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Structure of syndiotactic propylene–ethylene copolymers: Effect of the presence of ethylene units on the structural transitions during plastic deformation and annealing of syndiotactic polypropylene

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Abstract

Syndiotactic propylene–ethylene copolymers have been synthesized with a single-center C_s-symmetric syndiospecific metallocene catalyst. A study of the effect of the presence of ethylene comonomeric units on the polymorphic behavior of syndiotactic polypropylene (sPP) and on the structural transitions occurring during stretching is reported. For copolymer samples with low ethylene contents, in the range 2–7 mol%, crystals of the helical form I, present in the melt-crystallized samples, transform into the *trans*-planar form III by stretching at high deformation. Form III transforms in part into the helical form II by releasing the tension, as it occurs for sPP. Samples with ethylene contents in the range 8–10 mol% are crystallized from the melt as a mixture of crystals of helical form I and form II. Both helical forms transform by stretching at low values of deformation (lower than 300%) into the *trans*-planar mesomorphic form, which transforms into the *trans*-planar form III by further stretching at higher deformations (higher than 500%). For these samples form III transforms back into the mesomorphic form, rather than into the helical forms, by releasing the tension. Unoriented samples of copolymers with ethylene content in the range 13–18 mol% are mainly crystallized in the helical form II, which transforms into the *trans*-planar mesomorphic form by stretching. Upon releasing the tension the mesomorphic form remains stable and no polymorphic transition is observed. The presence of ethylene comonomeric units stabilizes the *trans*-planar forms in fibers of the copolymer samples. This has been confirmed by the result that for high ethylene contents the *trans*-planar form III and the mesomorphic form do not transform in helical forms by annealing of fibers stretched at high deformations.

Keywords: Syndiotactic propylene–ethylene copolymers; Polymorphic transitions during stretching; Thermoplastic elastomers

1. Introduction

The deformation behavior and the mechanical properties of syndiotactic polypropylene (sPP) are strongly related to its complex polymorphic behavior [1–6]. Four crystalline forms [1,7–14] and one mesomorphic form [15,16] have been found and different polymorphic transformations occurring during deformation have been described [1–6,17–22]. Form I and form II present chains in s(2/1)2 helical conformation [1,7,8,11–13], the crystalline form III and the mesomorphic form present chains in *trans*-planar conformation [9,15,16], and form IV is characterized by chains in a $(T_6G_2T_2G_2)_n$ helical conformation [10,14].

The plastic deformation of sPP is associated with a polymorphic transition from the stable form I with chains in two-fold helical conformation, generally present in unstretched powder samples of sPP, into the metastable form III, characterized by chains in *trans*-planar conformation [1–6]. The deformation behavior of sPP is complicated by the fact that the associated polymorphic transformations strongly depend on the microstructure of sPP macromolecules and condition of deformation [17–22]. In particular, the polymorphic behavior of sPP in both powder and fiber samples, is strongly influenced by the degree of stereoregularity [12,13,18–20,23,24]. In fact, the pure *trans*-planar form III is obtained only by stretching at room temperature highly stereoregular sPP samples (with *rrrr* pentad contents higher than 90%), initially in the helical form I [1–4,9,13] or in the *trans*-planar mesomorphic form [21]. The lower the stereoregularity, the more difficult the formation of the *trans*-planar form III by stretching [2–4,13,18–20]. Stretching at high draw ratios of poorly syndiotactic samples (with *rrrr* pentad contents of 40–55%) produces, indeed, transformation of the helical form I into the *trans*-planar

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mesomorphic form [18–20]. The high concentration of defects of stereoregularity does not prevent formation of the *trans*-planar conformation but prevents the crystallization of the ordered form III by stretching, and only the disordered *trans*-planar mesomorphic form is obtained [18–20].

Different polymorphic transformations have been observed during the relaxation and elastic recovery of stretched fibers of sPP upon releasing the tension [2–4,17]. The *trans*-planar form III obtained by stretching of highly syndiotactic samples is unstable in unstrained samples and, generally, transforms into the more stable isochiral helical form II upon removing the tension from stretched fibers [2–4,13,17]. However, it has been shown that this transformation depends on a memory effect, that is, on the crystalline form present originally in the unstretched sample [21]. 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 [21].

The polymorphic transition between the helical form II and the *trans*-planar form III is reversible and occurs during successive mechanical cycles of stretching and relaxation of fibers, and is associated with the elastic recovery of sPP [2–4,17]. It has been recently suggested that this stress-induced phase transition is a martensitic phase transformation [4,17]. As in martensitic phase transitions it occurs readily and directly, supporting the idea that elasticity in sPP has a partial enthalpic character, providing an additional contribution to the elastic recovery, besides the entropic contribution as in conventional elastomers [4,17].

The polymorphic transformation occurring during fiber relaxation upon releasing the tension also depends on the stereoregularity [18–20]. In fact, in the case of poorly stereoregular sPP samples, with *rrrr* pentad contents of 40–55%, the *trans*-planar mesomorphic form, obtained by stretching, transforms into the antichiral helical form I by releasing the tension [18,20]. This transition is reversible and is associated with the good elastic recovery shown by these samples [18,19].

Both the metastable *trans*-planar form III and mesomorphic form of sPP also transform into the more stable helical forms by annealing at high temperatures [25], and fibers with mixtures of crystals of the antichiral form I and isochiral form II are generally obtained [1,13,25].

The polymorphic behavior of sPP is also strongly affected by the presence of comonomeric units. The structure and physical properties of copolymers of sPP with ethylene [26–34], butene [26–30,35–38], pentene [27–29], hexene [27–29], 4-methyl-1-pentene [26–29] or octene [39–43], have been recently studied. The effect of the presence of comonomeric units on the polymorphic behavior of sPP has been extensively investigated basically in as-prepared and melt crystallized samples of copolymers [30–37].

Copolymers of sPP with ethylene (sPPET) have interesting physical properties of thermoplastic elastomers [33,34]. The copolymer samples are crystalline up to an ethylene content of nearly 20 mol%, with melting temperatures decreasing with increasing ethylene content from 150 °C, typical of sPP homopolymer, to nearly 50 °C [32]. Ethylene units are partially included in the crystals of both as-prepared and melt-crystallized samples [31,32]. As-prepared sPPET samples basically crystallize in conformationally disordered modifications of form II of sPP, containing kink bands [31,32]. These modifications are characterized by portions of chains in *trans*-planar conformation in chains having a prevailing two-fold helical conformation, packed as in the isochiral helical form II of sPP [44,45]. These structures are metastable and transform by crystallization from the melt into the most stable antichiral helical form I or into the conformationally ordered helical form II, depending on the ethylene concentration [32].

sPPET samples having low ethylene content (up to 6–7 mol%) crystallize from the melt into the stable form I of sPP [32], even though disordered modifications of form I are always obtained [12]. Disorder consists into departures from the perfect alternation of helices of opposite chirality along *a* and *b* axes of the orthorhombic unit cell [12]. For higher ethylene content, mixtures of crystals of forms I and II are obtained by crystallization from the melt [32]. The fraction of form II increases with increasing crystallization temperature and ethylene content. The helical form II obtained by melt crystallizations does not present kink-band disorder, all chains being in the more stable two-fold helical conformation. This is the first example of crystallization of the isochiral helical form II of sPP from the melt at atmospheric pressure [32].

