Structural Transitions of the Trans-Planar Mesomorphic Form and Crystalline Form III of Syndiotactic Polypropylene in Stretched and Stress-Relaxed Fibers: A Memory Effect

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ABSTRACT: A study of polymorphic transitions occurring during the stretching of samples of syndiotactic polypropylene (s-PP) in the trans-planar mesomorphic form is presented. Samples in the pure trans-planar mesomorphic form or in mixture with crystals of the helical form I have been stretched at room temperature and at 4 °C. Both the stretching temperature and the crystalline modification of the starting material strongly influence the polymorphism of oriented s-PP fibers. Stretching procedures at room temperature induce the crystallization of the trans-planar form III, regardless of the crystalline modification of the starting unoriented sample. Both the trans-planar mesomorphic form and the helical form I transform at high deformation into the crystalline trans-planar form III. When the stretching is instead performed at 4 °C the structural transitions occurring upon stretching depend on the crystalline modification of the starting unoriented material. Indeed, if s-PP samples in the pure trans-planar mesomorphic form are stretched at 4 °C, only an orientation of the mesomorphic crystals occurs, and the transition into the crystalline form III is never observed, also for high deformation. When the s-PP samples are, instead, in mixtures of crystals of the mesomorphic and helical forms, stretching at 4 °C induces the transition of the helical form into the trans-planar form III at low deformations. At high deformations the mesomorphic form also transforms into the crystalline form III. In all the experiments, the removal of the tension in fibers stretched at room temperature and at 4 °C produces structural changes, which depend on the crystalline form of the starting unoriented samples and on the crystalline modifications formed during the stretching. The trans-planar form III transforms, indeed, into the crystalline forms present in the unoriented samples or formed during the stretching (helical form and/or mesomorphic form). These results indicate that the structural evolution of the trans-planar form III upon removing the tension in stretched fibers strongly depends on the memory of the crystalline forms present in the starting unoriented material and on the memory of the crystalline forms produced during the stretching.

Introduction

Highly stereo- and regioregular syndiotactic polypropylene (s-PP) has been synthesized thanks to the discovery of single center homogeneous metallocene catalysts.[1] The high crystallinity and melting temperature of the highly regular s-PP samples has allowed one to carry out more detailed studies of the complex polymorphism and of the physical properties of s-PP.

Four different crystalline forms of s-PP have been obtained and widely studied so far. Form I and form II present chains in the **s**(2/1)2 helical conformation,[2,3] whereas form III and form IV present chains in trans-planar[4,5] and $(T_6G_2T_2G_2)_n$ helical conformations,[6,7] respectively. Form I is the stable form of s-PP; it is obtained under the common conditions of crystallization, from the melt[8] and from solutions in powder and single crystals.[3,9−11] The metastable helical form II is obtained in oriented fibers, by stretching s-PP samples of low stereoregularity[2,12−14] or by removing the tension in fibers initially in the trans-planar form III stretched from highly stereoregular s-PP samples.[13−16] Recently it has also been obtained in powder samples by crystallization from the melt at elevated pressure[17] and in single crystals by epitaxial crystallization.[18]

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The trans-planar form III is obtained by stretching at low temperatures low stereoregular s-PP samples[4] or by stretching at room temperature highly stereoregular samples.[5,12−15] It is stable only under tension; when the tension is removed, the orientation of the sample is preserved and a phase transition from the trans-planar form III into the helical form II is observed.[13−16] A small amount of crystals in form III may remain in the relaxed fibers, the relative amount of helical and trans-planar forms being dependent on the stereoregularity of the s-PP sample, the stretching conditions (i.e., stretching temperature, draw ratio) and the time the fiber is kept under tension. The metastability of the trans-planar form III in the unstrained state seems to be mainly responsible for the elastic behavior of fibers of s-PP.[14−16]

Besides the four crystalline modifications, a mesomorphic form of s-PP, characterized by disorder in the lateral packing of chains in trans-planar conformation, has been recently obtained by quenching the melt at 0 °C and keeping the sample at 0 °C for long time.[19−21] The residence time at 0 °C plays a relevant role in the formation of the mesomorphic form of s-PP: samples kept for a short time at 0 °C crystallize at room temperature in the more stable helical form I, longer residences at 0 °C, instead, favor the stability of the trans-planar mesomorphic form and inhibit the normal crystallization into the helical form I when the sample

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is heated at room temperature.[19−24] These results have been interpreted considering that portions of chains in trans-planar and in helical conformations are in equilibrium in the amorphous state at 0 °C; the slight mobility of chains, still present at 0 °C, allows portions of chains in trans-planar conformation to aggregate forming small disordered crystalline bundles which originate the mesomorphic form. If the residence time at 0 °C is long enough, these bundles become stable enough to prevent the crystallization at room temperature in the more stable helical form I.[21−23]

The crystallization of the mesomorphic form also depends on the degree of stereoregularity of the s-PP sample; in particular, the stereoregularity influences either the rate of formation of the mesomorphic form at 0 °C, or the maximum amount of the mesomorphic form obtained in the sample at room temperature.[23] The higher the syndiotacticity of the s-PP sample is, the easier the formation of the mesomorphic form and the greater the fraction of material in the mesomorphic form present in the sample at room temperature, with respect to that in the helical form I.

Recently, the crystallization of the mesomorphic form of s-PP has been investigated at quenching temperatures different from 0 °C.[25−27] At any temperature in the range between −5 and +6 °C, mixtures of crystals of the trans-planar mesomorphic form and helical form I are obtained, and the relative amount of the two phases depends on the quenching temperature and the residence time at that temperature.[25,26] With increasing quenching temperature, an increase of the rate of formation of the mesomorphic form is observed, due to the increased mobility of the chains. However, an amount of mesomorphic form close to 100% of the total crystalline phase, measured at room temperature, is achieved only in s-PP samples quenched at 0 °C.[26] This is not in contrast with the results of dynamic FT-IR analysis, reported by Nakaoki et al.[25] In ref 25, indeed, an increase of the intensity of the IR bands sensitive to the T_2G_2 helical sequences is observed in s-PP samples kept at 0 °C for a time long enough to reach the equilibrium state and annealed at room temperature. This indicates a further crystallization of the chains in noncrystalline regions into the helical form I. These crystalline aggregates are, probably, very small and highly disordered so that the corresponding broad and low intensity diffraction is hardly observed in the X-ray powder diffraction profiles reported in ref 26.

