

Formation of High-Performance Fiber Morphologies

A. S. ABHIRAMAN, *Textile Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332*

Synopsis

Processes aimed at forming high-performance fiber morphologies from rigid, semirigid, and flexible polymers have been analyzed. Routes that rely at least partially on the favorable thermodynamic consequences of conformational rigidity imparted by intramolecular and polymer-solvent interactions are shown to offer much greater promise than those that rely entirely on externally applied deformation.

INTRODUCTION

Strength and modulus of synthetic fibers from conventional processes fall far below that of theoretical predictions for perfectly aligned structures. The properties of fibers with essentially homogeneous extended chain morphologies produced from liquid crystalline precursors of the nematic type^{1,2} show conclusively that theoretical predictions regarding practically attainable modulus and strength values³ are not unreasonable. The concept and the existence of liquid crystalline systems have been known from a time preceding the production of the first synthetic fiber.⁴ The commercial production of high-tenacity fibers from aromatic polyamides is indeed an excellent example of the benefits that can be derived by departing from traditional technology to incorporate newer physical principles.

Since rigidity in spatial configuration of isolated molecules is not directly involved in the strength of macromolecular bundles, the search for practical methods by which semirigid and flexible molecules can be assembled into perfectly aligned structures is continuing. These efforts have generally been guided by the fact that polymer molecules can indeed be stretched (oriented) by externally applied force fields, a popular example being the flow-induced precipitation of fibrous morphologies from dilute polymer solutions,^{5,6} which can yield, albeit slowly, fibers with superior mechanical properties.⁷

Rapid generation of high strength morphologies requires processes which involve one of the following two routes:

(1) Formation of macromolecular bundles in which the orientation and the conformation sequence of the components are the same as, or very close to, that of the desired final morphology and subsequent annealing to produce an essentially homogeneous crystalline morphology. An essential requirement of such a process is the absence of major segmental relaxation effects after the first step.

(2) In systems where significant disorienting relaxations are possible, the two steps have to take place essentially simultaneously.

We present here an analysis in order to identify possible kinetic restrictions on the rates of these processes.

HIGH-PERFORMANCE MORPHOLOGIES FROM LIQUID CRYSTALLINE PRECURSORS

Among the three major types of liquid crystals,⁸ nematic, smectic, and cholesteric, the cholesteric type does not possess the orientation desired in the precursor to a uniaxially oriented extended chain structure, and the moment of momentum in any flow process will tend to destroy the smectic order. The nematic state offers the ideal precursor structure for generating high-performance morphologies from linear polymers. The body of a fluid, upon its transition into the nematic state, separates into domains with essentially unidirectional order within each domain. Formation of extended chain morphologies from such a structured fluid is favored because of the following reasons:

- (1) Entanglements are removed except at the domain interfaces.
- (2) The conformational order of the molecule in the fluid is close to the order desired in the precipitated crystal.
- (3) The orientating moments exerted by the axial forces in a spinning process are high because of the large size of the ordered domains.

Order in Fluids of Rigid Polymer Molecules

Based on a statistical thermodynamic analysis of a solution of rodlike polymer molecules, Flory⁹ predicted the favoring of at least partial anisotropy above a critical volume fraction ϕ^* of the polymer in solution. In the absence of polymer-solvent interactions, the critical volume fraction is given by

$$\phi^* = (8/P)(1 - 2/P)$$

where

$$P = \text{length/diameter of rodlike molecule}$$

If $\phi > \phi^*$, one obtains a stable, at least partially anisotropic phase. Flory also obtained a more general result for the case of nonathermal solutions (polymer-solvent interaction parameter $\chi \neq 0$). For the case of perfect orientation in the anisotropic phase, the equations for phase equilibrium become

$$\ln(1 - \phi) + \left(1 - \frac{1}{P}\right)\phi + \chi\phi^2 = \ln \frac{1 - \phi'}{1 - \phi' + \phi'/P} + \chi\phi'^2$$

and

$$\ln \left(\frac{\phi}{P}\right) + (P - 1)\phi - \ln P^2 + \chi P(1 - \phi)^2 = \ln \frac{\phi'/P}{1 - \phi' + \phi'/P} + \chi P(1 - \phi')^2$$

where ϕ, ϕ' are the volume fractions of polymer in the isotropic and anisotropic phases, respectively. Figure 1 shows an example of the composition of the phases in equilibrium for $P = 150$, the parameters governing the phase diagram being the interaction parameter χ and the volume fraction of the polymer.