In this paper, the structure of oriented fibers of sPPET copolymer samples is studied as a function of ethylene composition. The effect of the presence of ethylene units on the stability of helical and *trans*-planar forms of sPP and on polymorphic transitions occurring during plastic deformation and elastic recovery is investigated.

2. Experimental section

Samples of sPPET copolymers having concentrations of ethylene in the range 2–20 mol% have been prepared using the single center metallocene catalyst (phenyl)$_2$-methylen(cyclopentadienyl)(9-fluorenyl)ZrCl$_2$ (Ph$_2$-C(Cp)(Flu)ZrCl$_2$), activated with methylaluminoxane (MAO), according to the method described in Refs. [31,32].

All copolymerizations were run at 10 °C in a 250 mL Pyrex reactor, agitated with magnetic stirrer, containing a toluene solution (100 mL) of the catalyst (2–3 mg) and MAO. The Al/Zr molar ratio was adjusted to 1000. Gas mixtures of ethylene and propene at the appropriate composition, prepared with vacuum line techniques and standardized by gas chromatography, were bubbled through the liquid phase at atmospheric pressure and a flow rate of 0.3 L/min. Under such conditions, total monomer conversions were lower than 10%, this ensuring a nearly constant feeding ratio. The copolymers were coagulated with excess methanol acidified with enough HCl (aqueous, concentrated) to prevent the precipitation of alumina from MAO hydrolysis, filtered, washed with further methanol, and vacuum-dried. Typical yields were 2–5 g with a

120 min reaction time. The conditions of polymerization for all sPPET samples are reported in Table 1.

The used catalyst has been reported to be highly syndiotactic specific and highly regioselective (the amount of regioirregularities due to 2,1 insertions of propylene units being less than 0.1%) [31].

The composition of the copolymers, reported in Table 1, was determined by analysis of the ^{13}C NMR spectra, recorded with a Varian XL-200 spectrometer operating at 50.3 MHz, of 10% w/v polymer solutions in deuterated tetrachloroethane (also used as internal standard) at 120 °C. The copolymers, according to this analysis, are random and homogeneous in the composition.

The melting temperatures were obtained with a differential scanning calorimeter Perkin–Elmer DSC-7 performing scans in a N_2 atmosphere at heating rate of 10 °C/min.

The intrinsic viscosities were measured in 1,2,3,4-tetrahydronaphtalene solutions at 135 °C, using standard Ubbelohde viscosimeter. The viscosity average molecular masses of sPPET samples were obtained from values of intrinsic viscosity using the parameters of Mark–Houwink equation reported for atactic polypropylene $\alpha = 0.96$, $k = 1.24 \times 10^{-5}$ dL/g [46].

Unoriented films used for structural analysis have been obtained by compression molding of as-polymerized samples. Powders of sPPET samples have been heated at temperatures 30–40 °C higher than the melting temperature of the as-prepared samples under a press at very low pressure, kept at this temperature for 10 min, and slowly cooled to room temperature.

Oriented fibers have been obtained by stretching at room temperature compression-molded films of initial length L_0 up to a final length L_f, keeping the fiber under tension for 2 h (deformation $\varepsilon = 100 \times (L_f - L_0)/L_0$), and then removing the tension.

X-ray diffraction patterns have been obtained with Ni-filtered Cu K_α 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 while 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. Diffraction patterns have also been recorded for stretched fibers after annealing for 20 min at temperatures 30 °C below the melting temperature of the as-prepared sample (see Table 1), keeping the fiber under tension.

3. Results and discussion

The X-ray powder diffraction profiles of some compression molded samples, slowly crystallized from the melt, of sPPET copolymers are reported in Fig. 1. The samples are crystalline up to an ethylene concentration of 18–20 mol% and the degree of crystallinity decreases with increasing ethylene content.

As discussed in our previous paper [32], sPPET samples with low ethylene contents (lower than 10 mol%) crystallize from the melt in the antichiral helical form I of sPP, as indicated by the presence of the 200 and 020 reflections of form I at $2\theta \approx 12$ and 16° in the diffraction profiles of Fig. 1(a) and (b). Disordered modifications of form I are obtained in these samples, as shown by the absence in the diffraction profiles of Fig. 1 of the 211 reflection at $2\theta = 18.8°$, typical of the ordered form I [12]. Structural disorder consists in departures from perfect alternation of right- and left-handed two-fold helical chains along *a* and *b* axes of the orthorhombic unit cell [12].

A small amount of the isochiral helical form II of sPP crystallizes from the melt, as indicated by the presence of the 110 reflection at $2\theta = 17°$ of form II, as a shoulder of the 020 reflection at $2\theta = 16°$, in the X-ray diffraction profiles of Fig. 1(b) and (c). The intensity of the 110 reflection of form II increases with increasing ethylene concentration, indicating an increase of the amount of crystals of form II (Fig. 1(d)). sPPET samples with ethylene content in the range 14–18 mol% are mainly crystallized in disordered modifications close to the isochiral helical form II of sPP (Fig. 1(e)), as indicated by the presence of the broad reflection centered at $2\theta = 17°$ in the diffraction profile of Fig. 1(e). The presence of ethylene units,

Table 1
Composition, melting temperature (T_m), intrinsic viscosity ($[\eta]$) and viscosity average molecular mass (M_v) of sPPET copolymer samples prepared with the catalytic system $Ph_2C(Cp)(Flu)ZrCl_2$/MAO

Sample	Feed composition (mol% ethylene)	Copolymer composition (mol% ethylene)	T_m (°C)	$[\eta]$ (dL/g)	$M_v \times 10^{-5}$
sPPET(1)	4.9	2.6	129.0	0.89	1.14
sPPET(2)	7.6	6.3	110.2	1.78	2.37
sPPET(3)	10.3	8.0	103.2	2.26	3.03
sPPET(4)	12.1	8.5	95.0	1.94	2.59
sPPET(5)	12.6	9.1	95.0	2.12	2.84
sPPET(6)	17.3	13.2	85.0	2.02	2.69
sPPET(7)	21.4	14.3	78.2	1.13	1.45
sPPET(8)	24.9	15.9	66.0	1.47	1.94
sPPET(9)	27.1	16.2	65.9	1.47	1.94
sPPET(10)	34.4	17.5	53.9	1.14	1.48

Polymerization temperature = 10 °C; pressure = 1 atm; solvent = toluene (100 mL); molar ratio Al/Zr = 1000; catalyst amount = 2–3 mg; reactor volume = 250 mL; polymerizzation time = 2 h; flow rate = 5 mL/s; yield = 2–5 g.

