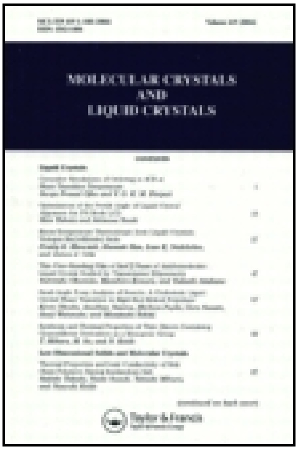

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Processing Rheology of Liquid Crystalline Polymers: A Review

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Processing Rheology of Liquid Crystalline Polymers: a Review

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Keywords: processing rheology, liquid crystalline polymer, copolyester, lyotropic, orientation, blend

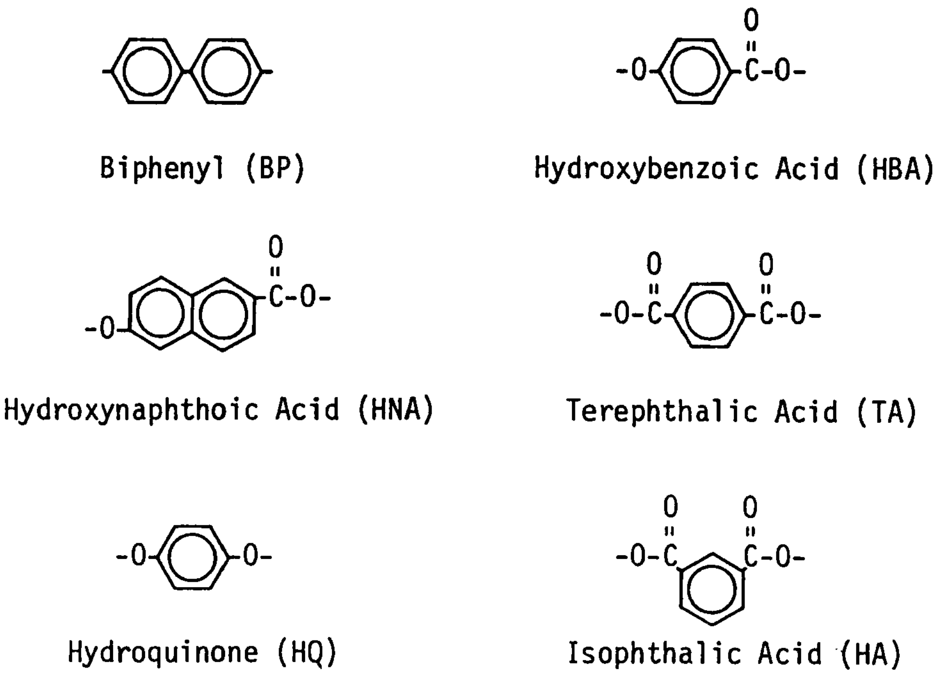
1. INTRODUCTION

The success realized by duPont with Kevlar and similar lyotropic polyaramides[1-8] has led to considerable interest in the processing and properties of liquid-crystalline polymers (LCPs). The attractiveness of lyotropic LCPs lies, for the most part, in their ease in attaining high uniaxial orientation. As a consequence, the fibers formed show excellent moduli and strengths.

The rheology of LCPs has been reviewed by Porter and Johnson,[9] Baird,[10] and Wissbrun.[11] The formation of fibers and other properties of LCPs have been reviewed by Black,[12] Chandrasekhar,[13] by Dobb and McIntyre,[14] and by White.[15] In addition, the book by Ciferri, Krigbaum, and Meyer[16] contains several useful reviews. The reader may also wish to refer to the bibliography recently compiled by Hinov[17] for a list of recent thermotropic references. We shall focus this review on recent developments concerning the effect of main-chain LCP rheology on processing variables and ultimate properties.

The aggressive solvents required to process lyotropic LCPs suggest the alternative of thermotropic liquid crystal polymers (TLCPs) to achieve similar results, while avoiding the costly and dangerous processing schemes inherent in lyotropic LCPs. The advantages of such systems also include the fact that conventional processing equipment can be employed.

