

# Polymorphism and Structural Disorder in Melt-Crystallized and Fiber Samples of Syndiotactic Copolymers of Propene with 1-Butene

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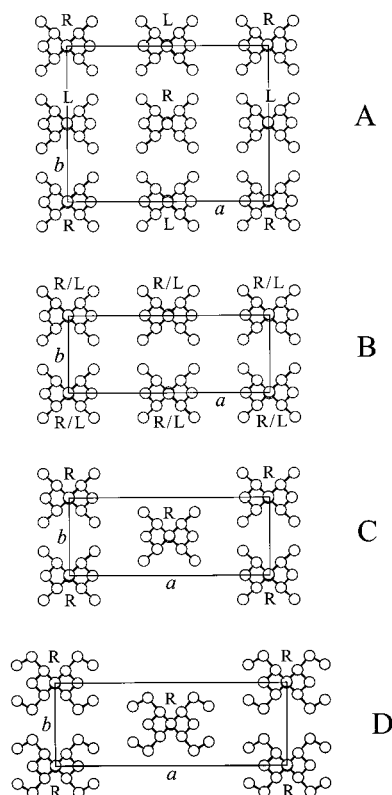
**ABSTRACT:** The structural characterization of melt-crystallized samples and oriented fibers of syndiotactic copolymers between propene and 1-butene is reported. Melt-crystallized samples of copolymers are crystallized in the form I of syndiotactic polypropylene (s-PP) up to a content of 1-butene of 60–70 mol %, although disorder in the alternation of right- and left-handed helical chains along both axes of the unit cell is present. More ordered modifications, close to the limit ordered, fully antichiral, form I of s-PP are obtained by crystallization at high temperatures only for samples containing small contents of 1-butene (1–2 mol %). The presence of 1-butene prevents that the order in the alternation of right- and left-handed helical chains develops at high crystallization temperatures. Samples with contents of 1-butene higher than 70 mol % crystallize in structures similar to that of form I of syndiotactic poly(1-butene). Fiber samples of copolymers with small content of 1-butene (1–2 mol %) present the same behavior of syndiotactic polypropylene. Stretched fibers are in the trans planar form III of s-PP, which transforms into the isochiral helical form II of s-PP upon the release of the tension. Mixtures of crystals in forms I and II of s-PP are obtained by annealing. With increasing the 1-butene content only the antichiral helical form I of s-PP is observed in the stretched fibers of the copolymers, as well as upon the release of the tension. The presence of 1-butene units, for contents higher than 4 mol %, prevents the formation of the trans planar form III of s-PP by stretching. For these samples the formation of form I of s-PP, instead of the isochiral form II, either in the stretched fibers or upon the release of the tension, is a further evidence that the isochiral helical form II of s-PP can be obtained only from fibers initially in the trans planar form III, through a cooperative conformational transformation which induce the formation of helical chains having the same chirality.

## Introduction

The structural characterization of syndiotactic copolymers of propene with 1-butene (PPBU) has been recently reported.<sup>1–5</sup> The copolymers are crystalline in a whole range of comonomer composition. An increase of *a* and *b* axes of the unit cell from the values of syndiotactic polypropylene (s-PP) to those of syndiotactic poly(1-butene) (s-PB), with increasing the content of 1-butene, has been observed.<sup>2,3</sup> This indicates that the comonomeric units, propene or 1-butene, are included in the unit cells of both homopolymers. The cocrystallization of the two comonomers has also been confirmed by the solid state <sup>13</sup>C NMR spectra of the copolymers, which indeed present resonances of the methylene carbons belonging to propene–butene sequences in the crystalline phase.<sup>5</sup>

The copolymers crystallize in modifications having structures intermediate between those of s-PP and s-PB.<sup>3</sup> This is due to the very similar crystal structures of s-PP and s-PB. Indeed, the most stable forms of both homopolymers are characterized by chains in *s*(2/1)2 helical conformation, packed in orthorhombic unit cells.<sup>6–15</sup>

Two different orthorhombic crystalline forms of s-PP (forms I and II), with chains in *s*(2/1)2 helical conformation, have been described.<sup>6–12</sup> The most stable form I is characterized, in the limit ordered modification, by a regular alternation of right- and left-handed helical chains along both axes of the unit cell (Figure 1A).<sup>7</sup>



**Figure 1.** Models of packing of the limit ordered form I of s-PP (A), the limit disordered form I of s-PP (B), form II of s-PP (C), and form I of s-PB (D). R = right-handed helix; L = left-handed helix.

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Depending on the conditions of crystallization, different amounts of disorder may be present in the structure of form I.<sup>8,11</sup> In samples crystallized from the melt at low temperatures<sup>11</sup> or in single crystals grown at low temperatures<sup>8</sup> disorder in the perfect alternation of right- and left-handed helices along both axes of the unit cell develops. As-prepared samples or samples quenched from the melt are characterized by a statistical disorder in the distribution of right- and left-handed chains; the limit disordered structural model can be described by the statistical space group *Bmcm* (Figure 1B).<sup>9,11</sup>

The metastable form II of s-PP can be obtained in oriented fibers of s-PP<sup>6,9,12</sup> and is characterized, in the limit ordered modification, by an isochiral packing of the helical chains according to the space group *C222<sub>1</sub>*<sup>6,9</sup> (Figure 1C). In particular the pure form II has been obtained in stretched fibers of samples having low stereoregularity.<sup>6,12</sup> By stretching of more stereoregular samples obtained with metallocene catalysts, fibers in the trans planar form III are obtained.<sup>9,12,16</sup> However, also for high stereoregular samples, the pure form II can be obtained upon the release of the tension in fibers initially in the trans planar form III.<sup>12</sup> In this conditions a recovery of the initial length of the fiber and a transition from the trans planar form III into the helical form II occurs.<sup>12,17</sup> This reversible conformational transition is responsible of the elastic behavior of s-PP.<sup>12,17</sup>