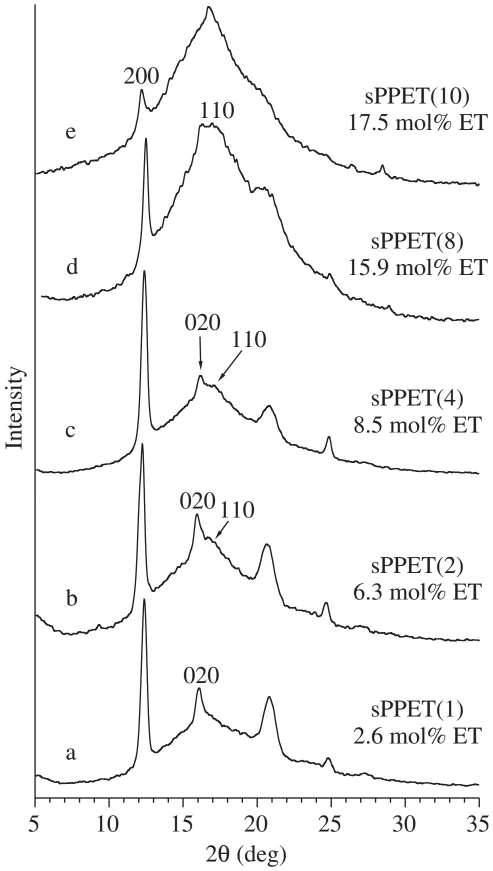

Fig. 1. X-ray powder diffraction profiles of compression molded films of sPPET samples of the indicated concentration of ethylene (ET) comonomeric units. The 020 reflection at $2\theta = 16°$ of the helical form I, and the 110 reflection at $2\theta = 17°$ of the isochiral helical form II are shown.

partially included in the crystalline lattice of sPP [31,32], prevents the crystallization from the melt of the ordered antichiral helical form I of sPP, characterized by order in the alternation of right- and left-handed helical chains along the axes of the unit cell, and induces, at high concentrations, crystallization of the helical form II. In any case, highly disordered crystals of form I and form II are obtained from melt-crystallizations. Both crystals of form I and form II present, indeed, structural disorder characterized by stacking faults and disorder in the statistical substitution of right and left-handed helical chains, as indicated by the broadness of the 020 and 110 reflections at $2\theta = 16$ and 17°, respectively, and the absence of the 211 reflection of form I at $2\theta = 18.8°$ in the diffraction profiles of Fig. 1. Stacking faults are due to shifts of *bc* layers of chains of *b*/4 along *b*, in crystals of form I (*b*/4 shifts disorder, $b = 11.2$ Å) [12,47], and of *b*/2 in crystals of form II ($b = 5.6$ Å for form II). These disorders induce departures from the fully antichiral packing of form I and fully isochiral packing of form II of sPP [32].

The possible structural transitions that may occur during deformation of sPPET copolymer samples have been studied recording the X-ray fiber diffraction patterns of fibers stretched at different deformations, and of the corresponding stress-relaxed fibers, that is, fibers kept in tension for 2 h and then relaxed by removing the tension. In addition, for each oriented specimen, in order to check the thermodynamic stability of the polymorphic form obtained by stretching, X-ray fiber diffraction patterns have been recorded after annealing the fiber (kept under tension) at temperatures 25–30 °C lower than the melting temperatures (see Table 1) of the copolymer sample.

The X-ray fiber diffraction patterns, and the corresponding diffraction profiles read along the equatorial layer lines, of fibers of the sample sPPET(1) obtained by stretching compression molded films at 300 and 500% deformations are shown in Fig. 2(A,A′) and (B,B′), respectively. It is apparent that the antichiral helical form I of sPP, originally present in this sample (Fig. 1(a)), transforms into the *trans*-planar form III already at 300% deformation, as indicated by the presence in the diffraction patterns of Fig. 2(A,A′) of the equatorial $(020)_t$ and $(110)_t$ reflections at $2\theta \approx 16$ and 18°, respectively, and of the $(021)_t$ and $(111)_t$ reflections on the first layer line, typical of the *trans*-planar form III of sPP [9] (subscript 't' standing for *trans*-planar form III). The equatorial reflections of form III of sPP are poorly resolved in Fig. 2(A′), indicating that the crystals have small dimensions. High degree of orientation of crystals of form III parallel to the stretching direction are obtained already for 300% deformation (Fig. 2(A)). Similar diffraction pattern is obtained by further stretching at 500% deformation (Fig. 2(B)), and only an increase of the degree of orientation of crystals of form III is observed.

A small amount of crystals of the helical form is present in the stretched fibers, as indicated by the presence of the 200 equatorial reflection at $2\theta = 12°$, of low intensity, of both helical forms I and II and of reflections on the first layer line corresponding to the helical periodicity, in the diffraction patterns of Fig. 2(A) and (B). It is not possible to establish if the helical form present in the fibers stretched at 300 and 500% deformations is form I or form II because the diagnostic reflections of these forms occur on the equator at $2\theta = 16°$ (020 reflection) and 17° (110 reflection), respectively [1], and are buried by the strong equatorial reflections of the *trans*-planar form III in the 2θ region between 15 and 18° ($(020)_t$ and $(110)_t$ reflections) [9]. Probably, in the stretched fibers of the sample sPPET(1) a small fraction of crystals of form I, originally present in the unoriented film, remains embedded in the polymer matrix without undergoing any structural transition. These crystals result poorly oriented in the patterns of Fig. 2(A) and (B), and do not feel the effect of the mechanical stress field. Previous studies have, indeed, indicated that the parameter mainly responsible for the structural transition from helical forms into the *trans*-planar form III is the value of the applied tensile stress [4,17,48–50]. Only the crystals that experience a stress higher than a critical value in the direction parallel to the stretching direction undergo phase transition [48–50]. In our case, crystals of form I unable to reach a high degree of orientation with chain axes parallel to the stretching direction at 300 and 500% deformations, do not undergo any phase transition.