The field of TLCPs was pioneered by such industrial workers as Economy,[18] who made wholly aromatic copolyesters of *p*-hydroxybenzoic acid (HBA) and terephthalic acid (TA), and copolyesters of hydroquinone (HQ), and HBA, TA, and 4,4′-biphenol (BP); Jackson and Kuhfuss,[19,20] who synthesized a copolyester of poly(ethylene terephthalate) and HBA; and Morgan,[21] who spun fibers from



Biphenyl (BP)

Hydroxybenzoic Acid (HBA)

Hydroxynaphthoic Acid (HNA)

Terephthalic Acid (TA)

Hydroquinone (HQ)

Isophthalic Acid (HA)

FIGURE 1 Typical structural components of thermotropic polymers.

aromatic polyazomethines. A number of fully aromatic TLCPs, including copolyester combinations of HBA, hydroxynaphthoic acid (HNA), and hydroquinone (HQ), have been made by Calundann and coworkers at Celanese.[22] Figure 1 summarizes the structures of some typical TLCPs.

2. CONTROL OF PROCESSING TEMPERATURE

The classic problem with TLCPs has been that of compromise: In order to obtain a processible system, it has been commonly deemed necessary to incorporate chain units to disrupt the otherwise rigid, linear aromatic chain. These disrupting units may take the form of random copolymerization, bent or "swivel" components. The common theme in each of these approaches is that they disrupt the crystalline structure and thus lower the crystal–nematic transition temperature, T_{kn}. While these randomizing and kinking components serve the recognized function of tractabilizing the polymers, they also limit the attainable modulus through imposing limitations on attainable crystallinity and on chain orientation. One scheme to resolve this dilemma is that of George and Porter,[23] who mixed a low-molecular weight liquid-crystalline species (LMLC) with a polymeric TLCP. In principle, by proper choice of LMLC and TLCP, the desired depression in T_{kn} can be achieved for ease of processing[24]; once the blend is formed into a fiber or shaped part, a solid-state transesterification can be induced by heat, resulting in a fully rigid, high-strength solid. Model experiments confirmed the premise of this scheme, including a lower melt viscosity of the blend and a higher thermal stability of the finished, heat-treated product; however, aided processing of a TLCP has not yet been further demonstrated.

3. THREE-REGION FLOW CURVE

One method for categorizing the rheology of LCPs is the three-region flow curve proposed by Onogi and Asada. Briefly, they describe a phenomenon, seen with some LCPs, where the η-$\dot{\gamma}$ curve can be divided into three sections: Regions I, II, and III. As Figure 2 shows, Regions I and III are shear-thinning; Region II shows slight or zero variation of viscosity with shear rate. This behavior contrasts with that observed for isotropic polymer melts and solutions, as Figure 2 also shows.

Generally, many LCPs show at least shear thinning at low shear rates (Region I). This has been described as yield, but this term is probably inexact for most LCP behavior. Metzner and Prilutski[25] observed, with lyotropic HPC solutions, that small bubbles rose out of the quiescent fluids, indicative of a finite zero-shear viscosity. In addition, the slope of the η-$\dot{\gamma}$ curve is not -1, which would be expected for systems showing a yield stress.

Rheo-optical observations suggest that flow in Region I occurs by motion of "domains," which become smaller in size and more oriented with increasing shear rate.[26]

