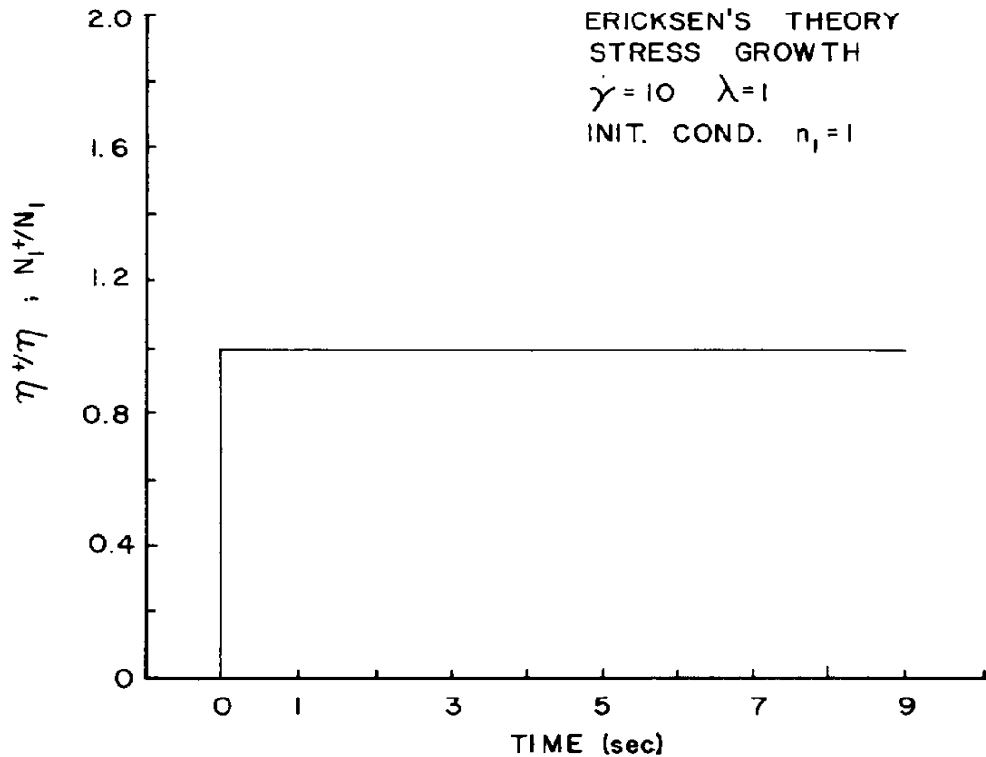
Fig. 1.   Predictions of Ericksen's theory for the viscosity and N_1 at the start up of shear flow: $\dot{\gamma} = 10 \text{ sec}^{-1}$, $\lambda = 1.0$, $n_1 = 1.0$ at $t = 0.0$.

within a plane of shear perpendicular to the flow direction. There would be no real driving force to reorient the director. Thus, the three director equations are zero specifying that steady state conditions have been achieved. Notice that this result is independent of λ or $\dot{\gamma}$.

For an initial condition of $n_1 = 1$, the results of the predictions of Ericksen's theory for stress growth are shown in Figure 1. For this case, the director's initial orientation is coincident with the flow direction. Since $\lambda = 1$, the initial condition is really the steady state solution to the director equations. As one can observe in Figure 1, the theory predicts instantaneous attainment of steady state values of stress with no overshoot.

The most interesting predictions of Ericksen's theory result from the case in which an initial condition of $n_2 = 1$ is specified. In this case, the director is initially oriented perpendicularly to the planes of shear. Upon inception of shear, the director equa-
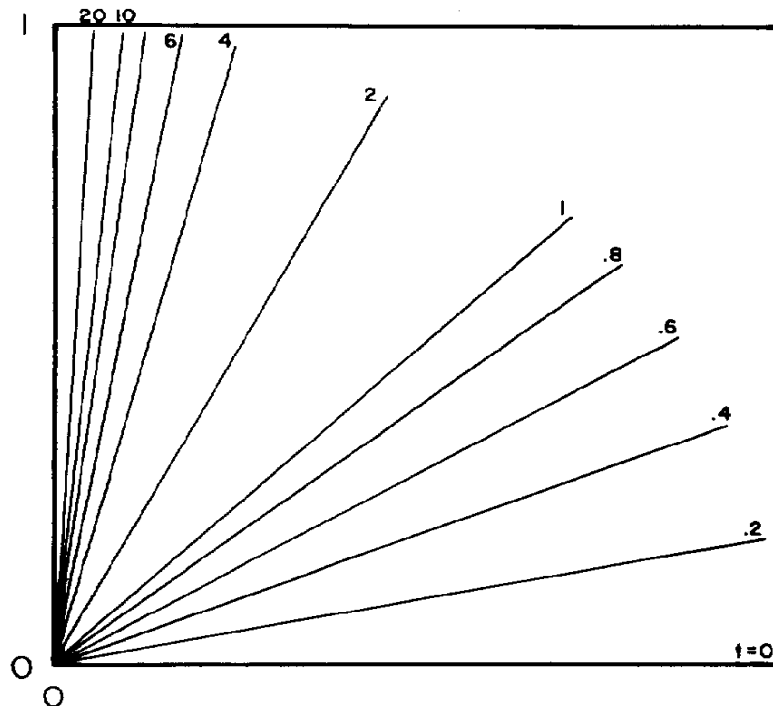
Fig. 2. Schematic representation of the path of the director for the following conditions: $\dot{\gamma} = 10 \ \text{sec}^{-1}$, $\lambda = 1.0$, $n_2 = 1.0$ at $t = 0.0$.

tions predict that the director rotates in order to align itself with the X1 axis ($n_1 = 1$). This rotation is schematically represented in Figure 2 in which the position of the director in the $n_1 - n_2$ plane is shown as a function of time. Notice that the magnitude of $\underset{\sim}{n}$ in the $n_1 - n_2$ plane is always unity. The rotation of the director depicted in Figure 2 gives rise to overshoot behavior in the shear and normal stresses. The reason for this overshoot is most clearly seen by taking the first derivative of Eq. (10) for the shear stress with respect to n_1. This operation is facilitated by noting that $\alpha_1 = 0$, and $n_2^2 = 1 - n_1^2$. Thus, the first derivative of Eq. (10) with respect to n_1 becomes:

$$\frac{\partial \tau_{12}}{\partial n_1} = [(1 - n_1^2)^{1/2} - n_1^2/(1 - n_1^2)^{1/2}] \frac{\alpha_5 \dot{\gamma}^2}{2} \qquad (17)$$

