Polymorphic Transitions Induced by Annealing in Stretched Fibers of Syndiotactic Polypropylene

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ABSTRACT: A study of the polymorphic transitions induced by annealing of fibers of syndiotactic polypropylene initially in the *trans*-planar form III and in the mesomorphic form is reported. Both the *trans*-planar form III and the mesomorphic form transform by annealing at high temperatures into a mixture of crystals of the antichiral helical form I and the isochiral helical form II. Annealing of the *trans*-planar mesomorphic form produces simultaneous formation of the isochiral form II and the antichiral form I, already at low temperatures (40−60 °C). The relative amounts of forms I and II increase with increasing the annealing temperature and fibers containing similar amounts of crystals of forms I and II are obtained at high temperature (120−130 °C). Fibers of the crystalline *trans*-planar form III transform mainly into the antichiral form I by annealing up to 80 °C. At higher temperatures also the isochiral form II develops, and fibers in a mixture of similar amounts of crystals of both helical forms are obtained at 120−130 °C. These results indicate that the formation of the isochiral helical form II is not necessarily linked to the presence of the *trans*-planar mesomorphic form, as suggested in the literature, but it can be obtained also starting from the crystalline form III. These experimental data are not consistent with the hypothesis reported in the literature that intermediate mesophases are necessarily precursors of the crystallization of the isochiral structure of syndiotactic polypropylene.

Introduction

The availability of syndiotactic polypropylene (s-PP) samples with high molecular weight and high stereoregularity, obtained with single center homogeneous metallocene catalyst,[1] has refocused the interest for s-PP and for its physical properties. The complex polymorphism of s-PP and the conditions of formation and interconversion of the various crystalline modifications have been extensively studied in the past 15 years.[2−13] Four crystalline forms and one mesomorphic form have been found and described so far. Form I and form II present chains in the s(2/1)2 helical conformation (chain periodicity = 7.4 Å),[2,14] the crystalline form III and the mesomorphic form present chains in the *trans*-planar conformation (chain periodicity = 5.1 Å),[11,15−17] and finally form IV is characterized by chains in a $(T_6G_2T_2G_2)_n$ helical conformation (chain periodicity = 11.6 Å).[12,13]

Form I is the most stable form of s-PP, and it is obtained in powder samples[6−8] and single crystals[2−5] by crystallization from the melt and from solution. In the limit ordered modification of form I left- and right-handed helical chains alternate along both axes of the unit cell;[2,5] disorder in the regular alternation of the helices can be present in powder samples crystallized from the melt at low temperatures[8] or in single crystals grown at low temperatures.[5]

The metastable helical form II, characterized by a packing of helices of the same chirality,[14] is obtained in oriented fibers by stretching at room temperature low stereoregular s-PP samples synthesized with the vanadium-based Ziegler−Natta catalysts[6,9,14] or by removing the tension in fibers initially in the *trans*-planar form III obtained by stretching highly stereoregular s-PP samples.[9,18,19] Recently, form II has also been obtained in unoriented samples by crystallization from the melt at elevated pressure[20] and in thin film by epitaxial crystallization.[21]

The *trans*-planar form III is obtained only in oriented fibers by stretching at room temperature highly stereoregular samples, prepared with metallocene catalysts, initially in the helical form I[6,9,11,18,19] or in the *trans*-planar mesomorphic form.[22,23] The formation of the form III depends on the stereoregularity; the pure *trans*-planar form III is, indeed, obtained only for highly syndiotactic samples (with *rrrr* pentad contents higher than 90%).[6,9,11] The lower the stereoregularity, the more difficult the formation of the *trans*-planar form III by stretching.[9,18,19] Stretching at high draw ratios of poorly syndiotactic samples (with *rrrr* pentad contents of 40−55%) produces, indeed, oriented fibers in the *trans*-planar mesomorphic form.[24]

The *trans*-planar form III is unstable in unstrained samples and, generally, transforms into more stable helical modifications upon removing the tension from stretched fibers. It has been shown that this transformation depends on memory effects.[22] In particular, form III transforms into the helical form II or into the *trans*-planar mesomorphic form upon releasing the tension if the initial unstretched sample was in the helical form I or in the *trans*-planar mesomorphic form, respectively.[22,23]

Stretched fibers in the *trans*-planar form III also transform into the helical forms by annealing at high temperature,[6,9,25,26] and fibers in mixtures of crystals of the antichiral form I and isochiral form II are generally obtained.[6,9]

The mesomorphic form of s-PP is characterized by chains in the *trans*-planar conformation and is obtained from highly stereoregular samples by quenching the

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melt to temperatures close to 0 °C.[16,17,27] Oriented fibers of the mesomorphic form can be obtained by stretching at low temperature (4 °C) samples in the mesomorphic form[22] or by removing the tension in fibers of form III obtained by stretching at room temperature samples originally in the mesomorphic form.[22,23] In low stereoregular samples, with *rrrr* pentad contents of 40−55%, the *trans*-planar mesomorphic form is obtained only in oriented fibers by stretching at high deformations compression-molded films initially in the helical form I.[24] When the tension is removed from these fibers, the *trans*-planar mesomorphic form transforms again into the helical form I.[24] As the crystalline *trans*-planar form III, the mesomorphic form transforms by annealing into the more stable helical modifications.[16d,17]