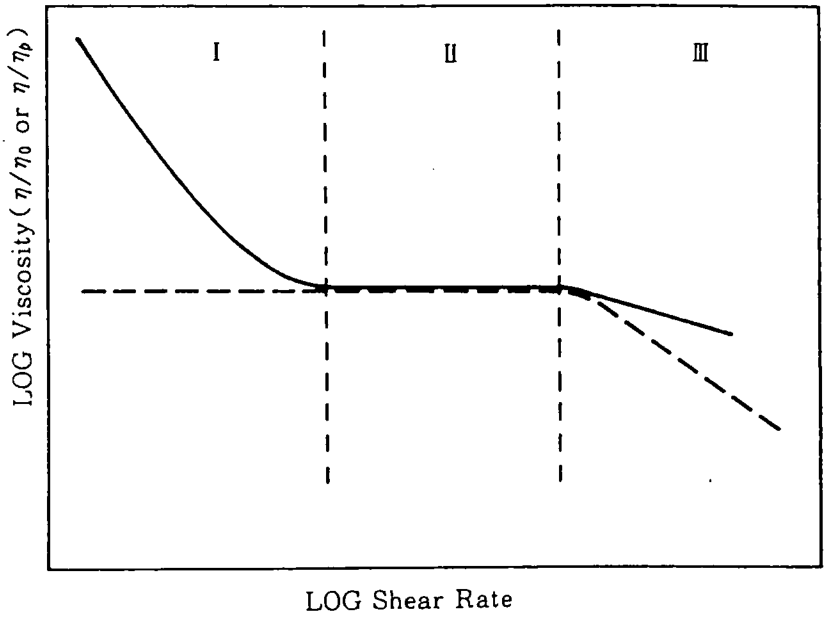


FIGURE 2 The Asada Three-Region Flow Curve. The solid line represents the proposed general curve for LCPs; the dotted line, the general curve for conventional polymer solutions and melts.

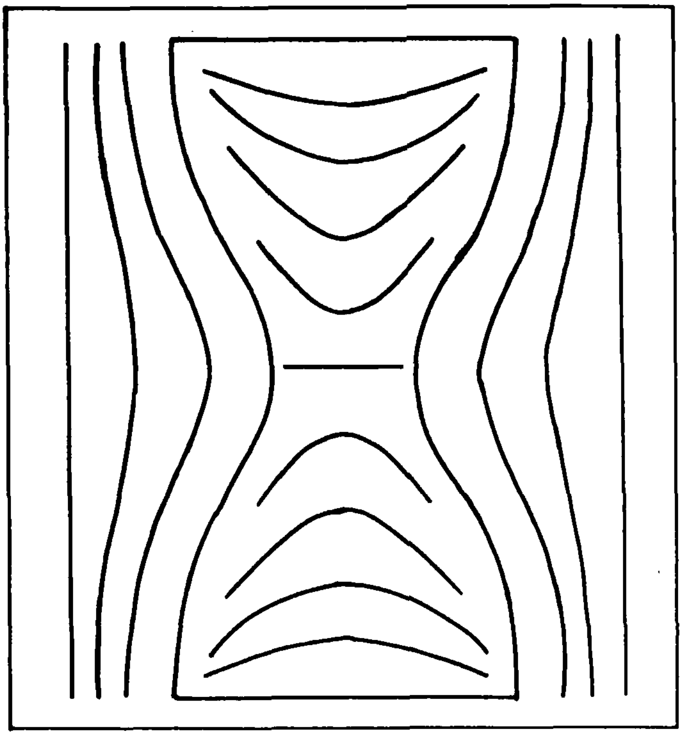


FIGURE 3 Marrucci's description of a "domain," i.e., a collection of liquid crystalline moieties exhibiting disclinations and no net orientation.

Many theoretical treatments have been advanced to describe Region I behavior. Marrucci[27] applied Asada's observations to a model which predicts Regions I and II. The model involves the concept that a "domain" is a set of disclinations in a director field such that there is no net orientation over the entire domain (Figure 3). This model, however, predicts an increase in net orientation of the domains with shear rate, and that the number of domains remains constant as they decrease in size.

A revision of the Marrucci model was made by Wissbrun,[28] including the same definition of a domain, but rejecting the assumption of flow-induced orientation, and allowing the number of domains to increase commensurate with their decrease in size. His calculations, with the aid of non-equilibrium molecular dynamics, result in a slope of the viscosity-shear rate curve which varies from $-\frac{1}{3}$ to -1, and no prediction of a Region II.

Asada et al. hypothesize that the 3-region curve is characteristic of all LCPs, lyotropic and thermotropic, to the extent of suggesting that this behavior can be recognized as a criterion of liquid-crystallinity in polymers.[29] However, this behavior may not be so general. In particular, many TLCPs show only Region I or III.[30–38] Asada claims to see I, II, and III with a PHB/PET thermotropic copolyester, "UT-4," but his data are not conclusive. For example, in Figure 4 the existence of Region I is claimed on the basis of only one datum.