Setting the left-hand side of Eq. (17) to zero and solving for n_1 shows that when the director passes through an angle of 45° to the flow direction, ($n_1 = n_2 = \frac{1}{2}$) a maximum in τ_{12} occurs. (The

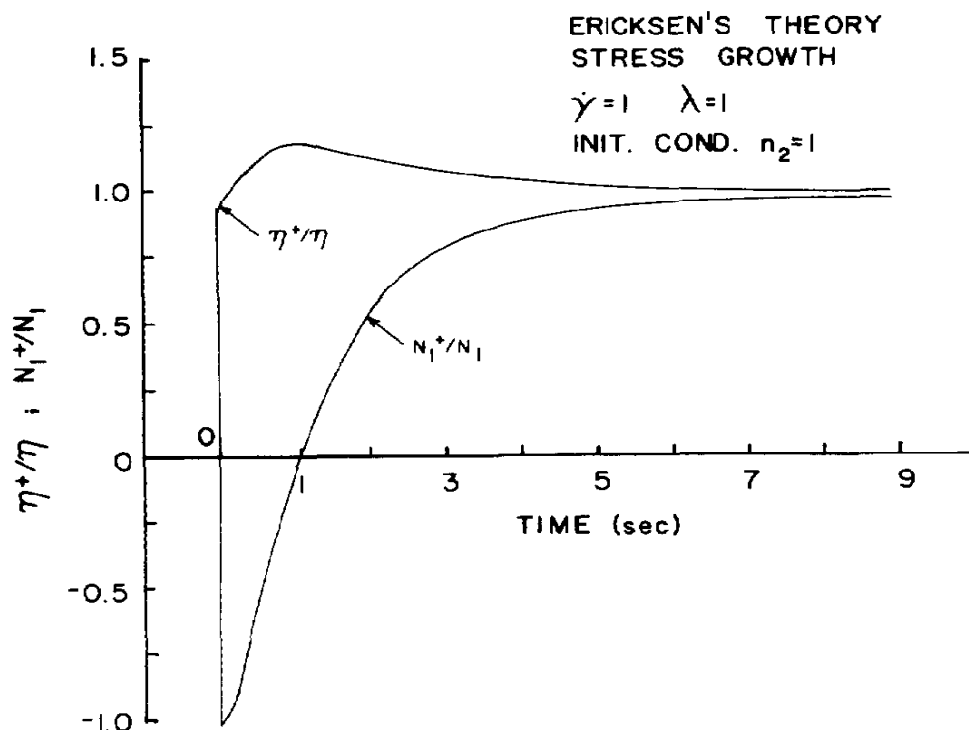Fig. 3. Predictions of Ericksen's theory for the viscosity and N_1 at the start up of shear flow: $\dot{\gamma} = 1.0 \sec^{-1}$, $\lambda = 1.0$, $n_2 = 1.0$ at $t = 0.0$.

same operation can be done with primary normal stress difference equation.) The results of the predictions of Ericksen's theory for the transient shear and normal stress behavior are shown in Figure 3. For a shear rate of $1 \sec^{-1}$, there is a slight overshoot in the viscosity and a negative undershoot in the normal stresses. In both cases, the extremuns occur at strain values of less than 1 strain unit. For a shear rate of $10 \sec^{-1}$, as shown in Figure 4, the same overshoot and negative undershoot behavior occurs in the shear and normal stresses. However, the extremuns now occur at smaller times, and the absolute magnitude of the overshoot peaks has increased. The fact that the overshoot peaks are predicted at smaller times for an increase in shear rate suggests that the theory predicts a constant strain value for overshoot behavior. The value of strain at the maximum in the overshoot appears to be less than 1.

In the figures given so far, no stress relaxation behavior has been shown. Inspection of the shear and normal stress equations
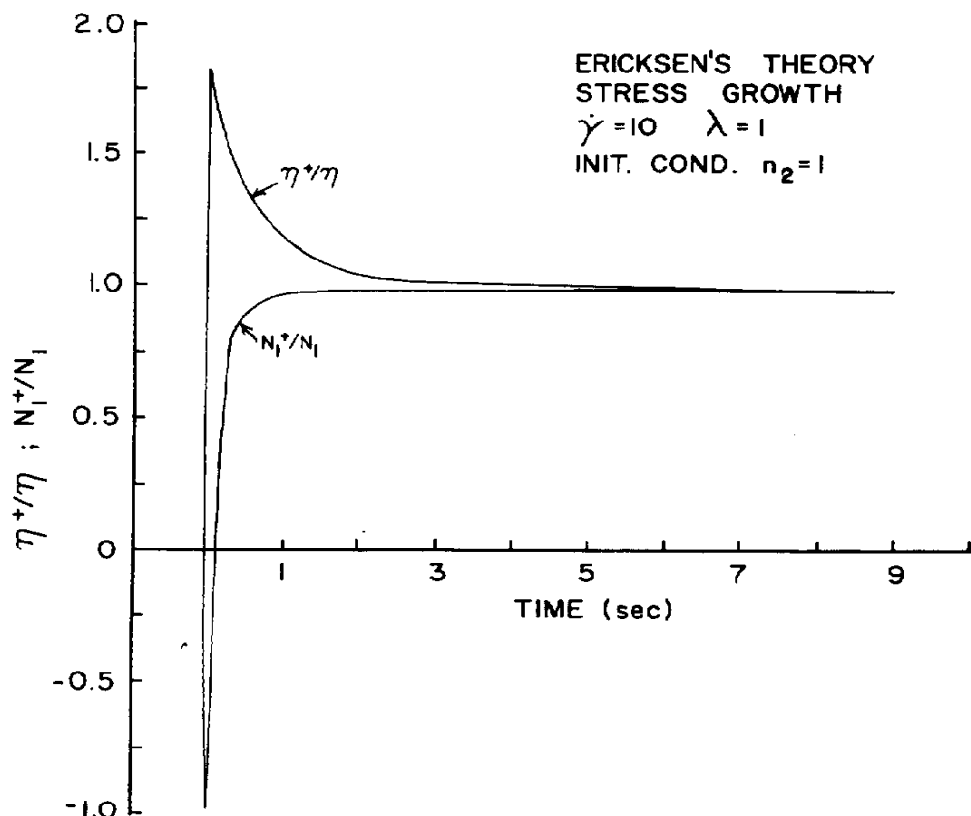
Fig. 4. Predictions of Ericksen's theory for the viscosity and N_1 at the start up of flow: $\gamma = 10 \text{ sec}^{-1}$, $\lambda = 1.0$, $n_2 = 1.0$ at $t = 0.0$.

reveals, however, that if the shear rate is set to zero, all stresses go to zero immediately, provided $\alpha_1 = 0$. Thus, the theory predicts instantaneous stress relaxation upon cessation of shear. Inspection of Eqs. (13) through (15) for the director indicates that for $\dot{\gamma} = 0$, all three $\dot{n}_i = 0$. Therefore, the theory predicts that an unoriented fluid will remain unoriented, and an oriented fluid will remain oriented indefinitely.

