Macromolecules **1989**, *22*, 1419–1422

Band Textures in Mesomorphic (Hydroxypropyl)cellulose Solutions

Benoît Ernst and Patrick Navard*

Centre de Mise en Forme des Matériaux, Ecole Nationale Supérieure des Mines de Paris, U.A. CNRS no. 852, Sophia-Antipolis 06565, Valbonne Cedex, France.

Received April 22, 1988; Revised Manuscript Received August 10, 1988

ABSTRACT: The formation of band textures in mesomorphic (hydroxypropyl)cellulose solutions has been investigated, on the basis of a comparison between rheooptical and rheological measurements. The influence of several physical parameters (molecular weight, concentration, sample thickness, etc.) on the formation of these bands is analyzed. It is shown that this peculiar texture is very stable and only observed when the molecules had been well oriented in the shear direction. It is proven that shear can be efficient for orienting molecules in the ordered state. It is unambiguously shown by small-angle light scattering that no band texture exists during the flow. A qualitative model is proposed to account for this texture and the first normal stress difference.

Introduction

Main-chain nematic or cholesteric liquid crystalline polymers have very interesting rheological behavior. The relaxation after shearing is particularly intriguing: after cessation of flow, it appears, after a certain time, a transient phenomenon giving long, equidistant, black lines, known as band texture, perpendicular to the shear direction, seen between crossed polarizers. This band texture originates from a serpentine position of the chain along the shear direction.[1,2] Less studied is the formation of such a band texture. One of us[3] followed the formation and deformation of this texture by optical microscopy and small-angle light scattering. Recently, Marsano et al.[4] and Marrucci[5] used a transparent rheometer to investigate the influence of both shear rate $\dot{\gamma}$ and shear deformation γ on the band formation in (hydroxypropyl)cellulose (HPC) liquid crystalline polymer solutions. Marsano et al.[4] have measured two parameters: t_s, the shear time at a given shear rate $\dot{\gamma}$, and t_b, the time after cessation of shear one needs for the band texture to appear, for several concentrations and molecular weights. Their main results are (i) there is a critical shear rate $\dot{\gamma}_c$ below which no band texture appears after cessation of shear; (ii) even if the shear rate $\dot{\gamma}$ is greater than $\dot{\gamma}_c$, there is a minimal shear time t^*_s below which no band texture appears after cessation of shear, showing that a minimal deformation is needed; and (iii) there are no concentration effects, but there is a slight influence of molecular weight on the two critical parameters $\dot{\gamma}_c$ and t^*_s.

Marrucci[5] also noticed an influence of the sample thickness on the band appearance. Fincher[6] used light diffraction to measure the band spacing S and he showed that neither sample thickness nor shear rate have an influence on S, while increasing concentration decreases S.

A model has been proposed by Marrucci,[7] but it does not seem to fit all the experimental facts. In order to get more quantitative and precise knowledge of the conditions of the appearance of this band texture, we extended the work of Marsano et al.,[4] compared it to the rheological behavior, performed flow–small-angle light scattering (SALS) measurements, and found new features about the formation of the band texture that must be taken into account in any comprehensive theory.

Experimental Section

The formation of the band textures was investigated on two samples of HPC Klucel E (M_w = 60 000) and L (M_w = 100 000) kindly supplied by Hercules. Five solutions, 40, 45, 50, 55, and 60 wt %, of HPC E and three solutions, 45, 50 and 55 wt %, of HPC L were prepared by mixing water with HPC at room temperature followed by centrifugation to remove air bubbles. All the solutions were fully cholesteric at rest except the 45 wt % ones, which were biphasic, and the 40 wt %, which is isotropic.

Rheooptical investigations were made at room temperature by using a modified Instron 3250 cone-and-plate made of highly polished quartz.