The trends predicted by Flory's lattice model of rigid polymer solutions have been verified, an excellent example being the results of Miller et al.,¹⁰ reproduced here in Figure 2. (Note: The situation is reversed when the ordinate is changed from the interaction parameter χ to temperature T because

$$\chi = \Delta H_m / kTN_s V_p$$

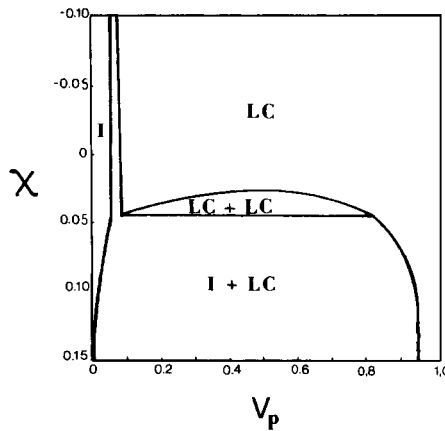


Fig. 1. Phase diagram predicted by lattice model (ref. 9) for rigid polymers with $P = 150$ (V_p , volume fraction of polymer; χ , interaction parameter; LC , liquid crystalline; I , isotropic) (from ref. 10).

where ΔH_m is the heat of mixing, N_s is the number of solvent molecules, and V_p is the volume fraction of polymer in solution.) Anisotropic phases under equilibrium conditions have also been obtained in polyparabenzamide and in poly-(paraphenylene terephthalamide) (PPTA),¹¹ a feature which has been successfully used in generating high-tenacity fibers from these polymers. Experimental phase diagrams for these two polymers are shown in Figures 3 and 4.

In the case of rigid polymers, formation of anisotropic solutions in the absence of external fields (electromagnetic or mechanical force fields) eliminates the rate at which disorder \rightarrow order transformation takes place as a factor of concern in practical processes to produce extended chain morphologies. The required time for completion of such transformation can be allowed in the precursor prior to fabricating the product in the desired geometry. However, since generation of anisotropic phases through the application of external force fields has been

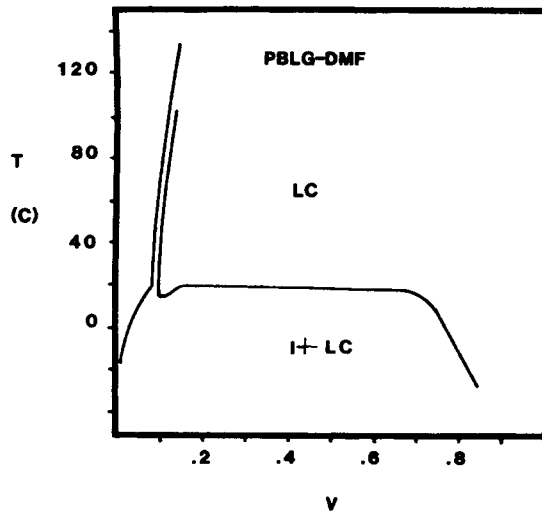


Fig. 2. Experimental phase diagram for PBLG ($M_w = 310,000$) in DMF (V_p , polymer volume fraction) (from ref. 10).

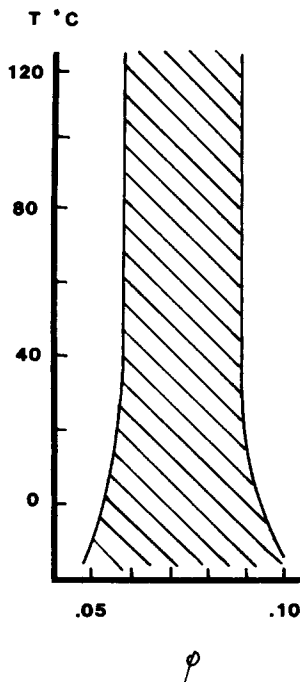


Fig. 3. Experimental phase diagrams for PBA-DMAA system (from ref. 11).

suggested (discussed in later sections), we examine the kinetics of isotropic \rightarrow ordered fluid transitions both in the absence and the presence of external stress fields.