The X-ray fiber diffraction pattern of the fiber of Fig. 2(B) stretched at 500% deformation after removing the tension is

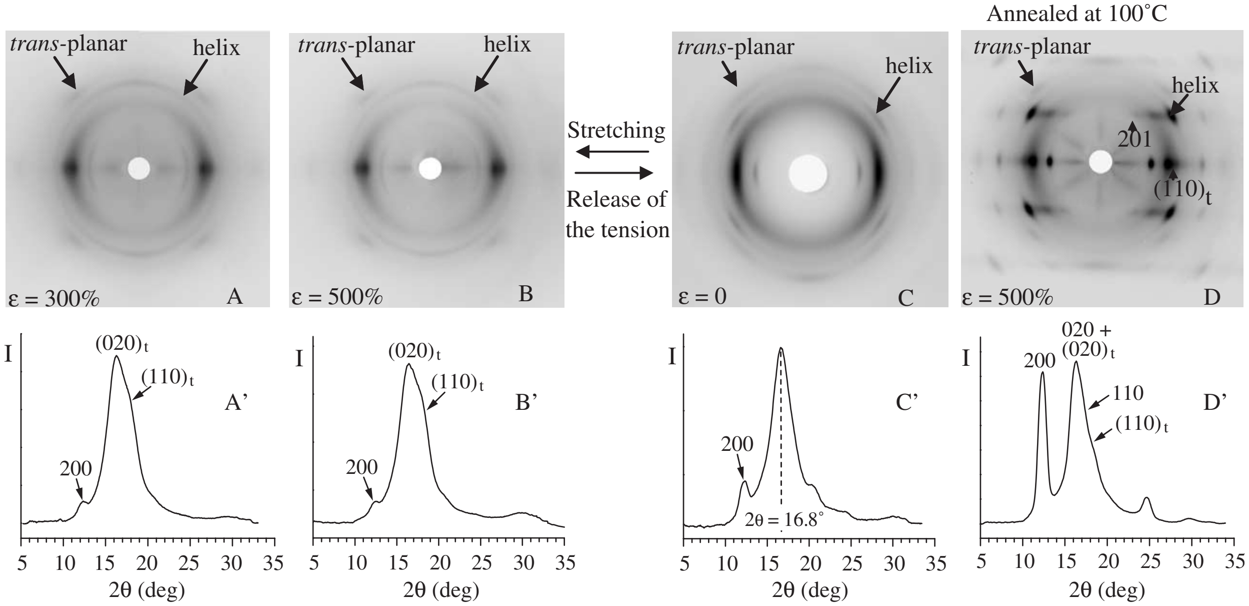

Fig. 2. X-ray fiber diffraction patterns (A–D) and corresponding diffraction profiles read along the equatorial layer lines (A′–D′), of fibers of the sample sPPET(1) with 2.6 mol% of ethylene, obtained by stretching compression molded films at 300% (A, A′) and 500% deformations (B, B′), after releasing the tension from 500% deformation (C, C′) and of fibers stretched at 500% deformation and annealed at 100 °C for 20 min while keeping the fiber in tension (D, D′). The $(020)_t$ and $(110)_t$ reflections of the *trans*-planar form III at $2\theta \approx 16$ and 18°, respectively, the 110 reflection at $2\theta \approx 17°$ of the helical form II, the 020 reflection at $2\theta \approx 16°$ of the helical form I and the 200 reflection at $2\theta \approx 12°$ of both helical forms are indicated. On the first layer line, reflections arising from the diffraction of crystals of the helical forms and the *trans*-planar form III are also indicated as 'helix' and '*trans*-planar', respectively. In C the position of the broad equatorial reflection at $2\theta \approx 17°$ and the reflection on the first layer line (indicated as '*trans*-planar') of the *trans*-planar mesomorphic form are also shown.

shown in Fig. 2(C). It is apparent that the intensities of the 200 reflection at $2\theta = 12°$ and of the reflection on the first layer line at $2\theta = 21°$ of the helical forms slightly increase, whereas those of reflections of the *trans*-planar form III decrease, by releasing the tension (Fig. 2(C,C′)). The equatorial $(020)_t$ and $(110)_t$ reflections of form III in the 2θ range 15–18° transform in a broad peak centered at $2\theta \approx 17°$, corresponding to the 110 reflection of form II. This possibly indicates that crystals of the *trans*-planar form III transform into the isochiral helical form II as the tension is released. This transformation is reversible and crystals of the helical form II transform back into the *trans*-planar form III by stretching again the relaxed fiber of Fig. 2(C) up to the maximum deformation achieved during the early stretching of the unoriented film (Fig. 2(B)).

The presence in the diffraction pattern of Fig. 2(C) of the reflection on the first layer line typical of crystals with chains in *trans*-planar conformation and the fact that in Fig. 2(C′) the intensity ratio between the 200 and 110 reflections at $2\theta \approx 12$ and 17°, respectively, is lower than that expected for the pure helical form II of sPP [1], indicate the presence in the stress-relaxed fiber of a not negligible amount of crystals with chains still in the *trans*-planar conformation. These crystals are probably in the *trans*-planar mesomorphic form of sPP [16,21], rather than in the crystalline form III, as suggested by the weakness of the reflection on the first layer line of the *trans*-planar form and the presence of the strong broad equatorial peak centered at $2\theta \approx 17°$ in the pattern of Fig. 2(C,C′), which can be attributed to the sum of the 110 reflection of form II and the typical equatorial reflection of the mesomorphic form. Therefore, stress-relaxed fibers of the sample sPPET(1) consist of a mixture of crystals of the helical form I, due to the crystals originally present in the unoriented sample that do not undergo any phase transition, of the helical form II and of the *trans*-planar mesomorphic form, which originate from transformation of the metastable *trans*-planar form III after removing the tension, although the presence of small amount of crystals of form III, which remain frozen in this state upon releasing the tension, may not be excluded.

The X-ray fiber diffraction pattern of the fiber of the sample sPPET(1) of Fig. 2(B) stretched at 500% deformation and annealed at 100 °C is shown in Fig. 2(D). It is apparent that the annealing produces a strong increases of the intensities of the equatorial 200 reflection at $2\theta = 12°$ of the helical forms, and of the reflection on the first layer line corresponding to the 121 or 111 reflections of the helical forms [1]. Moreover, a strong equatorial reflection with a maximum at $2\theta \approx 16°$ and a shoulder at $2\theta = 17°$, resulting from the overlapping of the 020 and 110 reflections at $2\theta = 16$ and 17° of the helical form I and form II, respectively, are clearly present in the pattern of Fig. 2(D). The presence of crystals of form II is also indicated by the diffraction maximum at $2\theta = 17°$ on the first layer line, corresponding to the 201 reflection of form II [1]. These data indicate that the stretched fiber originally in the *trans*-planar form III (Fig. 2(B)) transforms by annealing into a mixture of crystals of the helical form I and form II. Moreover, the high degree of orientation achieved in the stretched sample at room temperature is not lost during annealing while keeping the fiber in tension. A small amount of crystals of form III is also present in the annealed fibers, as indicated by the presence of the reflection on the first layer line of the *trans*-planar form in the diffraction pattern of Fig. 2(D) and by the shoulder at $2\theta\approx 18^\circ$ in the equatorial profile of Fig. 2(D′), corresponding to the $(110)_t$ reflection of form III [9].

