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Rheo-Optical Studies of Liquid Crystalline Solutions of Helical Polypeptides

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The shear dependence of structures of liquid crystalline solutions of Poly-γ-benzyl-L-glutamate PBLG in m-cresol was examined in a polarizing microscope using a specially constructed shearing stage and stroboscopic illumination. Three different textures were observed depending on shear rate. The shear rates at which the texture changes occurred correlated well with the changes in sign of the first normal stress difference reported earlier.[1,2] The region of negative first normal stress difference corresponded to a texture consisting of striations perpendicular to shear.

The transverse striations were also observed to develop over a period of seconds or minutes after cessation of shear at rates within the first positive region of N_1. These striations could be fixed in a dried film by using a volatile helicogenic solvent (1,4-dioxane).

A speculative model is proposed to account for the rheological observations in Refs.[1,2] and the rheo-optical observations reported herein.

INTRODUCTION

In Refs. 1 and 2 we have reported the observation of many unusual rheological phenomena in concentrated solutions of Poly-γ-benzyl-glutamate (single enantiomers as well as racemic mixtures, PBLG and PBDG), Poly-ε-carbobenzyloxy-L-lysine (PCBZL), and Poly-β-benzyl-L-aspartate (PBA) in the helicogenic solvent, m-cresol. We observed that the transition from isotropic to liquid-crystalline state at a critical concentration C^* of the rod-like helical polypeptide solute is manifested dramatically in all of the rheological properties which were examined.

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The observations reported in this paper will consist of photographs taken during shear, after cessation of shear, and of dried films made from solutions of PBLG in a volatile helicogenic solvent, 1,4-dioxane. In order to avoid unnecessary redundancy, background material which is available in Refs. 1 and 2 has been kept to a minimum and interested readers are referred thereto.

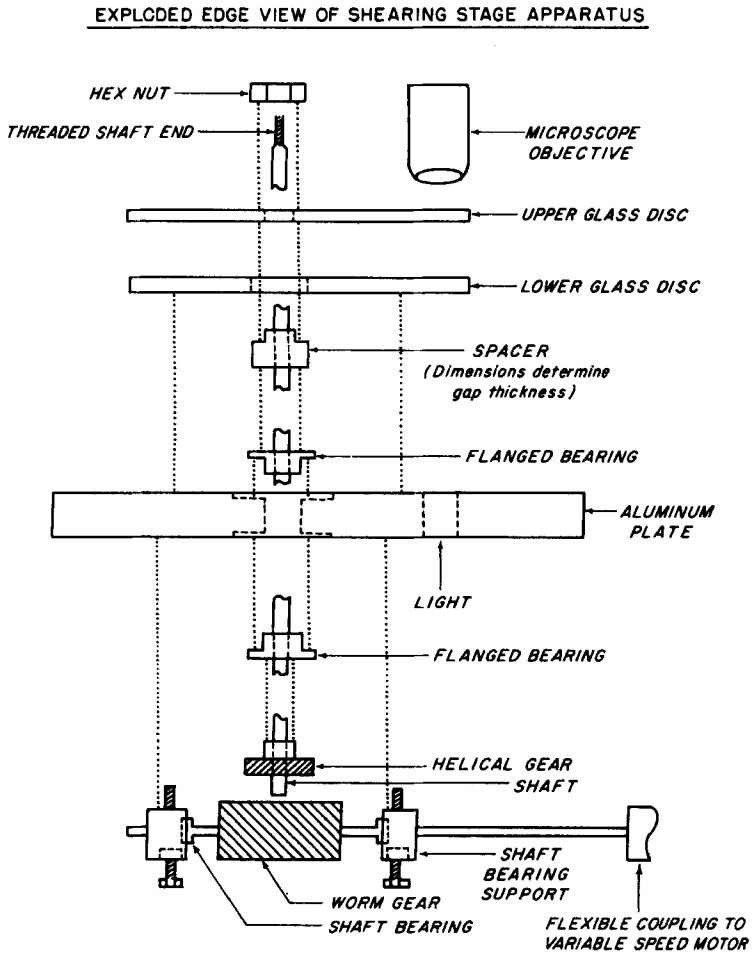


FIGURE 1 Exploded schematic diagram of shearing stage apparatus.

