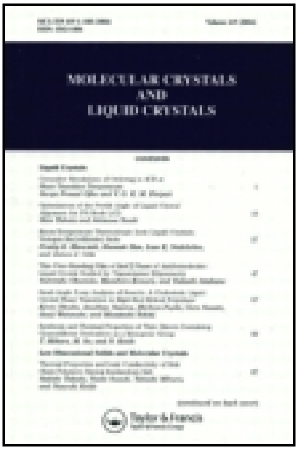

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Deformation Studies of Liquid Crystalline Polymers

Anagnostis E. Zachariades [a], Patrick Navard [a] & John A. Logan [a]
[a] Ibm Research Laboratory, San Jose, California, 95193

To cite this article: Anagnostis E. Zachariades, Patrick Navard & John A. Logan (1984): Deformation Studies of Liquid Crystalline Polymers, Molecular Crystals and Liquid Crystals, 110:1-4, 93-107

To link to this article: http://dx.doi.org/10.1080/00268948408074498

Mol. Cryst. Liq. Cryst. 1984, Vol. 110, pp. 93-107
0026-8941/84/1104-0093/$18.50/0

Printed in the United States of America

DEFORMATION STUDIES OF LIQUID CRYSTALLINE POLYMERS

ANAGNOSTIS E. ZACHARIADES
PATRICK NAVARD
JOHN A. LOGAN
IBM Research Laboratory
San Jose, California 95193

Oriented liquid crystalline polymers exhibit a macroscopic optical effect which appears as a sequence of bright and dark bands perpendicular to the orientation direction. Although these bands appear to be similar to the Williams domains in low molecular weight liquid crystals, their interpretation must satisfy not only the optical observations but also the rheological properties of the mesophases and the high mechanical properties typically exhibited by the oriented polymer morphologies produced by processing such mesophases. In view of these criteria, we discuss the formation of band patterns in thermotropic and lyotropic polymer systems and propose that the band patterns result from the ordering of macroscopic domains.

1. INTRODUCTION

The need for polymeric materials with greater mechanical, thermal and oxidative stability led polymer scientists to design new processing techniques and materials which contain aromatic and heterocyclic rings in the polymer chain backbone. New processing techniques have been developed mainly for processing flexible polymers and indeed, one of the most flexible polymers, polyethylene, has been processed recently into the strongest man-made fibers[1,2]. On the other hand, the design of new materials with aromatic and heterocyclic rings in the chain backbone has been pursued by linking together suitable mesogenic monomers through functional groups located at the ends of the mesogenic monomers. Depending on whether the functional groups are linked directly or indirectly, *e.g.*, through an alkylene chain segment, rigid or semi-rigid polymer backbone may result. Rigid and semi-rigid polymers exhibit liquid crystalline behavior upon heating and/or in solution and form thermotropic melts when the liquid crystalline behavior is brought about by a temperature change and lyotropic solutions for certain solution concentrations and temperatures. Because of their ability to orient in the melt or the solution, such polymers have been processed into highly oriented morphologies with ultra-high modulus and strength. Examples from this group of polymers are the poly(p-phenylene terephthalamide fibers with modulus ~120 GPa prepared by spinning the fibers from a lyotropic solution of poly(p-phenylene terephthalamide) in H_2SO_4 and the thermotropic copolyesters of poly(ethylene terephthalate) with p-acetoxybenzoic acid contents greater than 30 mole percent which have been injection molded into high modulus specimen (~12 GPa)[3].

Although the oriented morphologies of the flexible, semi-rigid and rigid polymers have certain common characteristics, that is they are fibrillar, exhibit a high degree of chain orientation and are birefringent, and have modulus (100-200 GPa) and strength (3-5 GPa) of the same order of magnitude, the oriented morphologies of the semi-rigid and rigid polymers, *i.e.*, the liquid crystalline behaving polymers exhibit a unique optical phenomenon which appears to be typical of the class of polymers with liquid crystalline order. This optical phenomenon, a series of bright and dark bands perpendicular to the orientation direction, is observed with cross-polarized light and has been reported to occur in various oriented thermotropic and lyotropic polymer systems[4-14].

