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Reversible changes induced by temperature in the spherulitic birefringence of nylon 6 9

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ABSTRACT

Spherulitic morphologies of nylon 6 9 as an example of an even-odd nylon were studied by optical microscopy. A well-defined dependence on crystallization temperature was found. In particular, positively birefringent spherulites were characteristic for temperatures higher than 232 °C, low birefringence spherulites developed between 232 and 225 °C, positive ringed spherulites were found between 225 and 220 °C, and finally negative fibrillar spherulites were formed at temperatures lower than 220 °C. These optical properties were clearly different from those observed with even–even nylons (e.g., negative and positive birefringence for high and low temperatures, respectively), and may derive from the peculiar crystalline structures determined for even-odd nylons. Furthermore, low birefringence spherulites were characterized by a flat-on lamellar disposition and reversibility of the birefringence sign in the 80–120 °C temperature interval (positive and negative values at high and low temperatures, respectively).

Real time WAXD profiles taken during heating and cooling processes demonstrated that different crystalline structures (named I, II and III) developed depending on the temperature and crystallization procedure of samples (e.g., from solution or from the melt state). Crystalline structures were characterized by the formation of hydrogen bonds along two crystalline directions in all cases, a peculiar arrangement that may account for the development of positive and negative spherulites in a more simple way than formulated for conventional polyamides having a single hydrogen bonding direction. DSC and FTIR data also showed a complex structural behavior with structural transitions in the 80–120 °C range, a region that corresponds to birefringence sign reversibility.

1. Introduction

Despite the tremendous importance of polyamides in society and enormous effort devoted to research and development of nylons, publications on the structure of non conventional nylons (i.e., those different from even and even–even series) are scarce. However, odd derivatives are gaining interest due to the development of materials based on renewable resources because of concerns over long-term availability of chemicals derived from fossil resources [1,2]. Nylons 5 6 [3–6], 6 9 [7] and 13 6 [8] can be considered in this context. Furthermore, the ferroelectric behavior of odd numbered polyamides has been discovered, with remanent polarization being linearly dependent upon the dipolar density of amide groups [9,10]. Specifically, nylon 6 9 has also been considered as a material with piezoelectric activity due to its peculiar structure [7].

The crystalline structure of conventional even–even nylons is defined by a stack of hydrogen bonded sheets that progressively (α-form) or alternatively (β-form) arranged themselves parallel to the plane of the sheet [11,12]. Fiber diffraction patterns of such structures are characterized by strong equatorial reflections at spacings close to 0.43 and 0.38 nm. Linear hydrogen bonds between molecules confined in the sheets could be formed for an all-trans conformation, giving rise to strong interactions and a minimum packing energy. A pseudohexagonal arrangement defined by strong

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equatorial spacings very close to 0.415 nm and named γ-form has been determined for several odd–odd nylons (e.g., nylon 7 7) [13]. In this case, amide groups are rotated from the plane defined by the methylene carbons in such a way that linear hydrogen bonds are established along a single direction between molecules of neighboring sheets.

More complex geometries have been postulated for the room temperature structures of polyamides containing glycine units [14] and also of several odd-even and even-odd nylons [8,15–26]. These structures were characterized by the establishment of hydrogen bonds along three and two directions as a consequence of the conformational preferences of glycine residues and the inability to establish a saturated intrasheet hydrogen bonding scheme when an all-trans molecular conformation was assumed and odd diamine or diacid units were involved (Fig. 1a).

The rotation of the two amide groups of the odd unit in opposite directions to the plane defined by the methylene carbon atoms allowed the formation of linear hydrogen bonds along two directions when neighboring chains were conveniently sheared parallel to the chain axis (Fig. 1b). This structure was consistent with the typical diffraction spacings of α- and β-forms and was defined by a centered monoclinic unit cell, with the chain axis projection corresponding to a rectangular unit cell whose diagonals matched the two hydrogen bonding directions. This peculiar structure has also been recently postulated for even polyoxamides with methyl side-groups i.e., poly(2-methyl-1,8-octamethyleneoxamide) [27].

It is worth mentioning that the structure of conventional nylons has usually a continuous evolution with temperature towards a pseudohexagonal packing that is achieved at the so-called Brill transition temperature [28–34]. Unfortunately, low resolution or ambiguous X-ray diffraction data do not provide a good understanding of this transition.