EXPERIMENTAL

An exploded schematic diagram of the shearing stage apparatus utilized in this study is shown in Figure 1. The apparatus consists simply of two glass discs, separated approximately 0.5 mm by a brass spacer, one fixed and one driven at any chosen speed, insertable into a polarizing microscope. Since the field of view of the microscope objective is small compared to the distance from the observed spot to the axis of rotation, it can be assumed that the shear rate is constant throughout the field of view. The range of accessible shear rates was approximately 0.5–200 sec^{-1}. It was found impossible to increase the shear rate further by reducing the spacing of the discs, since lack of precision in machining caused slight non-parallelism of the discs which would have produced unacceptably large variations in shear rate in the course of each revolution. The accuracy of the shear rate values given in this paper is approximately 30%.

Dried films were made from 1,4-dioxane solution by pressing a drop of solution between glass slides and pulling them apart lengthwise at various speeds for low and high shear. The films dried in approximately one minute.

The 350,000 M.W. PBLG used in this study was obtained from Biopolymer Corp. (Moreland Hills, Ohio) and the 150,000 M.W. PBLG was obtained from Sigma Chemical Co. (St. Louis, Mo.). Steady shear viscosity η and first normal stress difference N_1 for a 17 wt.% (liquid crystalline) solution of the 350,000 M.W. PBLG are shown in Figure 2. Note in particular the occur-

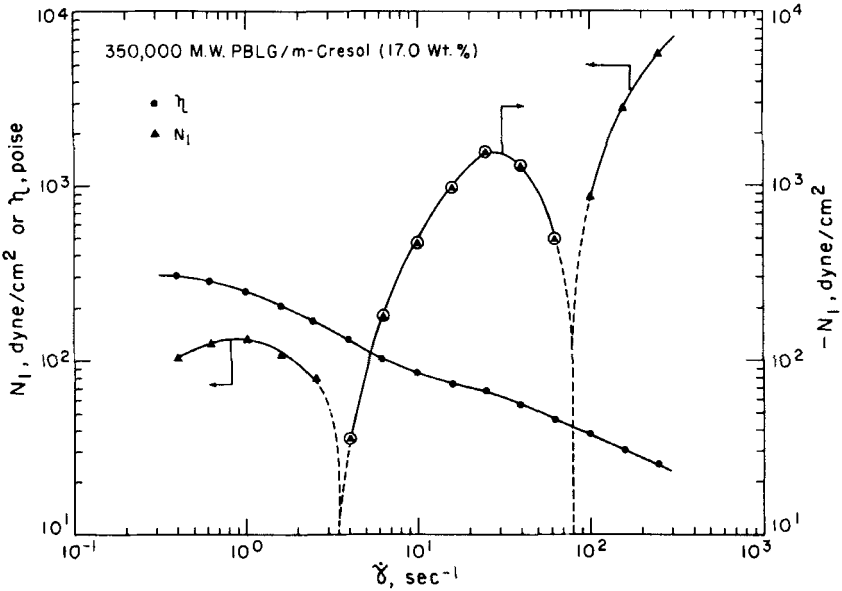


FIGURE 2 Steady shear viscosity and first normal stress difference versus shear rate for 17.0 wt% PBLG, M.W. 350,000.

rence of two sign changes in N_1 at shear rates of 3.5 and 80 sec^{-1}; this region of negative N_1 is a feature which we have observed in other liquid-crystalline polypeptide solutions but which has not appeared previously in the rheological literature.

RESULTS

During shear

Photomicrographs taken at a magnification of 170X between crossed polars with a flash lamp (duration on the order of 0.0001 sec) to freeze the structure at a variety of shear rates are shown in Figure 3. Some of the features which will be referred to in the description which follows may be obscure in reproduction, but were more clearly visible in the original Ektachrome slides due to the vivid birefringence colors. The direction of shearing is vertical in every case.