The polymorphic behavior and the mechanical properties of s-PP fibers in the mesomorphic form have recently been investigated.[28,29] It has been reported that stretching s-PP samples in the trans-planar mesomorphic form at room temperature induces a progressive orientation of the mesomorphic crystals, for values of the draw ratio up to 5, and the transition into the trans-planar form III for higher deformations. After the tension is released, the crystalline trans-planar form III transforms again in the mesomorphic form.[28,29] Analogous results have been obtained if s-PP samples, quenched from the melt at 0 °C, are directly stretched at 0 °C, kept at 0 °C under tension for 10 days, and then, analyzed at room temperature. The trans-planar form III obtained by stretching at 0 °C transforms into the mesomorphic form upon relaxation.[30] In these studies, the transition of the trans-planar form III into the helical form II, observed in other papers,[13,14,16] has not been observed. These data indicate that the evolution of the trans-planar form III in stretched fibers upon releasing the tension depends on many parameters, as for instance the stretching temperature and the crystalline forms present in the starting unoriented material.

In this paper, this issue is analyzed by performing a study of the polymorphic behavior of s-PP fibers stretched at room temperature and at 4 °C starting from samples initially in the mesomorphic form or in mixture with crystals of the helical form I.

Experimental Section

The s-PP sample was synthesized at 80 °C with the single center metallocene catalyst isopropylidene(cyclopentadienyl)-(9-fluorenyl)zirconium dichloride activated with methylaluminoxane according to standard procedure.[1] The polymer is characterized by a fully syndiotactic pentad *rrrr* content of 91%, molecular weight M_w of 1.64×10^5 ($M_w/M_n = 2.2$), and melting temperature of 147 °C.

Two samples containing different amounts of the trans-planar mesomorphic form were prepared by melting the polymer powder in a hot press at 170 °C, then, rapidly quenching at 0 °C, and keeping the so obtained film (0.3 mm thick) at 0 °C for 90 min (sample sPPA) and for 10 days (sample sPPB).

Oriented fibers of s-PP were obtained by stretching at room temperature and at 4 °C sPPA and sPPB samples at different values of deformation ϵ ($\epsilon = 100[(L_f - L_i)/L_i]$, with L_f and L_i the final and the initial lengths of the specimen, respectively). The fibers were kept under tension at room temperature for the time necessary to perform the X-ray diffraction measurement (2 h), and then the tension was removed, allowing the fibers to relax.

X-ray diffraction patterns were obtained with Ni-filtered Cu Kα radiation. The powder profiles were obtained with an automatic Philips diffractometer, whereas the fiber diffraction patterns were recorded on a BAS-MS imaging plate (FUJIFILM) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800). The X-ray fiber diffraction patterns have been recorded for stretched fibers soon after the stretching and keeping the fiber under tension, as well as for relaxed fibers, that is, after keeping the fiber under tension for 2 h and then removing the tension, allowing the complete relaxation of the specimens.

Results and Discussions

Unoriented Samples. Two samples, sPPA and sPPB, containing different amounts of the trans-planar mesomorphic form have been obtained by quenching the melt at 0 °C and keeping the sample at 0 °C for 90 min and 10 days, respectively. The X-ray powder diffraction profiles recorded at room temperature of sPPA and sPPB samples are reported in Figure 1.

It is apparent that the sample sPPA is characterized by a mixture of crystals of the helical form I and the trans-planar mesomorphic form, as indicated by the presence of the 200 and 020 reflections at $2\theta = 12$ and 16°, respectively of the helical form I, and the broad peak at $2\theta = 17°$ of the mesomorphic form, in the diffraction profile of Figure 1A. Moreover, the absence of the 211 reflection at $2\theta = 18.8°$ indicates that the crystals of form I are characterized by statistical disorder in the position of right- and left-handed helical chains in the unit cell.[8] The residence time of 90 min at 0 °C is not sufficient to stabilize the trans-planar mesomorphic form,[23] and a large amount of crystals in the helical form I are present in the sPPA sample. The sample sPPB, which was kept at 0 °C for longer time, is instead essentially in pure trans-planar mesomorphic form, as indicted by the presence of only two broad

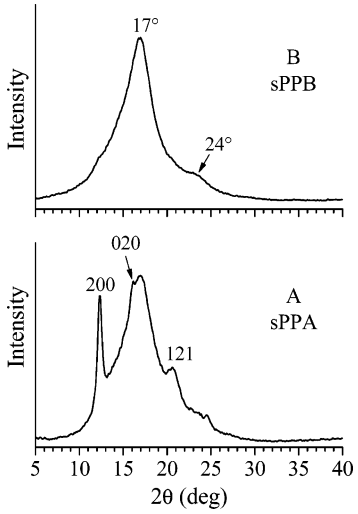


Figure 1. X-ray powder diffraction profiles of sPPA (A) and sPPB (B) samples, obtained by quenching the melt at 0 °C and keeping the samples at 0 °C for 90 min (sample sPPA) and 10 days (sample sPPB). The 200, 020, and 121 reflections of the helical form I and the broad peaks at $2\theta = 17$ and 24° of the trans-planar mesomorphic form are indicated.

peaks centered at $2\theta = 17$ and 24°, in the diffraction profile of Figure 1B.[19,21]

The X-ray diffraction patterns of Figure 1 arise from the contributions of three phases: the trans-planar mesomorphic phase, the helical crystalline form I and the amorphous phase, which can be easily separated knowing the patterns of the three single phases. In particular, the X-ray diffraction pattern of the amorphous phase has been obtained from an atactic polypropylene sample, whereas the patterns of pure trans-planar mesomorphic form and helical crystalline form I have been obtained from a s-PP sample quenched from the melt at 0 °C and kept at 0 °C for 10 days and few seconds, respectively. Hence, the fractions of the three phases have been evaluated by the ratios between the area subtending the diffraction profile of the single phase and the area of the whole diffraction profile.

The total fraction of crystalline phase, that is the sum of the trans-planar mesomorphic form and helical form I, in both sPPA and sPPB samples, evaluated by the X-ray diffraction profiles of Figure 1 as described before, is around 30%. It corresponds to the maximum value of crystallinity achievable at room temperature, regardless of the residence time at 0 °C.[23,26] Moreover, the amount of the trans-planar mesomorphic form, also evaluated from the X-ray diffraction profile, is equal to 12% (40% of the total crystalline phase) for the sample sPPA and to ≈30% (almost 100% of crystalline phase) for the sample sPPB.