The transitions from the *trans*-planar forms into the helical forms induced by annealing of oriented s-PP fibers has been recently investigated.[25] In the ref 25, it has been observed that annealing of fibers in the *trans*-planar mesomorphic form or in the crystalline *trans*-planar form III produces different results. However, in this study fibers in the mesomorphic form and in the crystalline form III were subjected to different thermal treatments.[25] In fact, fibers in the mesomorphic form have been progressively annealed from 40 up to 130 °C, whereas fibers in the *trans*-planar form III have been annealed only up to 60 °C.[25] The results of this study have shown that annealing of the mesomorphic form up to 130 °C produces fibers in a mixture of the isochiral helical form II and antichiral helical form I, whereas the annealing of the *trans*-planar form III at 60 °C produces fibers in a mixture of the *trans*-planar form III and the antichiral helical form I, and no crystals of the isochiral helical form II are obtained.[25]

The authors of ref 25 have considered these results as evidence of the fact that the isochiral helical form II can be obtained only from the mesomorphic form (in this case by annealing), which is therefore considered as a precursor of the isochiral structure of s-PP. According to this idea, the annealing experiments of the fibers of s-PP in the *trans*-planar mesomorphic form, containing a small fraction of crystals of the helical form II, have been interpreted assuming that annealing up to 60 °C produces progressive transformation of the mesomorphic form into the isochiral helical form II.[25] At higher temperatures (above 60 °C), when the mesophase is completely transformed and is virtually absent in the fiber, further development and perfecting of form II occurs up to 120 °C. The annealing determines further crystallization of the amorphous phase into form II, nucleated by the form II crystals already present in the sample.[25] This explains the increasing amounts of form II obtained by annealing above 80 °C. At higher temperatures, melting of form II starts, giving rise to a reorganization of the fiber and recrystallization into form I, so that at 130 °C a mixture of forms I and II is obtained.[25]

As further evidence of the fact that the isochiral helical form II can be obtained only from the mesomorphic form, the authors of ref 25 have annealed fibers in the pure *trans*-planar form III (without traces of the mesomorphic form) only up to 60 °C and have found that no crystals of the helical form II are obtained, but form III transforms in part only into the antichiral helical form I. However, no results of annealing of form III at higher temperatures have been reported.[25] Data reported in the literature[6,9,26] have shown that form III transforms into a mixture of forms I and II by annealing at temperatures higher than 100 °C. In particular, in ref 26 it has been shown that annealing stretched thin films of s-PP in form III at temperatures higher than 80 °C produces a transformation into a mixture of the helical forms I and II. Moreover, the authors of ref 26 suggest that their data give an indication of a noncooperative process involving partial melting and recrystallization. Therefore, the conclusion outlined by the authors of ref 25 that their experimental results represent strong evidence that, in order for form II to develop, the *trans*-planar mesophase has to be present appears an interesting hypothesis, but it is not strongly supported by their experiments.

All the data reported in the literature, and the contrasting interpretation, have increased the debate about the role played by the mesomorphic form on the polymorphic transitions occurring in the solid state and as precursor of the crystallization of isochiral structures. Moreover, the polymorphic transformations between the helical forms (antichiral form I and isochiral form II) and the *trans*-planar form (form III and mesomorphic form) occurring in oriented fibers of s-PP by stretching or removing the tension and by annealing are of interest because they are often associated with the elastic recovery experienced by s-PP fibers upon releasing the tensile stress.[18,19] It has been suggested that these transitions provide an enthalpic contribution to the elasticity of s-PP.[18,19]

In this paper the structural transformations of the mesomorphic form and the crystalline form III induced by annealing of stretched fibers are compared aiming at understanding the role of the *trans*-planar mesomorphic form and crystalline form III on the formation of the isochiral helical form II.

Experimental Section

The s-PP sample was synthesized at 10 °C using a single center C_s-symmetric metallocene catalyst, isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride activated with methylaluminoxane (MAO).[1] The sample is highly stereoregular and is characterized by a concentration of the fully syndiotactic pentad *rrrr* of 93.4%, a molecular weight $M_w = 2.13 \times 10^5$ ($M_w/M_n = 2.4$), and melting temperature $T_m = 143$ °C.

Samples of s-PP in the *trans*-planar mesomorphic form were prepared by compression-molding, producing films of thickness 0.3−0.5 mm, and quenching the melt at 0 °C. The polymer powder is melted in a hot press at 180 °C and rapidly quenched at 0 °C in an ice−water bath and kept at 0 °C for 10 days. The residence time at 0 °C is long enough to prevent the crystallization at room temperature of the helical form I, and the sample turns out to be in the pure mesomorphic form.[16,17,22,27] Oriented fibers of s-PP in the *trans*-planar mesomorphic form (fiber sPPMeso) were prepared by stretching at 4 °C the so-obtained films in the mesomorphic form and then removing the tension. The stretching at 4 °C of s-PP films initially in mesomorphic form, indeed, does not induce any phase transition but only orientation of the mesomorphic crystals. After releasing the tension the crystalline orientation is preserved, and fibers in the *trans*-planar mesomorphic form are obtained.[22]

Samples of s-PP in the helical form I were prepared by compression-molding, producing films of thickness 0.3−0.5 mm, and cooling the melt to room temperature. The polymer powder is melted in a hot press at 180 °C, kept at 180 °C for 5 min, and cooled to room temperature. Oriented fibers in the pure *trans*-planar form III (fiber sPPIII) were obtained by stretching at 4 °C the film in the helical form I up to deformation $\epsilon = 600\%$ ($\epsilon = 100(L_f - L_i)/L_i$, with L_f and L_i final and initial lengths of the specimen, respectively).