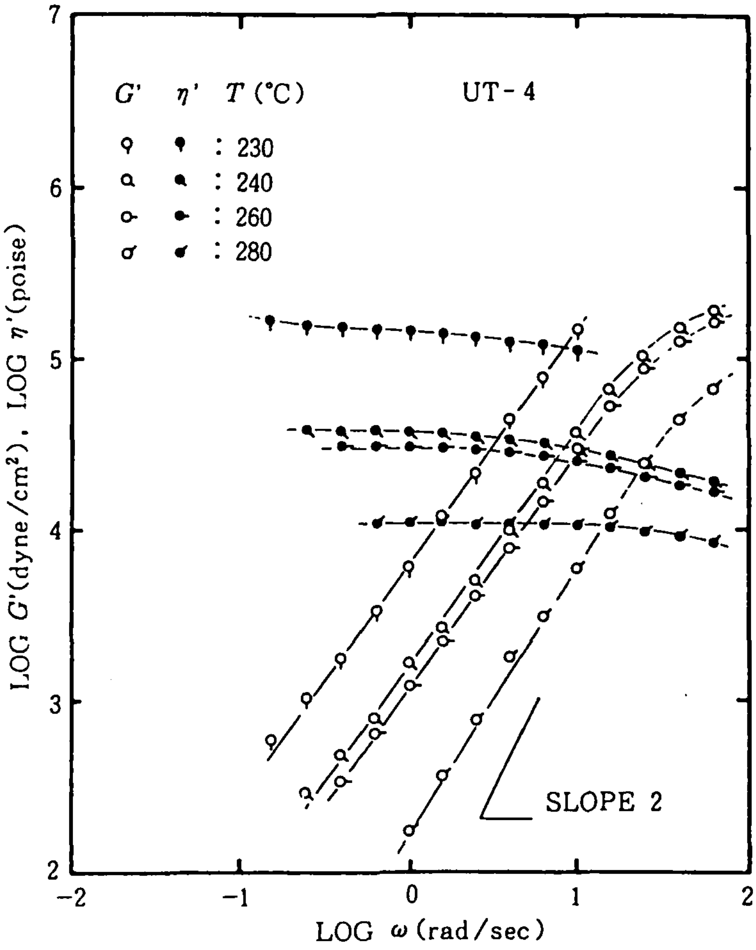


FIGURE 4 Viscosity vs. shear rate for a HBA/PET copolyester, "UT-4" (from Asada).

Even lyotropic LCPs do not comply uniformly with this "rule." Regions I, II, and III are seen by Yanase and Asada,[39] but not by Moldenaers and Mewis[40] with nematic solutions of PBG. The data were obtained for similar molecular weights, and over a similar range of shear rates, but Yanase's solutions were more concentrated. Einaga et al.[41] observed all three regions with nematic solutions of PBT, extending to shear rates as low as 10^{-4} s^{-1}. The importance of this last work must be emphasized, as many of the studies have been limited to shear rates in the range of 10^{-2} to 10^{4} s^{-1}. This can be seen as a limitation of many of the observations, i.e., the lack of all three regions can be attributed to insufficient data at low or high shear.

In fact, extending the shear range would be desirable. If orientation of molecules or breaking of a domain structure is to be accepted as the mechanism for the shear-thinning behavior, then "Newtonian" regions must be observable at sufficiently high and low shear rates. A dimensional analysis model by Chaffey and Porter[42] describes Regions II and III, as well as a high-shear plateau viscosity η_∞.

Incidentally, much of the data obtained have been based on oscillatory shear. This has some analogy to processing conditions, particularly when the "Cox-Merz" rule, indicating a direct equivalence between dynamic and steady shear, applies.[43] However, one must be cautious in drawing such analogies, because some LCPs show behavior that violates this rule.[44]