Figure 3a (1.1 sec^{-1}) clearly shows streaks parallel to the shearing direction. In Figure 3b (3.3 sec^{-1}) these streaks are disappearing and the beginnings of a structure exhibiting orientation perpendicular to the shearing direction is seen. In Figures 3c and 3d (16 and 19 sec^{-1}, resp.), the transverse striations are clearly visible and no streaks parallel to the shearing direction are in evidence. (We have nicknamed these transverse striations the "row-nucleated" texture due to the similarity of appearance with structures formed during stress-induced crystallization of polyethylene (Ref. 3, Figure 17). No assumptions about the origins of this texture are implied by this terminology). In Figure 3e (40 sec^{-1}) the row-nucleated texture is starting to fade. Note the air bubble elongated in the direction of shear. Finally, in Figure 3f (100 sec^{-1}) only a relative featureless field remains, with what appears to be occasional disclinations scattered throughout. It is apparent that the correlation between the appearance of the row-nucleated texture and a negative value of N_1 is quite close.

After cessation of shear

Photographs taken after the cessation of shear for a 14.1 wt.% solution of the 150,000 M.W. PBLG are shown in Figures 4–6. (This solution did not exhibit negative N_1 at shear rates within the range of the shearing stage and the row-nucleated texture did not appear in photographs taken during shear.) In Figure 4a, taken immediately after the cessation of shear at 3.3 sec^{-1}, long thin streaks, oriented parallel to shear and speckled in appearance, are visible. In Figures 4b and 4c (0.3 min and 1 min after cessation) the appearance is only slightly changed with slight coarsening of the

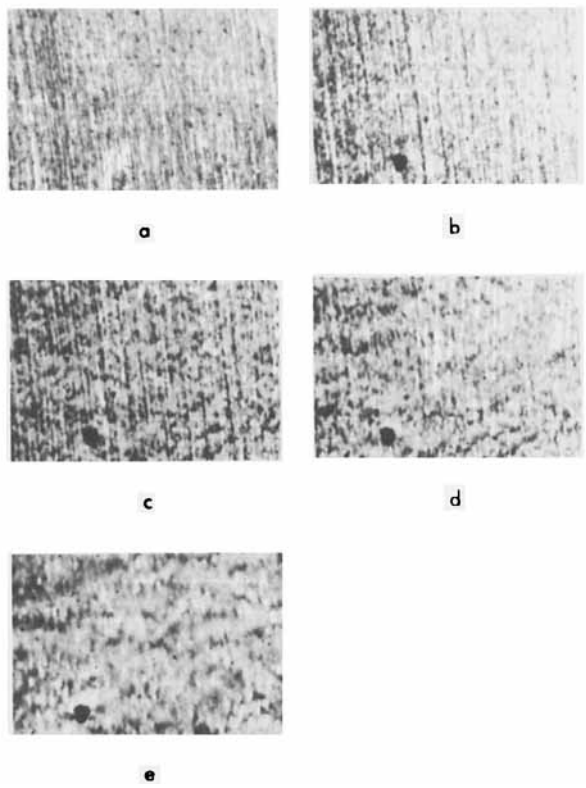


FIGURE 4 Polarized light micrographs of 14.1 wt % 150.000 M.W. PBLG at various times after shearing at 3.3 sec^{-1} 170X. (a) immediately; (b) 0.1 min; (c) 0.3 min; (d) 2 min; (e) 5 min.

speckling and thickening of the streaks. In Figure 4d (2 min) the coarsening is more visible and the first hint of horizontal organization appears. Finally, in Figure 4e (5 min), the coarsening is very pronounced so that the streaks have become lines of ellipsoidal regions. Ellipsoidal regions of the same color have come roughly into horizontal register so that a coarse, irregular variation of the row-nucleated texture results.

