Shish Kebab and High-Performance Morphologies

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Synopsis

A new model of shish kebab morphology is obtained based on objective analysis of its mechanism of formation in elongational flow. The problems and limitations of deformation processes leading to the transformation of flexible polymers into extended chain morphologies are analyzed.

INTRODUCTION

Generation of high-performance morphologies through mechanically induced ordering of polymer molecules is of great interest in synthetic fiber research. One of the most important manifestations of this activity is the flow-induced precipitation of polymers in the form of shish-kebab morphologies (Fig. 1) from solutions. In simple terms, the solution of a polymer is subjected to a specific flow situation, and one observes, when sufficient strength of the deformation rate is reached, the separation of polymer into a solid precipitate which has the appearance as shown in Figure 1. These structures have been obtained from several elongational flow experiments and from shear flow after the inception of instabilities leading to the formation of the familiar "Taylor vortices."[2,3] Several questions regarding the shish kebab morphology remain unresolved, particularly the structure of the core (shish). A popular model is that of the successive shish segments being parts of a single, essentially homogeneous extended chain crystal, with the periodic rings, kebabs, being the overgrowth on this central structure. However, critical examination of the structure and the possible consequences strongly favor the model of a shish consisting of discrete "foldless" crystalline segments connected by a hitherto undetermined structure. Bolhuis and Pennings[4] obtained, from stirred solutions of amylose, long fibrils with only some of them showing the transverse striations characteristic of shish kebabs. Treatment of the fibrillar crystals with iodine showed, however, that only discrete portions were stained. Conclusive experimental evidence is still lacking, and the following analysis is based on an objective view of the separation and growth of a fibrous polymer solid from either its melt or a solution in elongational flow.

EXPERIMENTAL

Consider the elongational flow of a polymer solution along the y-direction (Fig. 2), where the entropy of the polymer solution, S_σ, is a function of the y coordinate, and let

$$\frac{dS_\sigma}{dy}\bigg|_{y < y_c} < 0$$

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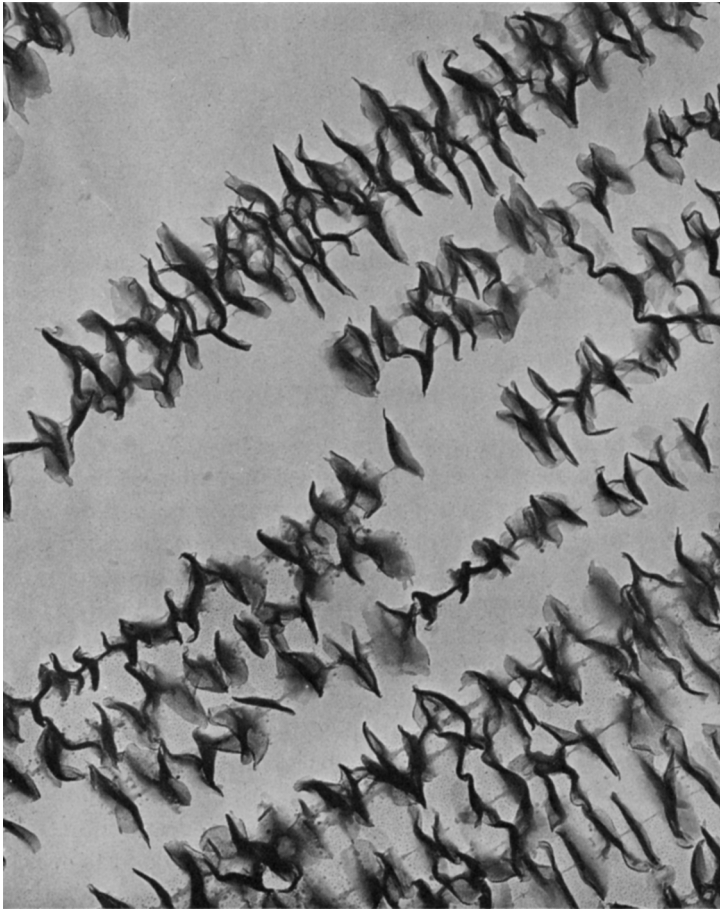
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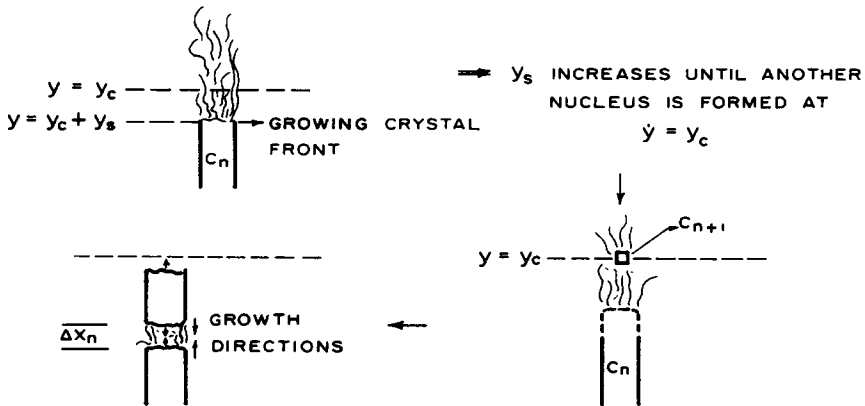
Fig. 1. Shish kebab morphology (from ref. 1).