The predictions of Ericksen's theory for the stress growth/ relaxation behavior of anisotropic fluids suggests that certain transient tests are of importance for liquid crystalline fluids. If the predictions of the theory are correct, then a stress overshoot peak should be observed at small strain values. This overshoot peak would occur due to reorientation of the fluid particles. Once oriented, the fluid particles would remain oriented. Thus, in an

interrupted shear test, one would not expect to see any overshoot behavior once the fluid had been oriented. On cessation of shear, the shear and normal stresses should go to zero instantaneously. In the next section, we look at the transient behavior of several liquid crystalline polymer systems to see if they behave as predicted by the theory of Ericksen.

Stress Growth and Relaxation

The results presented in the previous section indicate that interrupted stress growth experiments may yield important information concerning the behavior of liquid crystalline fluids. In order to test the predictions of Ericksen's theory for stress growth and relaxation behavior, the transient response of several liquid crystalline polymers was investigated. At the present time, only the transient shear stress response results are given. The normal stress response was sometimes cyclic and at other times exhibited negative undershoot. These results are presented elsewhere.[16,17]

Figure 5 shows the transient shear stress response of the 60-mole % PHB/PET copolymer at 275°C for a range of shear rates. Several important features of the traces are worth discussing. An overshoot peak is exhibited at all shear rates tested. As the shear rate increases, the magnitude of the overshoot peak increases and the overshoot occurs at shorter times. The overshoot peak appears to be occurring at a constant strain value of less than one. The material also exhibits a second overshoot peak at higher shear rates. This peak occurs at a constant strain value of 50–60 strain units. At this time there are no reasonable explanations for the occurrence of this secondary peak. Furthermore, upon cessation of shear, the shear stresses go to zero almost instantaneously. This suggests that the fluid does not exhibit a yield stress and the choice of $\alpha_1 = 0$ in Ericksen's theory would seem to be valid.

Figure 6 shows the results of interrupted stress growth experiments for the 60-mole % PHB/PET system at a shear rate of 10 sec^{-1} and a temperature of 275°C. A range of rest periods between cessation and continuation of shear, ranging from 1 to 180 seconds, was investigated. Upon inception of shear flow, the first and second overshoot peaks are exhibited in a manner similar to that observed in Figure 5. However, after interruption of shear flow, the first overshoot peak is noticeably absent. Even after
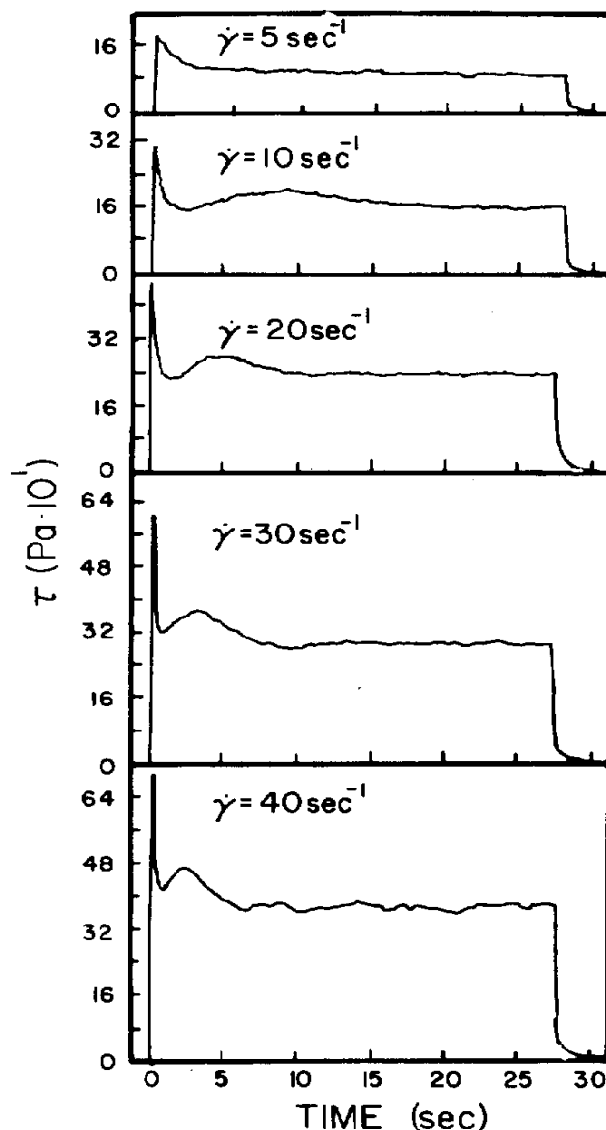
Fig. 5. Stress growth and relaxation of shear stress as a function of shear rate for 60-mole % PHB/PET at 275°C: 50 mm cone-and-plate with a 0.04 rad cone.

three minutes of rest at the melt temperature, the first peak remains nearly absent. Notice that the second overshoot peak and the stress relaxation behavior are unaffected by the period of rest in the interrupted shear experiment.