Photographs taken after cessation of shear at 19 sec^{-1} are shown in Figure 5. Figure 5a (immediately after cessation) once again shows speckled streaks parallel to the shearing direction. Figure 5b (0.1 min) still shows the parallel streaks, but superimposed is the beginnings of transverse striations. In Figure 5c (0.3 min) the row-nucleated texture superimposed on the streaks is well-developed, with greater overall perfection and finer scale than the texture which developed in five minutes after cessation of shear at 3.3 sec^{-1} (cf. Figure 4e). In Figure 5d (1 min) the row-nucleated texture is

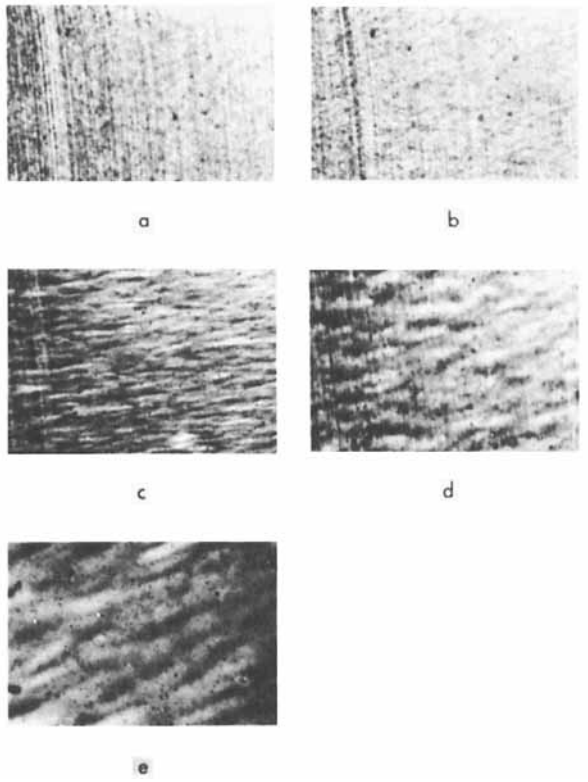


FIGURE 5 Polarized light micrographs of 14.1 wt% 150,000 M.W. PBLG at various times after shearing at 19 sec^{-1} 170X. (a) immediately; (b) 0.1 min; (c) 0.3 min; (d) 2 min; (e) 5 min.

already starting to fade, with coarsening and loss of definition. After 5 minutes (Figure 5e) the row-nucleated texture has almost completely disappeared.

Photographs taken after the cessation of shear at 100 sec^{-1} are shown in Figure 6. Figure 6a (immediately after cessation) reveals only a uniform speckled appearance. After only 0.05 minutes, very fine and well-defined transverse striations have already formed (Figure 6b). After 0.1 minute (Figure 6c), the striations are slightly more perfect, and neighboring striations are much better differentiated on the basis of color. By 0.3 minutes (Figure 6d), the row-nucleated texture is already thickening and losing definition. This process continues and after 2 minutes (Figure 6e) the striations are quite thick, though still reasonably well-defined.