Experimental data on the kinetics of formation of an ordered phase under conditions where the final state is either a single anisotropic phase or a mixture of isotropic and anisotropic phases have been presented by Miller et al.¹² Figure 5 shows the rate at which the ordered phase appears when an isotropic solution of poly- γ -benzyl glutamate in dimethyl formamide at 80°C is rapidly quenched to the temperature indicated. The corresponding equilibrium states are shown in Figure 6. It is important to note the long times—at least several minutes—required for the transformation when compared to the time of deformation in fiber fabrication processes, which is only a fraction of a second. The kinetic data shown here are analogous to the nature of crystallization of polymers under quiescent conditions. The well-known increase by several orders of magnitude in the rate of crystallization of polymers under stress suggests that we should also examine the influence of external force fields on the rate and extent of isotropic \rightarrow nematic transformation in polymer solutions.

The anisotropy of diamagnetic susceptibility along and normal to the chain axis creates magnetic moments tending to align the chains along the direction of the externally applied magnetic field stress. The kinetic data on solutions of polyparabenzamide (PBA) in DMAA are, however, far from encouraging in this respect (Fig. 7). In the case of solutions that exhibit only partial anisotropy in the absence of an external magnetic field (curves 1 and 2 in Fig. 7; continuous phase is isotropic) there is only a marginal effect of the magnetic field on the extent of anisotropy, with the rate of realignment induced by the field being slow.

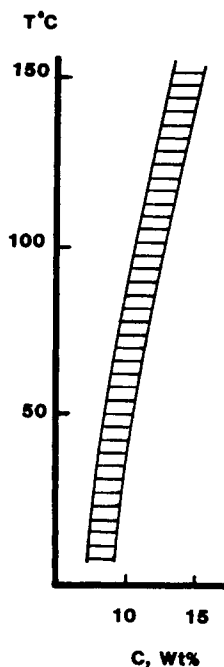


Fig. 4. Experimental phase diagrams for PPTA-H₂SO₄ system (from ref. 11).

As one would expect from the increase in anisotropic domain size, the rate of realignment increases with concentration. The process, however, still extends over several minutes.

Rapid alignment of internally ordered anisotropic domains in a flow field is clearly indicated by the successful generation of extremely high degrees of axial orientation in fibers spun from nematic precursors.¹⁴ Anisotropic solutions of *para*-linked aromatic polyamides, e.g., poly(*para*-benzamide) and poly(*para*-phenylene terephthalamide), have been spun into fibers with tenacities at least three times those of commercial industrial fibers from aliphatic polyamides.² The process utilizes a nematic precursor solution which is then spun with an air gap between the spinneret and the coagulation bath to allow the moment exerted

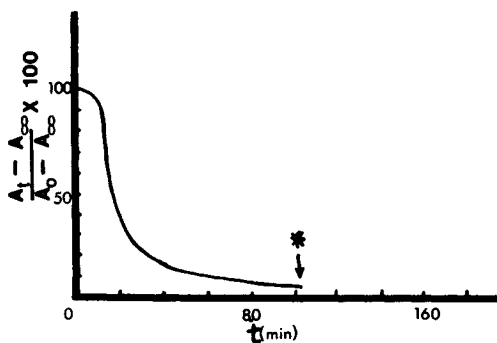


Fig. 5. Rate of appearance of ordered phase measured by polarized light transmission through 13.3 wt % polycarbonylene ($M_w = 1.5 \times 10^6$) in DMF (temperature of ordered phase formation, = 10.2°C) (from ref. 12).