A similar polymorphic behavior has been observed for the sample sPPET(2) with ethylene content of 6.3 mol%. The mixture of crystals of forms I and II, originally present in the unoriented compression-molded film (Fig. 1(b)), transforms by stretching into the *trans*-planar form III. Crystals of form III partially transform into the helical form II by releasing the tension; portion of them remains frozen in the polymer matrix, or transforms into the *trans*-planar mesomorphic form of sPP. Annealing of the stretched fiber at 90 °C, keeping the fiber in tension, produces a mixtures of crystals of form I and form II, with small amounts of crystals of form III.

Therefore, the polymorphic behavior and the mechanical properties of sPPET copolymer samples with low ethylene content, up to 6–7 mol%, are similar to those of sPP. The irreversible plastic deformation of unoriented samples occurring by stretching is associated with a stress-induced phase transition from the helical form I into the *trans*-planar form III, as for sPP homopolymer [2–4]. In oriented fibers, the *trans*-planar form III obtained by stretching transforms into the helical form II by removing the tension. The latter phase transition is reversible and the fibers show elastic behavior [33,34]. In these samples elasticity has an enthalpic contribution due to the associated polymorphic transition. Annealing at temperatures 20–30 °C below the melting temperature produces mixtures of crystals of the helical forms I and II, as in sPP [1,13,25]. It should be noticed, however, that in the sPPET samples the presence of ethylene units as constitutional defects with content in the range 3–7 mol%, seems to slightly increase the stability of the *trans*-planar form III with respect to the sPP homopolymer, because the transformation of form III into the helical forms upon releasing the tension or annealing is not complete (Fig. 2).

The polymorphic behavior of fibers of sPPET samples with ethylene content in the range 8–10 mol%, (samples sPPET(3), sPPET(4) and sPPET(5) with 8, 8.5 and 9.1 mol% of ethylene, respectively), is different from that of sPP. The X-ray fiber diffraction patterns and the corresponding equatorial profiles of fibers of the sample sPPET(4) with 8.5 mol% of ethylene, obtained by stretching compression molded films at 300, 500 and 800% deformations, are reported in Fig. 3(A)–(C).

Crystals of the helical forms I and II, originally present in the unoriented sample (Fig. 1(c)), gradually transform into *trans*-planar forms. In fact, the intensities of the equatorial 200 reflection at $2\theta=12^\circ$ and of reflections on the first layer line of the helical forms are strongly reduced already at 300% deformation (Fig. 3(A)) and gradually disappear with increasing deformation, and are, finally, absent at 800% deformation (Fig. 3(C)). Correspondingly, the intensities of reflections on the equator and on the first layer line of the *trans*-planar forms gradually increase (Fig. 3(A)–(C)). At 300% deformation, a broad equatorial peak centered at $2\theta\approx 17^\circ$ and a weak reflection on the first layer line corresponding to the *trans*-planar periodicity are apparent in the X-ray diffraction pattern of Fig. 3(A,A′). This indicates that at low deformations the helical form transforms into the *trans*-planar mesomorphic form [16,21]. At higher deformation (500%) crystals of the mesomorphic form gradually transform into the *trans*-planar form III (Fig. 2(B,B′)). At 800% deformation, a well-formed *trans*-planar form III is apparent, as indicated by the presence of $(020)_t$ and $(110)_t$ equatorial reflections at $2\theta\approx 16$ and 18° and $(021)_t$ and $(111)_t$ reflections on the first layer line [9] in the diffraction pattern of Fig. 3(C,C′). Therefore, the helical forms

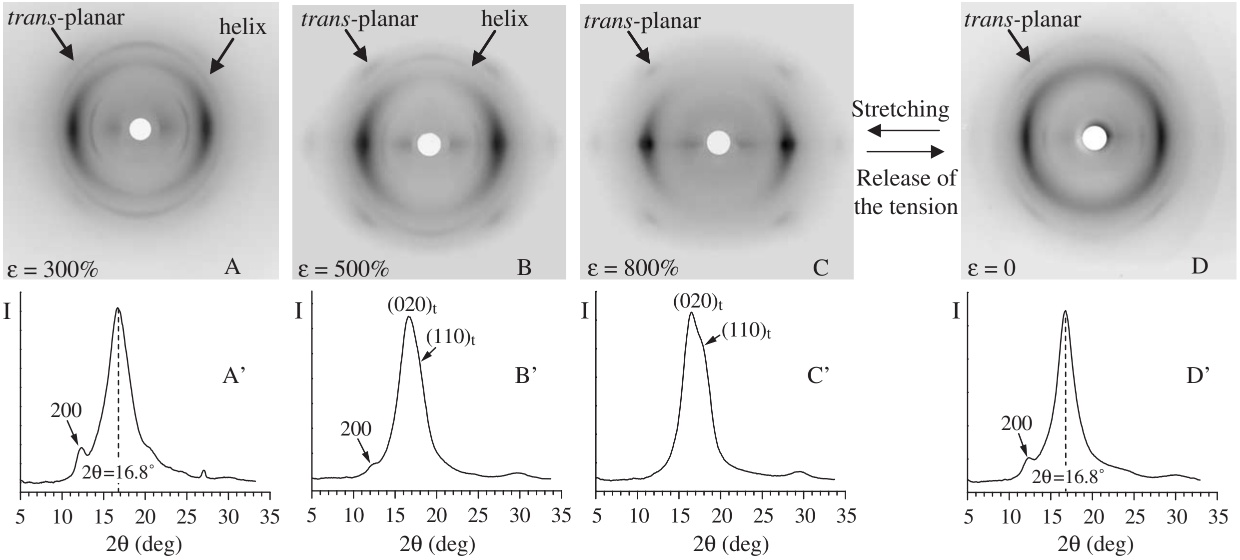

Fig. 3. X-ray fiber diffraction patterns (A–D) and corresponding equatorial diffraction profiles (A′–D′) of fibers of the sample sPPET(4) with 8.5 mol% of ethylene obtained by stretching compression molded films at 300% (A,A′), 500% (B,B′) and 800% deformations (C,C′), and after releasing the tension from 800% deformation (D,D′). The $(020)_t$ and $(110)_t$ reflections of the *trans*-planar form III at $2\theta\approx 16$ and 18°, respectively, and the 200 reflection at $2\theta\approx 12$ of the helical forms are indicated. On the first layer line, reflections arising from the diffraction of crystals of the helical forms and *trans*-planar form III are shown. In A and D the position of the broad equatorial reflection at $2\theta=16.8^\circ$ and the reflection on the first layer line of the *trans*-planar mesomorphic form are also indicated.

present in the melt crystallized sample transform into the intermediate *trans*-planar mesomorphic form at low deformations, and into the crystalline *trans*-planar form III at higher deformations.