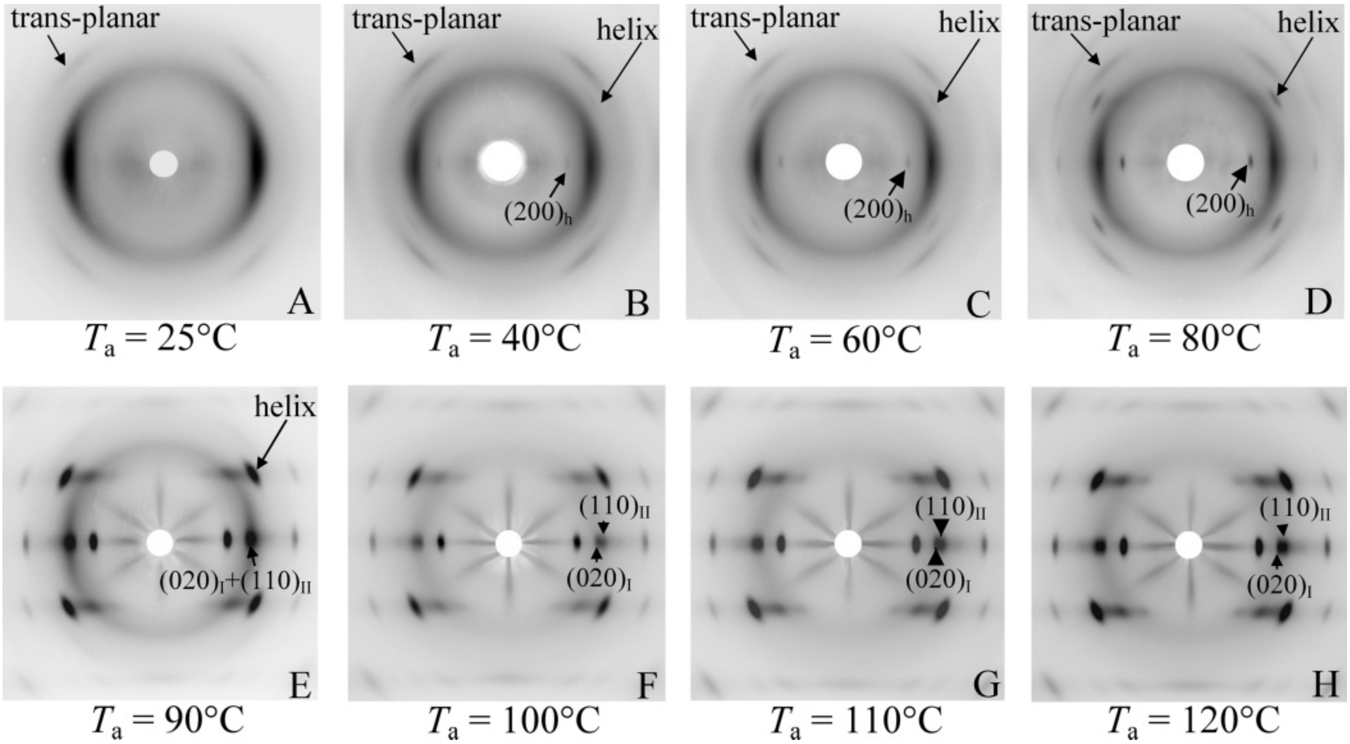

Figure 1. X-ray fiber diffraction patterns recorded at room temperature of the fiber sPPMeso in the *trans*-planar mesomorphic form (A) and of fibers obtained by annealing the fiber sPPMeso at the indicated temperatures (B−H). The $(200)_h$ reflection at $2\theta = 12°$ of the helical forms and the $(020)_I$ and $(110)_{II}$ reflections at $2\theta = 16°$ and 17° of the helical form I and form II, respectively, are indicated. On the first layer line reflections corresponding to helical and *trans*-planar conformations are also indicated.

The fibers in the *trans*-planar mesomorphic form (sPPMeso) and in the *trans*-planar form III (sPPIII) were annealed at different temperatures for 15 min, keeping the fibers under tension to avoid loosing of orientation, and then analyzed at room temperature by X-ray diffraction. The annealing temperatures were chosen in the range 25−120 °C for the fibers in the mesomorphic form and 25−130 °C for fibers in the crystalline form III. Annealing at higher temperatures induces softening of the fibers due to starting of melting.

The X-ray fiber diffraction patterns were obtained with Ni-filtered Cu Kα radiation at room temperature and recorded on a BAS-MS imaging plate (FUJIFILM) with cylindrical camera (radius 57.3 mm) and processed with a digital imaging reader (FUJIBAS 1800).