Oriented Samples: Stretching at Room Temperature. Oriented fibers of s-PP have been obtained by stretching, at room temperature, films of the samples sPPA and sPPB at different values of deformation. The X-ray fiber diffraction patterns and the corresponding X-ray diffraction profiles read along the equatorial layer line, of fibers of the sample sPPA, initially in a mixture of the helical form I and the mesomorphic form, stretched at room temperature at 200, 300, and 500% deformations, keeping the fibers under tension, are reported in Figure 2 parts A−C, respectively. For deformations up to $\epsilon = 300\%$, fibers in mixtures of crystals of the helical and trans-planar mesomorphic forms are obtained, as indicated by the presence on the equator of the 200 reflection at $2\theta = 12.3°$ of the helical form of s-PP and the broad reflection at $2\theta = 17°$, typical of the mesomorphic form (Figure 2, parts A, B, A′, and B′). On the layer lines reflections corresponding to both chain

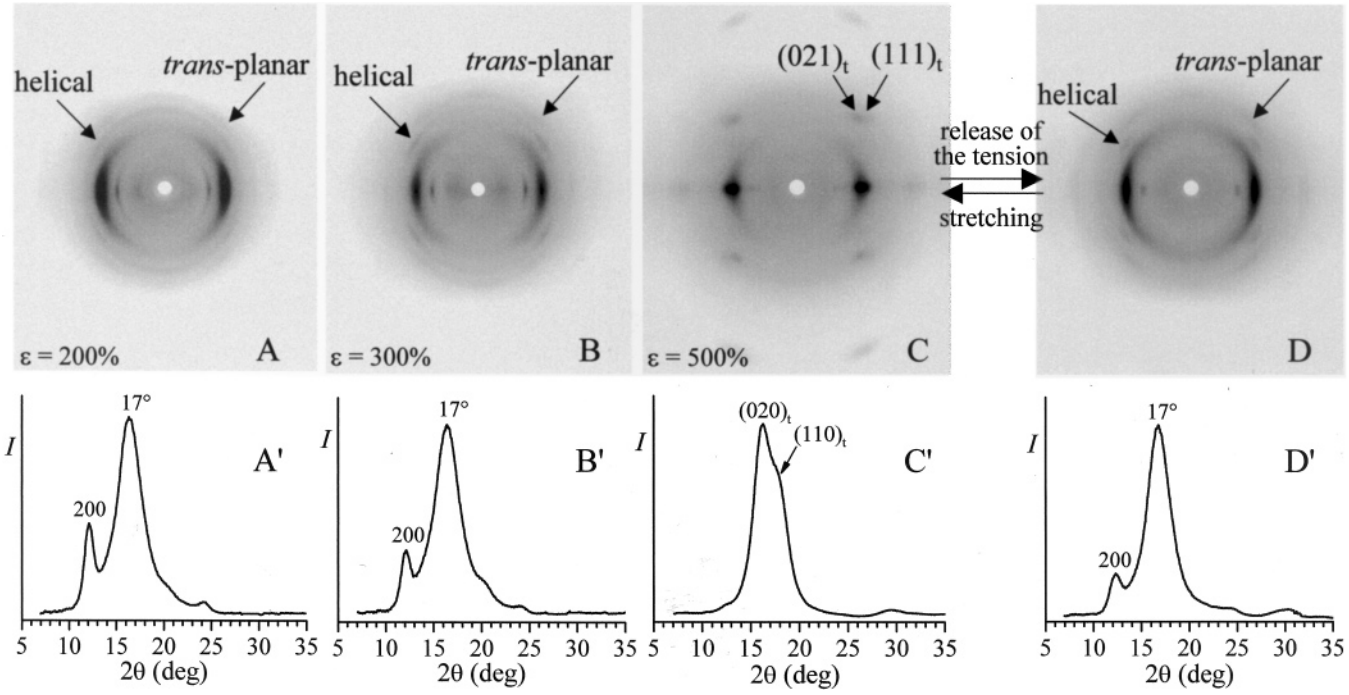


Figure 2. X-ray fiber diffraction patterns (A−D) and corresponding profiles read along the equatorial lines (A′−D′) of fibers obtained by stretching at room temperature and at different deformations ϵ the sample sPPA, keeping the fibers under tension (A−C, A′−C′), and after removing the tension from deformation of 500% (D, D′). The 200 reflection of the helical form I, the $(020)_t$ and $(110)_t$ reflections of the trans-planar form III and the broad peak at $2\theta = 17°$ of the mesomorphic form are indicated. On the first layer line, the reflections arising from the diffraction of crystals in helical and trans-planar forms ($(021)_t$ and $(111)_t$ reflections in the case of crystalline form III) with chain periodicity of 7.4 and 5.1 Å, respectively, are also indicated.

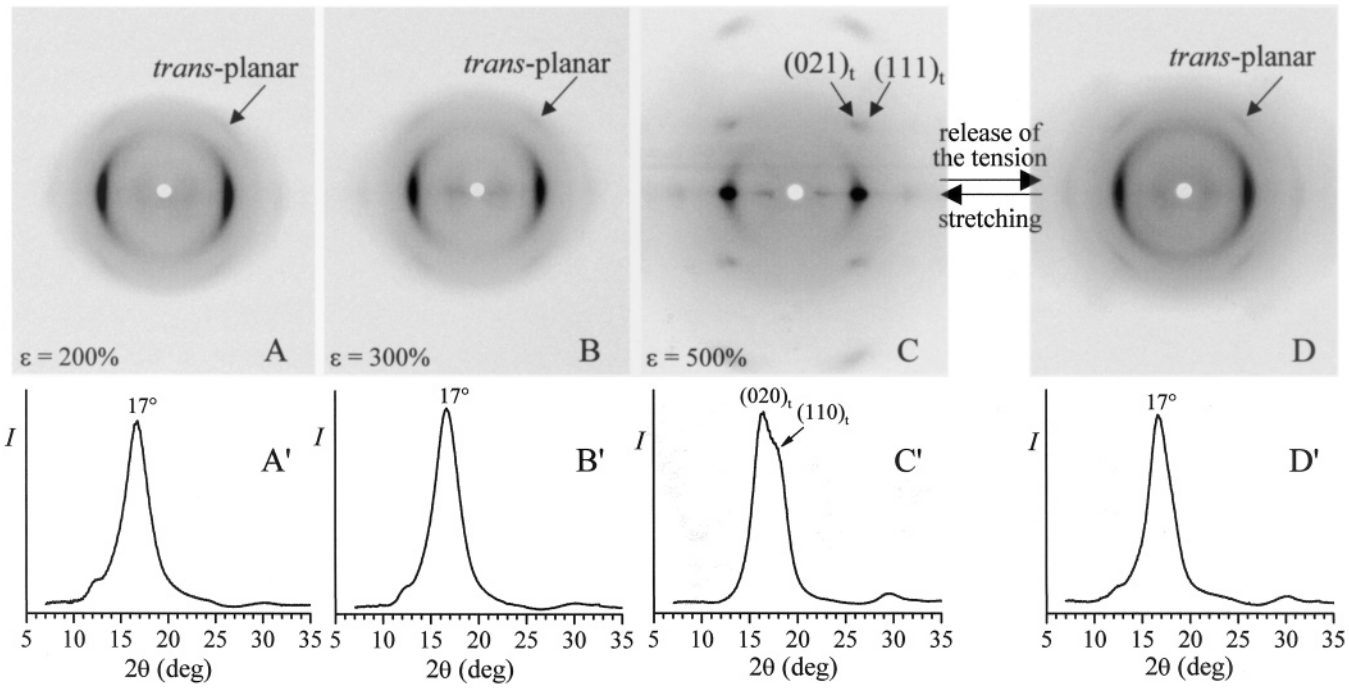


Figure 3. X-ray fiber diffraction patterns (A−D) and corresponding profiles read along the equatorial lines (A′−D′) of fibers obtained by stretching at room temperature and at different deformations ϵ the sample sPPB, keeping the fibers under tension (A−C, A′−C′), and after removing the tension from deformation of 500% (D, D′). The $(020)_t$ and $(110)_t$ reflections of the trans-planar form III and the broad peak at $2\theta = 17°$ of the mesomorphic form are indicated. On the first layer line, the reflections arising from the diffraction of crystals of the trans-planar forms ($(021)_t$ and $(111)_t$, reflections in the case of the crystalline form III) with chain periodicity of 5.1 Å are also indicated.