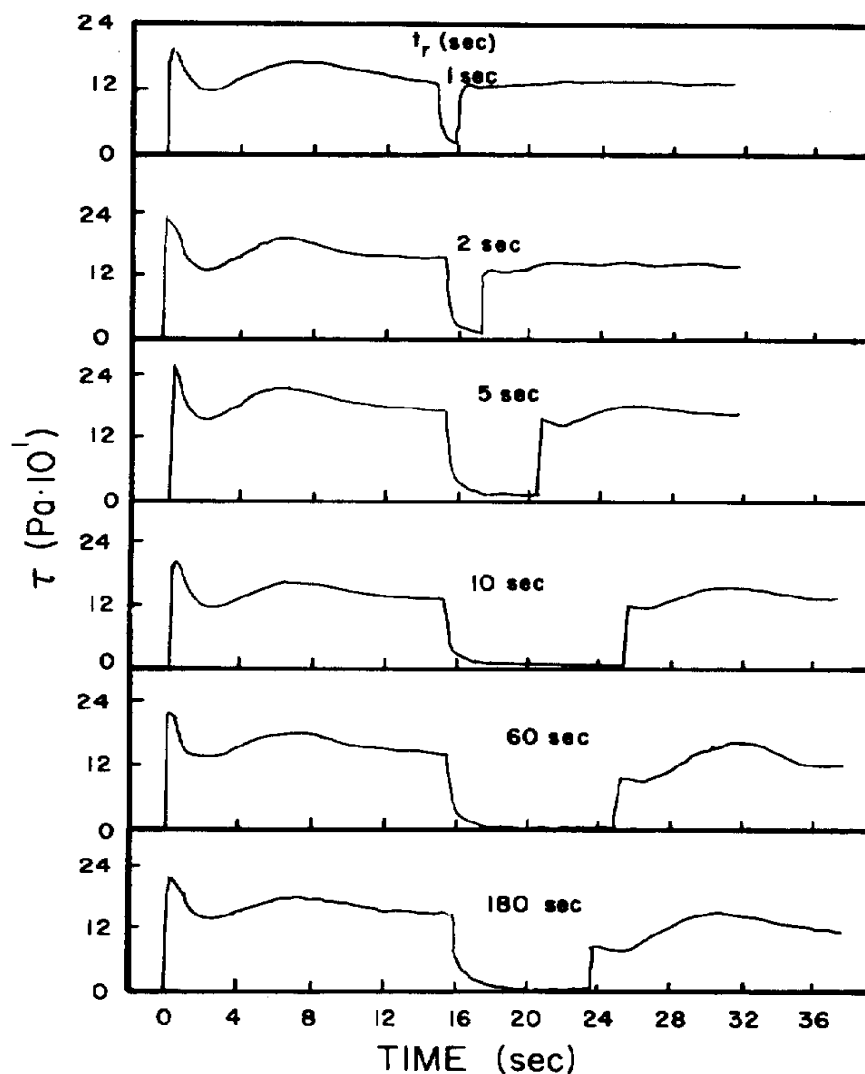At first sight these results are in qualitative agreement with the predictions of Ericksen's theory. As stated in the presentation

Fig. 6. Interrupted stress growth for various recovery times for 60-mole % PHB/PET at 275°C: 50 mm cone-and-plate, 0.04 rad. cone, $\dot{\gamma} = 10$ sec^{-1}.

of Ericksen's theory, the positive and negative director directions are assumed equivalent (i.e., $\underset{\sim}{n} = -\underset{\sim}{n}$). For an oriented fluid, therefore, Ericksen's theory would predict the same flow behavior independent of shear direction. Figure 7 shows the results of an interrupted stress growth experiment for the 60-mole % PHB/ PET system at 275°C in which the shear direction is reversed. Notice that in comparison to the case in which continuation of shear flow was in the same direction, no difference in shear stress
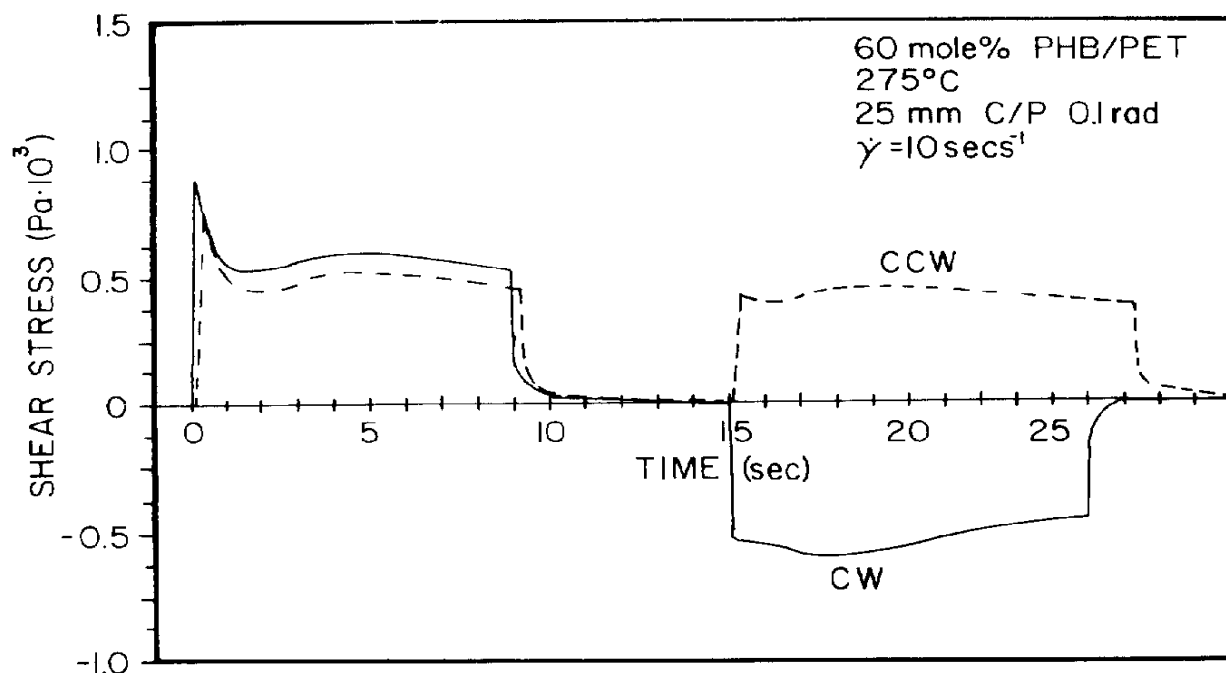
Fig. 7. Interrupted stress growth for 60-mole % PHB/PET system at 275°C: 25 mm cone-and-plate with a 0.1 radian cone and $\dot{\gamma}$ = 10.0 sec^{-1}. The broken line (- - -) represents a reversal in the flow direction on the start up of flow.

response exists. The first overshoot peak is nearly absent from both response curves. Again this is in qualitative agreement with the ideas of Ericksen's theory.

The results presented thus far have been for the 60-mole % PHB/PET system. In order to be able to generalize the results, the transient response of the 80-mole % PHB/PET and Kevlar[R] systems were also investigated. Figure 8 shows a transient shear stress response curve for the 80-mole% PHB/PET system at 320°C. After one minute of shearing at a rate of 3 sec^{-1}, the shear direction was reversed. The initial stress growth response is quite similar to the behavior exhibited by the 60-mole % PHB/PET system. Both the first and second overshoot peaks are present. Upon reversal of shear direction, no stress overshoot peaks are exhibited. This result is consistent with the predictions of Ericksen's theory and the behavior exhibited by the 60-mole % PHB/PET system. We also note that upon cessation of shear, the shear stresses relax to zero instantaneously.