Approximate values of the relative amounts of the helical form I and form II present in the annealed fibers have been evaluated from the intensities of the $(020)_I$ reflection at $2\theta = 16°$ of form I ($I(020)_I$) and of the $(110)_{II}$ reflection at $2\theta = 17°$ of form II ($I(110)_{II}$) in the diffraction profiles read along the equator of the X-ray fiber diffraction patterns. The fraction of crystals of the helical form II is calculated as $f_{\text{form II}} = I(110)_{II}/[I(110)_{II} + RI(020)_I]$, with $R = (|F(110)_{II}|^2 Lp(110)_{II})/(|F(020)_I|^2 Lp(020)_I)$ the ratio between the squares of the calculated structure factors (multiplied by the appropriate multiplicity factor for fiber diffraction) of the $(110)_{II}$ reflection of form II in the space group $C222_1$ and of the $(020)_I$ reflection of form I in the space group *Ibca*, taken from ref 6, corrected by the Lorentz and polarization factor $Lp = 1 + \cos^2 2\theta/2\sin 2\theta$. The experimental intensities of $(110)_{II}$ and $(020)_I$ reflections ($I(110)_{II}$ and $I(020)_I$, respectively) have been obtained from the area of the corresponding diffraction peaks at $2\theta = 17°$ and 16°, respectively, in the equatorial profile after the subtraction of the diffraction of the amorphous contribution. The area of the two diffraction peaks at $2\theta = 17°$ and 16° have been estimated by deconvolution of the broad equatorial peak into the different contributions (see Supporting Information). The error in the estimated fractions of different phases is about 3%. The amorphous halo along the equatorial line has been obtained from the equatorial diffraction profile of the X-ray diffraction pattern of an atactic polypropylene, after scaling by a suitable factor.

The degrees of crystallinity of oriented s-PP fibers have been evaluated from the X-ray fiber diffraction patterns. Monodimensional X-ray intensity profiles as a function of 2θ have been obtained from the bidimensional diffraction patterns by integrating the intensity along the azimuthal angle with constant value of 2θ, at interval of $\Delta 2\theta = 0.4°$, in the 2θ range 10°−30°. The diffraction profile of the amorphous phase has been evaluated performing the same procedure from the bidimensional X-ray diffraction pattern of a sample of atactic polypropylene obtained with the same cylindrical camera. The amorphous profile was then scaled and subtracted from the X-ray diffraction profiles of the crystalline fibers. The degree of crystallinity was therefore calculated from the ratio of the so-obtained crystalline diffracting area and the total area of the X-ray diffraction profiles.

Results and Discussion

The X-ray fiber diffraction patterns of the fiber sPPMeso in the *trans*-planar mesomorphic form and of fibers obtained by annealing the fiber sPPMeso at different temperatures are reported in Figure 1A−H. The corresponding X-ray diffraction profiles read along the equatorial line are reported in Figure 2A−H.

The X-ray diffraction pattern of the fiber sPPMeso is characterized by a strong and broad equatorial reflection at $2\theta = 17°$ (Figures 1A and 2A), typical of the *trans*-planar mesomorphic form, and a broad reflection of lower intensity on the first layer line corresponding to the *trans*-planar chain periodicity of 5.1 Å. At the annealing temperature of 40 °C the *trans*-planar mesomorphic form starts transforming into the more stable helical forms, as indicated by the appearance of the $(200)_h$ equatorial reflection at $2\theta = 12°$ and of reflections on the first layer line corresponding to the helical chain

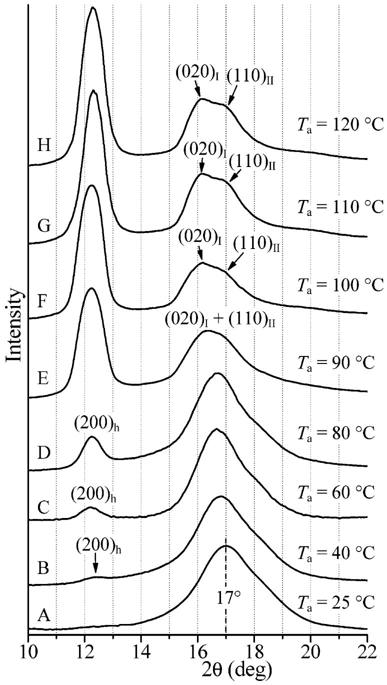

Figure 2. X-ray diffraction profiles read along the equatorial line of the X-ray fiber diffraction patterns of Figure 1A–H of the fiber sPPMeso in the *trans*-planar mesomorphic form (A) and after annealing at the indicated temperatures (B–H). The (200)$_h$ reflection at $2\theta = 12°$ of the helical forms and the (020)$_I$ and (110)$_{II}$ reflections at $2\theta = 16°$ and 17° of the helical form I and form II, respectively, are indicated.

periodicity of 7.4 Å in the diffraction patterns of Figures 1B and 2B.

The amount of the helical form increases and that of the *trans*-planar mesomorphic form decreases with increasing annealing temperature, as indicated by the increase of the intensities of the (200)$_h$ reflection at $2\theta = 12°$ and of reflections on the first layer line corresponding to the helical chain periodicity (Figures 1C–E and 2C–E).

The *trans*-planar mesomorphic is still present in a nonnegligible amount up to the annealing temperature of 80 °C, as indicated by the fact the broad equatorial reflection at $2\theta = 17°$ and the reflection on the first layer line corresponding to the *trans*-planar chain periodicity are still present in the X-ray diffraction pattern of Figures 1D and 2D.