Two different crystalline modifications, form I and form II, have been found for s-PB.<sup>13</sup> The structure of the most stable form I<sup>14</sup> is very similar to that of form II of s-PP;<sup>6,9</sup> it is indeed characterized by chains in *s*(2/1)2 helical conformation<sup>13–15</sup> packed according to the space group *C222<sub>1</sub>*<sup>14</sup> (Figure 1D). The metastable form II of s-PB is characterized by chains in *s*(5/3)2 helical conformation<sup>13</sup> packed in a monoclinic unit cell according to the space group *P2<sub>1</sub>/a*.<sup>18</sup>

In ref 3 we have shown that as-prepared samples of syndiotactic poly(propene-*co*-1-butene) (PPBU) having small contents of 1-butene are crystallized in a structure similar to that of the antichiral form I of s-PP, and as occurs for the s-PP homopolymer,<sup>11</sup> disordered modifications of form I, characterized by statistical disorder in the alternation of right- and left-handed helices along both axes of the unit cell (Figure 1B), are obtained. At higher 1-butene content disorder in the stacking of *bc* layers of chains piled along *a*, characterized by shifts along *b* of *b*/4 among consecutive *bc* layers (*b*/4 shifts disorder) develops. With increasing 1-butene content (50–60 mol %), the amount of *b*/4 shifts disorder increases, and disordered modifications, having structures intermediate between those of form I of s-PP (Figure 1A,B) and form I of s-PB (Figure 1D), are obtained.<sup>3</sup> Samples with a content of 1-butene higher than 70 mol % crystallize in a structure similar to that of the isochiral form I of s-PB (Figure 1D), as well as of form II of s-PP (Figure 1C).<sup>3,5</sup>

In this paper, the polymorphic behavior of PPBU copolymers in the melt-crystallized samples and in oriented fibers are analyzed. The differences between the structures of the as-prepared samples, reported in the previous papers,<sup>3,5</sup> and the melt-crystallized and fibers samples are outlined. The effect of the presence of the butene units on the polymorphic behavior of the s-PP homopolymer in the melt-crystallized samples and oriented fibers is analyzed.

**Table 1. Composition and Melting Temperatures ( $T_m$ ) of the PPBU Copolymer Samples**

sample	mol % of 1-butene	$T_m$ (°C)
PPBU(1)	1.3	131
PPBU(2)	2.3	130
PPBU(3)	2.6	130
PPBU(4)	4.2	123
PPBU(5)	5.8	112
PPBU(6)	9.9	101
PPBU(7)	16.2	97
PPBU(8)	39.6	72
PPBU(9)	47.9	64
PPBU(10)	65.3	56
PPBU(11)	77.0	51
PPBU(12)	90.9	51
PPBU(13)	98.6	46

## Experimental Part

Samples of PPBU copolymers were synthesized with a single center syndiospecific catalyst composed of isopropylidene-(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminumoxane with the method described in ref 3. All the samples correspond to the samples reported in ref 3.

The composition and the melting temperatures of the copolymers are reported in the Table 1. The composition was determined by the analysis of the <sup>13</sup>C NMR solution spectra, recorded on a Bruker AM300 spectrometer at 120 °C in deuterated tetrachloroethane.<sup>3</sup> 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<sub>2</sub> atmosphere at heating rate of 10 °C/min.

Samples of PPBU copolymers were isothermally crystallized from the melt at various temperatures. The as-prepared samples were melted at temperatures in the range 100–200 °C, depending on the composition and kept, for 5 min at this temperature in a N<sub>2</sub> atmosphere; they were then rapidly cooled to the crystallization temperature  $T_c$  and kept at this temperature, still in a N<sub>2</sub> atmosphere, for a time  $t_c$  long enough to allow complete crystallization at  $T_c$ . The samples were then cooled to room temperature and analyzed by wide-angle X-ray diffraction.

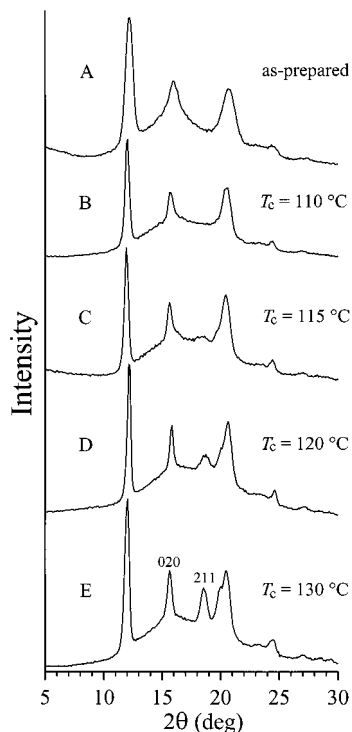
Oriented fiber samples of s-PP were obtained by stretching at room-temperature compression molded samples.

X-ray powder diffraction patterns were obtained with an automatic Philips diffractometer using Ni-filtered Cu K $\alpha$  radiation. X-ray fiber diffraction patterns were obtained with Ni-filtered Cu K $\alpha$  radiation on a BAS-MS imaging plate (FUJIFILM) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800).