4. THERMAL AND SHEAR DEPENDENCE OF VISCOSITY

LCPs are unique in the richness of variations in their behavior with respect to thermal and shear history. Variables which may often increase the viscosity of conventional polymers can have the reverse effect with LCPs, a phenomenon which has exciting implications for processing. One point of interest with TLCPs has been the anomalous temperature behavior of bulk viscosity η, as seen, for instance, in the work of Kiss,[45] with a HBA/HNA/HQ copolyester (Figure 5); Acierno, et al.,[46] with a series of PET/HBA polymers; Simoff,[47] with a bisphenol E/isophthalate-naphthalate terpolymer; and Tuttle et al.,[48] with an aromatic/aliphatic polyester. With these TLCPs, a lowering in viscosity with decreasing temperature has been observed. The lower energy requirements inherent in processing lower-viscosity materials may represent a significant advantage. This behavior was predicted as an analog to the behavior of viscosity with concentration in lyotropic polymers,[49] the proposed explanation lying in the ease of orientation of the liquid-crystalline domains. This would reduce the effective hydrodynamic volume of the system, and thus lower the viscosity.[50] This explanation conforms to the observation of a subsequent increase in viscosity with further increasing temperature, as the ease of orientation of domains is reduced.

Kiss explained his observations with the existence of a biphasic state: an "isotropic-anisotropic melt," produced in part by a variation in composition, and thus in chain stiffness, of the random copolymer. The competition between these phases is said to be influenced by composition, temperature, and shear, although no direct evidence to support his assertion of the existence of a biphasic melt is reported.

It must be emphasized that this phenomenon—increasing η with temperature—is not general for all TLCPs. For example, Bickel et al.[51] observed, for a modified PET-HBA-like polyester, a nearly monotonic decrease in η with T, with a shoulder seen in the curve in the vicinity of T_{kn}.

Complicating these phenomena is the observation of time- and shear-dependent rheology in TLCPs. Gochanour and Weinberg[52] observed, after shearing, increases in the dynamic viscosity η^*, in the non-Newtonian character, and in the elasticity of the melt. The explanation they advanced is that the content of a crystalline phase is continually increasing with time at elevated temperature. They offer support in the form of DSC studies of annealing.

Wissbrun and Griffin[53] observed interesting phenomena with an aromatic thermotropic polyester. In the isotropic phase, no history-dependence was observed,