From the X-ray diffraction patterns of Figures 1B–D and 2B–D it is not possible to determine whether the helical form obtained in the annealed fibers is the antichiral form I, the isochiral form II, or a mixture of both. The diagnostic reflections of forms I and II (the (020)$_I$ reflection at $2\theta = 16°$ of form I and the (110)$_{II}$ reflection at $2\theta = 17°$ of form II) are, indeed, concealed by the broad and intense equatorial peak at $2\theta = 17°$ of the mesomorphic form. However, with increasing the intensity of the (200)$_h$ reflection at $2\theta = 12°$ of both helical forms, no decrease of the peak at $2\theta = 17°$ is observed (Figure 2B–D), probably due to a balance between the progressive decrease of the amount of mesomorphic form and the increase of that of the helical form II, both characterized by a diffraction reflection at $2\theta = 17°$. Moreover, a slight shift of the peak at $2\theta = 17°$ toward lower values of 2θ is also observed (Figure 2B–D). This is probably due to development of the (020)$_I$ reflection at $2\theta = 16°$, indicating the formation of crystals of the helical form I. Therefore, the broad equatorial peak in the 2θ range 15°–18° in the diffraction patterns of the fibers annealed up to 80 °C of Figures 1B–D and 2B–D could be ascribed to the overlapping of the main peak of the mesomorphic form at $2\theta = 17°$ with the (020)$_I$ and (110)$_{II}$ reflections at $2\theta = 16°$ and 17° of the helical form I and form II, respectively. The crystalline portion of material in helical conformation formed in the fiber upon annealing up to 80 °C would be, most likely, constituted by a mixture of crystals of antichiral form I and isochiral form II.

This hypothesis is strongly supported by the results obtained at higher annealing temperatures (Figures 1E–H and 2E–H). At 90 °C the transition of the mesomorphic form into the helical forms is essentially complete, as indicated by the strong increase of the equatorial (200)$_h$ reflection and by the disappearance of reflections corresponding to the *trans*-planar chain periodicity on the first layer line in the X-ray fiber diffraction patterns of Figures 1E and 2E. The broad reflection at $2\theta = 17°$ of the mesomorphic form is replaced by the (020)$_I$ and (110)$_{II}$ reflections at $2\theta = 16°$ and 17°, respectively, of the antichiral helical form I and isochiral helical form II, respectively (Figure 2E). This clearly indicates that the crystalline portion of material in helical conformation is a mixture of crystals of both helical forms I and II. When the transition of the *trans*-planar mesomorphic form into the more stable helical modifications by annealing is complete, almost the same amount of the isochiral form II and the antichiral form I is obtained (Figures 1E and 2E).

At higher annealing temperatures (100–120 °C) the (020)$_I$ reflection of form I and the (110)$_{II}$ reflection of form II appear more clearly in the diffraction patterns of Figures 1F–H and 2F–H, indicating an improvement of crystallinity and dimensions of crystals. The relative amount of crystals of the helical form II present in the fibers annealed at temperatures higher than 90 °C remains constant at values of nearly 60%. This fraction has been obtained, as described in the experimental part (see also Supporting Information), from the intensities of the (110)$_{II}$ and (020)$_I$ reflections at $2\theta = 17°$ and 16° in the X-ray equatorial diffraction profile of Figure 2F–H. This probably indicates that when the *trans*-planar mesomorphic form is virtually absent (already transformed into the helical forms at 90 °C), the increase of the annealing temperature produces further crystallization of the amorphous phase into the helical forms and improvement of crystals size.

In summary, annealing fibers of s-PP in pure *trans*-planar mesomorphic form at high temperatures gives fibers containing a mixture of crystals of the helical form I and form II. The transition starts at the annealing temperature of 40 °C. The two helical polymorphs are simultaneously formed in the fiber already at 40 °C and their relative amounts gradually increase with increasing the annealing temperature. At 90 °C the *trans*-planar mesomorphic form is fully transformed into a mixture of the helical forms, and further increase of the annealing temperature basically produces an increase of crystallinity and dimensions of crystallites. The experimental data indicate that the antichiral form I is already present in the fibers annealed at low annealing temperatures (definitely at 90 °C, Figure 1E) and does not form after melting of form II and successive recrystallization, as suggested in ref 25.