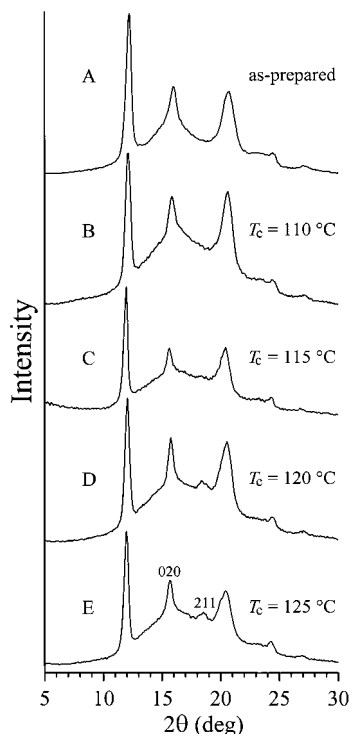
For PPBU samples crystallized in the antichiral form I of s-PP, an evaluation of the degree of order present in the structure was obtained from the X-ray diffraction patterns of the melt-crystallized samples, following the method used for the s-PP homopolymer and described in ref 11. Precisely, the ratio between the intensities of the 211 and 020 reflections, at  $2\theta \approx 18^\circ$  and  $15\text{--}16^\circ$ , respectively,  $R = I(211)/I(020)$  was used as a measure of the degree of order in the alternation of right- and left-handed helical chains. The intensities of the 211 and 020 reflections were measured from the area of the corresponding diffraction peaks arising above the diffuse halo in the X-ray powder diffraction profiles.<sup>11</sup>

## Results and Discussion

**Melt-Crystallized Samples.** The X-ray powder diffraction patterns of the as-prepared PPBU samples and of the corresponding samples obtained by isothermal crystallizations from the melt at various temperatures  $T_c$  are reported in Figures 2–5. For each sample, the position of the reflections in the X-ray diffraction patterns of the melt-crystallized samples (parts B–E of Figures 2–5) are the same as in the as-prepared

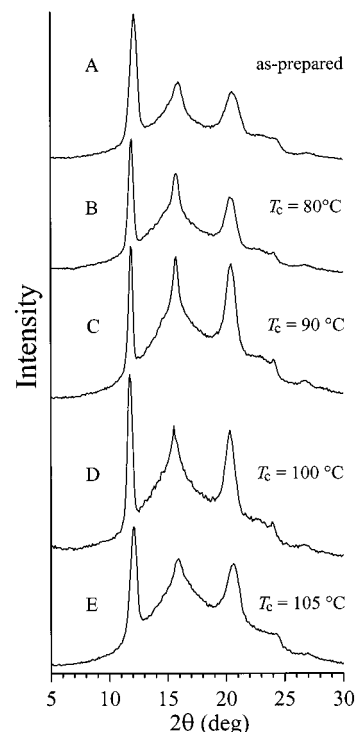


**Figure 2.** X-ray powder diffraction patterns of samples of the PPBU(2) copolymer with 2.3 mol % of 1-butene, isothermally crystallized from the melt at the indicated crystallization temperatures  $T_c$ . The indices  $hkl$  of the reflections are given for the unit cell of form I of s-PP of Figure 1A.

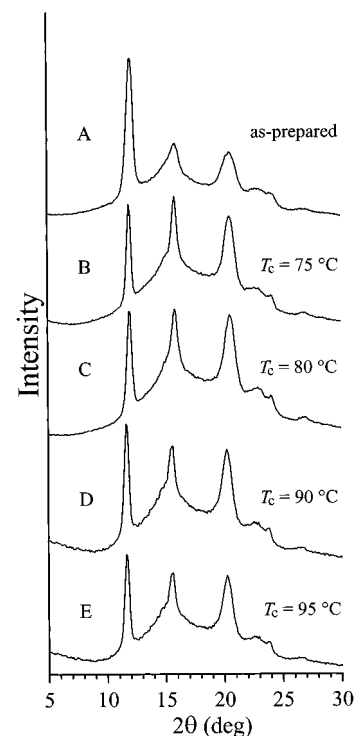


**Figure 3.** X-ray powder diffraction patterns of samples of the PPBU(4) copolymer with 4.2 mol % of 1-butene, isothermally crystallized from the melt at the indicated crystallization temperatures  $T_c$ . The indices  $hkl$  of the reflections are given for the unit cell of form I of s-PP of Figure 1A.

samples (Figures 2A–5A). This indicates that the parameters of the unit cells determined for the as-prepared samples in the ref 3, are nearly the same in the melt-crystallized samples. The values of the  $a$  and  $b$  axes of the melt-crystallized PPBU samples are

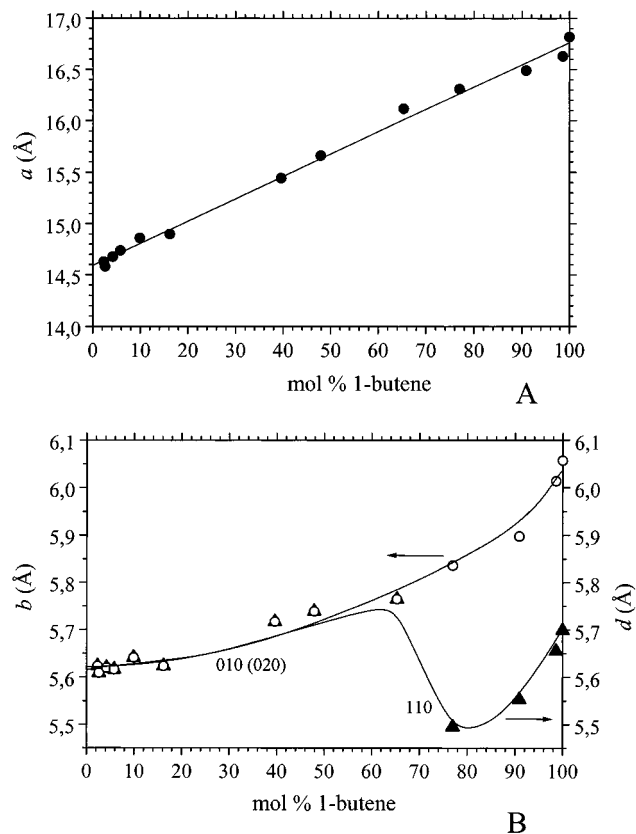


**Figure 4.** X-ray powder diffraction patterns of samples of the PPBU(6) copolymer with 9.9 mol % of 1-butene, isothermally crystallized from the melt at the indicated crystallization temperatures  $T_c$ .