periodicities of 5.1 Å (trans-planar conformation) and 7.4 Å (**s**(2/1)2 helical conformation) are clearly present (Figure 2, parts A and B). From the patterns of Figure 2, parts A and B, it is difficult to understand whether the fraction of the crystalline material in the helical modification present in the stretched fibers, giving the 200 reflection, is in the antichiral form I or in the isochiral form II or even in a mixture of both forms. In fact, only a quite broad peak in the 2θ range between 14 and 19° is apparent in the equatorial profiles of Figure 2, parts A′ and B′; in this 2θ range, the 020 reflection at $2\theta = 16°$ of the antichiral form I[3] and the 110 reflection at $2\theta = 17°$ of the isochiral form II[2] are hidden by the broad diffraction peak at $2\theta = 17°$ of the mesomorphic form.[21]

With increasing deformation, the intensity of the 200 reflection decreases, and at $\epsilon = 500\%$ the crystalline trans-planar form III of s-PP is obtained, as indicated by the presence of the $(020)_t$ and $(110)_t$ reflections at $2\theta = 15.9$ and 18.8°, respectively, of form III[5] in the diffraction pattern of Figure 2, parts C and C′. On the first layer line, the corresponding $(021)_t$ and $(111)_t$ reflections of the trans-planar form III are also apparent (Figure 2C).

The X-ray fiber diffraction pattern, and the corresponding equatorial profile, of the fiber in form III of Figure 2C after releasing the tension are reported in Figure 2, parts D and D′. It is apparent that the trans-planar form III (Figure 2C) is metastable and transforms in a mixture of crystals of the trans-planar mesomorphic and helical forms upon releasing the tension, as indicated by the presence of the 200 reflection at $2\theta = 12°$ of the helical form and the broad peak at $2\theta = 17°$ of the mesomorphic form, and spots on the first layer line corresponding to both helical and trans-planar chain periodicities, in the diffraction pattern of Figure 2, parts D and D′. It is worth noting that the equatorial peak at $2\theta = 17°$ present in the X-ray diffraction profile of the stress-relaxed s-PP fiber of Figure 2D′ is sharper than those observed in the stretched fibers of Figure 2, parts A′ and B′, and no shoulders at lower values of 2θ are present. This indicates that the helical modification obtained after releasing the tension is possibly the isochiral form II of s-PP. This hypothesis is in agreement with data reported in the literature, which indicate that the trans-planar form III transforms into the helical form II upon releasing the tension in stretched fibers.[13−16] It has recently been demonstrated that the transformation from the trans-planar form III into the helical form II is a crystal−crystal phase transition occurring through a cooperative process imposed by steric constraints.[16,31]

These data indicate that when the starting material used to prepare oriented fibers by stretching is in a mixture of the helical and trans-planar mesomorphic forms, the trans-planar form III, obtained by stretching at high deformation, transforms into a similar mixture of crystals of the helical and mesomorphic forms. This transition is reversible upon successive stretching and relaxing of fibers. It is worth mentioning, however, that whereas the helical form present in the unoriented film is the antichiral form I, the helical form in the stress-relaxed fiber is the isochiral form II.

The X-ray fiber diffraction patterns, and the corresponding X-ray diffraction profiles read along the equatorial layer line, of fibers of the sample sPPB, initially in the trans-planar mesomorphic form, stretched at room temperature at 200, 300, and 500% deformations, keeping the fibers under tension, are reported in Figure 3, parts A−C, respectively. It is apparent from Figure 3 that stretching at low deformations, up to 300%, induces orientation of the mesomorphic crystals (Figure

3, parts A and B), whereas a transition into the crystalline trans-planar form III is observed at higher deformation ($\epsilon = 500\%$, Figure 3C). In fact, in the X-ray diffraction patterns of the fibers stretched at $\epsilon = 200$ and 300%, only the equatorial peak at $2\theta = 17°$, typical of the trans-planar mesomorphic form, and a broad peak at $2\theta \approx 24°$ on the first layer line, corresponding to the chain periodicity of 5.1 Å, are apparent (Figure 3, parts A, A′, B, and B′). With increasing deformation the transition of the mesomorphic form into the crystalline form III progressively occurs, as indicated by the splitting of the diffraction peak at $2\theta = 17°$ into the $(020)_t$ and $(110)_t$ reflections at $2\theta = 15.9$ and 18.8°, respectively (Figure 3, parts C and C′), typical of the form III of s-PP. The transformation into the crystalline form III is also apparent by the diffraction on the first layer line, where the broad peak of the mesomorphic form at $2\theta \approx 24°$ is replaced by two sharper reflections corresponding to the $(021)_t$ and $(111)_t$ reflections of the crystalline form III[5] (Figure 3C).

The X-ray fiber diffraction pattern, and the corresponding equatorial profile, of the fiber in form III of Figure 3C after releasing the tension are reported in Figure 3, parts D and D′. It is apparent that after releasing the tension the crystalline trans-planar form III transforms back into the mesomorphic form (Figure 3, parts D and D′), as indicated by transformation of the two $(020)_t$ and $(110)_t$ reflections at $2\theta = 15.9$ and 18.8° of form III into the broad peak at $2\theta = 17°$ of the mesomorphic form. The transition between the trans-planar form III and the mesomorphic form is reversible upon successive stretching and relaxing of the fiber.

It is worth noting that a peak at $2\theta = 12°$ of low intensity is apparent in the equatorial profiles of Figure 3, parts A and B, indicating that a small amount of crystals in the helical form of s-PP is present in the fibers stretched at low deformations. This negligible fraction of material in the helical form is initially present in the unoriented sPPB film (Figure 1B) and disappears by stretching at high deformation (Figure 3C), but appears again upon removing the tension (Figure 3, parts D and D′).