Optical observations made with a polarizing WILD-LEITZ microscope allowed the formation of band textures to be observed just after shearing. Samples were injected into the gap between the transparent cone and plate. The solutions are then sheared at given shear rates $\dot{\gamma}$ for a certain time t_s. After shearing is stopped, it takes a certain time, t_b, for the band texture to be formed, and the band texture stays a time t_d before vanishing. The three parameters t_s, t_b, and t_d are then determined at given $\dot{\gamma}$.

Flow–SALS experiments were conducted with a 633-nm wavelength laser using the three 40, 45, and 60 wt % solutions of HPC E. The flow and the relaxation of the band texture were followed by H_v light scattering, the analyzer being parallel to the flow direction.

The steady-state rheological behavior was investigated by using the standard rheometer equipped with cone and plate made of the same material used for the rheooptics.

Results and Discussion

Optical Microscopy. The formation of the band textures during and after shear in HPC–water solutions has been followed by optical microscopy. The purpose of this study is to get a more quantitative description of this very peculiar phenomenon. The following results have been obtained, measuring t_s, t_b, and t_d versus $\dot{\gamma}$ for each solution.

1. No band texture is visible under shear, just looking into the microscope. Only dark lines running along the flow direction have been observed. Due to the large flow birefringence, which is generated under shearing, this result does not prove the nonexistence of bands during shearing. This important question will be discussed in the next chapter.

2. The isotropic 40 wt % E solution and the two biphasic 45 wt % E and L solutions did not exhibit band textures after shearing even when they were sheared at high shear rates ($\dot{\gamma} > 100$ s^{-1}) for several minutes. So, one condition necessary for band formation after shearing in (hydroxypropyl)cellulose solutions is to have a completely anisotropic solution. This rule does not seem to be general since a band texture has been reported for a biphasic solution.[8]

3. There is a critical shear rate $\dot{\gamma}_c$ below which no band texture appears, in the limit of shearing time $t_s \leqslant 30$ min. This critical shear rate is nearly independent of concentration in the studied concentration range but depends on molecular weight. For HPC L, $\dot{\gamma}_c{}^L = 1.1$ s^{-1}, while for HPC E, $\dot{\gamma}_c{}^E = 2.6$ s^{-1}. Figure 1 shows the comparison between $\dot{\gamma}_c$ and the flow curve viscosity η versus shear rate $\dot{\gamma}$.

0024-9297/89/2222-1419$01.50/0

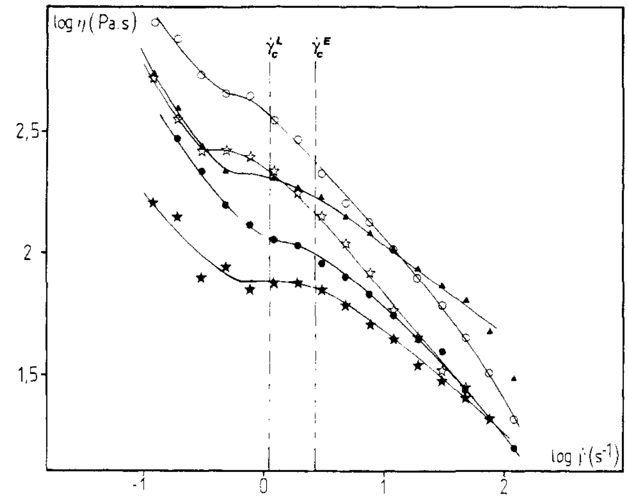

Figure 1. Comparison between the optical critical shear rate $\dot\gamma_c$ with the flow curve viscosity η versus shear rate $\dot\gamma$: (○) L 55%; (☆) L 50%; (▲) E 60%; (●) E 55%; (★) E 50%.