**Figure 5.** X-ray powder diffraction patterns of samples of the PPBU(7) copolymer with 16.2 mol % of 1-butene, isothermally crystallized from the melt at the indicated crystallization temperatures  $T_c$ .

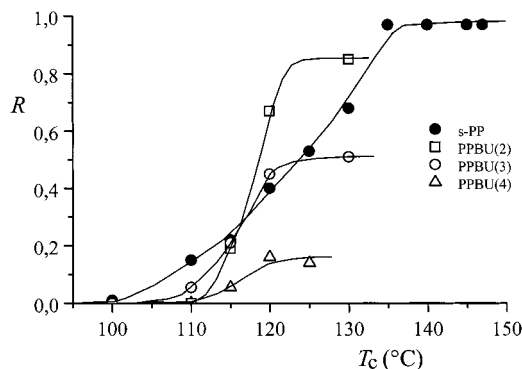
reported in Figure 6 as a function of the copolymer composition. Also for the melt-crystallized samples the  $a$  and  $b$  axes increase with increasing the content of 1-butene from the values typical of s-PP up to the values typical of s-PB. Therefore, both comonomeric units are still included in the unit cells of the two homopolymers



**Figure 6.** Values of the *a* (A) and *b* (B) axes of the unit cell of melt-crystallized samples of PPBU copolymers as a function of the 1-butene content. In part B, the values of the Bragg spacing *d* of the reflection at  $2\theta = 15\text{--}16^\circ$  ( $\blacktriangle$ ) are also reported as a function of the 1-butene content.

even when the samples are slowly crystallized from the melt at high temperatures.

The structures of the PPBU copolymers described in refs 3 and 5 for the as-prepared samples at different compositions are stable and remain unchanged in the melt crystallization, and no segregation of the comonomeric units in the amorphous phase has been observed. In particular, it is apparent from Figure 6B that also for the melt-crystallized samples, the Bragg spacing of the reflection at  $2\theta = 15\text{--}16^\circ$  increases with increasing the 1-butene content up to a concentration of 60–70 mol % and decreases for a further increase of the 1-butene content. This indicates that, as it occurs for the as-prepared samples,<sup>3</sup> PPBU samples having contents of 1-butene up to 60–70 mol % are crystallized from the melt at any temperature in a structure similar to that of the *B*-centered form I of s-PP (Figure 1A,B)<sup>21</sup> and the diffraction peak at  $2\theta = 15\text{--}16^\circ$  is indexed as 020 or 010 reflection, for the unit cell of Figure 1, part A or B, respectively. Melt-crystallized samples with a content of 1-butene higher than 70 mol % crystallize in a isochiral *C*-centered structure similar to that of form I of s-PB (Figure 1D), as well as of form II of s-PP (Figure 1C). In these samples the diffraction peak at  $2\theta = 15\text{--}16^\circ$  is indexed as 110 reflection (Figure 6B). Disorder in the stacking of *bc* layers of chains piled along *a*, implying *b*/4 shifts among consecutive *bc* layers (*b*/4 shift disorder),<sup>3</sup> is present also in the melt-crystallized samples. It increases with increasing 1-butene content, and for compositions of 50–60 mol % of 1-butene, disordered modifications having structures intermediate between those of the *B*-centered form I of s-PP (Figure



**Figure 7.** Values of the order parameter *R* of the PPBU copolymers crystallized from the melt reported as a function of the crystallization temperature *T<sub>c</sub>*, and compared with the values of the s-PP homopolymers taken from ref 11. Key: ( $\bullet$ ) s-PP; ( $\square$ ) PPBU(2), 2.3 mol % of 1-butene; ( $\circ$ ) PPBU(3), 2.6 mol % of 1-butene; ( $\triangle$ ) PPBU(4), 4.2 mol % of 1-butene.

1A,B) and the *C*-centered form I of s-PB (Figure 1D) are obtained.

For the PPBU samples having small content of 1-butene (1–4 mol %), an ordering process develops in the samples crystallized from the melt at high temperatures (Figures 2 and 3). It is apparent from Figures 2 and 3 that the as-prepared samples, or the samples crystallized from the melt at low temperatures, disordered modifications of the *B*-centered form I of s-PP, characterized by a statistical disorder in the positioning of right- and left-handed helical chains (Figure 1B, space group *Bmcm*), are formed, as demonstrated by the absence of the 211 reflection at  $2\theta = 18\text{--}19^\circ$  in the X-ray powder diffraction patterns of Figures 2A,B and 3A–C.<sup>11</sup> We recall that for the s-PP homopolymer the 211 reflection at  $2\theta = 18.8^\circ$  is typical of the packing characterized by the regular alternation of 2-fold helices of opposite chirality along the *a* and *b* axes (Figure 1A).<sup>7</sup> This reflection is present in the X-ray diffraction patterns of the melt-crystallized PPBU samples and its intensity increases with increasing the crystallization temperature *T<sub>c</sub>* (Figures 2C–E and 3D–E). The profiles of Figures 2 and 3 indicate that with increasing the crystallization temperature, more ordered crystals of form I of s-PP are obtained. However, only for PPBU samples having a very low content of 1-butene (1–2 mol %), modifications close to the limit ordered, fully antichiral form I of s-PP (Figure 1A) are formed at high crystallization temperature (Figure 2E).