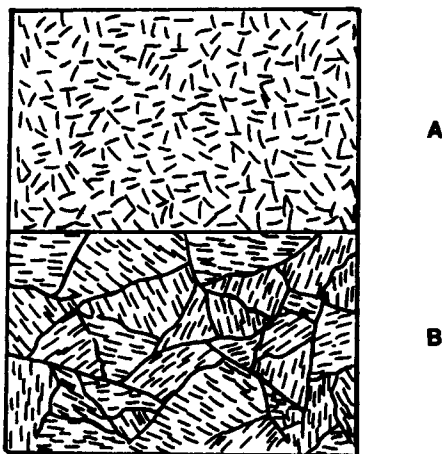


Fig. 6. State of organization in the initial isotropic phase (A) and in the anisotropic phase (B) denoted by * in Fig. 5 (from ref 12).

by the axial spinline stress to align the anisotropic domains prior to precipitation. The moment exerted by the deformation-induced stresses is increased significantly by the much larger size of these domains when compared to single molecules. The long time required for the generation of the anisotropic domains under quiescent conditions does not pose serious practical problems because it does not affect the rates of fabrication processes.

What would be of special interest is the extent, if any, to which a flow field can favor the formation of an anisotropic phase in systems that would otherwise be isotropic. The analysis of Marrucci and Ciferri¹⁵ predicts a significant flow induced reduction in the critical concentration at which the anisotropic phase appears in a solution of rodlike molecules. The predictions refer to the equilibrium response of the system. The shear viscosity data presented by Kiss and Porter¹⁶ and Miller et al.¹⁰ indicate that the concentration at the isotropic \rightarrow partially anisotropic phase boundary decreases, but only slightly, with shear rate (Fig. 8). If the minimum in the viscosity-concentration data which occurs at high concentrations is interpreted as the boundary of complete anisotropy, the

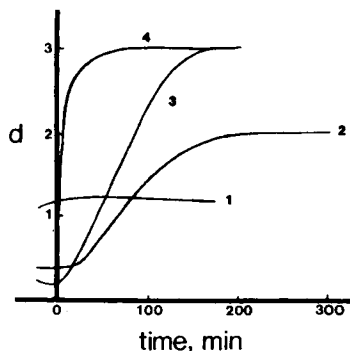


Fig. 7. Rate of reorientation in a magnetic field (maximum field strength, 700 G) of PBA-DMAA measured by dichroism of a band at 860 cm^{-1} (concentrations in wt % (1) 3.73; (2) 5.15; (3) 7.24; (4) 12 (d , dichroic ratio) (from ref. 13).

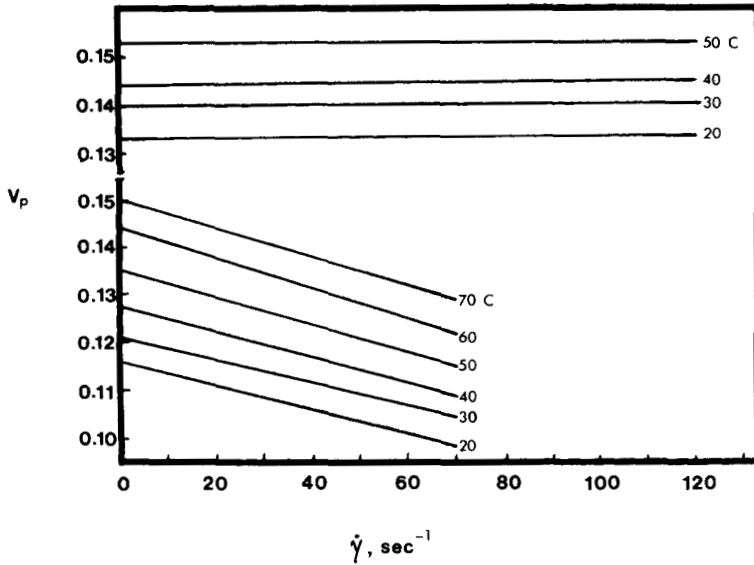


Fig. 8. Influence of shear rate on the isotropic (O) and liquid crystalline (●) phase boundaries for PBLG ($M_w = 310,000$) in DMF determined from shear viscosity measurements ($\dot{\gamma}$ = shear rate, sec^{-1} ; V_p , volume fraction of polymer) (from ref. 10).

concentration at this boundary is essentially independent of the rate of deformation.

The transformation from an initially isotropic solution to an equilibrium anisotropic state requires cooperative response of segments adding up to macromolecular dimensions. Such processes are governed by relaxation times much larger than those encountered in, for example, localized segmental crystallization of macromolecules. Alfonso et al.¹⁷ report approximately 10 min for attaining steady-state viscosity in shear deformation, indicating the longer time scale for flow-induced development of a steady structural state as compared to the duration of deformation processes in fabrication.