The X-ray diffraction pattern of the fiber of the sample sPPET(4) stretched at 800% deformation (Fig. 3(C)) after releasing the tension is reported in Fig. 3(D,D′). It is apparent that crystals of form III obtained by stretching (Fig. 3(C)) transform back into the mesomorphic form, upon releasing the tension; only a small portion of these crystals transforms into the helical form II of sPP, as indicated by the small intensity of the 200 and 111 reflections of form II in the pattern of Fig. 3(D,D′). The structural transition of form III into the mesomorphic form upon releasing the tension is reversible; the *trans*-planar mesomorphic form transforms back into the crystalline *trans*-planar form III by stretching again. These data confirm recent results obtained for sPP homopolymer that have indicated that the structural evolution of the *trans*-planar form III depends on a memory of the crystalline forms formed during the stretching [21,22]. In fact the *trans*-planar form III obtained at high deformation transforms upon releasing the tension into the mesomorphic form that forms during stretching at low deformations (Fig. 3(A) and (B)).

It is worth noting that the *trans*-planar mesomorphic form present in the fiber stretched at 300% deformation (Fig. 3(A)) remains stable upon releasing the tension. Only a negligible portion of mesomorphic crystals transforms reversibly into the helical form by removing the tension from 300% deformation (data not shown). Moreover, fibers of the sample sPPET(4), as well as of samples sPPET(3) and sPPET(5) with ethylene contents in the range 8–10 mol%, show elastic behavior independent of the maximum deformation achieved in the early stretching of unoriented samples [34]. In the case of the fibers prepared by stretching the unoriented samples up to 300% deformation and then removing the tension, the elastic recovery [34] is not associated with polymorphic transitions because the *trans*-planar mesomorphic form present in the stretched fiber (Fig. 3(A)) remains stable by releasing the tension and only a small portion of mesomorphic crystals transforms into the helical form II. In the case of fibers prepared by stretching unoriented samples up to 500 or 800% deformation, instead, a polymorphic transition occurs during elastic recovery. The crystalline *trans*-planar form III present in the stretched state (Fig. 3(B) and (C)) transforms into the *trans*-planar mesomorphic form by releasing the tension (Fig. 3(D,D′)). Also in this case a perfect elastic recovery is observed [34].

The annealing of fibers of the samples sPPET(3)-sPPET(5) with ethylene content in the range 8–10 mol%, produces different results depending on the crystalline forms originally present in the stretched fibers. The X-ray fiber diffraction patterns of fibers of the sample sPPET(4) stretched at 300, 500 and 800% deformations (Fig. 3(A)–(C), respectively), after annealing at 70 °C for 20 min are shown in Fig. 4. Annealing of fibers stretched at 300% deformation, which were in the *trans*-planar mesomorphic form with a small amount of the helical form (Fig. 3(A)), produces an increase of the degree of crystallinity and a transformation of the mesomorphic form

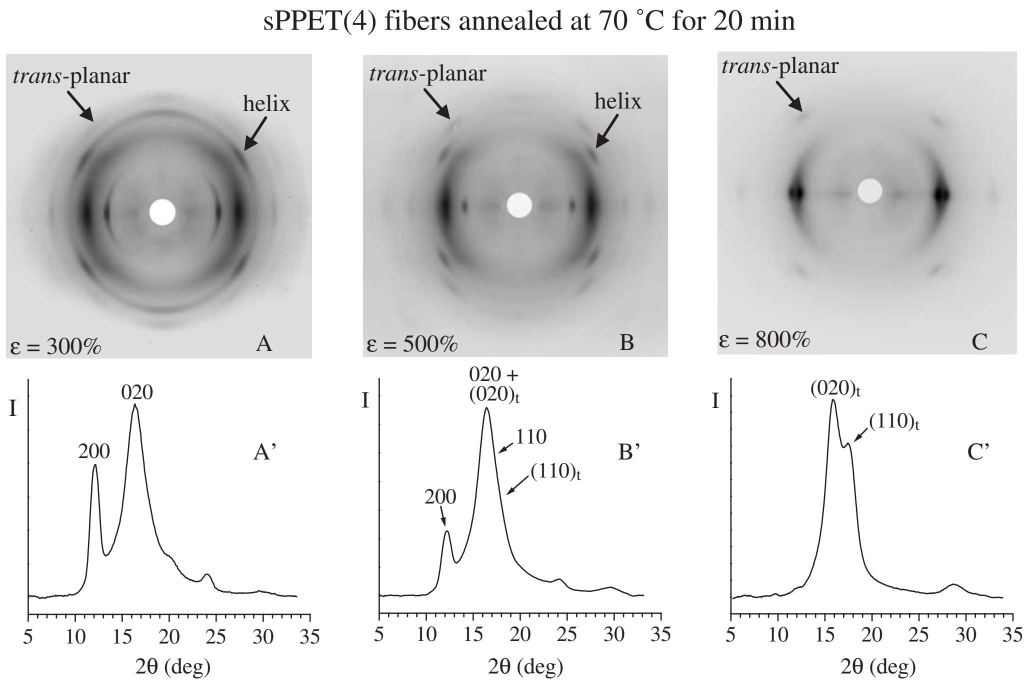

Fig. 4. X-ray fiber diffraction patterns (A–C) and corresponding equatorial diffraction profiles (A′–C′) of fibers of the sample sPPET(4) with 8.5 mol% of ethylene obtained by stretching compression molded films at 300% (A,A′), 500% (B,B′) and 800% (C,C′) deformations and then annealed at 70 °C for 20 min. The 110 reflection at $2\theta \approx 17°$ of the isochiral helical form II, the 020 reflection at $2\theta \approx 16°$ of the antichiral helical form I, the 200 reflection at $2\theta \approx 12°$ of both helical forms, and reflections on the first layer line arising from the diffraction of crystals of helical forms are indicated in A and B. The $(020)_t$ and $(110)_t$ equatorial reflections at $2\theta \approx 16$ and 18°, respectively, and the $(021)_t$ and $(111)_t$ on the first layer line of the *trans*-planar form III are also indicated in B and C.

into the helical form I (Fig. 4(A)). This is indicated by the strong increase of the intensities of the 200 reflection at $2\theta = 12°$ and of the 121 reflection at $2\theta = 21°$ on the first layer line and the presence of the 020 reflection at $2\theta = 16°$ of the antichiral helical form I in the X-ray fiber diffraction pattern of Fig. 4(A). Crystallization of portions of chains of the amorphous phase into the helical form I may also occur. However, a not negligible amount of crystals of the *trans*-planar mesomorphic form of sPP is still present, as indicated by the presence of the very weak reflection on the first layer line typical of the mesomorphic form in the pattern of Fig. 4(A) and by the intensity ratio between the 200 and 020 equatorial reflections at $2\theta \approx 12$ and 16°, respectively, which is lower than that expected for the helical form I (Fig. 4(A′)).