The results of the investigation of the transient response of the
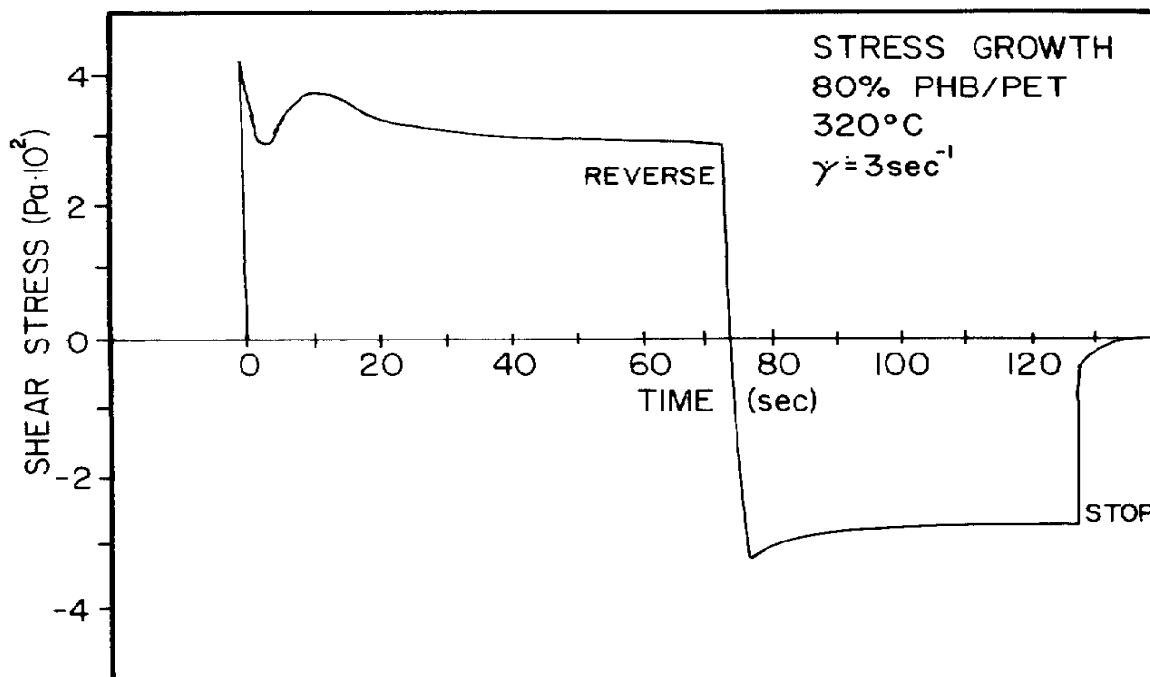
Fig. 8. Shear stress response on reversal of shear direction for 80-mole % PHB/PET copolymer at 320°C: 25 mm diameter cone-and-plate with a 0.1 radian cone.

Kevlar system are shown in Figures 9 and 10. These figures show the stress response curves for an interrupted shear test at a shear rate of 10 sec^{-1}. Upon inception of shear, a large stress overshoot is exhibited at a strain value of less than 1. After three minutes of relaxation at the test temperature (60°C) the overshoot peak remains greatly reduced. There is no second overshoot peak exhibited by the Kevlar material. This result implies that the second overshoot peak exhibited by the PHB/PET systems is probably not a phenomenon generally associated with liquid crystallinity, but may be related to the copolymer nature of the system. In all other respects, however, the behavior of the Kevlar system is consistent with the behavior of the PHB/PET systems. Upon cessation of shear the stresses relax to zero immediately. Figure 11 shows the results of tests in which the shear direction has been reversed. After the initial shearing has taken place, the overshoot peak is noticeably absent.

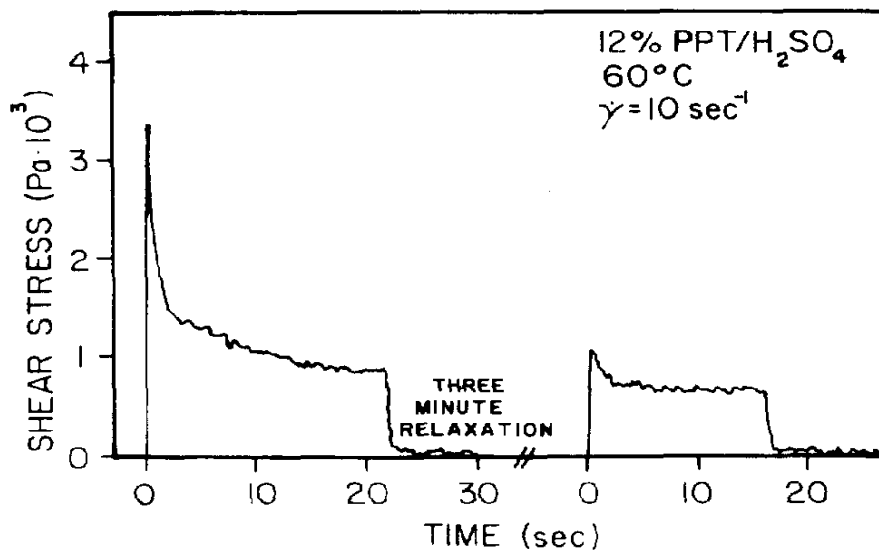The transient stress response of the materials tested are in

Fig. 9.   Interrupted shear stress growth for a 12 wt% PPT/H_2SO_4 solution at 60°C: 25 mm cone-and-plate with a 0.1 radian cone and $\dot{\gamma} = 10$ sec^{-1}.
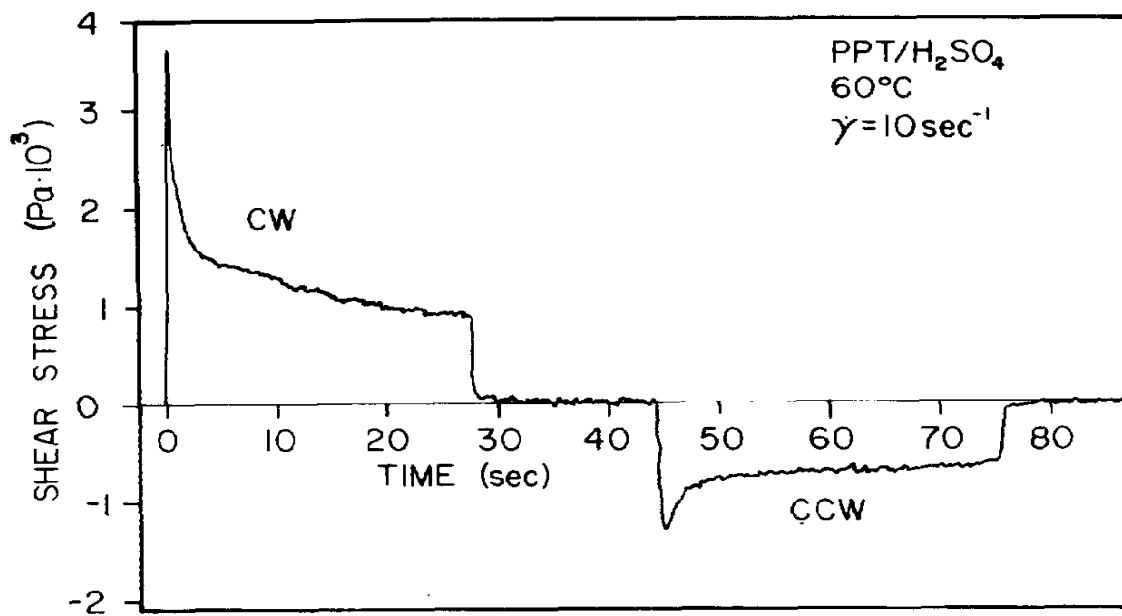