In any case, generation of flow-induced isotropic \rightarrow anisotropic transition, if it can be obtained, would be of practical interest only in systems that do not exhibit a liquid crystalline phase transition under quiescent conditions. No particular advantage can be gained by lowering the critical concentration for nematic order in rigid polymer systems which exhibit a lyotropic phase transition under quiescent conditions. The characteristic low viscosity of such nematic solutions enables the economically advantageous use of high concentration in spinning solutions.

High-Performance Fibers from Semirigid Polymers

Flow-induced lowering of critical concentration can, nevertheless, be of advantage in semirigid polymer systems where the isotropic \rightarrow nematic transition is expected to occur at much higher concentrations when compared to rigid polymers. Lowering the critical concentration here can help reduce the large

“viscosity barrier” imposed by the increase in viscosity with concentration in the isotropic region. Among the factors favoring the formation of high-performance morphologies from anisotropic precursors, the most important is the generation of conformational sequences in macromolecules close to that of the precipitated crystal. The cooperative phenomenon involved in generating the sequence required for rodlike spatial geometry can be aided by flow fields exerting the desired orienting stresses. In principle, one can look at the effect of such fields as increasing the persistence length of the nonrigid polymer. The effect of flow-induced increase in persistence length can be important, particularly in the case of “semirigid” polymers where experimental evidence shows a significant reduction in the concentration at which the isotropic \rightarrow nematic transition occurs.¹⁷ For example, the data of Alfonso et al. (Fig. 9) shows that the critical concentration at which the anisotropic phase appears is significantly decreased when the shear rate is increased. Also, the rates of such thermodynamically favored transition can be increased by flow-induced intermolecular disentanglement and alignment. It should be noted here that no practical advantage is gained in the *fabrication process* by going from rigid to such semirigid polymers, both of which are not thermoplastic and present the same difficulties in generating a fiber via the solution spinning process. In fact, as observed by Alfonso et al.,¹⁷ the conditions under which high-performance fibers can be generated are more stringent in the case of the X-500 polymer when compared to, e.g., PBA which forms quiescent anisotropic solutions. The real advantage to be gained from such studies, besides their contribution to scientific knowledge of anisotropic polymer solutions, is in leading the way toward a *wider choice* of materials.

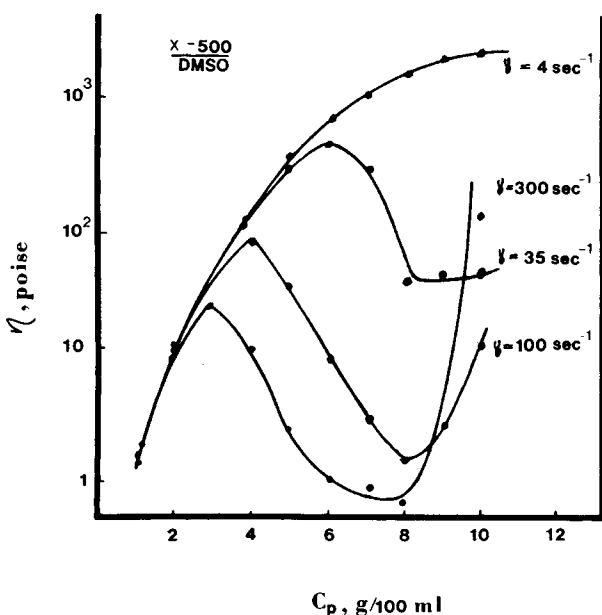


Fig. 9. Influence of shear rate on the isotropic (relative maxima) and anisotropic (relative minima) phase boundaries for X-500 polymer $[-(\text{NH}-\text{C}_6\text{H}_4-\text{CO}-\text{NH}-\text{NH}-\text{CO}-\text{C}_6\text{H}_4-\text{CO})_n-]$ in DMSO (from ref. 17).