It is worth noting that studies of isothermally melt-crystallized samples of syndiotactic propene/1-butene copolymers have been already reported by Naga et al.<sup>19</sup> However, in this paper, ordered modifications of form I of s-PP have never been obtained, even for samples with low 1-butene content crystallized at high temperatures.<sup>19</sup> In all the X-ray diffraction patterns of Figure 7b of ref 19, the 211 reflection is absent or has very low intensity. From our data of Figure 2, it is apparent that we have obtained more ordered modifications of form I of s-PP by melt-crystallization of the PPBU samples, as indicated by the higher intensity of the 211 reflection in the X-ray diffraction pattern of Figure 2E. Moreover, the authors in ref 19 have interpreted the absence of the 211 reflection in the X-ray diffraction patterns of the copolymer samples, assuming a model for the crystal structure characterized by an alternation of right- and left-handed helical chains only along the *a* axis and a succession of isochiral chains along the *b* axis (space

group  $Pca2_1$  or  $Pcaa$ ).<sup>7</sup> It is instead well established that the absence of the 211 reflection is an indication of a structure characterized by a statistical disorder in the distribution of right- and left-handed helices along the axes of the unit cell, described by the statistical space group  $Bmcm$  (Figure 1B).<sup>9,11</sup>

For PPBU samples with higher 1-butene content the intensity of the 211 reflection is low or absent even at high crystallization temperatures (Figures 3–5). Already for a composition of 4.2 mol % of 1-butene, the intensity of the 211 reflection is very low (lower than that expected for the ordered structure of form I of s-PP<sup>11</sup> of Figure 1A) and does not increase with increasing the crystallization temperature (Figure 3). For concentration of 1-butene higher than 4.2 mol % the 211 reflection is always absent in the X-ray diffraction patterns of the melt-crystallized samples whatever the crystallization temperature (Figures 4 and 5). For these samples the ordering process in the alternation of right- and left-handed helices along the axes of the unit cell, typical of the s-PP homopolymer,<sup>8,11</sup> does not occur and  $B$ -centered disordered modifications, characterized by statistical disorder in the positioning of right- and left-handed helical chains (Figure 1B), are obtained at any crystallization temperature.

The intensity of the 211 reflection at  $2\theta = 18-19^\circ$  can be used as a measure of the degree of order present in the crystals of the  $B$ -centered form I. Precisely, since the intensity of the 020 reflection is constant with  $T_c$ , we use the ratio between the intensity of the 211 and 020 reflections, at  $2\theta = 18-19$  and  $15-16^\circ$ , respectively,  $R = I(211)/I(020)$ , to eliminate any dependence on the crystallinity and the thickness of the samples.<sup>11</sup>

The values of  $R$  of the PPBU melt-crystallized samples are reported in Figure 7 as a function of  $T_c$  and compared with the values of  $R$  of the s-PP homopolymer taken from the ref 11. It is apparent that while for the homopolymer  $R$  increases with  $T_c$  from  $R = 0$ , corresponding to the limit disordered structure of Figure 1B, to a constant value  $R \approx 1$ , corresponding to the limit ordered structure of Figure 1A,<sup>11</sup> for the PPBU copolymers the limit values of  $R$  are lower than 1 and decrease with increasing butene content.

These data clearly indicate that the presence of 1-butene does not affect the usual crystallization of s-PP in the most stable  $B$ -centered form I, but prevents the formation of the ordered antichiral packing (Figure 1A) even at high crystallization temperatures. This behavior can be easily explained considering that a disorder in the stacking of  $bc$  layers of chains piled along  $a$  ( $b/4$  shifts disorder) is present in the copolymer samples, as demonstrated by the broadening of the 020 reflection at  $2\theta = 15-16^\circ$  in the X-ray diffraction patterns of the as-prepared samples (Figures 2A–5A).<sup>3</sup> This kind of disorder, observed also in the s-PP homopolymer samples crystallized at low temperature,<sup>8,11</sup> destroys any correlation at long distances between the chirality of the helices along the  $a$  and  $b$  axes of the unit cell. Antichiral packing of first neighboring chains may still be preserved locally and lost in the long range because of the occurrence of the  $b/4$  shifts disorder.

For PPBU samples with high 1-butene content, the amount of  $b/4$  shifts disorder increases and disordered modifications having structures intermediate between those of the  $B$ -centered form I of s-PP (Figure 1B) and the isochiral  $C$ -centered form I of s-PB (Figure 1D), or  $C$ -centered form II of s-PP (Figure 1C), are obtained,

although the packing mode of the  $B$ -centered form I of s-PP (Figure 1B) is still prevalent up to a composition of 70 mol % of 1-butene.<sup>3</sup> Crystallization from the melt of these samples does not induce any ordering process; a slight narrowing of the 020 reflection is only observed for samples crystallized at high temperature (Figure 5), indicating an increase of the size of the domains characterized by the  $B$ -centered structure (Figure 1B), but without any correlation among the chirality of the neighboring helices.