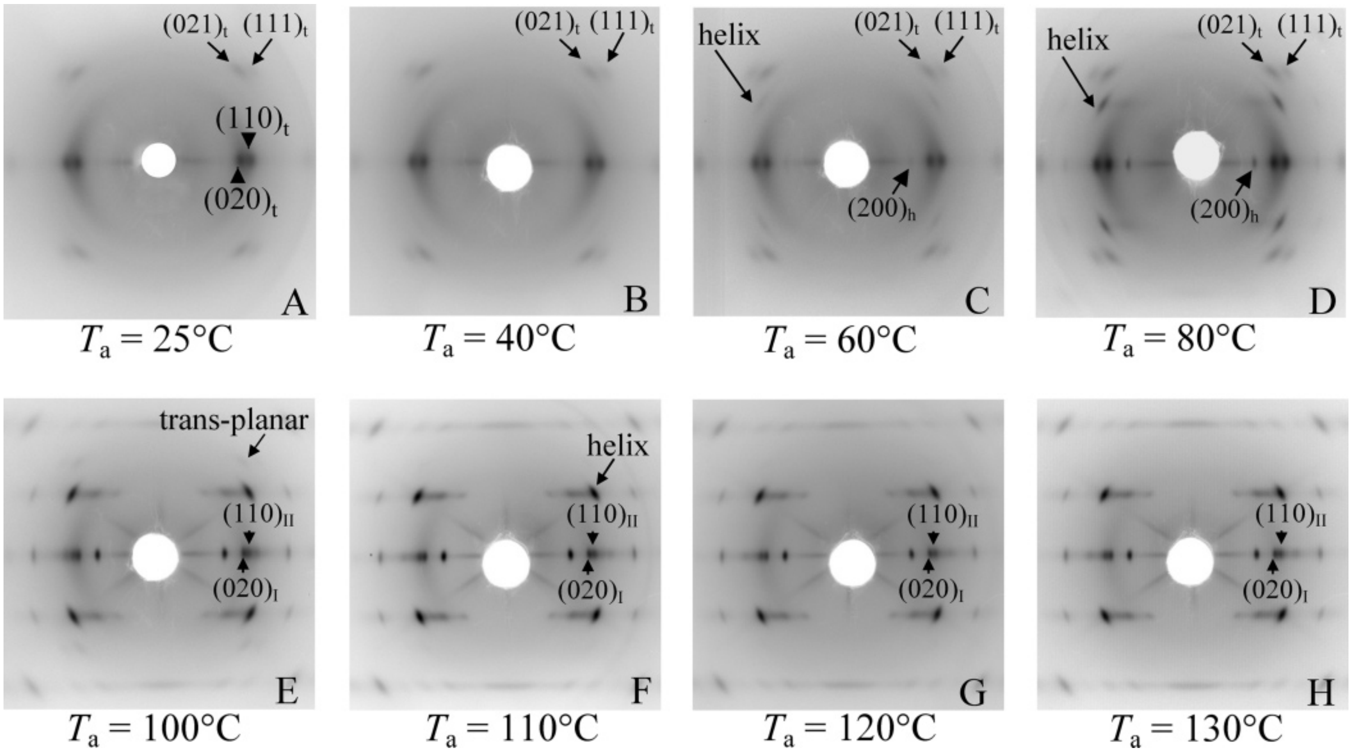

Figure 3. X-ray fiber diffraction patterns recorded at room temperature of the fiber sPPIII in the *trans*-planar form III (A) and of fibers obtained by annealing the fiber sPPIII at the indicated temperatures (B–H). The $(200)_h$ reflection at $2\theta = 12°$ of the helical forms, the $(020)_t$ and $(110)_t$ reflections at $2\theta = 16.2$ and $18.3°$, respectively, of form III and the $(020)_I$ and $(110)_{II}$ reflections at $2\theta = 16°$ and $17°$ of the helical form I and form II, respectively, are indicated. On the first layer line reflections corresponding to helical and *trans*-planar conformations are also indicated.

It is worth noting that the degree of crystallinity of s-PP fibers in the pure *trans*-planar mesomorphic form does not change upon annealing treatments up to 80 °C and amounts to about 35%. At annealing temperatures higher than 80 °C the degree of crystallinity gradually increases due to crystallization of the amorphous phase, and a plateau value of ≈51% is achieved by annealing at temperatures of 100−110 °C. The X-ray diffraction patterns of Figures 1 and 2 indicate that the following processes may occur upon annealing s-PP fibers originally in the pure mesomorphic form: (a) direct crystallization of the mesomorphic form; (b) crystallization of part of the amorphous polymer; (c) melting of the mesophase, followed by recrystallization. Since the degree of crystallinity does not change upon annealing up to 80 °C, the formation of helical form II at low temperatures could be due to direct transformation of the *trans*-planar mesomorphic form (mechanism a). The formation of crystals in the helical form I could instead possibly involve melting of the mesomorphic form and successive recrystallization (mechanism c). At temperatures higher than 80 °C the crystals of the two forms originating from transformation of the *trans*-planar mesomorphic form nucleate the further crystallization of the amorphous phase, leading to an increase of the degree of crystallinity (mechanism b), whereas the relative amount of the two forms remains nearly constant up to higher annealing temperatures.

The X-ray fiber diffraction patterns of the fiber sPPIII in the crystalline *trans*-planar form III and of fibers obtained by annealing the fiber sPPIII at different temperatures, keeping the fibers under tension, are reported in Figure 3A–H. The corresponding X-ray diffraction profiles read along the equatorial line are reported in Figure 4A–H. The X-ray fiber diffraction

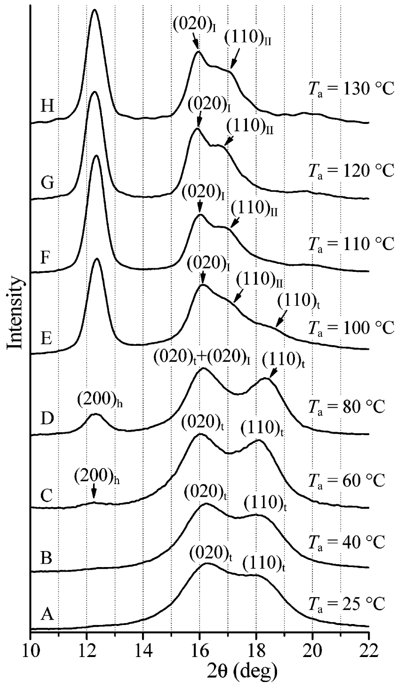

Figure 4. X-ray diffraction profiles read along the equatorial line of the X-ray fiber diffraction patterns of Figure 3A–H of the fiber sPPIII in the *trans*-planar form III (A) and after annealing at the indicated temperatures (B–H). The $(200)_h$ reflection at $2\theta = 12°$ of the helical forms, the $(020)_t$ and $(110)_t$ reflections at $2\theta = 16.2$ and $18.3°$, respectively, of form III and the $(020)_I$ and $(110)_{II}$ reflections at $2\theta = 16°$ and $17°$ of the helical form I and form II, respectively, are indicated.