The observation of these band structures has been explained by various workers independently on the basis of interference patterns resulting from the periodic occurrence of light scattering sources along the orientation direction,[6] the focusing effects of hydrodynamic instabilities that are known to occur in low molecular weight liquid crystals,[15] or a serpentine motion of molecules[12-14]. Since the band structures are observed with highly oriented morphologies having ultra-high modulus and strength as well as with moderately sheared morphologies with low mechanical properties, an explanation of the band structures must satisfy the criteria of (a) optical observations, (b) rheological properties and (c) mechanical performance of the oriented morphologies. Unfortunately, the hitherto proposed explanations consider only the first two criteria – and these in essence separately – and neglect the third criterion which addresses the issues of molecular extension and continuity within the oriented morphology for load transfer. In this article, we discuss the generation of the band structure in liquid crystalline polymers and propose an explanation in view of three criteria.

2. RESULTS

The optical observation of ordered band structures perpendicular to the flow direction were made in our laboratory during the preparation of highly oriented morphologies with the thermotropic copolyesters of poly(ethylene terephthalate) (PET) and 60 and 80 mole% acetoxybenzoic acid (PHBA) by compression molding under torsional flow conditions in a custom built optical plate-plate rheometer for

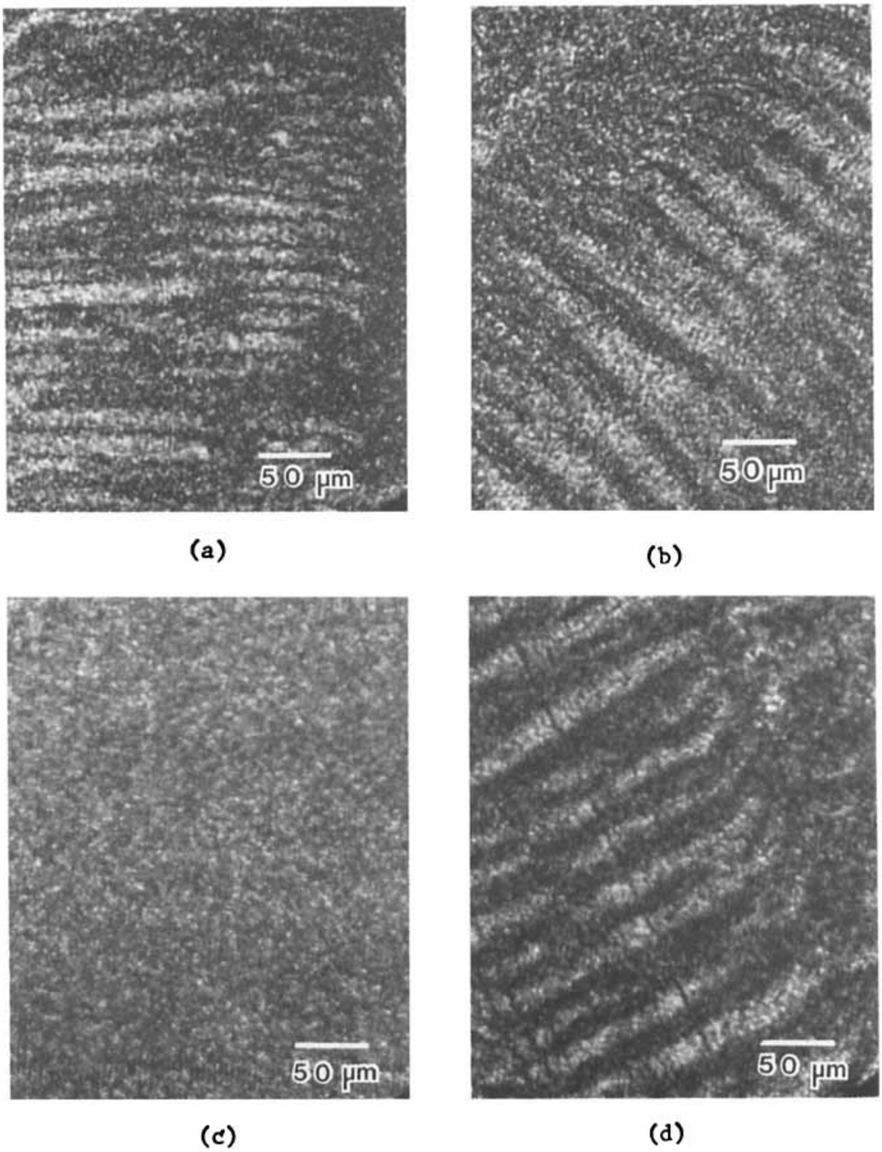

FIGURE 1 Optical micrographs of oriented PET/PHBA copolyester films showing band patterns using cross-polarized light. Band structure (a) parallel, (b) at 45°, (c) at 90° and (d) at 135° to analyzer direction.

