

Structure development in the early stages of crystallization during melt spinning

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Abstract

The earliest stage of crystallization during melt spinning was examined for four polymers: HDPE, PVDF, nylon 6 and poly(oxy-methylene). The four polymers have very similar melt viscosities. Of particular interest is the dependence of the time for the onset of detectable crystallization on the take-up speed. The results for all four polymers lie on the same onset time versus take-up speed curve, indicating that this condition depends chiefly upon chain orientation and not appreciably on chain chemistry or specific undercooling. The result is consistent with a condition of critical strain level. A similar, but less stringent, result is found for further crystallization in the spinline. © 2002 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The crystallization of polymers from highly oriented melts is technologically pervasive, and understanding the mechanisms by which such crystallization takes place has been scientifically challenging. Perhaps nowhere is an understanding of the mechanisms more important than in the melt spinning and subsequent heat-treatment of polymer fibers. In this technological sector, detailed control of crystallization and of non-crystalline region orientation is used to provide fibers with very different strengths, stiffnesses, bulk and dyeability.

Models to explain the development of structure in fiber spinning and heat-treatment have followed two distinct paths. In one of the scenarios, conformational defects migrate along the oriented chains, forming a continuous and periodic modulation of defects—and consequently of density—along the orientation direction [1,2]. The amplitude of this modulation is to grow with time, ultimately changing to a discontinuous, but still periodic alternation of crystalline and non-crystalline phases. This mechanism is a type of spinodal decomposition, in which the components, which are to be separated, are defective and perfect

chain sequences. The signature of such a spinodal mechanism is the formation of a small-angle scattering signal (marking the periodic density modulation) before the appearance of a crystalline diffraction signal (which must await the creation of sufficiently perfect crystals). The search for this signal is generally done using small- and wide-angle X-ray scattering (SAXS and WAXS), and the sequence expected for a spinodal process is *SAXS before WAXS*.

The opposing scenario is one of nucleation and growth (N&G). Here, crystalline nuclei form first, followed by a growth phase. The fingerprint of this scenario should be that SAXS and WAXS signals appear simultaneously. However, it has been pointed out that signal sensitivity and the formation of very small or very imperfect crystals could cause the WAXS signal to become visible only after a SAXS signal is observed [3]. There are several variations to the N&G scenario.

1. While, in general, nucleation is a thermally activated process and consequently sporadic in time, under the very high orientation conditions of high-speed spinning, the activation barrier to nucleation disappears and nucleation is instantaneous [4,5].
2. There may be an early step, in which a highly oriented, threadlike (and not necessarily crystalline) domain is created, followed by crystallization of or on this domain [6–9].

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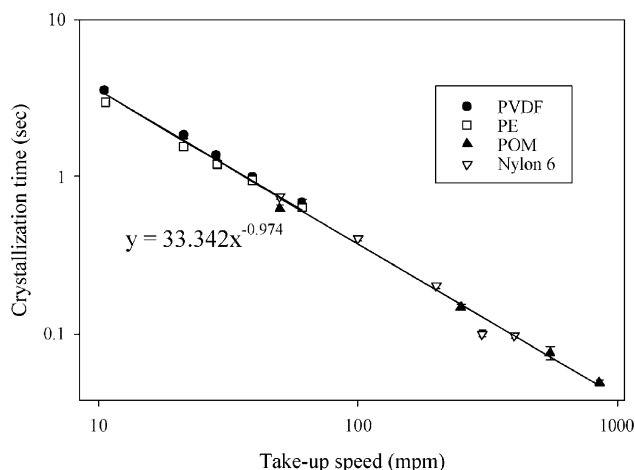


Fig. 1. The onset of crystallization data of the four polymers of this note, plotted against fiber take-up speed. Note the power law behavior.

- In further detail, the nuclei are described as micro-fibrillar and the growth occurs through the propagation of lamellar crystals outward from the micro-fibrils, resulting in a shish-kebab morphology [10–12].

In many cases, SAXS before WAXS has been observed [2,13–17], while in others SAXS and WAXS signals are observed to form simultaneously [18,19]. It is not the purpose of this note to answer questions about the conditions for or the correctness of the earlier models. Rather, we report here an observation common to the melt spinning of four polymeric materials which exhibit features consistent with N&G. These features suggest that a condition of critical molecular strain is crucial to initiate the nucleation event.

2. Experimental background

The X-ray scattering experiments for this study were conducted at Beamline A2 of the Hamburg Synchrotron Radiation Laboratory (HASYLAB) at the Deutsches Elektronen-Synchrotron (DESY). The synchrotron radiation is monochromatized to a specific wavelength (0.154 nm for PE, PVDF, PA6; 0.150 nm for POM) by Bragg reflection from a sagittal germanium crystal monochromator, and shaped and collimated with a cylindrical horizontal mirror in combination with a series of horizontal and vertical slit assemblies. An extruder is placed above the beampath so that fibers are spun downward, through the beam, and finally wound on a variable speed take-up reel situated below the beampath. The extruder is moved vertically, in order to probe positions along the spinline. Two-dimensional SAXS and WAXS data are collected using two image plates. A central hole with a diameter of 2 cm was cut in the WAXS image plate to allow the passage of the SAXS signal to a more distant image plate.

PE, PVDF, POM and nylon 6 are all polymers for which our previous work has demonstrated that the sequence of events during low-speed spinning begins with the formation of micro-fibrillar entities, followed by lamellar growth normal to the fibrils. For PE and PVDF, a SAXS signal appeared before crystalline WAXS was noted, but the SAXS signal was a narrow streak normal to the fiber axis, not the azimuthal nodes which would indicate an axial density modulation [20]. During POM spinning, SAXS and crystalline WAXS scattering appear simultaneously [19]. For nylon 6, WAXS data only were collected, but these data also suggested transformation via a shish-kebab model [21]. The interested reader should refer to the original papers for pertinent experimental details. The universal features during the early stages of crystallization are summarized in the following.