pattern of the fiber sPPIII in the pure crystalline form III, obtained by stretching compression-molded film of s-PP at 4 °C up to 600% deformation, is characterized by the $(020)_t$ and $(110)_t$ equatorial reflections at $2\theta = 16.2°$ and 18.3° and the $(021)_t$ and $(111)_t$ first layer line reflections, typical of the *trans*-planar form III (Figures 3A and 4A). Deconvolution of the diffraction profile of Figure 4A has indicated that only the $(020)_t$ and $(110)_t$ reflections of form III contribute to the diffraction, and there is no evidence of the presence of a possible contribution of the equatorial reflection at $2\theta = 17.0°$ of the mesomorphic form (see Supporting Information, Figure S2). This indicates that in the fiber sPPIII the mesomorphic form is absent.

Annealing up to temperatures lower than 60 °C does not induce any polymorphic transformation of the *trans*-planar form III, but only an improvement of crystallites of form III is observed, as indicated by the sharpening of the $(020)_t$ and $(110)_t$ equatorial reflections at $2\theta = 16.2°$ and 18.3° of form III in the X-ray diffraction profiles of Figure 4B,C. Similar sharpening is observed for the $(021)_t$ and $(111)_t$ reflections on the first layer line of the diffraction patterns of Figure 4B,C (see Supporting Information, Figure S3).

At the annealing temperature of 60 °C the *trans*-planar form III starts transforming into the helical forms, as indicated by the appearance of the $(200)_h$ equatorial reflection at $2\theta = 12°$ and of reflections on the first layer line corresponding to the helical chain periodicity, in the diffraction patterns of Figures 3C and 4C. At this temperature the $(020)_t$ and $(110)_t$ equatorial reflections at $2\theta = 16.2°$ and 18.3° of form III are well-separated and of high intensity, indicating further improvement of perfection of crystals of form III.

With increasing the annealing temperature we observe an increase of the intensities of the $(200)_h$ reflection at $2\theta = 12°$ and of the equatorial peak at $2\theta = 16°$ (Figures 3D,E and 4D,E) and a decrease of the intensities of the reflections of form III (the $(110)_t$ reflection at $2\theta = 18.3°$ and the reflections on the first layer line). This indicates that the helical form that develops by annealing up to 80 °C is basically the antichiral form I, although it may not be excluded the presence of a small amount of the isochiral form II. The increase of the intensity of the reflection peak at $2\theta = 16°$ is, indeed, due to the development of the $(020)_I$ reflection of form I at $2\theta = 16°$, which overlaps to the $(020)_t$ reflection of form III. Since the degree of crystallinity does not greatly change up to 80 °C, remaining constant at about 43%, local melting of the smallest and imperfect crystals of form III, followed by crystallization in the antichiral helical form I, probably occurs in this small range of temperature.

At the annealing temperature of 100 °C the relative amount of crystals in the *trans*-planar form III strongly decreases, accompanied by a slightly increase of the degree of crystallinity, and the amount of crystals in the helical forms increases, as indicated by the strong intensity of the $(200)_h$ reflection at $2\theta = 12°$ in the patterns of Figures 3E and 4E. The helical modification formed in the fiber up to 100 °C is basically the antichiral form I, as indicated by the strong $(020)_I$ peak at $2\theta = 16°$ (Figure 4E). However, the presence of a shoulder at $2\theta = 17°$, corresponding to the $(110)_{II}$ reflection of the isochiral form II, indicates that crystals of form II are also produced by annealing at 100 °C. A nonnegligible amount of the *trans*-planar form III is, however, still present in the annealed fiber, as indicated by the presence of the $(110)_t$ reflection of the form III at $2\theta = 18.3°$ (Figures 3E and 4E) and reflections corresponding to the *trans*-planar conformation on the first layer line (Figure 3E).

Upon annealing at 110 °C the crystals of form III disappear, and the sample results almost completely crystallized in the helical forms. In fact, the equatorial $(110)_t$ reflection at $2\theta = 18.3°$ and reflections on the first layer line corresponding to the *trans*-planar chain periodicity are basically absent in the patterns of Figures 3F and 4F. Moreover, at the annealing temperature of 110 °C the shoulder at $2\theta = 17°$ transforms into a well-defined peak corresponding to the $(110)_{II}$ reflection of form II, indicating the clear presence of crystals of the isochiral form II. The relative amount of crystals of the isochiral form II present in the fiber annealed at 110 °C is nearly 60%.

With increasing the annealing temperature up to 130 °C improvement of perfection and size of crystals is observed, as indicated by the sharpening of the $(020)_I$ and $(110)_{II}$ reflections at $2\theta = 16°$ and 17°, respectively, of the helical forms I and II (Figures 3F–H and 4F–H). The amount of crystals of form II present in the fibers annealed at 120 and 130 °C remains constant and equal to nearly 60%.