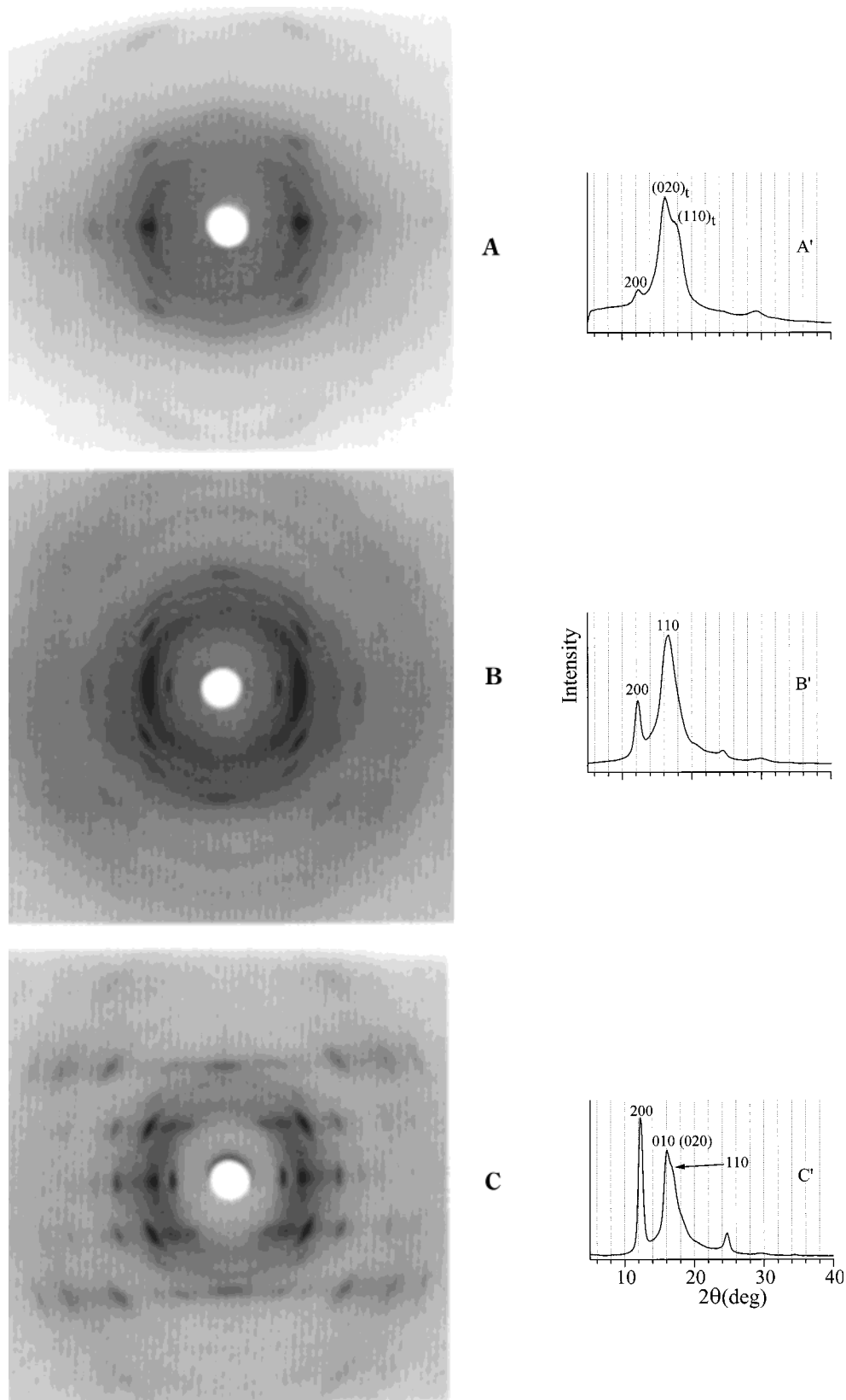
As-prepared PPBU samples with a content of 1-butene higher than 70 mol % crystallize in a structure similar to that of the isochiral  $C$ -centered form I of s-PB (Figure 1D), as well as of the  $C$ -centered form II of s-PP (Figure 1C).<sup>3,5</sup> As reported in ref 3, these samples behave like s-PB; they are amorphous just after the polymerization but crystallize if kept at room temperature for several days. The melt-crystallized samples show a similar behavior; the samples do not crystallize from the melt by cooling to room temperature but slowly crystallize at room temperature after few weeks. Structures similar to the  $C$ -centered form I of s-PB (Figure 1D) are obtained.

**Oriented Samples.** Oriented fibers of PPBU copolymers were obtained by stretching, at room-temperature, compression-molded samples.

In the X-ray fiber diffraction patterns of all the copolymer samples showing the structure of the 2-fold helical forms of s-PP and s-PB (Figure 1), the Bragg spacings of the first strong equatorial 200 reflections are nearly the same as the values observed in the melt-crystallized and as-prepared samples.<sup>3</sup> This indicates that also in the fiber samples the comonomeric units are included in the crystals of both homopolymers.

The X-ray fiber diffraction patterns of the oriented PPBU samples having low contents of 1-butene comonomeric units are very similar. In Figure 8A the X-ray fiber diffraction pattern of the PPBU(2) sample containing 2.3 mol % of 1-butene, is shown, as an example. The X-ray diffraction profile read along the equatorial line of the pattern of Figure 8A is also reported in Figure 8A'. Typical 020 and 110 equatorial reflections of the trans planar form III of s-PP at  $2\theta \approx 16$  and  $18^\circ$  (Cuko, Figure 8A') and spots on the layer lines corresponding to a chain periodicity of 5.1 Å are present in the pattern of Figure 8A. This indicates that, as occurs for s-PP homopolymer samples having a high degree of stereoregularity,<sup>9,12,16</sup> the trans planar form III of s-PP is obtained by stretching, even though small amounts of the helical form are also present as indicated by the presence of the 200 equatorial reflection at  $2\theta = 12^\circ$  (Figure 8A').