The behavior of this solution after the cessation of shear can be summarized

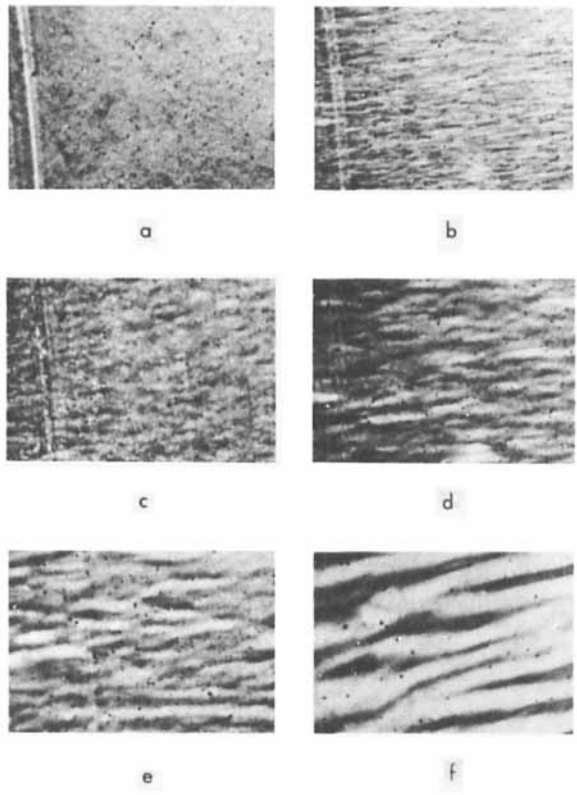


FIGURE 6 Polarized light micrographs of 14.1 wt% 150,000 M.W. PBLG at various times after shearing at 100 sec^{-1} 170X. (a) immediately; (b) 0.05 min; (c) 0.1 min; (d) 0.3 min; (e) 1 min; (f) 2 min.

as follows: with increasing rate of prior shear the row-nucleated texture forms more rapidly, with better definition and thinner striations, and also degenerates more quickly. It is significant that the solution shown in Figures 4–6 did not exhibit negative values of N_1 at the shear rates used, nor did they show the row-nucleated texture immediately upon cessation of shear. Thus the transverse striations were not present during shear, but formed spontaneously after cessation. However, the propensity of the molecular superstructure to re-organize into the row-nucleated texture increased with rate of prior shear, i.e., as the sign change in N_1 was approached. One final observation linking the negative normal stress phenomenon and the row-nucleated texture: in those solutions which were birefringent at rest (liquid crystalline) but did not exhibit negative N_1 values, the row-nucleated texture was not observed under any circumstances, either during or after cessation of shear.

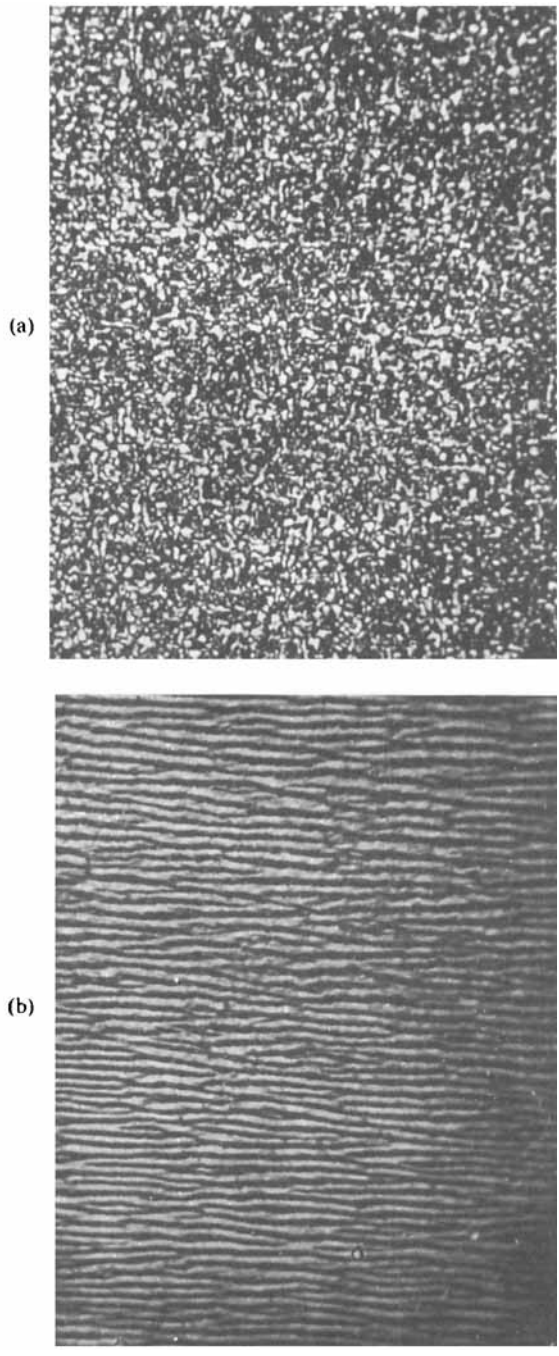
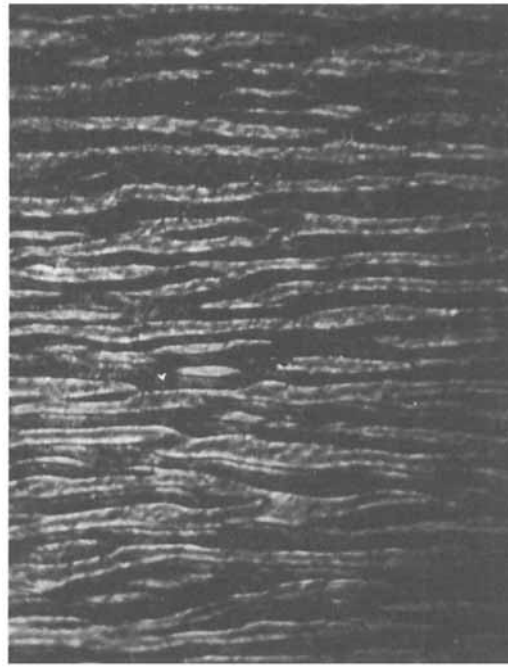