rheo-optical studies. The band structures were formed during shearing between the plates when the copolyesters formed a nematic mesophase, the PET/PHBA 40/60 composition in the temperature range 265-295°C and the PET/PHBA 20/80 composition at ~300°C. Oriented films of the two copolyester compositions with band structures perpendicular to the orientation direction were prepared by shearing the anisotropic melt of each copolyester in a shear rate range of $10–2\times10^2$ sec^{-1} as it was cooled to ~200°C. The average thickness of the so produced films was 100-160 μm. Figure 1 shows an optical micrograph of the ordered band structure observed in an oriented film of the PET/PHBA 40/60 copolyester composition. The bands were observed using cross-polarized light when the shear direction of sample was orthogonal to and at 45° to the cross-polarizers. More specifically, three bands, for example, parallel to one another and lined up with analyzer appeared bright. When the specimen was turned to 45° from the cross-polarizers, the center band became dark with respect to the outer two bands. When the specimen was rotated parallel to the polarizer, the three bands appeared dark. On further rotation to 135° from the starting point, the outer two bands become dark and the center band was bright. Maximum extinction of individual bands appeared at ~40° from the shear direction, that is the bands becoming brighter on either side of this angle. The band spacing was 1-10 μm and did not change with different light sources. The bands were formed during shearing and within a viscosity range which for the nematic mesophase of the PET/PHBA 40/60 copolyester composition at 275°C and the PET/PHBA 20/80 composition at 330°C was 10-100 poise[16,17] Furthermore, the band structures which were formed by shearing the thermotropic melts of the two copolyester compositions had long relaxation times ($\tau_t >> 10^3$ sec) after shear

TABLE I Variation of mechanical properties of oriented films of the PET/PHBA copolyesters.

Sample Thickness (mm)	Young Modulus (GPa)	Tensile Strength (MPa)
0.1	12	100-110
0.5	8	90

cessation. Also, the band population increased with shear rate and their spacing decreased to 0.3-0.8 μm at higher shear rates ($\dot{\gamma} > \sim 10^3$ sec^{-1}) used during the extrusion of fibers through capillary dies. It is important to notice that the mechanical properties (Young modulus and strength) of the compression molded films under torsional flow conditions of the two copolyester compositions increased as the thickness of the specimen decreased (Table I) similarly to the earlier observations with the same copolyesters by Jackson and Kuhfuss[17] for injection molded samples of varying thickness.

Similar observations were made when lyotropic solutions of 40%(w/w) cellulose triacetate in trifluoroacetic acid and 47% hydroxypropyl cellulose in water were sheared between a microscope slide and a cover slip. Ordered bands with spacing 1-5 μm were formed perpendicular to the shear direction and near the surface of the glass slide.

3. DISCUSSION

The development of ordered band structures perpendicular to the orientation direction appears to be an optical effect observed with oriented thermotropic and lyotropic polymer systems. A similar optical effect is observed with low molecular weight liquid crystals in the presence of electric and magnetic fields which is known to associate with the formation of Williams domains[18] and has been explained by Williams[19,20] and Helfirch[21] independently using theories analogous to the theories explaining the formation of domains in ferroelectric and ferromagnetic materials and by Penz[15] by the formation of electro-hydrodynamic instabilities which result in an array of focusing elements. Because of the analogy of the observed domain patterns in the low molecular weight liquid crystals with the band structures in liquid crystalline behaving polymers in the presence of electric fields or under shear flow conditions, it was reasonable to assume that the domains observed in the low molecular weight liquid crystals and the band structures liquid crystalline polymers have the same origin. Thus, Krigbaum *et al.*[22,23] assumed that the Williams domains generated with the thermotropic melt of the aromatic copolyester of poly(ethylene terephthalate) and 60 mole% p-acetoxybenzoic acid in the presence of an electric field was due to the formation of the hydrodynamic instabilities described by Penz for p-azoxyanisole[15]. Similarly, we reported in an earlier publication[4] an analogy between the band structure observed in thermotropic copolyesters of poly(ethylene terephthalate) and p-acetoxybenzoic acid under shear and the Williams domains decribed previously[18]. Although the observed optical phenomena in low molecular weight liquid crystals and liquid crystalline behaving polymers are comparable, it is difficult to justify their origin to the same source. For example, the generation of electro-hydrodynamic instabilities proposed by Penz for liquid crystals occur at a molecular level and when the Reynold's number of the nematic mesophase is ~100. However, the spacing of the ordered band structures in the thermotropic and lyotropic polymer systems – particularly at low shear rate – is ~10 μm, that is one order of magnitude larger even than the pitch of the cholesteric solutions of cellulose triacetate in trifluoroacetic acid and hydroxypropyl cellulose in water which are difficult to envisage how they will remain cholesteric in the presence of electro-hydrohynamic instabilities. Also, the Reynold's numbers of the thermotropic melts of the copolyesters of PET/PHBA 40/60 at 275°C and the PET/PHBA 20/80 at 330°C are 10^{-3}–10^{-5}, *i.e.*, very low for fluid flow instability to occur. Krigbaum *et al.*[22] report that they were unsuccessful to obtain aligned[23] domains with the thermotropic melt of the PET/PHBA 40/60 copolyester in the presence of electric fields. Also, we were unable to determine the focal planes of the shear induced band structures in the same copolyester in our studies. The observations of Donald *et al.*[12-14] that the oriented molecules remain always in parallel planes to the shear direction supports further that the kind of hydrodynamic instabilities described for Williams domains do not occur in liquid crystalline polymer systems. Although Izuka[24] reports that regular band patterns may develop when reversing a dc electric field applied to a cholesteric polypeptide solution, it is difficult to relate this electro-optical effect to the Williams domains and the Penz's theory.