The X-ray fiber diffraction pattern of the PPBU(2) sample of Figure 8A after the release of the tension is reported in Figure 8B, while the X-ray diffraction profile read along the equator is reported in Figure 8B'. As occurs for the s-PP homopolymers,<sup>12</sup> a transition from the trans planar form III into the helical form of s-PP occurs upon the release of the tension, as indicated by the presence of reflections on the layer lines corresponding to a chain periodicity of 7.5 Å (Figure 8B). In addition, the presence of the equatorial 110 reflection at  $2\theta = 16.7^\circ$  (Figure 8B') indicates that the helical  $C$ -centered form II of s-PP (Figure 1C) has been obtained.<sup>6,9,12</sup> This conformational transition is reversible; that is, the trans planar and helical forms transform



**Figure 8.** X-ray fiber diffraction patterns of the PPBU(2) sample with 2.3 mol % of 1-butene (A–C) and corresponding X-ray diffraction profiles read along the equatorial line (A'–C'). Key: (A and A') stretched sample; (B and B') fiber A after the release of the tension; (C and C') fiber A annealed at 90 °C for 20 min. In part A', the Miller indices  $(020)_t$  and  $(110)_t$  indicate reflections of the trans planar form III of s-PP, while the indices 200 indicate the reflection of the helical forms of s-PP. In parts B' and C', the 200 reflection corresponds to both the helical forms I (Figure 1A,B) and II (Figure 1C) of s-PP, while the indices 020 and 010 are given for the unit cells of form I of s-PP of Figure 1, parts A and B, respectively, and the indices 110 for the unit cell of form II of s-PP of Figure 1C.

each other by successive stretching and releasing of the tension.

The X-ray fiber diffraction pattern of the oriented PPBU(2) sample in the trans planar form III of Figure

8A after annealing at 90 °C for 20 min (holding the fiber sample under tension) and the corresponding equatorial profile are reported in Figure 8, parts C and C', respectively. It is apparent the presence, in the pattern of Figure 8C, of both 020 and 110 reflections at  $2\theta = 16$  and 17°, respectively (Figure 8C'), typical of the *B*-centered form I (Figure 1A,B) and the *C*-centered form II (Figure 1C) of s-PP, respectively. For the PPBU(2) copolymer, fibers with a mixture of crystals of form I and form II of s-PP are obtained by annealing fibers in the trans planar form III.<sup>9,12</sup> The same result is obtained by annealing the fiber samples in the *C*-centered form II of Figure 8B. This behavior is similar to that of the s-PP homopolymer.<sup>12</sup>

PPBU copolymer samples with small contents of 1-butene (PPBU(1–3)) present the same behavior as the PPBU(2) sample. With increasing the content of 1-butene a different behavior has been observed. The X-ray fiber diffraction pattern of the PPBU(4) sample with 4.2 mol % of 1-butene and the corresponding X-ray diffraction equatorial profile are reported in Figure 9, parts A and A', respectively. It is apparent that both layer lines corresponding to the periodicities of 5.1 Å (trans planar) and 7.5 Å (helical) are present in the pattern of Figure 9A, indicating that a mixture of the trans planar form III and the helical form of s-PP has been obtained. The higher content of 1-butene favors the formation of the helical form by stretching.