FIGURE 7 (a) dried film from 6.8 wt % 350,000 M.W. PBLG in dioxane, 100X; (b) dried film from 15.0 wt % 350,000 M.W. PBLG in dioxane, high shear 100X;



(c)

FIGURE 7 (c) dried film from 15.0 wt% 350,000 M.W. PBLG in dioxane, low shear 100X.

Dried films

Experiments were conducted with 6.8 wt. % (isotropic) and 15.0 wt. % (liquid crystalline) solutions of the 350,000 M.W. PBLG in 1,4-dioxane. This solvent was chosen since it is helicogenic and moderately volatile so that the structures formed after shearing could be made permanent by evaporation of the solvent. An assumption inherent in this procedure is that the structures formed by shear (and after cessation) are the same in m-cresol and dioxane solution, i.e., that they result from inter-molecular interactions (steric or electrostatic) and not from specific solute-solvent interactions. This assumption is supported by the similarity of appearance of the m-cresol solutions and the dried films.

Films made from the isotropic solution (6.8 wt.%) revealed a uniform spherulitic morphology, regardless of the rate of prior shear (Figure 7a). Recall that the "row-nucleated" texture was not observed in any circumstances for isotropic m-cresol solutions, nor for the anisotropic m-cresol solutions which did not exhibit the negative normal stress effect.

Films made from the anisotropic (15 wt. %) solution after shearing showed the transverse striations characteristic of the "row-nucleated" texture. As

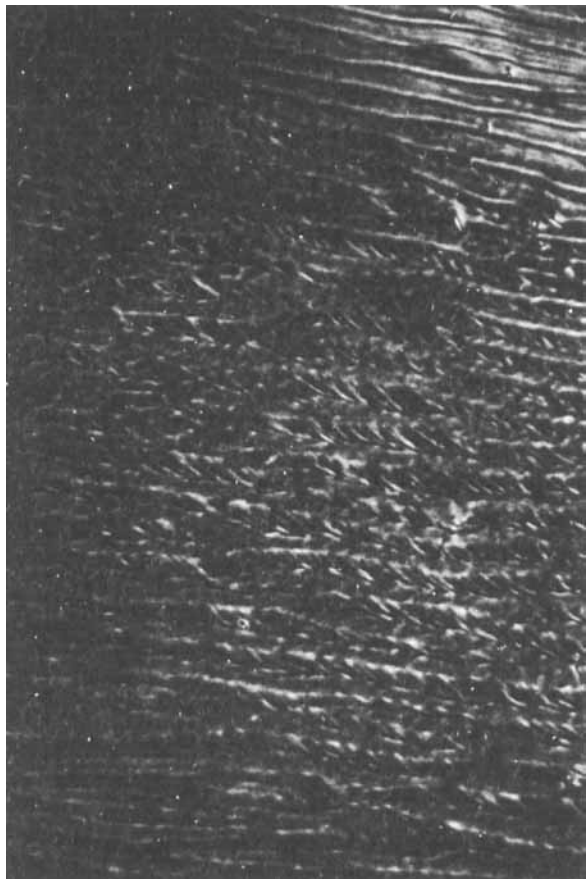


FIGURE 8 Helical transverse striations in dried film of 350,000 M.W. PBLG in dioxane 100X.

