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# Axially oriented guest induced crystallization in syndiotactic polystyrene unstretched fibers

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ABSTRACT

Guest-induced crystallization of amorphous s-PS fibers, although prepared with slow take-up speeds (e.g., 80 m/min) and in the absence of mechanical stretching, unexpectedly leads to high degrees of axial orientation ($0.7 < f_c < 0.8$) of co-crystalline phases. Similar high degrees of axial orientation can be maintained after suitable guest removal procedures, leading to nanoporous-crystalline (NC) phases. High degrees of orientation are even maintained after high temperature (e.g., 200 °C) treatments leading to dense crystalline α phases, although this phase transition implies change of polymer conformation from helical to zig-zag planar. Hence, guest induced crystallization of amorphous s-PS fibers not only leads to NC forms (suitable for removal of organic pollutants from the environment) or to co-crystalline forms with active guests (e.g., suitable for antimicrobial release) but also lead, without stretching, to axial orientation. For the disordered NC form, fiber patterns are for the first time reported, showing only four diffraction peaks, which suggest the occurrence of a hexagonal packing of chain axes of $s(2/1)2$ polymer helices. The NC nature of this disordered crystalline form is clearly confirmed by tests of perchloroethylene uptake, from dilute aqueous solutions (500 ppb).

## 1. Introduction

Crystalline phase orientations, axial and planar, can be generally obtained for polymers by axial and biaxial stretching, respectively [1–5].

For co-crystalline phases (CC) between polymer hosts and low-molecular-mass guest molecules, different kinds of planar orientations can be easily prepared, even in the absence of mechanical stretching. These phenomena have been deeply studied for syndiotactic polystyrene (s-PS) [6–14], poly(2,6-dimethyl-1,4-phenylene)oxide (PPO) [15,16] and poly(L-lactic acid) (PLLA) [17].

For s-PS films, different kinds of uniplanar orientations, i.e. of preferential orientation of a crystalline plane with respect to the film plane, have been obtained depending on the film preparation procedure as well as on the chemical nature of the guest [6–14].

In particular, three different kinds of uniplanar orientations were obtained both for δ clathrates [11] as well as for ε clathrates [13]. Going in more detail, for δ clathrates, the observed uniplanar orientations correspond to the three simplest orientations of the high planar-density *ac* layers (of close-packed alternated enantiomorphous helices) with respect to the film plane ($a_{//}c_{//}$, $a_{\perp}c_{//}$, $a_{//}c_{\perp}$) [11]. For ε clathrates the three observed uniplanar orientations exhibit one of the axes of the orthorhombic unit cell perpendicular to the film plane ($a_{\perp}$, $b_{\perp}$, $c_{\perp}$) [13].

Uniplanar orientations of s-PS can be maintained [9] not only after guest-exchange [18,19] but also after suitable guest removal procedures leading to nanoporous-crystalline (NC) δ [20–24] and ε [25,26] phases [6,9,13].

It is also worth adding that for s-PS by combining axial or unbalanced biaxial stretching with co-crystallization procedures, as induced by selected guest molecules, two different kinds of uniplanar-axial orientations have also been achieved [14]. These orientations exhibit the polymer chain axis (*c*-axis) parallel to the main draw direction and a crystal plane parallel or perpendicular to the film plane.

Moreover, high degrees of axial orientation can be obtained for CC [27–34] NC (δ [20,22] and ε [25]) and dense crystalline (α, β, γ) [35–40] phases of s-PS by usual axial stretching procedures on polymer films and fibers as well as by high-speed melt spinning processes [41].

In this paper, we show that guest-induced crystallization of essentially unoriented amorphous melt-spun fibers can lead to high degrees of axial orientation of s-PS crystalline phases. To our knowledge, this

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