One can argue that $\dot\gamma_c$ corresponds to the onset $\dot\gamma^*$ of the second shear thinning region (region III in the terminology of Onogi and Asada[9]). According to Doi and Edwards,[10] $\dot\gamma^*$ is given by the following equation for a nematic rodlike polymer solution:

$$\dot\gamma^* \propto D_r C \qquad (1)$$

where D_r is the rotational diffusion constant and C is the concentration.

$$D_r \propto C^{-2} M^{-7} \log M \qquad (2)$$

so

$$\dot\gamma^* \propto C^{-1} M^{-7} \log M \qquad (3)$$

Equation 3 shows that $\dot\gamma^*$, and thus $\dot\gamma_c$, is strongly inversely dependent on M and slightly sensitive to concentration. Equation 3 explains why we did not observe a dependence on concentration, owing to the small concentration range used. The inverse dependence of $\dot\gamma^*$ (and $\dot\gamma_c$) on M is observed, but without quantitative agreement.

The relation between $\dot\gamma_c$ and $\dot\gamma^*$ is interesting. It means that for having a band texture, the applied shear rate has to be larger than the inverse of the longest relaxation time, which means that the rodlike molecules will orient in the flow. Thus, a well-oriented state has to be reached for inducing a band texture.

4. If $\dot\gamma > \dot\gamma_c$, another condition has to be added for the band texture to be formed. The shearing time t_s must be larger than a certain time which depends on $\dot\gamma$. If $\gamma = \dot\gamma t_s$, then γ_c is the minimum shear deformation above which the band texture can be formed. Once γ_c has been calculated for each solution at different shear rates, the condition to get a band texture after shearing can be expressed as

$$\dot\gamma > \dot\gamma_c \quad \text{and} \quad \gamma_c \dot\gamma^{0.3} = a \qquad (4)$$

a was found to be about 140 for HPC E and about 120 for HPC L. All this supports the hypothesis that the molecules must be well oriented in the flow direction in order to give a band texture. The minimum shear deformation γ_c is very large. This is a new result and has an interesting consequence. Several authors[11,12] compared the efficiency of shear and elongation for orienting thermotropic polymer. The conclusion is not clear, some authors concluding that shear might be efficient while others draw the inverse conclusion.[12] If our hypothesis concerning the relation between the formation of a band texture and the existence of a well-oriented state is correct and valid for nematic polymer, eq 4 may explain their results. The shear deformation needed to have the molecules oriented in the flow direction must be large.

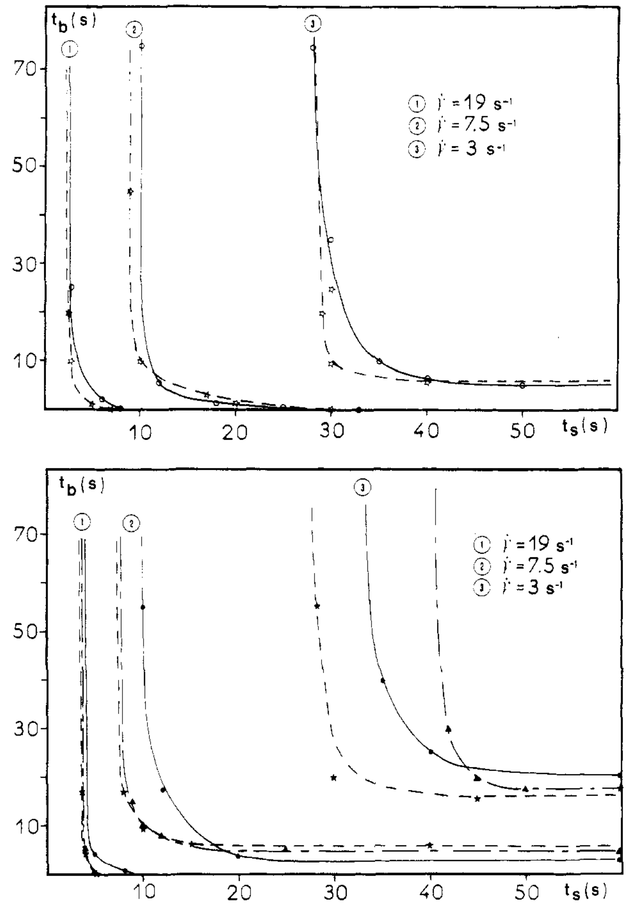

Figure 2. Evolution of t_b the time the bands need to appear after shearing as a function of the shear time t_s at different shear rates for the HPC L solutions (top) and the HPC E solutions (bottom): (○) L 55%; (☆) L 50%; (▲) E 60%; (●) E 55%; (★) E 50%.