with the m-cresol solutions, films made at high shear exhibited fine striations (approx. 10μ width, Figure 7b) and those made at low shear exhibited wider striations (approx. 30 μ width, Figure 7c). The length of the striations was indeterminate, although occasional terminations were visible. Also, striations were occasionally observed to fork into two striations, which then continued side-by-side.

In most cases the striations appeared smooth but on occasion consisted of long runs of a very pronounced helical structure, always of the same sense. In these regions the field of view had the appearance of a series of coarse ropes strung perpendicular to direction of shearing (see Figure 8).

Insertion of a first order red plate at 45° to the crossed polaroids gave

alternately blue and yellow colors to the striations, indicating that the molecules within the striations were alternately parallel and perpendicular to the red plate. The molecules were therefore oriented alternately $\pm 45°$ to the shearing direction. This was observed both for the smooth striations and the helical, ropy striations.

DISCUSSION

Previous reports of a feature similar to the "row-nucleated" texture described above, formed by various means, have appeared in the literature. Toth and Tobolsky[4] report that an electric field gradient perpendicular to a thin film of 15% PBLG in $CHCl_3$ produces a dark field between crossed polars due to perpendicular orientation of the solute molecules, however slight mechanical shearing instantaneously restored birefringence colors in the form of "parallel, multi-colored bands whose long direction is perpendicular to the direction of shear." 15% methylene dibromide solutions of PBLG allowed to stand for 20 hours in a magnetic field of 9600 Gauss formed a structure consisting of lines perpendicular to the magnetic field.[5] The same authors also stated that "rubbing" the solution also yielded lines perpendicular to the direction of rubbing. A similar effect is reported by Iizuka upon reversal of an electrostatic field in a 14.0% solution of PBLG in CH_2Br_2.[6] A series of photographs taken during the process (Ref. 6, Figure 6) is strikingly similar to Figure 6 of this work. Initially the structure was that of speckled streaks parallel to the electric field. Upon reversal of the field many equidistant lines perpendicular to the electric field were rapidly formed (less than 2 sec). After 140 sec the perpendicular pattern had visibly decayed.

None of these authors advanced speculations concerning the mechanism of formation of these structures. The model which we will propose presently for structural re-arrangement within liquid crystalline solutions under shear must be consistent with the important results of our rheological and rheo-optical investigations, viz. two changes in sign in N_1 corresponding to two distinct changes in texture, and negative values of N_1 correlating with the appearance of the transverse striations characteristic of the "row-nucleated" texture.

The results of the microscopic investigation of dried sheared films of anisotropic solutions indicate that molecules within striations are oriented $\pm 45°$ to the direction of shear. We make the assumption that the transverse striations observed in m-cresol solutions under conditions such that a negative value of N_1 is measured comprise the same structure. We propose that the transverse striations seen in thin films form planes on the order of