Fig. 10.   Interrupted shear stress growth for 12 wt% PPT/H_2SO_4 solution at 60°C: 25 mm cone-and-plate with a 0.1 radian cone and $\dot{\gamma} = 10$ sec^{-1}.
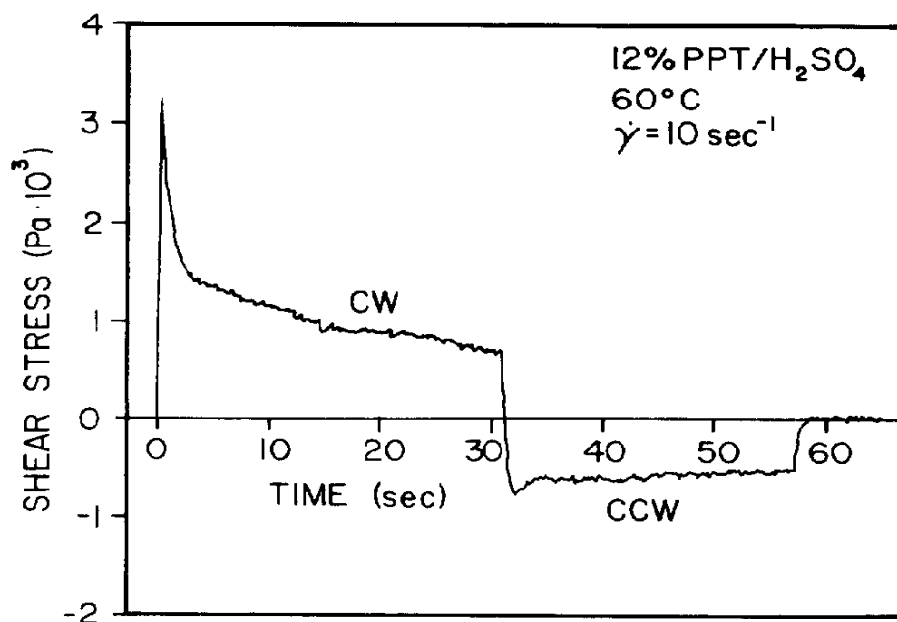
Fig. 11.   Transient shear stress response on the reversal of shear direction for 12 wt% PPT/H$_2$SO$_4$ solution at 60°C: 25 mm cone-and-plate with a 0.1 radian cone at $\dot\gamma$ = 10 sec^{-1}.

qualitative agreement with the predictions of Ericksen's theory. Upon inception of shear, a stress overshoot peak is exhibited at strain values of less than one. This peak is shear history dependent and can be removed completely. Once destroyed, the overshoot peak remains absent, even after three minutes of relaxation at the melt temperature. Also, the fluids appear to be insensitive to changes in shear direction once the overshoot peak has been removed. Finally, upon cessation of shear, the shear stresses relax to zero immediately. Clearly, some form of structural rearrangement is taking place within the fluid with the application of shear flow. This rearrangement is exhibited as a stress overshoot peak and appears to be irreversible, although it may just possess a very long time for recovery. Ericksen's theory qualitatively accounts for the experimentally observed behavior in terms of molecular orientation effects. However, it is not certain that a high degree of molecular orientation is being generated in shear flow. To further test the theory, wide angle x-ray scattering studies were performed on samples of the 60-mole % PHB/PET copoly-

mer subjected to known temperature and shear histories. These
results are presented next.

Wide Angle X-Ray Scattering

As a further test of the predictions of Ericksen's theory, spe-
cially prepared samples of the 60-mole % PHB/PET copolymer
were examined using wide angle x-ray scattering (WAXS) tech-
niques. Figure 12 shows the WAXS pattern exhibited by an ex-
tended ribbon of the 60-mole % PHB/PET copolymer. The sample
was prepared at a temperature of 275°C and an average extension
rate of 2.5 sec^{-1}. The flow direction is along the vertical axis in
the figure. The sample possesses a high degree of molecular orien-
tation with respect to the flow direction. This is evidenced by the
azimuthal dependence of scattering intensity observed in the pat-
tern. The sharp rings in the pattern indicate the presence of PHB
and PET crystallinity. In contrast, Figures 13a and 13b show the
WAXS patterns exhibited by sheared samples of the 60-mole %