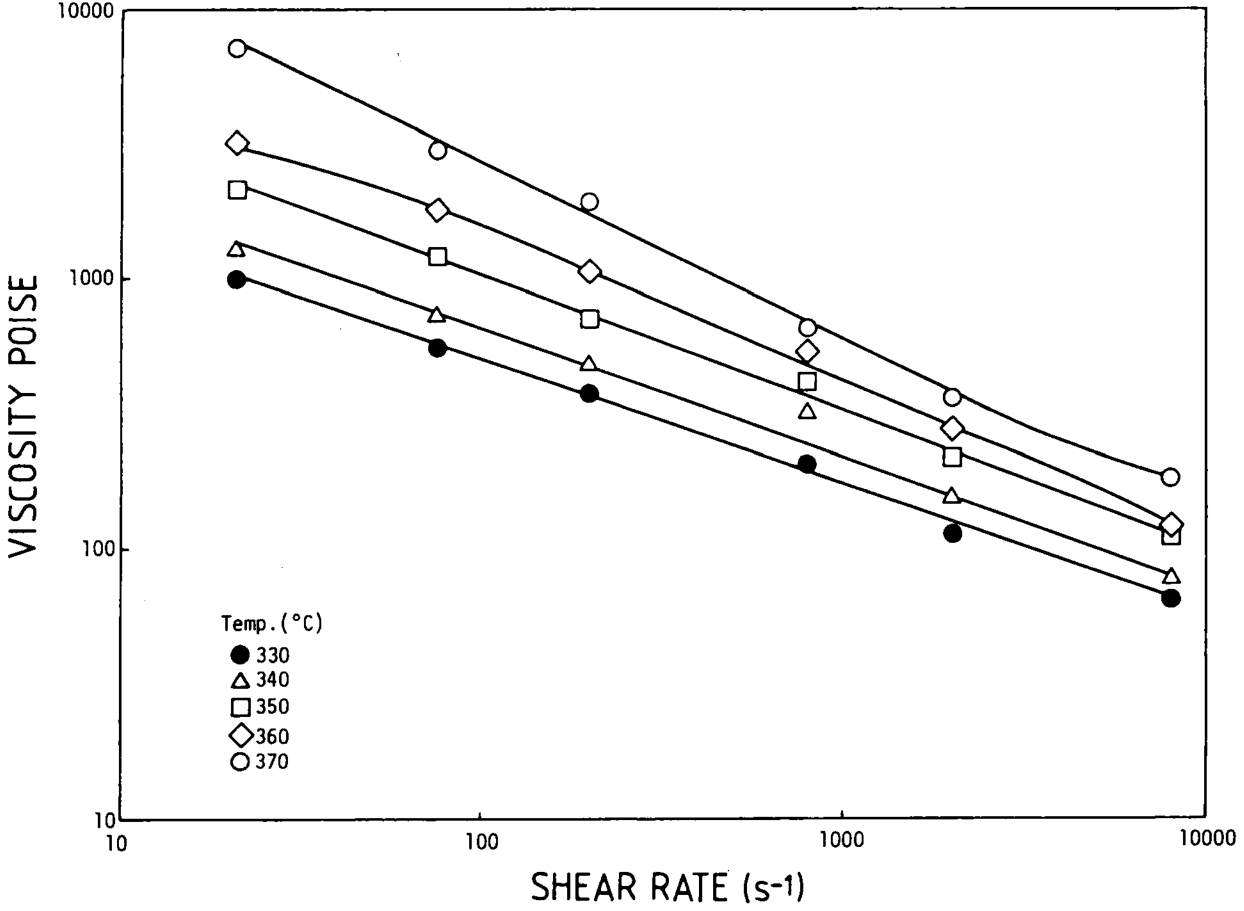


FIGURE 5 Viscosity vs. shear rate at several temperatures for a HBA/IA/HQ copolyester TLCP, showing anomalous behavior.[75]

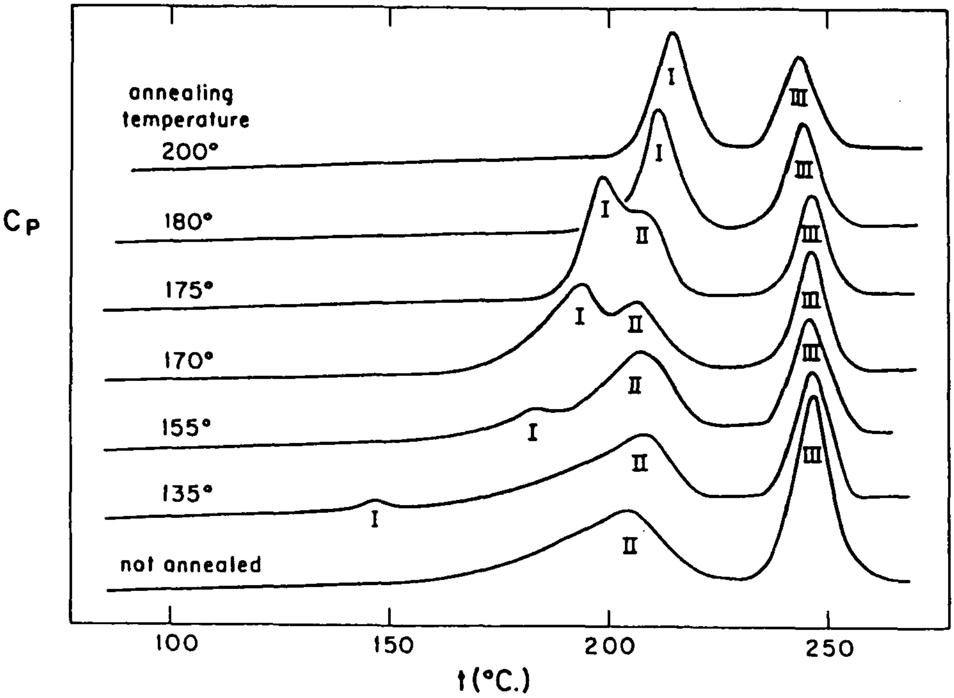


FIGURE 6 DSC scans for a PET/HBA TLCP, showing the influence of thermal history on the phase behavior.[76]

but the dynamic loss modulus and viscosity in the nematic state decreased markedly after being subjected to steady shear. This behavior was erased after reheating to the isotropic phase. No explanation was offered, but this behavior may be due to thermally-reversible orientation of domains in the nematic state.