In summary, the stretching at room temperature of s-PP samples induces the transition into the trans-planar form III, whatever the crystalline modification of the starting unoriented material. Both the helical form and the mesomorphic form transforms by stretching at high deformation into the crystalline form III. When the tension is removed the crystalline trans-planar form III transforms back into the crystalline modifications initially present in the unoriented films. In particular, if the starting s-PP sample is in mixtures of crystals of the trans-planar mesomorphic and helical forms, the trans-planar form III transforms into a mixture of mesomorphic and helical forms. Either fibers stretched at low deformations or stress-relaxed fibers are in mixtures of helical and mesomorphic forms; the helical crystalline modification is the antichiral form I in the stretched fibers and the isochiral form II in the stress-relaxed fibers. If the starting material is, instead, in the pure trans-planar mesomorphic form, the trans-planar form III, obtained by stretching at high deformations, transforms into the mesomorphic form after releasing the tension. These results are in agreement with the literature data[28,29] and indicate that the memory of the crystalline forms initially present in the unstrained material has a relevant effect on the polymorphic transitions occurring in the s-PP fibers upon removing the tension.

Oriented Samples: Stretching at 4 °C. Oriented fibers of samples sPPA and sPPB have also been obtained by stretching at 4 °C. The X-ray fiber diffraction patterns, and the corresponding X-ray diffraction profiles read along the equatorial layer line, of fibers of the sample sPPA, initially in mixture of the helical form I and mesomorphic form (see Figure 1A), stretched at 4 °C at 100, 200, 300, and 500% deformations, keeping the fibers under tension, are reported in Figure 4, parts A−D, respectively. It is apparent that the trans-planar form III is already obtained at low deformations. The comparison with data of Figure 2 shows that while at room temperature the trans-planar form III is obtained by stretching the sPPA sample at high deformations (e.g., $\epsilon = 500\%$ in Figure 2, parts C and C′), at 4 °C the transition has already occurred at $\epsilon = 200\%$, as indicated by the presence of the equatorial reflections $(020)_t$ and $(110)_t$ at $2\theta = 15.9$ and 18.8°, respectively, of the crystalline form III of s-PP in the diffraction pattern of Figure 4, parts B and B′. Moreover, the equatorial reflection at $2\theta = 12.3°$ of the helical form of s-PP and reflections on the first layer line corresponding to the chain periodicity of 7.4 Å of **s**(2/1)2 helical conformation, are never observed in the diffraction patterns of Figure 4, parts A−D. This indicates that the helical form I of s-PP, initially present in the unoriented film in a non-negligible amount (≈ 60% of the total crystalline fraction, Figure 1A), rapidly transforms by stretching at 4 °C into the trans-planar form III at very low deformations (at least starting from $\epsilon = 100\%$).

At deformation of 100% only a broad equatorial peak at $2\theta \approx 17°$ is present in the diffraction profile of Figure 4A′, indicating that most of the material is in the trans-planar mesomorphic form. The asymmetric shape of the peak at $2\theta = 17°$ suggests that at very low deformations mixtures of crystals in the trans-planar form III and the mesomorphic form are obtained. With increasing deformation also the crystals of the mesomorphic form transform into the form III, as indicated by the splitting of the peak at $2\theta = 17°$ into the $(020)_t$ and $(110)_t$ reflections of form III (Figure 4, parts B′ and C′). At a deformation of 500%, the equatorial $(020)_t$ and $(110)_t$ reflections of form III and the corresponding $(021)_t$ and $(111)_t$ reflections on the first layer line are well separated, indicating that the crystallization in the form III is complete (Figure 4, parts D and D′).

These results can be explained considering that, as reported in the literature,[4] cold drawing procedures of s-PP favor the formation of the trans-planar form III, also in samples of low stereoregularity. Therefore, when the sPPA sample initially in a mixture of crystals of the helical form I and the trans-planar mesomorphic form is stretched at low temperature, the crystals of the helical form transforms rapidly into the trans-planar form III even at low deformations, whereas the crystals of the trans-planar mesomorphic form are only oriented. At higher deformations also the mesomorphic form transforms into the crystalline form III.

The X-ray fiber diffraction pattern, and the corresponding equatorial profile, of the fiber in form III of Figure 4D after releasing the tension are reported in Figure 4, parts E and E′. It is apparent that the trans-planar form III transforms into the mesomorphic form upon removing the tension. Also in this case the helical form is not obtained, as indicated by the absence of the