As shown in Fig. 3(B), fibers of the sample sPPET(4) stretched at 500% deformation are basically in the *trans*-planar form III, although a small amount of crystals of the helical form are still present. The annealing at 70 °C of these fibers induces, as before, a neat increase of crystallinity, while form III transforms in part in a mixture of crystals of the helical form I and form II (Fig. 4(B)). A not negligible amount of crystals of form III does not transform upon annealing and remains in the annealed fibers. This is indicated by the presence of the equatorial 200 and 020 reflections of the antichiral helical form I at $2\theta = 12$ and 16°, respectively, the 110 reflection at $2\theta = 17°$ of isochiral helical form II, and of reflections on the first layer line corresponding to both helical and *trans*-planar periodicities in the diffraction pattern of Fig. 4(B,B′). The higher intensity of the equatorial diffraction peak at $2\theta \approx 16°$ with respect to that of the 200 reflection at $2\theta \approx 12°$ in the experimental profile of Fig. 4(B′) is clearly due to the contribution of the $(020)_t$ reflection at $2\theta \approx 16°$ of the *trans*-planar form III, whereas the shoulder at $2\theta = 18°$ is due to the $(110)_t$ reflection of form III (Fig. 4(B′)). It is also apparent that the amount of the helical forms obtained by annealing decreases with increasing degree of deformation achieved in the preparation of the fibers, as indicated by the lower intensity of the 200 reflection at $2\theta = 12°$ in the diffraction pattern of Fig. 4(B′) than that in the pattern of Fig. 4(A′).

Finally, annealing at 70 °C of the fiber of the sample sPPET(4) stretched at 800% deformation, originally in the pure *trans*-planar form III (Fig. 3(C)), induces only improvement of crystals of the *trans*-planar form III and no polymorphic transformation is observed (Fig. 4(C,C′)). This indicates that when the fibers are stretched at very high deformation, the *trans*-planar form III obtained by stretching does not transform into helical forms by annealing. The amount of helical form in the annealed fibers decreases with increasing deformation and disappear at very high strain.

These results clearly indicate that the *trans*-planar form III in sPPET copolymer samples is more stable than in sPP homopolymer. It is worth noting that the result of Fig. 4(C) represents the first example of stabilization of the *trans*-planar form III by annealing at high temperatures. The presence of ethylene comonomeric units with concentration in the range 8–10 mol% induces formation of long sequences in *trans*-planar conformation, which in turn stabilizes the crystals of form III. In the case of sPP homopolymer prepared with metallocene catalysts the *trans*-planar form III always transforms by annealing into the more stable helical forms [1,13,25].

It is worth noting that a partial stabilization of the *trans*-planar form III has been observed also in sPP homopolymer samples prepared with octahedral non-metallocene catalysts based on titanium chlorides bearing phenoxyimine ligands [51]. It has been, indeed, found that in these samples when the fibers are stretched at values of deformation higher than 300%,

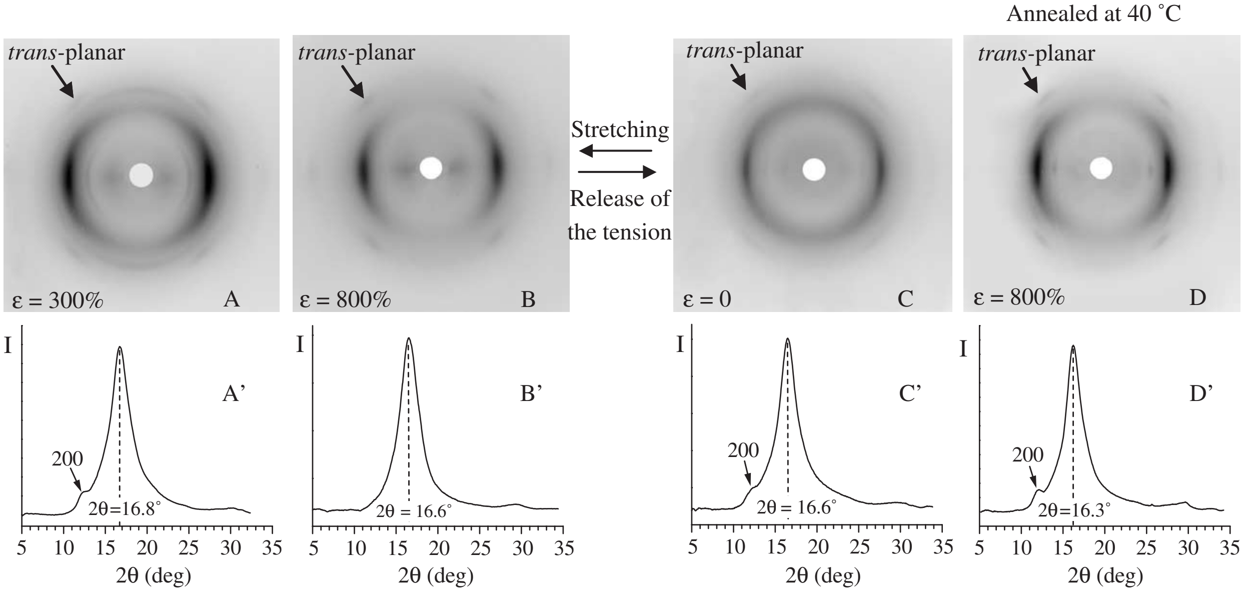

Fig. 5. X-ray fiber diffraction patterns (A–D) and corresponding equatorial diffraction profiles (A′–D′) of fibers of the sample sPPET(8) with 15.9 mol% of ethylene prepared by stretching compression molded films at 300% (A,A′) and 800% (B,B′) deformations, after releasing the tension from 800% deformation (C,C′) and of fibers stretched at 800% deformation and annealed at 40 °C for 20 min keeping the fiber in tension (D,D′). The equatorial reflection at $2\theta = 16$–17° and the reflection on the first layer line of the *trans*-planar mesomorphic form and the 200 reflection at $2\theta = 12°$ of the helical form are indicated.

the *trans*-planar form III obtained by stretching does not transform completely into the helical forms by annealing. The amount of form III that transforms into the helical form by annealing decreases with increasing deformation [51]. A remarkable amount of crystals of the *trans*-planar form III does not transform and remains stable even at high annealing temperatures in fibers stretched at high deformation [51]. These results have indicated that in these sPP samples the *trans*-planar form III obtained in stretched fibers is more stable than in the case of the metallocene-made sPP. This has been explained considering that the sPP samples prepared with the octahedral non-metallocene catalysts are characterized by a slightly different microstructure of the polymer chains, more similar to that of chains of propylene–ethylene copolymers, because of the presence of a non-negligible amount of defects of regioregularity (1,2 primary insertions of propylene units in a prevailing 2,1 enchainment), which produces formation of vicinal methylene carbon atoms $–CH_2–CH_2–$ along the polymer chains [51]. The presence of ethylene sequences favors, locally, the formation of *trans*-planar sequences, which, in turn, may stabilize the *trans*-planar form III in stretched fibers [51], as in the case of sPPET copolymers.