5. If $\dot\gamma > \dot\gamma_c$ and $\gamma > \gamma_c$, the band texture appears after stopping the shearing for times t_b ranging from 0 (meaning either that the band texture is formed immediately after stopping or that this texture was present during the shearing) to about 70 s depending on concentration, molecular weight, shear rate, and shear time, as shown in Figure 2. It must be noticed that the time t_b is difficult to determine at low shear rates since the band texture appears very slowly as a continuous phenomenon. Independent measurements repeatable to within ±15% give confidence in the present results.

6. Kiss and Porter[13] have suggested a correlation between the occurrence of a band texture during the shear and the measurements of a negative normal force for polypeptide solutions. Marsano et al.[4] suggested that this did not seem the case for HPC solutions, contrary to an early report of one of us.[3] We performed careful rheological and rheooptical experiments under the same conditions. In Figure 3 we compare the shear rate at which t_b becomes zero, suggesting that a band texture could be present in the flow, with the first normal stress difference N_1 versus shear rate $\dot\gamma$ curves. It appears clearly that the occurrence of $t_b = 0$ is not correlated with a negative normal force during flow but rather with the onset of the decrease of the positive normal force in flow.

7. This peculiar mode of relaxation does not last a long time. After some time, the bands begin to lose their parallelism, then they form elongated domains, and they

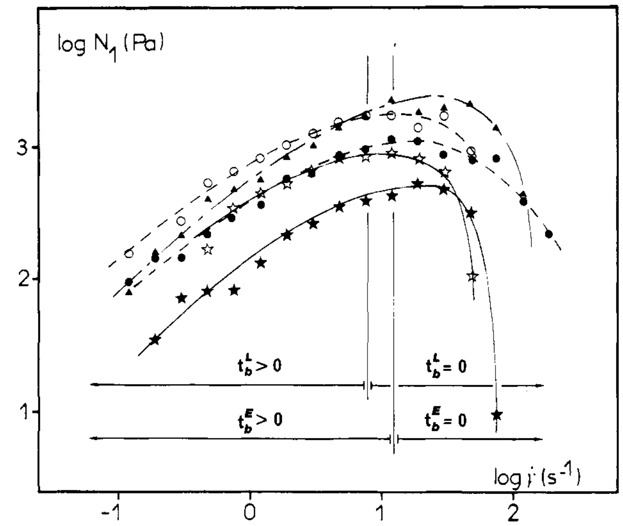

Figure 3. Comparison between the first normal stress difference N_1 versus shear rate $\dot{\gamma}$ curves with the critical shear rate at which t_b becomes zero: (O) L 55%; (☆) L 50%; (▲) E 60%; (●) E 55%; (☆) E 50%.

finally transform into an equilibrium texture close to the undeformed state. This duration time of the band textures is very sensitive to the molecular weight and to the applied shear rate while it is not influenced by the concentration nor by the deformation. The higher the molecular weight is, the longer the solutions will exhibit the band patterns: at $\dot{\gamma} = 3\ s^{-1}$, $t_d = 8$ min for the HPC L solutions, while $t_d = 2$ min for the HPC E solutions. The influence of the shear rate on t_d is also significant since t_d varies, for the HPC L solutions, from about 10 min at $\dot{\gamma} = 1.2\ s^{-1}$ to 5 min at $\dot{\gamma} = 30\ s^{-1}$.