Fig. 12.   WAXS pattern of a quenched sample of 60-mole % PHB/PET system
subjected to extensional flow at $\dot{\epsilon}$ = 2.5 sec^{-1} and a temperature of 275°C. Flow
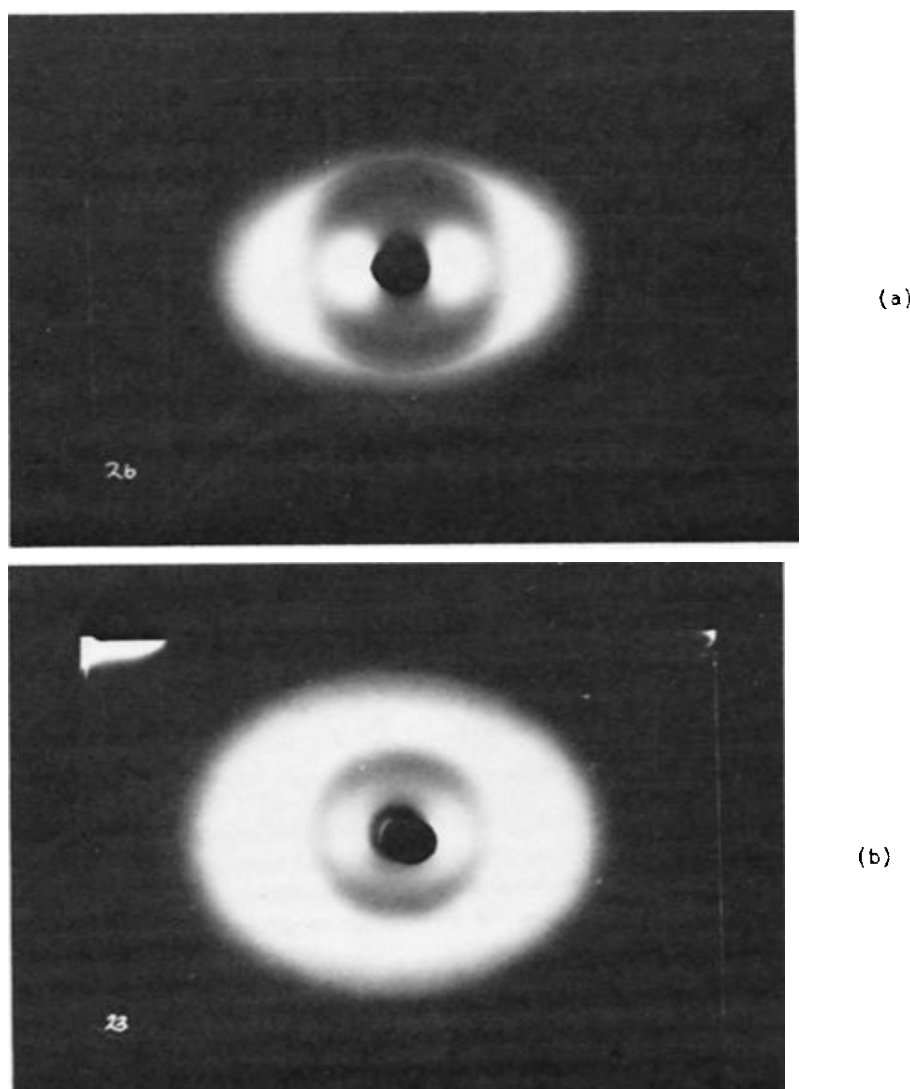direction is along the vertical axis.

Fig. 13. WAXS pattern of a quenched sample of 60-mole % PHB/PET system subjected to shear flow a) $\dot{\gamma} = 10$ sec $^{-1}$, b) $\dot{\gamma} = 50$ sec^{-1} at $T = 275°C$. Flow direction is along the vertical axis.

PHB/PET system. These samples were prepared by shearing the copolymer melt at 275°C and a shear rate of 10 sec^{-1} and 50 sec^{-1}. The low degree of azimuthal dependence of scattering intensity exhibited qualitatively indicates that the samples do not possess a high degree of molecular orientation. The WAXS patterns discussed so far indicate that the 60-mole % PHB/PET material ap-

(a)   (b)

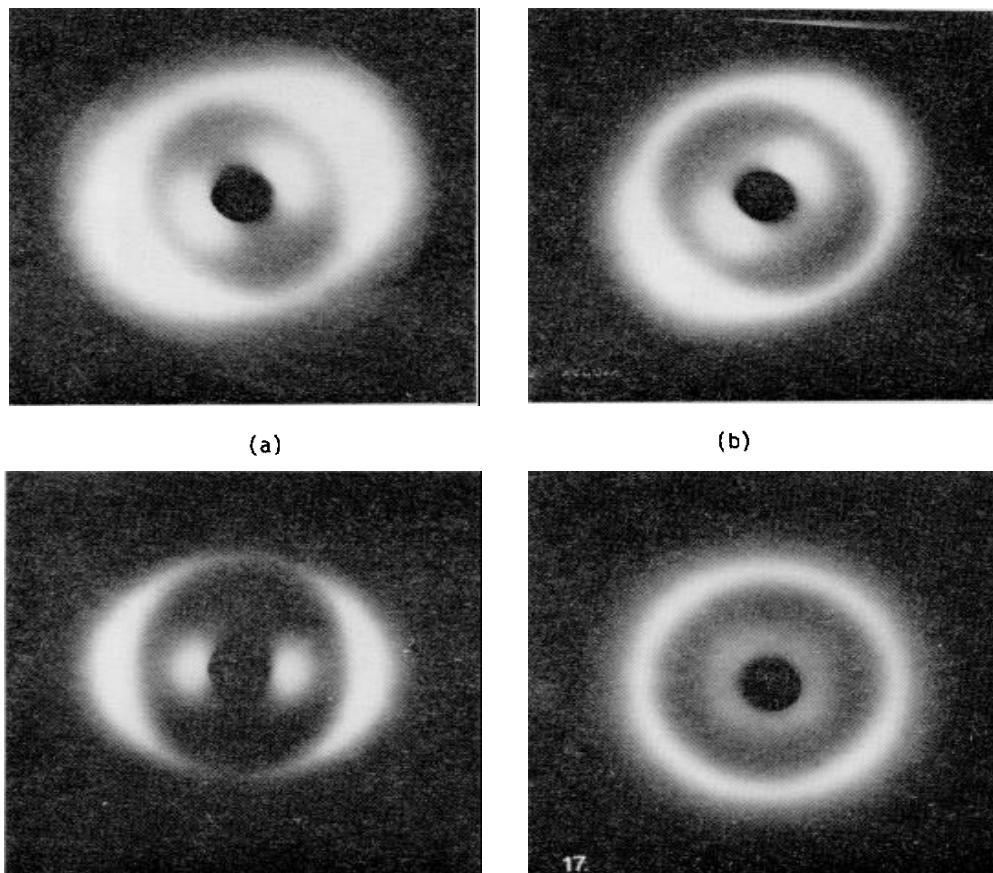(c)   (d)

Fig. 14.   WAXS pattern of 60-mole % PHB/PET system, initially subjected to extensional flow and then annealed at 275°C for varying times. a) $t = 0$; b) $t = 30$ seconds; c) $t = 1$ minute; d) $t = 5$ minutes; and $\dot{\epsilon} = 2.5$ sec^{-1}. Flow direction is along the vertical axis.

pears to orient well in extension, but not in shear flow. (The extension experiments are somewhat questionable because of the non-isothermal nature of the experiment since deformation and cooling occur simultaneously.)

Figure 14 shows the WAXS patterns exhibited by extended samples which have been annealed at the melt temperature for times ranging from 0 to 5 minutes. According to Ericksen's theory, orientation will remain indeffinitely if the fluid is left undisturbed. Additionally, if the experimentally observed stress overshoot peaks are due to the development of molecular orientation (as Ericksen's theory predicts) then this rearrangement of structure should be stable for at least three minutes at the melt

temperature. This last postulate follows directly from the interrupted stress growth results. The WAXS patterns in Figure 14 do not support the above conclusions. Even after 30 seconds at the melt temperature, most of the initial molecular orientation has been destroyed. This is seen by comparing the degree of azimuthal dependence of scattering intensity in Figure 14a to that in Figure 14b. It appears that after 5 minutes (see Figure 14d), all of the initial molecular orientation present has been destroyed.