Similar observations have been reported with another TLCP by Cogswell,[54] who observed a lowering in the viscosity after preshearing. This observation is consistent with the work of Krigbaum and Salaris,[55] by whose DSC studies they showed a dependence of phase behavior on thermal history for the same copolyester (Figure 6). The explanation advanced by Cogswell is that of a heterogeneous "melt," similar to Kiss' suggestion.

5. MECHANISM OF HIGH ORIENTATION

A problem of considerable interest, from both academic and industrial points of view, is the mechanism for the high orientation obtainable in LCPs. In fact, the initial rationale for synthesizing TLCPs, production of inexpensive high-strength fibers and films, has met with disappointment. Table I compares the fiber properties of several LCPs with those of other materials. It is seen that the tensile moduli of TLCPs do not compare favorably with those of lyotropic LCPs or many other

TABLE I

Properties of high-strength, high-modulus fibers

Material	Strength		Modulus		Elongation to break, %
	GPa	*g/d*	*GPa*	*g/d*	
Lyotropics					
Polyazomethines[78]		38		1012	4.4
PBT[79]	2.4	20	250	2000	
X-500[80]	2.5	20	102	800	
Aramid fiber	2.8	22	124	970	2.8
PPT, PBA dry-spun	1.1		65		3.1
annealed	2.2		137		1.9
PPT/PPA as-spun	2.2	17	76	570	4.5
heat-treated	2.5	19	265	2000	1.0
Kevlar 29 wet-spun	2.6	21	59	460	4.0
49	2.6	21	128	1000	2.4
Thermotropics					
HBA/HNA as-spun	1.2	10	74	600	
heat-treated[82]	2.4	20	124	1000	
PET/HBA	1.7	14	40	320	
Other Thermoplastics					
Nylon yarn	1.0	9.8	6	55	18
Polyester yarn	1.1	9.2	14	110	15
Polyethylene (gel-spun)[83]	3.9	44	124	1400	
Nomex	0.7	5.7	17	140	22
Other Materials					
E-HTS glass	2.4	11	69	310	3-4
S-glass	3.3	14.5	88	390	3-4
Steel wire	3.1	4.5	210	300	2-3
Carbon I	2.0	11.6	40	2300	0.5
II	2.6	16.8	260	1700	1.0

materials. The reason for interest in orientation behavior is then clear: An understanding of the orientation mechanism would contribute to improved properties of fibers, as well as allowing orientation to be inhibited when that is desirable.

Significant strides have been made in this area lately. The classical theory of Ericksen,[56] Leslie[57] and Parodi[58] describes the flow of a low-molecular-weight liquid crystal (LMLC) in terms of ordering of the director in shear. Many of the qualitative predictions of this theory have been borne out with LCPs. A difficulty with this model is that it describes the base fluid as Newtonian, a questionable assumption with LCPs. Akay and Leslie[59] address this shortcoming with a model which describes well the orientation of LCPs and fiber-reinforced thermoplastics in converging and diverging flow.

Recently it has been shown experimentally that, especially with TLCPs, a shearing flow field alone is not sufficient to form a highly oriented system. In particular, the work of Viola and Baird[60] has shown that, not only does shear flow not always generate exceptional orientation, but the orientation induced, even by extensional flow, can relax at a high rate. Their amendment to the commonly accepted model suggests that the behavior seen with LCPs is due to a disruption of a domain

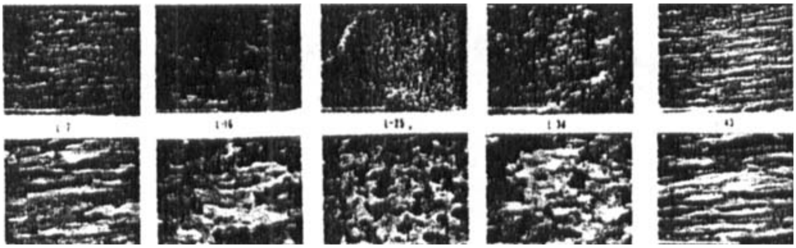


FIGURE 7 Photomicrographs of an extruded PHB/PET TLCP, showing skin-core morphology.[77]

structure, rather than the alignment of rod-like molecules in a domain. This model, and Viola and Baird's observations of a lack of orientation, is consistent with the wide observation of a "skin-core" morphology (Figure 7) in fibers spun and parts molded from thermotropic polymers.[61] Although the difficulty in attaining and holding high degrees of orientation in shear flow is not unique to TLCPs, this problem is perhaps particularly acute with TLCPs, since the low degree of crystallinity which they often possess[62] results in a strict requirement of orientation development for exceptional properties.