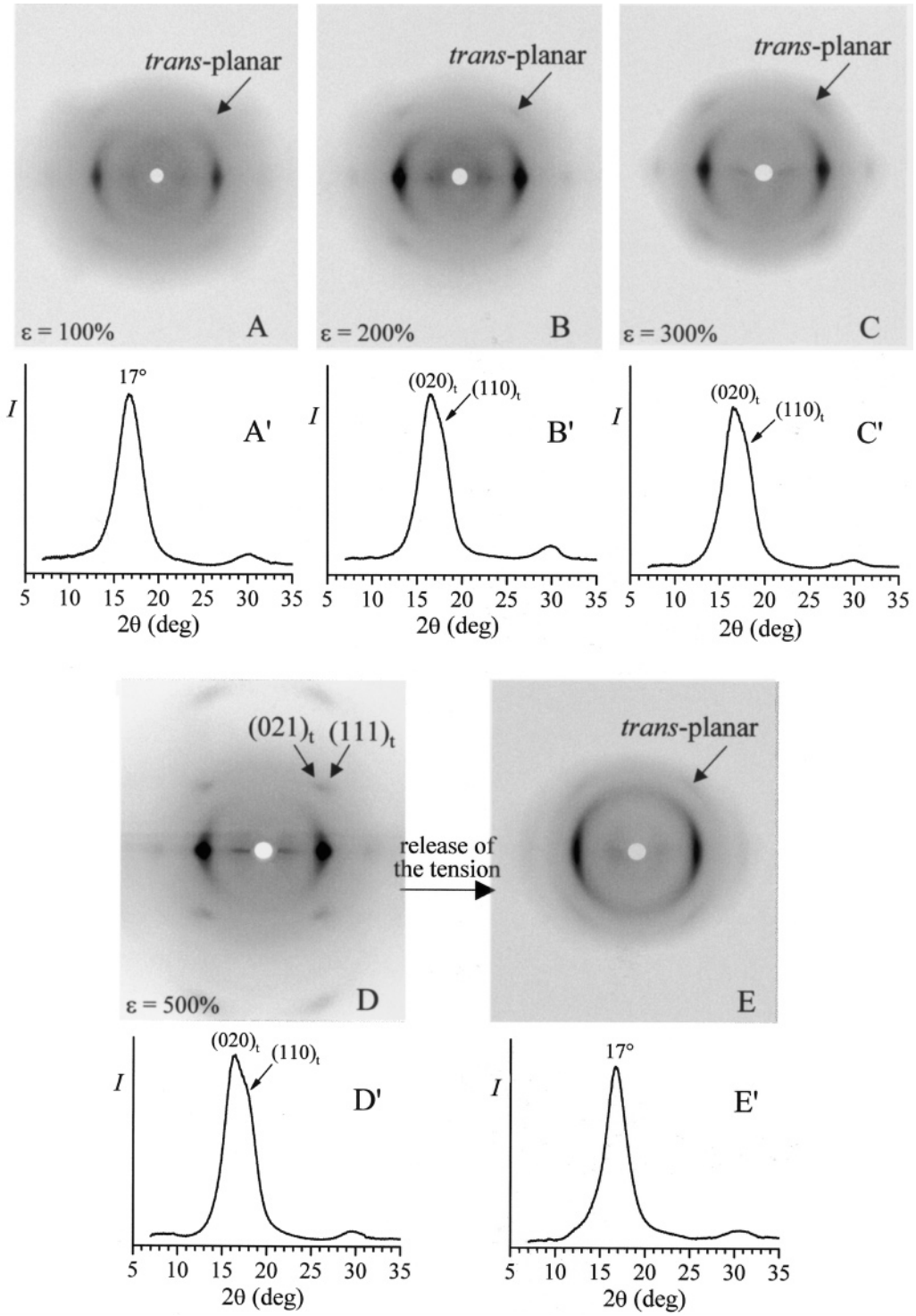


Figure 4. X-ray fiber diffraction patterns (A−E) and corresponding profiles read along the equatorial lines (A′−E′) of fibers obtained by stretching at 4 °C and at different deformations ϵ the sample sPPA, keeping the fibers under tension (A−D, A′−D′), and after removing the tension from deformation of 500% (E, E′). The $(020)_t$ and $(110)_t$ reflections of the trans-planar form III and the broad peak at $2\theta = 17°$ of the mesomorphic form are indicated. On the first layer line, the reflections arising from the diffraction of crystals in the trans-planar forms ($(021)_t$ and $(111)_t$ reflections in the case of the crystalline form III) with chain periodicity of 5.1 Å are also indicated.

peak at $2\theta = 12°$ on the equatorial profile of Figure 4E′ and the absence of layer lines reflections corresponding to the chain periodicity of 7.4 Å (Figure 4E).

The comparison of the data of Figures 2 and 4 relative to fibers prepared by stretching the same sPPA sample, clearly indicates that the structural evolution of the trans-planar form III (Figures 2C and 4D) upon removing the tension (Figures 2D and 4E) is different even though the crystalline form present in the starting unoriented material is the same. This suggests that the structural change of the form III depends not only on the memory of the crystalline forms initially present in the unoriented films but also on the crystalline forms formed during the stretching. In fact, during the stretching at 4 °C of the sample sPPA, the crystalline form I, present in the starting unstretched material, immedi-

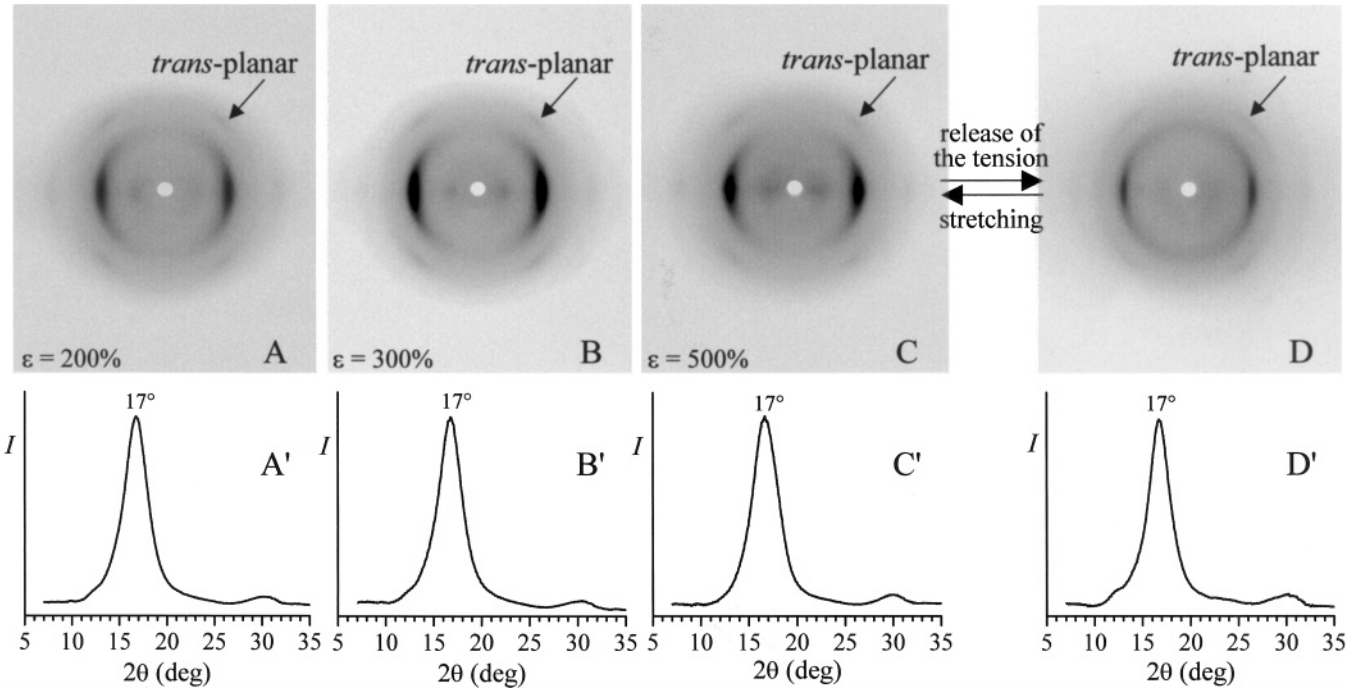


Figure 5. X-ray fiber diffraction patterns (A−D) and corresponding profiles read along the equatorial lines (A′−D′) of fibers obtained by stretching at 4 °C and at different deformations the sample sPPB, keeping the fibers under tension (A−C, A′−C′), and after removing the tension from deformation of 500% (D, D′). The broad equatorial peak at $2\theta = 17°$ of the mesomorphic form and the reflection on the first layer line corresponding to trans-planar conformation with chain periodicity of 5.1 Å are indicated.

ately disappears, already transforming into the trans-planar form III at very low deformations. As a consequence, no memory of this form remains in the stress-relaxed fiber, and upon removing the tension the form III does not transform into the helical form, but a fiber in pure trans-planar mesomorphic form is obtained (Figure 4E).