Fig. 2. Formation of shish kabab in elongational flow.

where $y = y_c$ is the plane where the conditions for phase separation are satisfied. Let the process velocity across $y = y_c$ be V_c and the velocity of growth of the trailing front of the precipitated crystal be V_g. In order to *maintain* the process of *elongational flow induced* precipitation, it is necessary to have $V_c > V_g$.

Figure 2 shows the growth process occurring under these conditions, where at some arbitrary time t the growing front of the crystal C_n is gradually displaced from the plane of phase separation Y_c until another nucleus C_{n+1} is formed, which in all probability is formed from segments of chains already anchored on the crystal C_n. The growth processes proceed on both C_n and C_{n+1} as far as the constraints imposed by the material in the intermediate region would allow. The probability of the necessary cooperative phenomenon existing to enable perfect coalescence of C_n and C_{n+1} is extremely small. The growth patterns on the two crystal fronts are bound to conflict with each other in the region Δy_n. Since the average constraints in the periodic process remain the same, the interfacial energy between the alternating crystals and the constrained regions of lower order is essentially constant in a given process. This accounts for the ratio of the lateral dimension to the longitudinal dimension of the shish segments produced in a given process being distributed closely around an average value. Stochastic fluctuations of a very complex nature exist due to the interactions between the variations in growth rates, nucleation sites, etc. The kinetics of nucleation and growth is an important factor in determining quantitatively the morphological dimensions. Increased chain extension which is required for phase separation to take place at higher temperatures should result in a larger volume fraction of the individual shish segments in the core and thus in improved mechanical properties.[5]

Thus, one obtains a description of the core of a shish kebab structure as segments of "foldless" crystals alternating with oriented regions which may be classified as low-order paracrystals. The constraints imposed by neighboring shish segments on each other make the process of melting of such a structure similar to that of extended chain crystals, thus accounting for possible elevations in melting temperature. The periodic appearance of the kebab segments suggests itself from the discrete nature of the central substrate. It should be noted here, however, that kebab-like overgrowths have also been observed to take place in crystallization from supersaturated solutions of low-D.P. cellulose seeded with native cellulose I fibrils[6] and poly(oxymethylene) on needlelike extended chain crystals of the same.[7] These observations show that periodicity in the central region is not a necessary condition for the development of morphologies similar in appearance to hydrodynamically induced shish kebabs. In the growth of a polymeric crystal from solution, the activation energy is provided by the reduction in configurational entropy of a molecule as it approaches the crystal surface, because it is restricted to lie in the half-space defined by that surface. The reduction in configurational entropy is even greater when a molecule is in the region enclosed on two sides by the shish and an existing kebab, thus making it more probable for successive kebab segments to be separated by a distance (Fig. 3).

Morphologies Associated with High-Strength Fibers

The properties of essentially extended chain fibers from liquid crystalline precursors of the nematic type have shown conclusively that theoretical predictions regarding practically attainable modulus and strength values were 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.
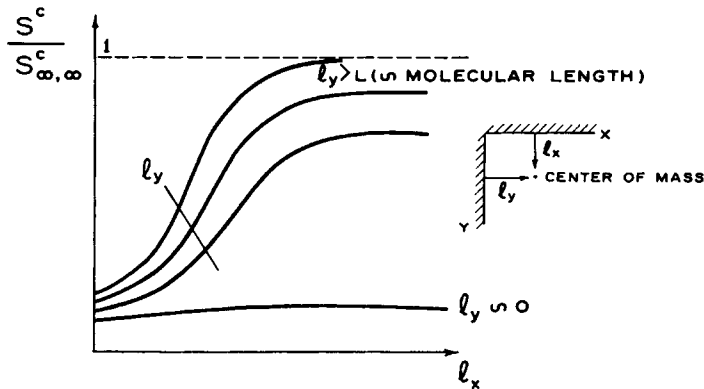
Fig. 3. Configurational entropy of spatially confined chain ($S_{\infty,\infty}^c$, − configurational entropy of chain far removed from confining barriers).