Two other explanations which have been proposed for the observation of band structures in oriented polymer systems are based on their optical or rheological properties and bear no relevance to the electro-optical effects described for low molecular weight liquid crystals. For example, it has been suggested[6,25] that the ordered bands (band spacing ~0.3 μm) observed with high modulus Aramid fibers is due to an interference pattern generated by a pleated structure in which the bends or folds between the pleats could be locations for density differences which could act as light scattering centers. Although this explanation may satisfy, in contrast to the previous explanation, the requirements for the high modulus and strength of the Aramid fibers, that is molecular chain orientation, extension and continuity, it is based on a structural variation occurring at a molecular level again which cannot explain the macroscopic optical observations with other lyotropic and thermotropic polymer systems. This zig-zag orientation structure in the Aramid fibers is similar to the orientation patterns observed by Takahashi[7] and Shimamura[9] with hydroxypropyl cellulose fibers obtained from a liquid crystalline solution and to the orientation patterns in our studies with the thermotropic PET/PHBA copolyesters; however, the average band spacing (0.3-1.5 μm) of the band structure in the fiber products is one order of magnitude smaller in comparison to the band spacing in the oriented films of the copolyesters at relatively low shear rate. A "piled domain" model proposed by Asada *et al.*[26,27] to explain the rheological properties of liquid crystalline polymers also does not provide support for the formation of aligned domain patterns because it does not predict any special arrangement of the domains which could lead to such patterns. The last explanation proposed by Donald *et al.*[5,12-14] suggests the molecules in shear deformed thermotropic melts have a serpentine motion in a plane perpendicular to the shear direction. However, this kind of molecular motion does not correlate well with electron microscope observations and also fails to explain the fast transformational of the band structure after short annealing.

Thus, it becomes evident that there is a need for a better explanation for the band structures and their alignment in the presence of flow fields. In the following, we hope to provide a reasonable explanation for these optical effects which satisfies the criteria of optical and rheological properties and the mechanical performance of the oriented morphologies of lyotropic and thermotropic polymers.

The first point is to recognize that there is a relation between the band structure and the domains described in the domain theory proposed by Asada *et al.*[26,27]. Despite the fact that the nature of these domains is not clear, there is evidence for their existence; yet the rheological properties of lyotropic solutions and thermotropic melts can be explained on the basis of their existence. Also, the size of the domains at rest is of the same order of magnitude as the band spacing in the generated band structures upon shearing. For example, when a solution of cellulose triacetate in trifluoroacetic acid (40% w/w) was sheared between two glass slides, band patterns were generated perpendicular to the shear direction with an average band spacing of 3-5 μm[28]. The same solution at rest exhibited domains the size of which was determined by wide-angle light scattering[23] and optical microscopy to be 5-10 μm[24]. Similarly, the band spacing of the ordered band patterns in Iizuka's studies with the cholesteric solution of poly-benzyl-glutamate in m-cresol was of the same size as the size of the domains at rest[24].