Recent works based on FTIR data suggest that high temperature pseudohexagonal arrangements are a result of the conformational disorder of polymethylene segments rather than of disruption of hydrogen bonds [35–37].

Morphology and optical properties of melt crystallized spherulites of polyamides also show some puzzling features. Thus, even–even nylons (e.g., nylon 6 6) render negative spherulites at crystallization temperatures near their melting point and positive spherulites at lower temperatures [12,38]. The change in optical properties of these nylons was explained by the stacking of their constitutive hydrogen bonded sheets. Specifically, linear hydrogen bonds were oriented along the spherulite radial (positive birefringence) and tangential (negative birefringence) directions. Nevertheless, the reason why the growth mechanism varied so drastically (radial or tangential direction of hydrogen bonds or sheets) at a given temperature remains unclear.

Properties of spherulites of even-odd nylons have been less studied, but pioneering and phenomenological works of Magill [39] performed with nylons 4 9, 6 7 and 6 9, and more recently results reported for nylon 4 7 indicate a peculiar behavior [19]. Thus, a reversible change in birefringence induced by temperature was detected. This feature is highly interesting since cannot be explained by a simple change in the sheet arrangement inside the spherulite as was postulated for structures having a single hydrogen bonding direction. It should be emphasized that birefringence of spherulites is still a hot topic [40–42], especially when different lamellar orientations (e.g., edge-on and flat-on) are considered. To the best of our knowledge, no explanations for reversible changes in birefringence of nylons induced by temperature have been reported. In some binary systems e.g., poly(hydroxyl butyrate)/poly(methyl acrylate blend), reversibility of birefringence was accounted for by a crystallization-induced phase separation [43].

The present work is focused on nylon 6 9 due to its peculiar structure based on two hydrogen bonding directions. The main objective is the study of thermally induced structural transitions and their influence on optical properties of spherulites. New data can help the understanding of the complex behavior of polyamides that arises from the relevance of the hydrogen bonding intermolecular interactions.

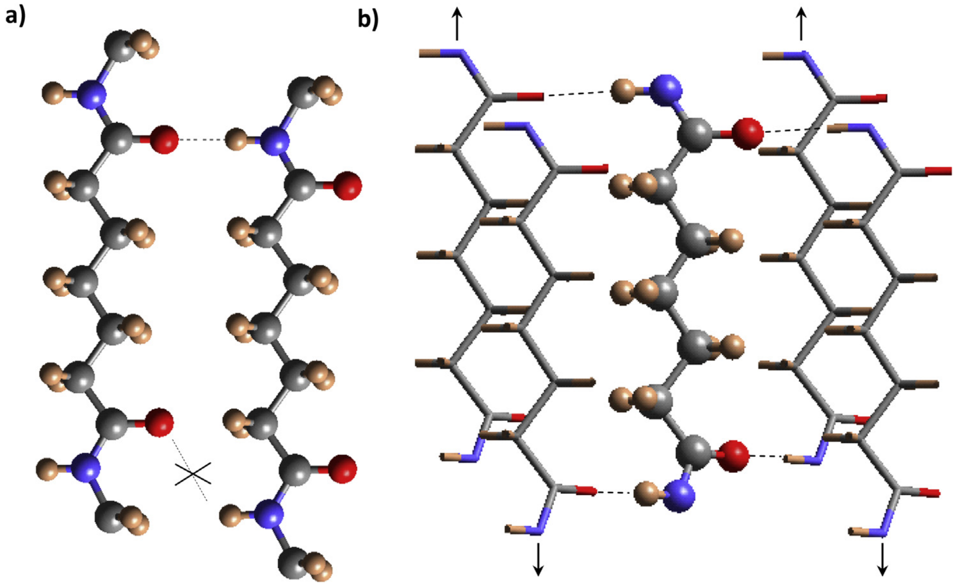

Fig. 1. a) Scheme of the unfavorable hydrogen bonding geometry between odd carboxamide (i.e., pimelamide) units having an all-trans conformation. b) Scheme showing the formation of hydrogen bonds along two directions when the two amide planes of the carboxamide unit rotate in opposite directions to the plane defined by its methylene carbon atoms. External chains (stick representation) should be shifted along the chain axis direction (see arrows) with respect to the central chain (ball and stick representation), thus giving rise to a monoclinic unit cell. Color code: nitrogen, blue; oxygen, red; carbon, gray; hydrogen, brown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)