The X-ray fiber diffraction patterns, and the corresponding X-ray diffraction profiles read along the equatorial layer line, of fibers of the sample sPPB, initially in the trans-planar mesomorphic form, stretched at 4 °C at 200, 300, and 500% deformations, keeping the fibers under tension, are reported in Figure 5, parts A−C, respectively. It is apparent that only an orientation of the mesomorphic crystals occurs by stretching at 4 °C and the transition into the crystalline form III is never observed, at least up to $\epsilon = 500\%$ which is, however, the maximum deformation achieved at 4 °C before the break. In fact, in all the diffraction patterns of Figure 5, only an equatorial peak at $2\theta = 17$ and a peak at $2\theta \approx 24°$ on the first layer line corresponding to the chain periodicity of 5.1 Å, typical of the trans-planar mesomorphic form are present (Figure 5, parts A−C and A′−C′).

After releasing the tension no structural transition is observed and a fiber in the trans-planar mesomorphic form is obtained (Figure 5, parts D and D′). Only a slight loss of orientation is observed in the stress-relaxed fiber (Figure 5D).

The comparison with the previous results, obtained by stretching at 4 °C the samples sPPA initially in mixtures of crystals of helical form I and trans-planar mesomorphic form (Figure 4), allows one to conclude that the formation of the crystalline form III, observed in stretched fibers, originates at low deformations from the transformation of the fraction of crystals in the helical form (Figure 4, parts A−C and A′−C′). At high deformations also the mesomorphic form transforms into form III at 4 °C (Figure 4, parts D and D′), probably thanks to a nucleating effect of the crystals of form III already present and formed at low deformations. In the case of the sample sPPB in the pure trans-planar mesomorphic form, in which crystals of the helical form are not initially present, the trans-planar form III is never observed by stretching at 4 °C, even at high deformation (Figure 5).

Concluding Remarks

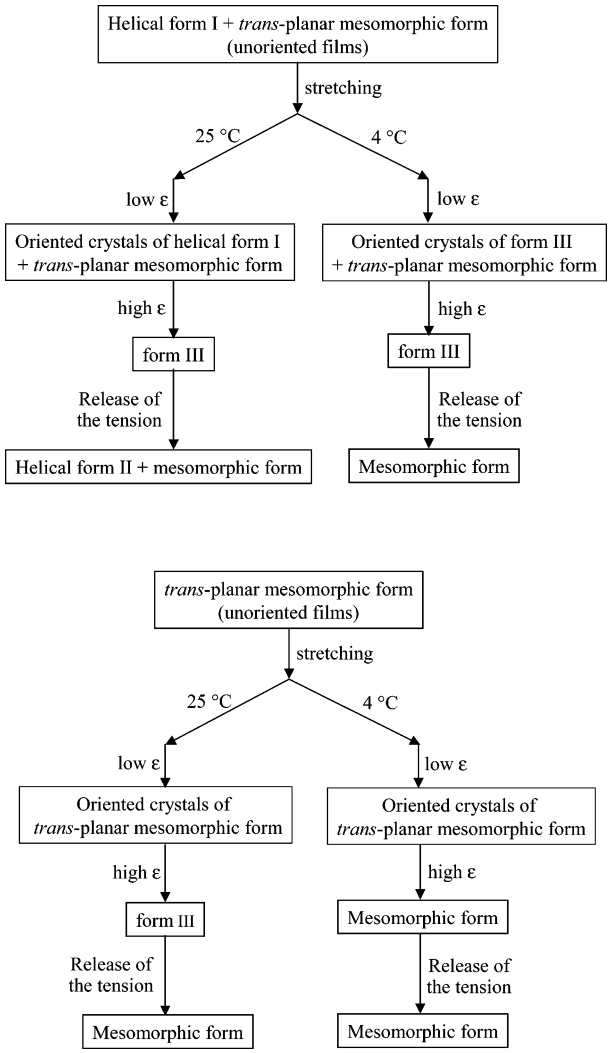
The polymorphic behavior of oriented fibers of s-PP, obtained by stretching samples crystallized from the melt at 0 °C, has been investigated as a function of the crystalline modification of the starting unoriented material and the stretching temperature.

s-PP fibers have been obtained by stretching at room temperature and at 4 °C samples of s-PP containing different amounts of the trans-planar mesomorphic form. The unoriented s-PP films have been prepared by quenching the melt at 0 °C and keeping the samples at 0 °C for suitable times in order to obtain samples in the pure trans-planar mesomorphic form and in mixtures of crystals of the mesomorphic form and the helical form I.

The results of the structural analysis of the stretched and stress-relaxed fibers are summarized in Scheme 1. Both the stretching temperature and the crystalline modification of the starting material strongly influence the polymorphism of oriented s-PP samples.

Stretching procedures at room-temperature induce the crystallization of the trans-planar form III, regardless of the crystalline modification of the starting unoriented sample. In particular, when s-PP samples containing mixtures of crystals in the trans-planar mesomorphic form and in the helical form I are stretched at 25 °C, orientation of both crystals occurs at low

Scheme 1. Structural Changes Occurring during the Stretching at Room Temperature and at 4 °C and, upon Releasing the Tension, of s-PP Samples Initially in Mixtures of Crystals of Trans-Planar Mesomorphic Form and Helical Form I (Sample sPPA) and in the Pure Trans-Planar Mesomorphic Form (Sample sPPB)[a]



[a] ϵ indicates the deformation.

deformations (up to $\epsilon = 300\%$), whereas the transition into the crystalline trans-planar form III occurs at higher deformation ($\epsilon = 500\%$). The trans-planar form III transforms into the mixture of crystals in the helical and mesomorphic forms upon releasing the tension. Analogously, stretching at 25 °C of s-PP samples in the pure trans-planar mesomorphic form induces orientation of the mesomorphic crystals at low values of deformation (up to 300%), and the transition into the crystalline form III at higher deformations (500%). In this case the trans-planar form III transforms into the mesomorphic form upon releasing the tension (Scheme 1).

Different results are obtained when the stretching is performed at 4 °C. In the case of s-PP samples initially in mixture of crystals of trans-planar mesomorphic form and helical form I, the low stretching temperature already induces the transition of the crystals in the helical form into the trans-planar form III at low deformations ($\epsilon = 200\%$), and only orientation of the crystals in the mesomorphic form is observed.

At higher deformations, the crystals in the mesomorphic form also transform into the crystalline trans-planar form III. As the tension is removed, the trans-planar form III transforms into the mesomorphic form with preserved orientation. When s-PP samples in the pure trans-planar mesomorphic form are stretched at 4 °C, only orientation of the trans-planar mesomorphic crystals is observed, while the transition into the crystalline form III never occurs, even for high values of deformation (Scheme 1).

Therefore, the crystalline trans-planar form III is always obtained by stretching at room temperature s-PP samples at high deformations, either starting from materials in mixtures of crystals of the trans-planar mesomorphic form and helical form I or starting from materials in the pure mesomorphic form. At room temperature both crystals in the helical form I and in the trans-planar mesomorphic form transform into the crystalline form III. At 4 °C, instead, the transition into the crystalline form III does not occur if the starting unoriented material is in the pure mesomorphic form, whereas it occurs only if crystals of the helical form I are present in the starting materials.