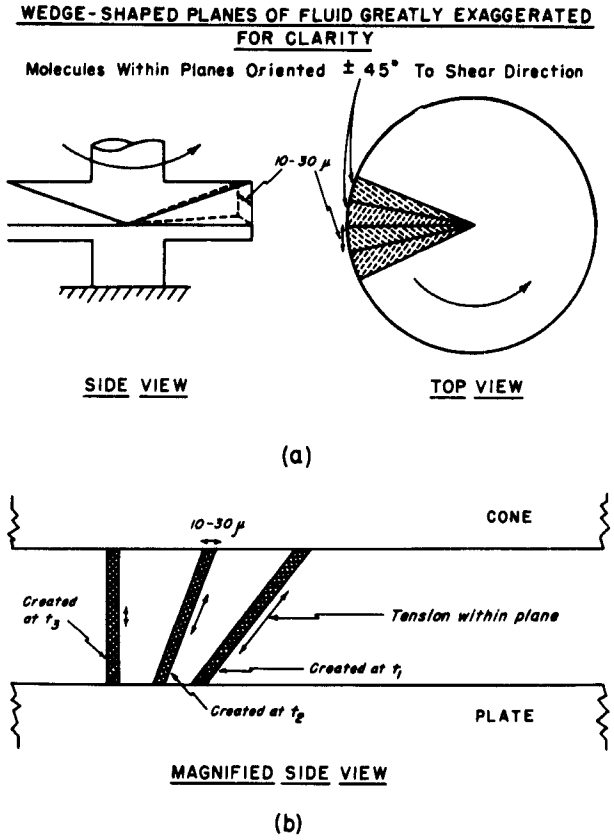


FIGURE 9 Proposed model linking "row-nucleated" texture and negative stress effect in cone-and-plate rheometer. (a) sideview and top view; (b) magnified side view.

10–30 μ in width which traverse the entire sample volume in the cone-and-plate rheometer, forming a physical link between the cone-and-plate (Figure 9a). We propose that the negative normal stress is the result of elasticity within these planes which are stretched as the cone rotates (Figure 9b). We envision a dynamic steady state as these planes are continuously stretched, broken, and re-created in a constantly fluctuating orientation pattern. Adjacent striations do not coalesce since molecules within them are perpendicular to each other.

The sequence of events occurring as a liquid crystalline solution is sheared at ever-increasing shear rates in a transparent cone-and-plate rheometer would be as follows:

Low shear—Molecules orient parallel to shear direction, observe streaks parallel to shear and positive values of N_1.

Medium to high shear—Molecules orient $\pm 45°$ to shear direction in wedge-shaped planes 10–30 μ wide. Observe transverse striations from top view (planes seen edge-on) and negative values of N_1 (due to tension within planes)

Very high shear—Planes break up into rapidly tumbling domains. Observe featureless field and positive values of N_1.

This speculative model accounts for the principal observations of this work: three regimes of normal stress including one with negative values, and three different shear-dependent textures including one characterized by striations perpendicular to shear direction. It also accounts for the correlation between the "row-nucleated" texture and the negative normal stress effect.

The crucial unanswered question is why the molecules assume the $\pm 45°$ orientation. Once they are thus oriented it is not surprising that they should come into register to form the transverse striations. Significantly, it appears that the $\pm 45°$ orientation possesses a degree of stability. Recall that liquid crystalline solutions sheared at rates within the first positive regime of N_1 were oriented parallel to shear immediately upon cessation, but evolved into the row-nucleated texture (cf. Figures 4–6) within seconds or minutes. Eventually, of course, Brownian motion destroyed these textures. It is also significant that the rate of prior shear in these cases influenced the rate of evolution into the row-nucleated texture, the degree of perfection of the texture, and the width of the striations. This was also noted for the dioxane solutions and evaporation of the solvent served to further enhance the perfection of the texture (cf. Figures 7b and 7c).

The 90° change in orientation of molecules within alternate planes (striations) makes this model resemble the phenomenon of "alignment-inversion walls" which has been observed in *p*-azoxyanisole[7] and treated theoretically.[8] The creation of alignment-inversion walls in closed shells was proposed as the mechanism leading to formation of tactoidal shell defects in PBLG/dichloromethane solutions under the influence of a magnetic field.[9] Possibly shear fields as well as magnetic fields are capable of creating alignment-inversion walls in liquid crystalline solutions of helical polypeptides.

This model is as yet highly speculative and could prove to be entirely unrealistic, at which point we will painlessly abandon it. It is, however, consistent with all rheological and rheo-optical observations we have made to date on PBG and PCBZL solutions. Significantly, another recent study of the rheo-optics of liquid crystalline PBLG solutions also resulted in the observation of three different textures depending on shear rate.[10] Although the model proposed differs in detail from ours, there are points of similarity, such as the feature of "domain-uniting." It is not yet clear whether the model proposed in Ref. 10 can account for the negative normal stress effect.

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