8. The band texture is energetically very stable. This has been deduced following the experimental procedure given below. First the solutions are sheared so that the band texture will appear after the shear flow. When the bands are fully formed, a shear deformation is applied by rotating the cone with a low angular velocity, in such a way that $\dot{\gamma} < \dot{\gamma}_c$. The rotation destroys very quickly the optical aspect of the band. After a time T, the rotation is stopped. Since $\dot{\gamma} < \dot{\gamma}_c$, no bands are formed. The rotation is then reversed with the same angular velocity. When the reversed deformation equals the initial deformation, the optical aspect of the band texture is instantaneously reformed. If the reversed sense of rotation is continued, the bands are destroyed as in the first rotation but are reformed when changing the sense of rotation again and going back to the initial position and so on. We saw that it is possible to apply a shear deformation of up to 10 shear units to the band texture and restore the original molecular arrangement when applying the same reversed deformation. The limit of this mechanism is when the time $2T$ necessary for shearing and coming back to the initial position is larger than the time t_d, the duration of the bands after stopping shear (see point 7). It is possible also to shear, stop for some time, shear back, and restore the original band texture, but only if the overall time is less than t_d. This experiment shows that a laminar shear (no tumbling) is applied to the sample at low shear rate ($\dot{\gamma} < \dot{\gamma}_c$) and that the band texture is not confined in a small layer of the sample, like near the surface. The laminar shear puts out of register in the thickness direction the orientation of the molecules, so that the optical aspect disappears, despite that each layer, in the thickness, has kept its original orientation. Reversing the shear flow aligns again in register the orientation. Finally such an experiment shows that the band texture is an energetically stable configuration of the molecules. In the absence of any external forces, its destruction is probably only due to the Brownian motion of the molecules.

9. No effect of sample thickness has been observed. By shifting the eyepiece under the quartz plate from the edge to the center of the plate we observed that the bands appear simultaneously in all the sample. Moreover, by focusing our observation, at a given distance from the center of the plate, through the sample thickness we observe no modification of the formation of the band texture. Until now there was a discrepancy between some authors about the influence of the sample thickness (plate–plate geometry). Several authors[5,14] showed that the appearance of the bands is governed by the thickness while the other[6] observed exactly the contrary. Our observations, corresponding to a situation of variable thickness, are in accordance with the conclusion of the later one.

10. The band spacing d is found to be 4.5 ± 0.3 μm with the 55 wt % HPC E solution. This result is consistent with a previous work.[3] Due to the narrow molecular weight and concentration ranges used we were not able to observe any influence of these two parameters on d. However, it has been recently shown that the concentration of the polymer solution has a very large effect on d.[6] By varying the shear rate $\dot{\gamma}$ from 4 to 75 s^{-1}, we also observed that $\dot{\gamma}$ has no influence on the band spacing. In addition, the same behavior has been observed when bands are generated in elongational flow. These two later results show that the periodicity of the band texture is independent of the flow condition.

Light Scattering. The flow–SALS technique has been used in order to investigate the flow-induced structure. The relaxation of the band texture has also been followed by SALS and the results are similar to those given in an earlier work.[3] Thus, we will focus our attention on the evolution of the molecular ordering induced by the flow.

Figure 4 shows the H_v patterns of the 60 wt % solution of HPC E. The quiescent pattern (Figure 4a) undergoes some deformation when subjected to shear. At low shear rates, corresponding to region I as defined by Onogi and Asada,[9] the H_v pattern transforms into a somewhat elliptical pattern with the long axis perpendicular to the flow direction (Figure 4b). At the onset of region III the pattern changes again into the characteristic pattern for oriented and deformed anisotropic rodlike superstructures as observed by Samuels,[15] Stein and Rhodes,[16] and Hashimoto et al.[17] (Figure 4c–e) in addition to a strong and sharp vertical streak. At very high shear rates, up to 1000 s^{-1}, only the vertical streak remains (Figure 4f). Two main results follow from these data. First, it is clearly shown that the supermolecular structure undergoes important changes when submitted to shear. At low shear rates this structure is slightly deformed without any relevant feature while at high shear rates the molecules tend to orient in the flow direction, the degree of orientation increasing with shear rate. After stopping the shear, a band texture appears only when the H_v profile was similar to the pattern of Figure 4c–f. This again shows that a condition for having a band texture as a relaxation mechanism is that the molecules are well oriented in the flow direction. Second, the answer to the question about the existence of a band texture during the flow has been unambiguously found. The occurrence of a band texture immediately after stopping the shear ($t_b = 0$) let us suggest that bands could exist during shear. Since microscopic observations are quite difficult and affected by the relative motion of the supermolecular structure at high shear rates, we used SALS measurements to elucidate this important question.