In the domain theory of Onogi and Asada,[27] the flow behavior of a liquid crystalline polymer is described by a three flow region curve. At very low shear rates, the domains flow with significant rotation and slippage; as the shear rate increases, the domains deform and at high shear rates they transform into a continuous "monodomain" phase. From the flow curves of the thermotropic melts of PET/PHBA copolyesters at different temperatures[16,31-33] and the rheological studies of Kiss and Porter[8] with lyotropic solutions of poly-benzyl-glutamate, it appears that the band structures are generated in the low to intermediate shear rate range also which is the region I and II of the three flow-region curve proposed by Onogi and Asada[27]. The relaxation behavior of the band structures[8] and the domains[34] after shear cessation is similar in that both relax faster as the shear rate increases. This could imply that the size of the domain decreases as the shear rate increases which explains also the fact that the band spacing of the band structure decreases with shear rate. These data are in agreement with the observation of smaller band spacings in the Aramid and the hydroxy-propyl cellulose fibers and indicate that the band structure possible result from organization of the domains upon shearing.

The second point to notice is that the deformation of the domains is non-uniform and appears to be dependent on the thickness of the sample. Such non-uniform deformation occurs because the domains close to the polymer-wall interface deform more effectively by shearing *versus* the domains in the bulk of the sample which may slip or rotate and can be demonstrated by two important effects: (a) the development of ordered optical effects which may arise from the hydrodynamic instabilities at the interface between the homogeneously sheared layer of the mesophase near the wall and the bulk of the mesophase and (b) the dependence of the mechanical properties (modulus and strength) of the oriented samples prepared by molding and extrusion processes on the thickness of the sample. Oswald *et al.*[35] showed that a network of focal conic defects occurs in a smeltic A phase upon slight dilation, and that this network retains upon shearing a regular domain pattern perpendicular to the shear direction at the interface between the top of the defects and the homogeneously sheared smectic layer. The regular pattern occurs in a low to medium range of shear rate. At high shear rates, the domain patterns are destroyed. In our rheo-optical studies with the thermotropic melts of the PET/PHBA 40/60 and 20/80 copolyesters, ordered band structures were formed upon shearing only thin samples which after solidification had significantly improved modulus and strength. Thicker specimen did not exhibit ordered band structures and had lower mechanical properties. Also, Jackson and Kuhfuss[17] reported that the flexural modulus and strength of oriented PET/PHBA 40/60 copolyester specimens prepared by injection molding depended on the thickness of the specimen. The flexural modulus increased by a factor of six and the strength was doubled as the thickness of the specimen was decreased from 1.3 to 0.13 cm. These data indicate that in order to achieve a high degree of molecular orientation and extension which is a prerequisite for the development of high modulus and strength, the polymer must be processed in a suitable shear rate viscosity range in which the domains can be shear deformed into smaller domains. This process should occur beyond the yield stress – at which the domains may reorient with respect to the shear direction by slippage and rotation – by cleavage of the domains along shear sensitive planes into smaller domains and result in the drawing of molecular chains which could link the smaller domains.

Thus, we propose that the formation of band structures upon shearing lyotropic and thermotropic polymers originates from an ordering of domains which in an intermediate shear rate range deform into smaller domains which like their predecessors act as independent birefringent elements. Since the deformation of the domains is not uniform across the thickness of the sheared mesophase, it may result in a skin-core type of structure in which the skin is composed of a homogeneously sheared "monodomain" phase, whereas the core is composed of interconnected domains with their director axes deviating from the shear direction up to ±40°. Since the nature of the domains is unknown, a theoretical approach to the reason of the deviation of domains' directors from the shear direction is fairly difficult. Nevertheless, this explanation, though purely speculative, meets many experimental results; it satisfies the optical observations, that is it is an orientation and not an interference or a focusing effect and satisfies the rheological data assuming the validity of the domain theory. The dependence of the relaxation time of the domain patterns on the shear rate suggests that the size of the domains decreases with shear rate and explains the decrease of domain spacing upon shearing at higher shear rates. Such an explanation based on a domain rather than molecular nature explains also the fast transformation of the band patterns perpendicular to the shear direction to elongated domains along the shear direction after annealing[14]. Since the transformation involves a domain rather than a molecular reorganization, any small disorientation of the domains will lead to a disordered structure. Finally, a skin-core structure generated upon shearing and composed the skin of a highly oriented monodomain phase and the core of interconnected domains with an average deviation ±40° from the shear direction has macroscopic molecular chain orientation and extension to lead to the generation of high modulus and strength.