3. Results and discussion

The data shown in Fig. 1 give further insight into the specifics of the nucleation mechanism that is occurring during the melt spinning process. This figure shows a compilation of the onset of crystallization time results as a function of take-up speed for PE, PVDF, POM, and nylon 6. The data from the four polymers studied fall along the same line, with a slope of -0.97 , on the log–log graph, or

$$\Delta t = 33.3V^{-0.97} \quad (1)$$

where Δt is the time (in s) for the onset of crystallization and V is the take-up velocity of the fiber (in m/min).

This result (Eq. (1)) is consistent with a simple model for the onset of crystallization. Suppose that adjacent chains align themselves spontaneously in crystal registry once the chains are strained to a critical extent ε_c . Under a constant rate of strain $\dot{\varepsilon}$, the critical strain is reached in a time Δt , or

$$\varepsilon_c = \dot{\varepsilon}\Delta t \quad (2)$$

The strain rate is proportional to the take-up velocity,

$$\dot{\varepsilon} \propto V \quad (3)$$

Combining Eqs. (2) and (3),

$$\Delta t \propto V^{-1} \quad (4)$$

in agreement with the experimental result of Eq. (1). This is the central point of this note: that for this limited range of polymeric materials crystallization appears to be triggered at a critical molecular extension.

Further commentary on the result is useful. First, the constant of proportionality in Eq. (3) should depend only on the viscosity of the polymer (a measure of the relaxation rate of the chains). The four polymers whose results are shown in Fig. 1 have very similar molecular weights and viscosities. Zero shear viscosities were measured using a Rheometric ARES dynamic parallel plate rheometer with frequency sweeps from 0.1 to 100 rad/s. Fig. 2 shows the

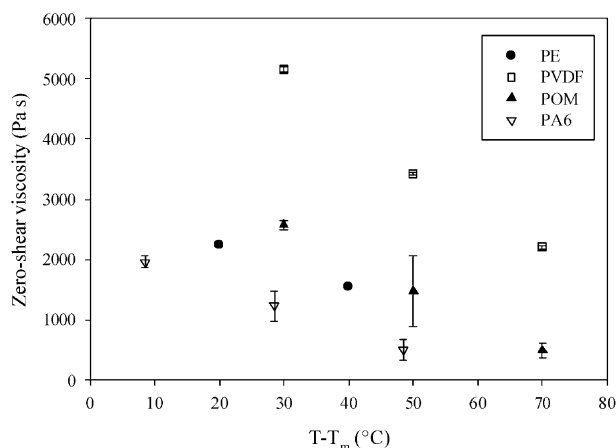


Fig. 2. Zero shear viscosities of the four polymers used in this note.

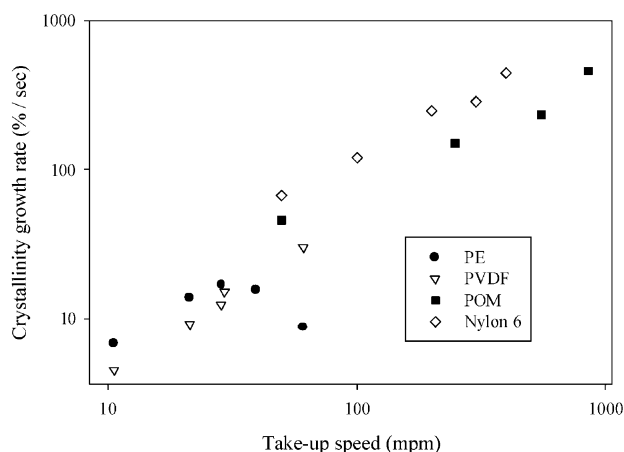


Fig. 3. A compilation of the crystallinity growth rates for the four polymers of this note. Note that for all polymers the crystallinity growth rate is take-up speed dependent.

result of these measurements. As the viscosities of the four polymers are similar, the extension-induced molecular orientation (reflecting the relaxation spectra of the chains) should be the same. And since the molecular orientations are similar, their individual results should lie on the same line in Fig. 1, as observed. This result carries with it then the inference that it is only the rheological behavior of the system that is important; for the systems studied here, the chemical makeup of the system is of secondary importance.

Second, in Eq. (2) it was assumed that the strain rate is constant during the fiber draw-down. However, this assumption is to some extent not necessary. In general, Eq. (4) should be replaced by $\Delta t \propto f(V)$, where $f(V)$ need not be $1/V$. In this more general case, all results for materials of

similar rheology should still lie on a common curve, but the curve in a log–log plot would not be a straight line.

Another aspect of the studies on these four polymers (PE, PVDF, POM and nylon 6) is shown in Fig. 3. In this figure, the rate at which crystallinity grows (as measured by WAXS) as a function of fiber take-up speed is shown. The crystallinity growth rate results fall in a more or less linear band in this log–log plot. Since we know that lamellar crystals (kebabs) grow, transverse to the fiber axis, at this stage, it is tempting to conclude that there is a very large effect of molecular strain on the lamellar growth rate. However, it is likely that both N&G occur simultaneously in this time range, and consequently it is not simple to determine if there is a major effect of spinline velocity on lamellar crystal growth, or if the behavior in Fig. 3 is an extension of the effect on nucleation to later times.

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