The polymorphic behavior of fibers of sPPET samples with ethylene content in the range 10–18 mol% (samples sPPET(6)-sPPET(10)) is shown in Fig. 5, in the case of the sample sPPET(8) with 15.9 mol% of ethylene, as an example. These samples are poorly crystalline in the unstretched state and result mainly crystallized in the isochiral helical form II of sPP (Fig. 1(d) and (e)). The helical form II transforms into the *trans*-planar mesomorphic form by stretching at 300% deformation as indicated by the presence of a weak reflection on the first layer line and of a broad equatorial reflection centered at $2\theta \approx 17°$, typical of *trans*-planar mesomorphic form of sPP [16,21], in the X-ray fiber diffraction pattern of Fig. 5(A). The small intensity of the 200 equatorial reflection at $2\theta = 12°$ in the diffraction pattern of Fig. 5(A) indicates that only a small amount of crystals of the helical forms is present in the fiber stretched at low deformations. At higher values of deformation (800%) a fiber in the pure mesomorphic form is obtained (Fig. 5(B,B′)). Therefore, the mesomorphic form already formed at low deformations (Fig. 5(A)) does not transform into the crystalline form III at higher deformations (Fig. 5(B)), as instead occurs for sPPET samples with lower ethylene content (Fig. 3).

The X-ray fiber diffraction patterns of fibers of the sample sPPET(8) stretched at 800% deformation after releasing the tension and after annealing at 40 °C are shown in Fig. 5(C) and (D), respectively. It is apparent that the mesomorphic form obtained in the stretched samples (Fig. 5(A) and (B)) remains stable upon releasing the tension (Fig. 5(C)) as well as after annealing (Fig. 5(D)). The fraction of crystals which transforms into the helical forms upon releasing the tension and annealing is very small, as indicated by the small increase of the intensity of the 200 reflection at $2\theta = 12°$ in the diffraction patterns of Fig. 5(C) and (D).

Analysis of the mechanical properties has shown that sPPET samples with ethylene content in the range 10–18 mol% (samples PPET(6)–PPET(10)) show good elastic behavior in the unstretched state, as well as in oriented fibers [33,34]. During stretching and preparation of oriented fibers, the helical forms present in the unoriented film transform into the *trans*-planar mesomorphic form (Fig. 5(A) and (B)). In oriented fibers, the *trans*-planar mesomorphic form does not transform into helical forms during recovery upon releasing the tension (Fig. 5(C)). Therefore, elasticity in sPPET samples with ethylene content in the range 10–18 mol% is not associated with any polymorphic transformation and has a pure entropic origin as in conventional thermoplastic elastomers [33,34].

These data indicate that the presence of ethylene comonomeric units induces a stabilization of polymorphic forms of sPP with chains in *trans*-planar conformation, the crystalline form III and the disordered mesomorphic form at low and high ethylene concentrations, respectively. All samples present novel thermoplastic elastomeric properties regardless of ethylene concentration.

4. Conclusions

Syndiotactic propylene–ethylene copolymers, with ethylene concentration variable in the range 2–20 mol%, have been produced with a single-center C_S-symmetric syndiospecific metallocene catalyst. The samples are crystalline up to 18–20 mol% of ethylene. The effect of the presence of ethylene comonomeric units on the polymorphic behavior of sPP in oriented fibers and on the structural transformations occurring during plastic deformation and elastic recovery of sPP has been analyzed.

For sPPET copolymer samples with ethylene content in the range 2–7 mol%, crystals of the helical form I of sPP present in the compression molded films, transform into the *trans*-planar form III, by stretching. The form III, in turn, transforms in part into the helical form II of sPP by releasing the tension, as occurs for sPP. This phase transition between form III and form II is reversible.

sPPET samples with ethylene content in the range 8–10 mol% crystallize from the melt as a mixture of crystals of form I and form II of sPP. The helical forms transform by stretching at low values of deformation (lower than 300%) into the *trans*-planar mesomorphic form. The mesomorphic form transforms into the *trans*-planar form III by further stretching at deformations higher than 500%. For these samples form III transforms back into the *trans*-planar mesomorphic form, rather than into the helical forms, by releasing the tension.

Unoriented samples of sPPET copolymers with ethylene content in the range 13–18 mol% are mainly crystallized in helical form II of sPP, which transforms into the *trans*-planar mesomorphic form by stretching at low, as well as, high deformations. The mesomorphic form remains stable upon releasing the tension and no polymorphic transition occurs during elastic recovery.

Therefore, the presence of ethylene comonomeric units, partially included in the crystals of sPP, increases the relative stability of the polymorphic forms of sPP with chains in *trans*-planar conformation, that is, the form III in fibers of sPPET samples with ethylene contents in the range 2–10 mol%, and of the mesomorphic form for ethylene concentrations in the range 10–18 mol%. This is due to the easier formation of *trans*-planar sequences in sPP chains in the presence of ethylene units.

These results indicate that the elastic behavior of most crystalline sPPET copolymers with low ethylene contents (lower than 6–7 mol%) is associated with a reversible polymorphic transition between the *trans*-planar form III and the helical form II occurring during stretching and relaxation cycles, which provides an enthalpic contribution to the elasticity [33]. Lower crystalline sPPET samples with higher ethylene concentrations (higher than 10 mol%) show similar elastic properties, which are not associated with any polymorphic transitions and elasticity has a pure entropic origin as in conventional thermoplastic elastomers [33].

The enhanced stability of the *trans*-planar form III and mesomorphic form of sPP in sPPET copolymer samples has been confirmed by annealing of stretched fibers. In fact, while in the case of sPP homopolymer annealing induces transformation of the *trans*-planar form III, originally present in the stretched samples, into the more stable helical forms I and II [25], in sPPET copolymer samples with ethylene content in the range 2–8 mol% the *trans*-planar form III transforms only partially into the helical forms by annealing. Moreover, in the case of sPPET samples with higher ethylene content, in the range 8–10 mol%, the *trans*-planar form III does not transform by annealing fibers stretched at high deformations and improvement of crystallinity of the form III is obtained. Finally, the mesomorphic form of sPP obtained in stretched fibers of samples with ethylene content in the range 13–18 mol% remain stable even upon annealing.

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