Acierno et al.[63] note that, in some cases, the nematic phase constitutes little advantage in fiber formation. With the HBA/PET samples which they spun into fibers, they found that those spun from an isotropic melt showed a higher modulus than fibers spun from the nematic state. This was explained by chain entanglements in the melt; especially with polymers of lower molecular weight than that required for facile entanglements, the desired orientation may in fact reduce entanglement density, lowering the attainable modulus.

6. TRANSVERSE PROPERTIES

Highly oriented LCP fibers necessarily mean that secondary forces (e.g., hydrogen bonding) are responsible for all strength in directions perpendicular to the fiber axis.[64] This leads to weakness in any loading other than tensile. Thus, compressive, transverse, or cyclic loading can result in fibrillation in fibers and delamination in films. One approach to minimizing this weakness is the synthesis of block copolymers. Takayanagi and coworkers have synthesized block copolymers of nylon and Kevlar[65]; Dickstein and Lillya[66] have synthesized unique lyotropic and thermotropic radial block LCPs. Hwang et al.[67] formed triblocks of poly(*p*-phenylene benzobisthiazole) with aromatic thermoplastics. The rationale for each of these syntheses is that the amorphous components can form interlamellar tie chains, resulting in improved strength in the transverse direction, perhaps with some loss of properties in tension. Although each of those techniques can result in a molecular composite, ultimate properties have not thus far been tested.

7. BLENDS WITH ISOTROPIC POLYMERS

Another interesting idea utilizing TLCPs is that of forming blends with isotropic polymers, both crystalline and amorphous. Blends prepared by Kiss,[68] a series of blends of poly(ether sulfone) (PES) and naphthalene-containing polyesters; Cogswell et al.,[69] of several thermoplastics and TLCPs; and Apicella et al.,[70] of polystyrene with a copolyester, have shown several advantages: improvement in mechanical properties (i.e., an in situ composite), lowering of viscosity of the melt, lowering of processing temperature, and avoidance of wear on processing equipment. All of these studies differ from that of Huh et al.,[71] who blended LMLCs with polystyrene, with the intent of having the low-viscosity LMLC phase separate and lubricate the isotropic polymer in processing.

8. NORMAL STRESSES AND DIE SWELL

Another observation of great practical interest had its roots in the observation of a negative normal stress in some lyotropic systems.[72] It was postulated that this would lead to negative "extrudate swell." While the origin of this unusual normal stress behavior is poorly understood, the effect—negative extrudate swell—has been observed for some systems,[73] while very low extrudate swell has commonly been seen with TLCPs. This feature is clearly very attractive to those interested in the design of dies and injection cavities for TLCP processing, particularly for thin sections.

The mechanism for this behavior is not well understood. A dimensional analysis by Chaffey and Porter[74] describes the phenomenon in terms of a dumbbell model and a compressive force along the streamlines. The magnitude of the predicted negative normal stress and the shear-rate range over which it occurs are underestimated, perhaps due to their assumptions in the intermolecular interaction potential.

9. SUMMARY

The processing rheology of TLCPs is complex. There are several issues in need of solution. Perhaps the greatest of these lies in the measure and control of orientation. While TLCPs have found some applications as moderately high-strength, low-weight, high-temperature materials, they lag the lyotropics. More work needs to be done in terms of a complete characterization of orientation in extensional and biaxial flow fields. More data are required in steady shear flow, also, for careful application of rheological data to processing conditions.

Regarding the three-region flow curve, it appears that this is a characteristic of several, but not all, lyotropic systems and few or no thermotropic systems. In pursuit of an explanation of the curve, extension of the data on several systems to low shear rates would be highly enlightening to see if indeed there is a low-shear limit justifying the liquid aspect of thermotropic polymer liquid crystals.

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