The result of the annealing tests clearly contradict the predictions of Ericksen's theory. It appears that even if a high degree of molecular orientation develops in shear flow, it may be lost in as little as 30 seconds. The theory would predict that any orientation produced during deformation of the fluid would remain indefinitely. It is also evident that the experimentally observed stress overshoot peaks are not related to the development of molecular orientation. If this were true, the overshoot peak would reappear after 30 seconds of relaxation at the melt temperature. It is more reasonable to assume, therefore, that some other type of structural rearrangement takes place during shear flow. Further discussion of this structural rearrangement is carried out in the next section.

DISCUSSION

An attempt has been made to use Ericksen's anisotropic fluid theory to model the transient flow behavior of several liquid crystalline polymers. The theory can qualitatively predict many features of the experimentally observed stress growth/relaxation behavior. The theory predicts this behavior solely on the basis of a reorientation of the director. Wide angle x-ray studies on sheared and extended samples indicate that the 60-mole % PHB/PET system may orient in extension, but not in shear flow. This result is well within the capabilities of the theory (i.e., $\lambda \neq 1$). However, the results of annealing experiments invalidate the theory's prediction that stress overshoot is due to the development of molecular orientation. The WAXS studies also indicate that the fluid particles may lose their orientation within a few seconds, which is not in agreement with the theory.

Clearly, some other form of structural rearrangement is occurring within these fluids during shear flow. Onogi and Asada[10]

have theorized that the internal structure of liquid crystalline
materials is based on the existence of a polydomain structure.
Within each domain there exists a high degree of molecular
orientation. From domain to domain, however, the axis of orien-
tation may change. On a global scale, therefore, the fluid appears
to be unoriented. Onogi and Asada claim that all liquid crystal-
line materials should exhibit a three-region flow curve. A shear
thinning region [Region I] followed by a plateau region [Region
II] followed by another shear thinning region [Region III]. Ac-
cording to Onogi and Asada, the existence of these three flow
regions is due to the successive destruction of the polydomain
structure with the application of shear flow. There is experimen-
tal evidence which suggests that this may be true. Horio[11] has
observed for lyotropic systems that shear flow can break large
domains into smaller spherical domains that rotate as they flow.
Asada[12] and Onogi et al.[13] have also shown, through the use of
rheo-optical methods, that shearing can break up the polydomain
structure into a single phase. These same investigators report,
however, that in extensional flow, strong birefringence was ob-
served. This would indicate the presence of a high degree of
molecular orientation.

The results of the previous investigators indicate that shear
flow may tend to break up the polydomain structure, while exten-
sional flow may consolidate and orient it. A schematic represen-
tation of this mechanism is given in Figure 15. The initial polydo-
main structure is affected differently by shear than extensional
flow. Thus, extensional flow seems to be more effective than shear
flow in producing molecular orientation. Ide and Ophir[14] and
Viola and coworkers[15] have shown that this is true for the PHB/
PET system.

With regard to the present study, the idea of disruption in the
polydomain structure during shear flow is consistent with the
experimentally observed behavior. The first stress overshoot peak
exhibited by the liquid crystalline materials tested is most proba-
bly due to the destruction of the initial polydomain structure into
smaller domains. The reformation of the initial polydomain struc-
ture must take a very long time, as the stress overshoot peak can
remain absent even after three minutes of relaxation at the melt
temperature. Once the polydomain structure has been disrupted,
there appears to be no long-range cohesive structure within the
fluid. Thus, upon cessation of shear flow, the stresses relax to zero
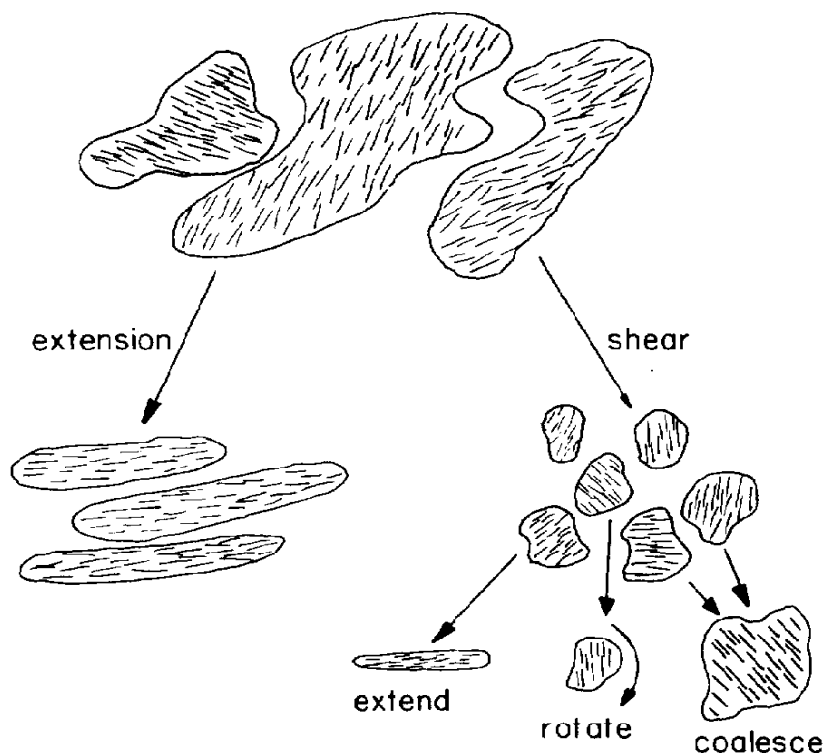
INITIAL POLYDOMAIN STRUCTURE

Fig. 15. Schematic representation of the destruction of the polydomain structure.

almost immediately. Ericksen's theory is most likely predicting the experimentally observed behavior for the wrong reasons. Molecular orientation effects are not the cause of the stress overshoot peak exhibited upon inception of steady shear flow.

CONCLUSIONS

Although it may be anticipated that the anisotropic fluid theory of Ericksen cannot quantitatively describe the flow properties of LCP's, our results go beyond just confirming this anticipation. The transient shear flow properties of two thermotropic copolyesters and a lyotropic system cannot be explained through orientation changes in the domains. Not only is this what is predicted by the theory but it may coincide with the intuition of others. It is believed the shear flow causes a disruption of the polydomain structure within the liquid crystalline fluid, such as

in the reduction of size of domains and the degree of interaction between domains. It is this rearrangement of structure which leads to the stress overshoot peaks on the inception of shear flow. Constitutive theories for these fluids should reflect changes in domain structure rather than just orientation changes.

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