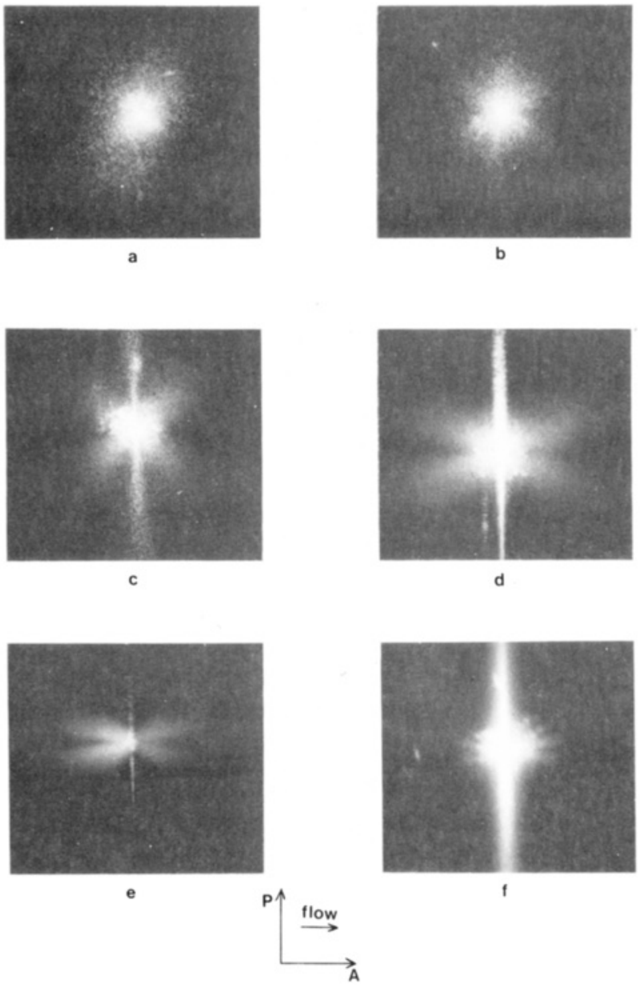

Figure 4. H_v light scattering patterns during the shear flow (60% HPC (E)–water solution): (a) at rest; (b) $\dot{\gamma} = 0.03\ s^{-1}$; (c) $\dot{\gamma} = 0.3\ s^{-1}$; (d) $\dot{\gamma} = 3\ s^{-1}$; (e) $\dot{\gamma} = 30\ s^{-1}$; (f) $\dot{\gamma} = 300\ s^{-1}$.

As shown in Figure 4 no H_v profile specific of a band texture (an horizontal two-point pattern, see ref 3) has been observed during the shear flow even in the shear rate range where the first normal stress difference becomes negative.

So, first we showed clearly that the bands are due to a relaxation mechanism as indicated by Fincher,[6] and second, contrary to Kiss and Porter,[13] we found evidence of the absence of any correlation between the occurrence of a band texture during the flow and the measurements of negative normal forces.