Therefore, annealing at high temperatures of fibers in the *trans*-planar form III produces a mixture of crystals of the helical form I and form II, as observed in the case of the annealing of the fiber initially in the *trans*-planar mesomorphic form (Figures 1 and 2). The relative amounts of crystals of form I and form II developed by annealing of fibers of form III are nearly the same as those formed by annealing of fibers initially in the *trans*-planar mesomorphic form. The only difference seems the temperature at which the transition starts. The *trans*-planar form III is stable up to 60 °C whereas for the mesomorphic form the transition begins already at 40 °C. Moreover, the annealing of form III produces first transformation into the antichiral helical form I (at 80–100 °C) and, then, formation of the isochiral helical form II (at 100–130 °C). Annealing of the fibers initially in the mesomorphic form, instead, produces contemporarily formation of crystals of form I and form II already at low temperature.

The experimental result that in the s-PP fiber in the pure *trans*-planar form III the helical form II appears only by annealing at temperatures higher than 80 °C, whereas the helical form I already develops at 60 °C may be explained considering that in order for the isochiral form II to develop its formation should be kinetically favored. At low annealing temperatures the smallest and most imperfect crystals of form III melt followed by crystallization of the amorphous phase in the antichiral helical form I. At the annealing temperature of 100 °C a sudden microscopic relaxation of chains, due to higher mobility, which alleviates the stress, occurs, so that the crystals of form III in part melt and in part transform into the helical form II. Meanwhile, the crystals of form I, already formed at low temperatures, nucleate the crystallization of the amorphous phase in the antichiral helical form I. At the annealing temperature of 110 °C the presence of crystals of the two helical forms nucleate crystallization of the amorphous phase, leading to a slight increase of the degree of crystallinity, whereas the relative amount of the two forms remains nearly constant, and at 130 °C only improvement of perfection and size of crystals is observed.

Concluding Remarks

The structural polymorphic transitions occurring in s-PP fibers initially in the *trans*-planar form III and in the mesomorphic form upon annealing at high temperatures have been analyzed. Both the *trans*-planar form III and the mesomorphic form transform by annealing at high temperatures into a mixture of crystals of the helical form I and form II. Annealing of the *trans*-planar mesomorphic form produces simultaneous formation of the isochiral form II and the antichiral form I, already at low temperatures (40−60 °C). The relative amounts of forms I and II increase with increasing annealing temperature, and fibers containing similar amounts of crystals of form I and II are obtained at high temperatures (120−130 °C). Fibers in the crystalline *trans*-planar form III transform mainly into the antichiral form I by annealing up to 80 °C; at higher temperatures also the isochiral form II develops, and fibers in a mixture of similar amounts of crystals of both helical forms are obtained at 120−130 °C.

These results clearly indicate that the isochiral helical form II can be obtained by annealing at high temperatures s-PP fibers initially either in the *trans*-planar mesomorphic form or in the crystalline form III. Therefore, the presence of the isochiral helical form II is not necessarily linked to the presence of the *trans*-planar mesomorphic form, as suggested in the literature.[25] The conclusion of ref 25 that, in order for form II to develop, the *trans*-planar mesophase has to be present seems rather forced and aimed at pursuing the general idea that intermediate mesophases are precursors of the crystallization of the isochiral structure of s-PP.[28] In fact, assuming valid the conclusions of ref 25, the origin of the presence of form II in fibers originally in the pure form III annealed at temperatures higher than 80 °C (Figure 3) may be due to the melting of form III, recrystallization of the *trans*-planar mesomorphic form, and then fast crystallization of the latter into the isochiral form II. An alternative route to the crystallization of form II could also be the crystallization of the amorphous phase via the precursor intermediate mesomorphic form. However, development of the *trans*-planar mesomorphic form of s-PP at temperatures higher than 80 °C is unlikely, since fibers originally in the pure mesomorphic form start transforming into the more stable helical form already at 40 °C, and at temperatures higher than 80 °C this transformation is almost complete (Figures 1 and 2). In any case the transformation of the *trans*-planar form III into the helical form II via the intermediate mesomorphic form is a speculation and deserves experimental evidences. Recent findings, indeed, have shown that form II can be obtained by melt-crystallization at high pressure,[20] or in single crystals grown in thin films,[21] where no reasons can be invoked to claim the presence of the mesomorphic form. Moreover, in recent papers we have also shown that in poorly stereoregular s-PP samples having high molecular mass, the pure mesomorphic form, obtained in fibers stretched at high deformations, transforms into the antichiral helical form I upon releasing the tension, and no traces of the isochiral form II have been observed.[24]

The data of the present paper are instead more compatible with the idea that in stretched fibers of s-PP form III transforms into the helical isochiral form II by releasing the tension through a crystal−crystal transition[9,19] involving a cooperative formation of gauche bonds of identical sign in contiguous chains,[29] without transformation into an intermediate phase. On the other hand, the evolution of the form III upon relaxation of stretched fibers depends on the memory of the crystalline form present in the unstretched samples or formed during the stretching. In fact, the *trans*-planar form III transforms into the *trans*-planar mesomorphic form upon removing the tension if the initial unstretched sample was in the mesomorphic form.[22] In the case of the annealing experiments at high temperatures, instead, the higher chain mobility or the possible partial melting and recrystallization allow formation also of the most stable antichiral helical form I, along with the isochiral helical form II.

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Supporting Information Available: Details of the experimental procedure used to evaluate the fraction of the helical forms I and II in the annealed fibers; deconvolution of the diffraction profiles read along the equator of the X-ray fiber diffraction patterns of form III and of annealed fibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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