HIGH-PERFORMANCE MORPHOLOGIES FROM FLEXIBLE POLYMERS

The search for devising a method to produce high-strength fibers from flexible polymers has been guided by the fact that polymer molecules can indeed be stretched (oriented) by externally applied force fields creating the desired flow or deformation, e.g., elongational and shear flows, hot and cold drawing, etc. The main difficulty in obtaining the extended chain-conformational sequence through mechanical stretching arises because of the fact that the end-to-end distance of a flexible molecule is changed primarily by out-of-plane rotations of bonds around the backbone axis and that the moment exerted by a unidirectional force to induce such rotations diminishes with increasing alignment of the backbone along the stretching direction. Also, in reacting to the force field, every segment in the molecule has to "know" the conformation in which it should exist prior to crystallization. This situation cannot be expected to result from a mechanical process where all the segments in a molecule react to the applied force field more or less simultaneously. In concentrated systems, one can expect such a cooperative action only in slow unidirectional growth of a polymer crystal, with the growth direction being parallel to the axis of the polymer molecule. The kinetics of rotations required to achieve conformational perfection beyond the initial orientation must be slow. At higher levels of uncoiling, the perturbation introduced by rotation of a backbone bond in the spatial location of segments of the same molecule far removed from it increases. Thus, the resistance from molecular inertia to conformational changes increases with overall molecular extension, diminishing the rates at which such changes can be accomplished. The observations in two-stage superdrawing experiments, where the second stage was necessarily restricted to low rates, are consistent with the hypothesis advanced here.^{18,19}

The attempts to form high-performance morphologies from concentrated solutions and melts of flexible polymers, e.g., cold extrusion,²⁰ superdrawing,¹⁹ etc., have been successful only when operating at extremely slow rates and increasing the rate of such processes has invariably led either to flow instabilities or to reduced order in the transformation product. Besides the physical barriers, the restriction imposed by the second law of thermodynamics on the kinetics of the required disorder-order transformation explains the need for slow rates if such transformation is to proceed to completion. Under steady state, the demand for positive entropy production and the need for the transformation to take place within an infinitesimal length along the process direction to avoid conflicts from multiple transformation sites restricts these processes to such slow rates.⁶ It is conceivable that, during crystallization, dissipation effects, along with any limitations on segmental relaxation, contribute to the development of semicrystalline structures with well-defined long periods. In flexible polymers the inhomogeneity depicted by such periodic fluctuations disappears only under conditions of slow deformation-induced transformation into ordered structures.¹⁹ In liquid crystalline systems, this restriction is avoided by separating the transformation process into two steps, viz., freezing the required molecular conformations and postannealing to complete the process of crystallization and minimization of defects.

Considerable rearrangement of conformations is required for the isotropic-

nematic transformation in flexible polymers. Even in the case of semirigid polymers, under conditions where thermodynamic considerations predict an equilibrium ordered state, the inability to obtain the required rearrangements because of insufficient mobility has been recognized.²¹ The complexity of the required intra- and intermolecular cooperative phenomenon would lead to the formation of domains of localized order where segments of a single molecule exist in more than one ordered domain. Flory suggests that our inability to obtain order in flexible polymers in the liquid state may possibly be due to spontaneous ordered liquid-crystal transformation being favored under conditions where an ordered liquid is predicted to be in equilibrium with the isotropic liquid. The consequent difficulty in achieving the required long-range conformational order prior to freezing is indeed a major stumbling block in the production of high-performance morphologies from flexible polymers.