In the case of the sample in the pure trans-planar mesomorphic form, the stretching at 25 °C probably induces either the crystallization of the mesomorphic form into form III, or further crystallization of the amorphous in form III. The high mobility of chains at 25 °C, combined with the stretching at high deformation, favors the crystallization of form III. At 4 °C, instead, the reduced mobility of the system prevents the crystallization of the mesomorphic aggregates, as well as of the amorphous chains, in the trans-planar form III, and the stretching at high deformations only produces orientation of the mesomorphic form.

The formation of the trans-planar form III by stretching at low temperature is easier when crystals of the helical form I are initially present in the starting material. In fact, despite the reduced mobility of the chains, the crystals of the helical form transform by stretching into the form III even at low deformations. In this case, as in the stretching at 4 °C of the sample in the pure mesomorphic form, crystallization of both mesomorphic aggregates and amorphous phase is prevented, but crystals of the helical form I transform into the trans-planar form III through a solid−solid phase transition, while crystals of the mesomorphic form are only oriented. At high deformations the mesomorphic form also transforms into the crystalline form III, probably because of the nucleating effect of the crystals of form III produced at low deformation.

In all the experiments, the removal of the tension in fibers stretched at room temperature and at 4 °C produces structural changes, which depend on the crystalline modification of the starting unoriented samples. When the trans-planar form III is produced by stretching at high deformations, it transforms back into the mesomorphic form upon releasing the tension, if the unoriented starting material was in the mesomorphic form. If the starting unoriented film contains crystals of the mesomorphic form and the helical form, the trans-planar form III, produced by stretching, transforms, upon releasing the tension, into a mixture of the mesomorphic and helical forms, if the stretching has been performed at room temperature, while it transforms into the mesomorphic form if the stretching has been performed at 4 °C.

These apparently contrasting results could be rationalized considering that during the stretching at room-temperature crystals of both the trans-planar mesomorphic form and helical form are oriented and are always present in the stretched fibers up to high values of deformation, when they finally both transform into the crystalline form III. During the stretching at 4 °C, instead, crystals of the helical form I rapidly transform, already at low deformations, into the trans-planar form III; as a consequence the helical form, present in the unoriented sample, is never present in the stretched fibers, which are instead characterized by mixtures of crystals of the mesomorphic form and the crystalline form III. Then, at high values of deformation the mesomorphic form transforms into form III. When the tension is removed the trans-planar form III transforms into the crystalline modifications produced during the stretching, that is, into mixtures of crystals of the trans-planar mesomorphic and helical forms if the stretching was performed at room temperature and into the trans-planar mesomorphic form if the stretching was performed at low temperature.

These data indicate that the structural evolution of the trans-planar form III upon removing the tension in stretched fibers strongly depends on the memory of the crystalline forms present in the starting unoriented material and of the crystalline forms produced during the stretching. This hypothesis is supported by the fact that these polymorphic transitions occur in the solid state, as for instance the reversible transition between the helical form II and the trans-planar form III,[13,16] and are probably related to the morphological and topological relationships between crystals.[16,31]

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References and Notes

(1) Ewen, J. A.; Jones, R.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988** *110*, 6255.
(2) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C* **1967**, *16*, 2477.
(3) Lotz, B.; Lovinger, A. J.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.
(4) Natta, G.; Peraldo, M.; Allegra, G. *Makromol. Chem.* **1964**, *75*, 215.
(5) Chatani, Y.; Maruyama, H.; Noguchi, K.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Part C* **1990**, *28*, 393.
(6) Chatani, Y.; Maruyama, H.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Polym. Phys. Ed.***1991**, *29*, 1649.
(7) Auriemma, F.; De Rosa, C.; Ruiz de Ballesteros, O.; Vinti, V.; Corradini, P. *J. Polym. Sci., Polym. Phys. Ed.* **1998**, *36*, 395.
(8) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1997**, *30*, 4137.
(9) Lovinger, A. J.; Lotz, B.; Davis, D. D. *Polymer* **1990**, *31*, 2253.
(10) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552.
(11) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J. *Macromolecules* **1993**, *26*, 3494.
(12) De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5711.
(13) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1998**, *31*, 7430.
(14) Auriemma, F.; Ruiz de Ballesteros, O.; De Rosa, C. *Macromolecules* **2001**, *34*, 4485.
(15) De Rosa, C.; Gargiulo, M. C.; Auriemma, F.; Ruiz de Ballesteros, O.; Razavi, A. *Macromolecules* **2002**, *35*, 9083.
(16) Auriemma, F.; De Rosa, C. *J. Am. Chem. Soc.* **2003**, *125*, 13143.
(17) Rastogi, S.; La Camera, D.; van der Burgt, F.; Terry, A. E.; Cheng, S. Z. D. *Macromolecules* **2001**, *34*, 7730.
(18) Zhang, J.; Yang, D.; Thierry, A.; Wittmann, J. C.; Lotz, B. *Macromolecules* **2001**, *34*, 6261.
(19) Nakaoki, T.; Ohira, Y.; Hayashi, H.; Horii, F. *Macromolecules* **1998**, *31*, 2705.
(20) Ohira, Y.; Horii, F.; Nakaoki, T. *Macromolecules* **2000**, *33*, 1801.
(21) Vittoria, V.; Guadagno, L.; Comotti, A.; Simonutti, R.; Auriemma, F.; De Rosa, C. *Macromolecules* **2000**, *33*, 6200.
(22) Ohira, Y.; Horii, F.; Nakaoki, T. *Macromolecules* **2001**, *34*, 1655.
(23) De Rosa, C.; Auriemma, F.; Ruiz de Ballesteros, O. *Polymer* **2001**, *42*, 9729.
(24) Ohira, Y.; Horii, F.; Nakaoki, T. *Macromolecules* **2000**, *33*, 5566.
(25) Nakaoki, T.; Yamanaka, T.; Ohira, Y.; Horii, F. *Macromolecules* **2000**, *33*, 2718.
(26) De Rosa, C.; Ruiz de Ballesteros, O.; Santoro, M.; Auriemma, F. *Polymer* **2003**, *44*, 6267.
(27) Grasruck, M.; Strobl, G. *Macromolecules* **2003**, *36*, 86.
(28) Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V. *Macromolecules* **2000**, *33*, 6023.
(29) Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V. *Macromolecules* **2001**, *34*, 2512.
(30) Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V.; Meille, S. V. *Macromolecules* **2002**, *35*, 3921.
(31) Lotz, B.; Mathieu, C.; Thierry, A.; Lovinger, A.; De Rosa, C.; Ruiz de Ballesteros, O.; Auriemma, F. *Macromolecules* **1998**, *31*, 9253.

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