REFERENCES

1. The Strength and Stiffness of Polymers, edited by A. E. Zachariades and R. S. Porter (Marcel Dekker, Inc., New York, 1983).
2. T. KANAMOTO, A. TSURUTA, K. TANAKA, M. TAKEDA and R. S. PORTER, Polymer J., 15 (1983).
3. Ultra High Modulus Polymers, edited by A. Cifferi and I. M. Ward (Applied Science Publishers Co., Barking, Essex, England 1979).

4. A. E. ZACHARIADES and J. A. LOGAN, *Polym. Eng. and Sci.*, 15, 797 (1983).
5. A. M. DONALD, C. VINEY and A. H. WINDLE, *Polymer*, 24, 155 (1983).
6. S. C. SIMMENS and J. W. S. HEARLE, *J. Polym. Sci., Polym. Phys. Ed.* 18, 871 (1980).
7. J. TAKAHASHI, K. SHIBATA, S. NOMURA and M. KUROKAWA, *Seni Gakkaishi*, 38, 375 (1982).
8. G. KISS and R. S. PORTER, *Mol. Cryst. Liq. Cryst.*, 60, 267 (1980).
9. K. SHIMAMURA, *Makromol. Chem. Rap. Comm.*, 4, 107, (1983).
10. E. D. T. ATKINS, W. S. FULTON and M. J. MILES, Fifth International Dissolving Pulp TAPPI Conference, Vienna, Austria, p. 208 (1980).
11. T. TANAKA, T. MORI, T. TSUTSUI, S. OHNO and R. TANAKA, *J. Macromol. Sci. – Phys.*, B17, 723 (1980).
12. C. VINEY, A. M. DONALD and A. H. WINDLE, *J. Mat. Sci.*, 18,1136 (1983).
13. A. M. DONALD and A. H. WINDLE, *J. Mat. Sci.*, 18, 1143 (1983).
14. A. M. DONALD and A. H. WINDLE, *Coll. Polym. Sci.*, in press.
15. P. A. PENZ, *Mol. Cryst. Liq. Cryst.*, 15, 141 (1971).
16. A. E. ZACHARIADES and J. A. LOGAN, Proceedings of the "European Science Foundation Sixth Polymer Workshop," September 1983, Lyngby, Denmark, to appear.
17. W. J. JACKSON, JR. and H. F. KUHFUSS, *J. Polym. Sci., Polym. Chem. Ed. 14*, 2043 (1976).
18. S. CHANDRASEKHAR and U. D. KINI, in *Polymer Liquid Crystals*, edited by A. Ciferri, W. R. Krigbaum and R. B. Meyer (Academic Press, New York, 1982), Ch. 8, (1982).
19. R. WILLIAMS, *J. Chem. Phys.*, 39, 384 (1963).
20. R. WILLIAMS, *Phys. Rev. Lett.*, 21, 342 (1968).
21. W. HELFRICH, *J. Chem. Phys.*, 51, 4092 (1969).
22. W. R. KRIGBAUM, H. J. LADER and A. CIFERRI, *Macromolecules*, 13, 554 (1980).
23. W. R. KRIGBAUM, C. E. GRANTHAM and H. TORIUMI, *Macromolecules*, 15, 592 (1982).
24. E. IISUKA, *Advances in Polymer Science*, 20, 80 (1976).
25. M. G. DOBB, D. J. JOHNSON and B. P. SAVILLE, *J. Polym. Sci., Polym. Phys. Ed.*, 15, 2201 (1977).

26. T. ASADA, H. MURAMATSU, R. WATANABE and S. ONOGI, Macromolecules, 13, 867 (1980).
27. S. ONOGI and T. ASADA, "Rheology and Rheo-optic of Polymer Liquid Crystals," in Rheology, Vol. I, edited by G. Astarita, G. Marrucci and L. Nicolais (Plenum Press, New York, 1980) pp. 127-147, papers presented at Eighth International Congress of Rheology, Naples, 1980.
28. P. NAVARD, unpublished results.
29. G. H. MEETEN and P. NAVARD, Polymer, 23, 1727 (1982).
30. G. H. MEETEN and P. NAVARD, Polymer, 24, 815 (1983).
31. A. E. JERMAN and D. G. BAIRD, J. Rheol., 25(2), 275 (1983).
32. D. G. BAIRD and G. L. WILKES, ACS Polymer Reprints, 22, 2 (1981).
33. K. F. WISSBRUN, Polymer, 163 (1980).
34. T. ASADA, K. TODA and S. ONOGI, Mol. Cryst. Liq. Cryst., 68, 231 (1981).
35. P. P. OSWALD, J. BEHAR and M. KLEMAN, Philosoph. Magazine, 46, 6, 899 (1982).