The commercialization 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.[8]

Among the three types of liquid crystals, viz., 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 body of a fluid, upon its transition into the nematic state, separates into swarms with essentially one-dimensional order within each swarm. Such a nematic precursor makes the formation of extended-chain fibrous morphologies favorable owing to the following reasons: (1) The entanglements are removed except at the swarm interfaces. (2) The long-range conformational order of the molecule is very close to the order desired in the precipitated crystal. (3) The orienting moments exerted by the axial forces in the spinning process are high due to the large size of the swarms.

Thus, the features of the spinning dope provide the *thermodynamic forces* to align and the *time* required to overcome, in large part, kinetic barriers such as entanglements. The precipitation process has to overcome only the less formidable problem of minimizing defects such as dislocations, voids, etc., a situation that is analogous to that of fabricating high-strength metallic filaments. Flory's thermodynamic analysis of solutions of semirigid and rigid polymers[9,10] predicts the possibility of, and the conditions (concentration, temperature, and degree of flexibility of the polymer) for, the development of nematic order. In the case of semirigid polymers, the phase transition, which has been predicted solely on the basis of intramolecular forces, has not been observed experimentally. As noted by Ciferri,[10] it is possible that the "isotropic–nematic" transition occurs below the crystallization temperature in the semirigid polymer solutions that have been examined so far. Some evidence exists to support the contention that the rigidity of semirigid polymer molecules could be increased through the choice of appropriate solvents to provide the proper polymer–solvent interactions.[11] What is required here is the kind of association of solvent molecules with adjacent segments in a polymer molecule that would make the conformation required for colinear succession of chain segments energetically much more favorable than all the other available conformations.

Morphologies Associated with Flexible Polymers

Strength and modulus of synthetic fibers from conventional processes, even under extremely severe conditions, fall far below those of theoretical predictions for perfectly aligned structures. The difficulty arises primarily owing to the following reasons: (1) The entropic force leads to complete or partial relaxation of any orientation introduced in the melt, solution, or amorphous states. This also leads to increased molecular entanglements which can inhibit the orientation as well as the crystallization process. (2) Activation energy barriers resulting from intra- and intermolecular constraints and from possible crystal growth mechanisms favor chain folding, regular or irregular, in flexible polymers. The reduction in strength arising from chain folding is widely discussed in the literature. (3) Multiple nucleation sites deny the development of homogeneous structure even in the case (discussed in the section on shish kebabs) where the nuclei are aligned and growth is essentially one-dimensional. This situation is usually further aggravated by multidirectional crystal growth patterns which result in structures analogous to the fringed micelle structure.

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. Mechanics can easily explain the orienting effects of such deformations. The main difficulty in obtaining the extended chain-conformational sequence through mechanical stretching arises due to 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 it should exist in 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 visualize such a cooperative action only in an extremely 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.

The attempts to form high-performance morphologies from concentrated solutions and melts of flexible polymers, e.g., cold extrusion,[12] superdrawing,[13] etc., have been successful by operating at extremely slow rates, and increasing the rate of such processes has invariably led either to 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" transormation explains the need for slow rates of transformation. Under steady state, the demand 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 such processes to extremely slow rates. In liquid crystalline systems, this restriction is avoided by separating the transformation process into two steps,

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*The equivalent segment length proposed by Kuhn[14] may be taken as the upper limit here.

viz., freezing the required molecular conformations and postannealing to complete the process of crystallization and minimization of defects—a process analogous to reducing the dislocations in metals.

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 due to insufficient mobility has been recognized.[9] 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[9] 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.

CONCLUSIONS

In the discussion here we have not included the limitations dictated by hydrodynamic instabilities on the rates of deformation processes. Designing "order generating" flow processes shall indeed require a thorough understanding of stability considerations in flow as well as transformation processes. It should come as no surprise that the rates of processes that have formed high-strength extended-chain fiber morphologies from *flexible* polymers (e.g., superdrawing, cold extrusion, etc.) have been below rates of practical interest.

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