The present study gives two important pieces of information: the bands do not exist during shear and the band texture is not a transient metastable state. In addition, SALS shows that there is a structure during shear. This gives the following model: under shear or elongation, defects (disclinations) are present but are strongly constrained by the molecules oriented by the flow, up to the point where no disclination is still stable. By optical microscopy we observed dark lines running along the flow direction. These lines are visible when $\dot{\gamma} > \dot{\gamma}_c$ and $\gamma > \gamma_c$. This means that the constrained defects are squeezed into regions between which the molecules are aligned. In other words, the flow is composed of long domains of well-oriented chains separated by squeezed-defect regions. The solution will have to rearrange the defects in space after cessation of flow. To relax the stored energy without loosing its nematic ordering, an in-plane periodic waving of the director will minimize the distortion energy while allowing the relaxation to occur. This qualitative model is in agreement with all the above reported features. As an elasticity driven mechanism, it explains why the time t_b decreases, increasing the stored energy. It also explains why an anisotropic solution is needed since the relaxation has to accommodate the nematic ordering. There is also a connection with the behavior of the normal forces, since the squeezed-defect regions will generate an extention perpendicular to the plane of shear. This gives a compression force in the plane of shear which may overcome the extention due to the first normal stress difference and leads to a negative normal force. The negative normal force and the band texture are two consequences of the structure of the flow.

Conclusion

The occurrence of a band texture in HPC–water solutions during and after shearing has been analyzed. Since no bands appear during the flow this phenomenon is shown to be a relaxation mechanism and is not correlated with a negative normal force. These bands appear only after the molecules have been well oriented in the flow direction. The minimum shear deformation necessary for orienting the molecules is very large, due probably to the stability of the defect (domainlike) texture present at rest and at low shear rates. The band texture is shown to be energetically very stable. A structural model is presented and seems to fit the observed results about the formation of a banded structure, at least for lyotropic polymers. The band texture which appears in thermotropic polymers had most probably the same origin, but the conditions of its formation have never been fully investigated. This investigation is presently carried out in several laboratories, including ours, and the results will be of great interest for understanding the flow behavior of anisotropic polymers.

Acknowledgment. We thank Dr. E. Marsano for making a preprint of ref 4 available to us and we are grateful to A. Le Floc'h, F. Fournier, and J. Lebris for help in the design and the realization of the transparent cone-and-plate rheometer.

Registry No. HPC, 9004-64-2.

References and Notes

(1) Viney, C.; Donald, A. M.; Windle, A. H. *Polymer* **1985**, *26*, 870.
(2) Navard, P.; Zachariades, A. E. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1089.
(3) Navard, P. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 435.
(4) Marsano, E.; Carpaneto, L.; Ciferri, A. *Mol. Cryst. Liq. Cryst.* **1988**, *158B*, 267.
(5) Marrucci, G.; Grizzuti, N.; Buonaurio, A. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 263.
(6) Fincher, C. R. A. *Mol. Cryst. Liq. Cryst.* **1988**, *155*, 559.
(7) Marrucci, G. *Pure Appl. Chem.* **1985**, *57*, 1545.
(8) Viney, C.; Windle, A. H. *Mol. Cryst. Liq. Cryst.* **1987**, *148*, 145.
(9) Onogi, S.; Asada, T. In *Rheology*; Astarita, G., Marrucci, G., Nicolais, L., Eds.; Plenum: New-York, 1980; Vol. 3, p 647.
(10) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Clarendon Press: Oxford, UK, 1986.
(11) Garg, S. K.; Kenig, S. In *High Modulus Polymers*; Zachariades, A., Porter, R. S., Eds.; Marcel Dekker: New York, 1988; p 71.
(12) Ide, Y.; Ophir, Z. *S.P.E. ANTEC Technol. Pap.* **1982**, *28*, 33.
(13) Kiss, G.; Porter, R. S. *Mol. Cryst. Liq. Cryst.* **1980**, *60*, 267.
(14) Fellers, J. F. Personal communication.
(15) Samuels, R. J. *J. Polym. Sci.* **1969**, *A2*(7), 1197.
(16) Rhodes, M. B.; Stein, R. S. *J. Polym. Sci.* **1969**, *A2*(7), 1539.
(17) Hayashi, N.; Murakami, Y.; Moritani, M.; Hashimoto, T.; Kawai, H. *Polym. J.* **1973**, *4*, 560.