INTRAMOLECULAR AND INTERMOLECULAR ORDER

The relative contributions toward the final morphology from intramolecular conformational order and intermolecular orientational order in the precursor deserve close scrutiny. Fibers with a very high degree of overall orientation can be produced at rapid rates from flexible polymers, but the strength of these fibers is far below what has been obtained from rigid polymers. The primary reason for the lower strength of morphologies derived from flexible polymers in practical processes is the low degree of connectivity between sequences of oriented crystallites.²² The high rate of localized crystallization arising from ease of backbone bond rotations leads unfortunately to a high degree of heterogeneity and chain folding—regular or random—in the structure formed from flexible polymers. The ease of relaxation also limits the degree of intermolecular alignment that can be obtained. An important inference here is the necessity of a high degree of order in intramolecular conformational sequence at the precursor stage. The probability of at least n trans conformations in sequence, in terms of the probability p that an arbitrary backbone bond is in the trans conformation relative to its immediate neighbor, is p^{n-1} , which decreases rather rapidly even for high values of p [e.g., for $p = 0.9$, $\text{prob}(n > 10)$ is ca. $\frac{1}{3}$]. Since the kinetics of cooperative rearrangement of long conformational sequences in a flow field is slow when compared to the duration of order-inducing flow processes in fiber fabrication, intrinsic molecular rigidity becomes absolutely essential for rapid generation of macromolecular bundles exhibiting high connectivity along the bundle axis. Such a structure, by the implied high orientation, would exhibit a high tensile modulus. The requirements for high strength, however, go beyond the necessary connectivity in the axial direction. It is necessary to have a spatial configuration of connecting chains (tie chains) which ensures a uniform load distribution among them.³ These two necessary and sufficient requirements imply essentially the disappearance in the axial direction of two-phase morphology in homopolymers.^{18,19}

CONCLUDING DISCUSSION

The successful commercial development of high-strength fibers from para-linked aromatic polyamides which form nematic liquid crystalline solutions has generated considerable interest in the field of high-performance morphologies.

The analysis presented here was conducted in order to help identify among the many processes that have been advanced for generating such morphologies those routes that offer reasonable kinetic rates.

The features of liquid crystalline spinning solutions, such as those from PBA and PPTA, provide the *thermodynamic forces* to align and the *time* required to overcome, in large part, kinetic barriers such as entanglements which inhibit the ordering processes. The precise level of intrinsic molecular flexibility which can be accommodated in the generation of a nematic precursor is still uncertain. Besides the solutions of X-500 polymer discussed earlier, indirect evidence of flow-induced nematic order exists also for cellulose acetate solutions (average degree of substitution, 1.9) at concentrations greater than 18% (Fig. 10). Since the time scale for the development of such order is greater than the duration of deformation processes in conventional fiber fabrication, modifications shall be necessary to subject the fluids to deformations at sufficient rates for the required period of time. It is also necessary to determine the rate at which relaxation of such flow-induced order takes place because short relaxation times would necessarily hinder successful harnessing of such order.

An avenue that has been suggested for generating nematic order in polymers while retaining thermoplasticity is by copolymerizing rigid and flexible components to give random sequences of rigid and flexible bonds in the backbone.²⁴ As correctly pointed out by Krigbaum and Salaris,²⁵ the order in melts of such polymers is necessarily significantly lower than that of polymers with uniformly rigid conformational sequences in the backbone. Also, the intrinsic disorder introduced by random copolymerization can only be detrimental to generating the high degree of homogeneity which is essential for realizing maximum strength.

The practical requirements for generating morphologies possessing high strength are rather severe, and gross deviations from such rigid requirements have so far failed to yield a promising route for the commercial production of

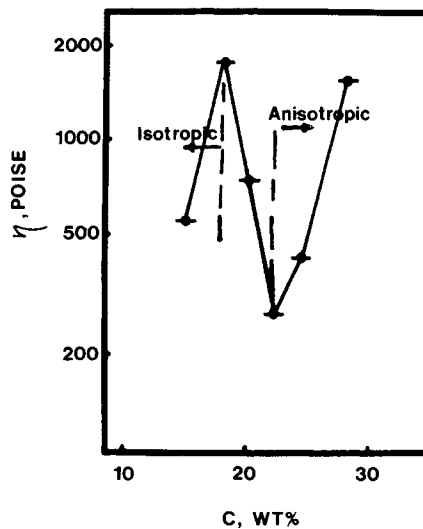


Fig. 10. Viscosity determined isotropic and anisotropic phase boundaries for cellulose acetate (degree of substitution, 1.9) in trifluoro acetic acid at 20°C (η , viscosity, poise; c , concentration, wt.%) (from ref. 23).

high-strength fibers. An important conclusion that can be drawn from the present analysis is that processes that utilize, at least partially, intramolecular and polymer-solvent interactions to impart conformational rigidity offer greater promise than those that rely entirely on externally applied deformation. In the latter case, the formidable kinetic restrictions imposed by hydrodynamic stability considerations, along with the requirement of positive entropy production in a necessarily unidirectional process, limit the rates to below those of practical interest.

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