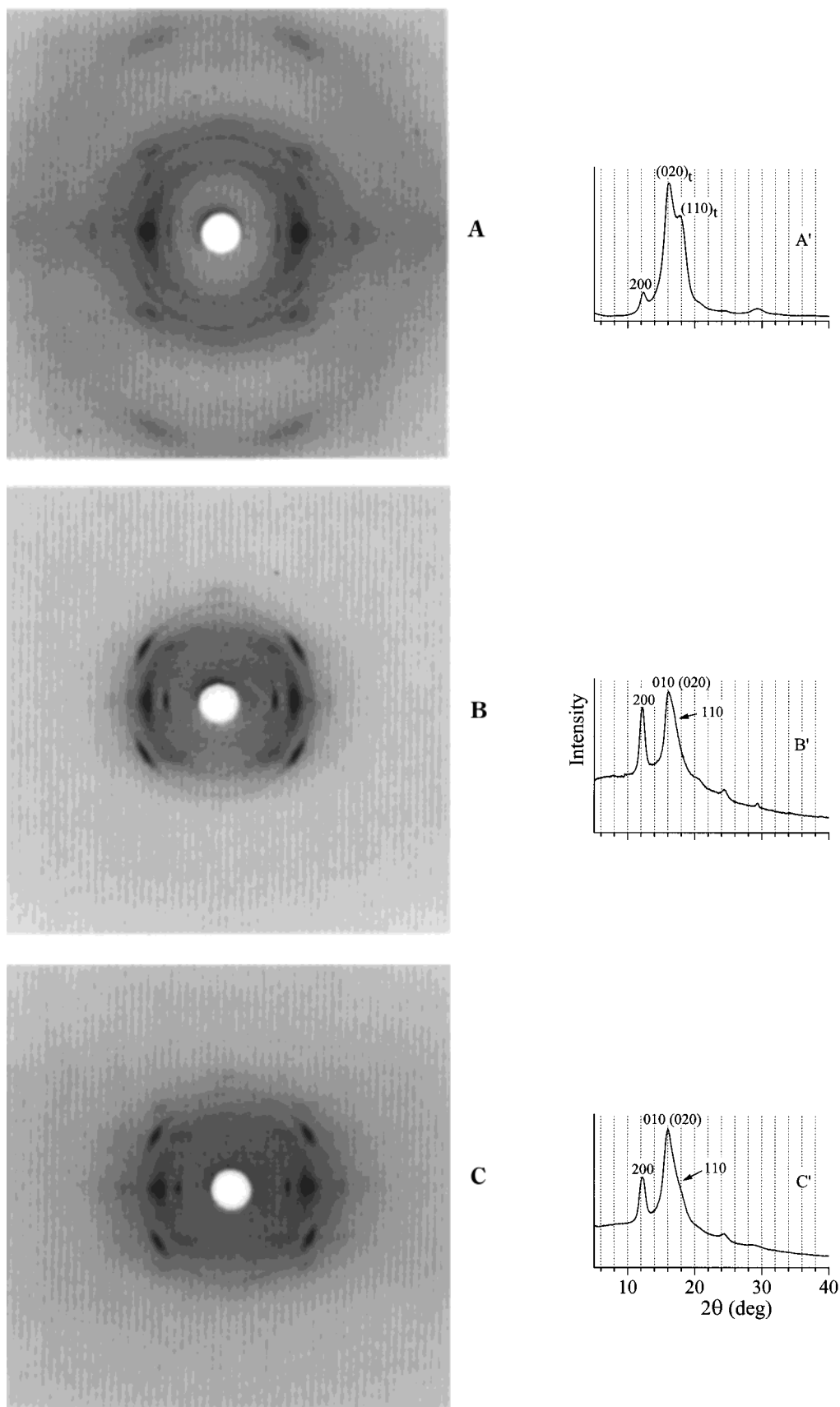
The X-ray fiber diffraction pattern of the PPBU(4) sample of Figure 9A after the release of the tension and the corresponding equatorial profile are reported in Figure 9, parts B and B', respectively. It is apparent that the reflections of the trans planar form present in the pattern of Figure 9A disappear after the release of the tension in Figure 9B and the helical form of s-PP is obtained. This is also indicated by the increase of the intensity of the 200 reflection at  $2\theta = 12^\circ$ , typical of the helical form of s-PP (Figure 9B'). The broad equatorial reflection peak centered at  $2\theta \approx 16^\circ$  (020 reflection) in Figure 9B', indicates that the fiber sample is basically in the helical *B*-centered form I of s-PP (Figure 1A,B). A shoulder at higher values of  $2\theta$ , due to the contribution of the 110 reflection, is also apparent in Figure 9B' and indicates the possible presence of a small amount of crystals of the *C*-centered form II of s-PP (Figure 1C) and/or the presence of a certain amount of *b/4* shift disorder (as discussed for the powder samples). Crystals of the helical *B*-centered form I of s-PP are probably already present in the stretched fiber (Figure 9A), whereas crystals in the isochiral *C*-centered form II of s-PP could be obtained from the crystals in the trans planar form III, which transforms into the helical *C*-centered form II upon release of the tension. By annealing the fiber samples of Figure 9A (trans planar plus *B*-centered form I) or Figure 9B (*B*-centered form I plus *C*-centered form II) at 80 °C for 20 min, a fiber basically in the stable *B*-centered form I of s-PP is obtained (Figure 9C). It is apparent that in the X-ray diffraction profile along the equatorial line of the pattern of Figure 9C, reported in Figure 9C', the 020 reflection centered at  $2\theta = 16^\circ$  presents the same shoulder at higher  $2\theta$  values as in Figure 9B', indicating that the annealed fiber is basically in the *B*-centered form I but still with a small amount of crystals in the *C*-centered form II of s-PP and/or with the presence of *b/4* shift disorder.

The X-ray fiber diffraction pattern of the oriented PPBU(7) sample with 16.2 mol % of 1-butene and the corresponding equatorial profile are reported in Figure 10, parts A and A', respectively. It is apparent that the helical form is obtained by stretching, as demonstrated by the absence of reflections of the trans planar form III of s-PP on the equator and on the first layer line and the presence of the 200 reflection at  $2\theta = 12^\circ$ , typical of the helical forms of s-PP and of reflections on the layer lines corresponding to a periodicity of 7.5 Å. The presence of the butene comonomeric units in this sample prevents the formation of the trans planar form III of s-PP by stretching. The second strong equatorial peak in the pattern of Figure 10 at  $2\theta = 15.9^\circ$  may be indexed as 010 (or 020) reflection indicating that the helical *B*-centered form I of s-PP (Figure 1A,B) has been obtained by stretching. It is apparent from Figure 10A' that this 020 reflection is sharp, sharper than the peak in Figure 9, parts B' and C', indicating that only the *B*-centered form I of s-PP is present in the stretched fiber of the sample PPBU(7).

Since the fiber of the PPBU(7) sample is in the helical form, no conformational transition is observed upon the release of the tension. The X-ray fiber diffraction pattern of the PPBU(7) sample of Figure 10A after the release of the tension (not shown) is very similar to that of Figure 10A. This means that after the release of the tension, the fiber remains in the helical *B*-centered form I of s-PP. The X-ray fiber diffraction pattern of the oriented PPBU(7) sample in the *B*-centered form I of Figure 10A does not change after annealing at 60–70 °C; no structural changes are observed upon annealing. It is worth nothing that, contrary to the behavior of the s-PP homopolymer or PPBU samples with low 1-butene contents, the isochiral helical *C*-centered form II of s-PP (Figure 1C) is never observed in this sample, neither in the stretched fibers, nor upon the release of the tension, nor in the annealed fibers.

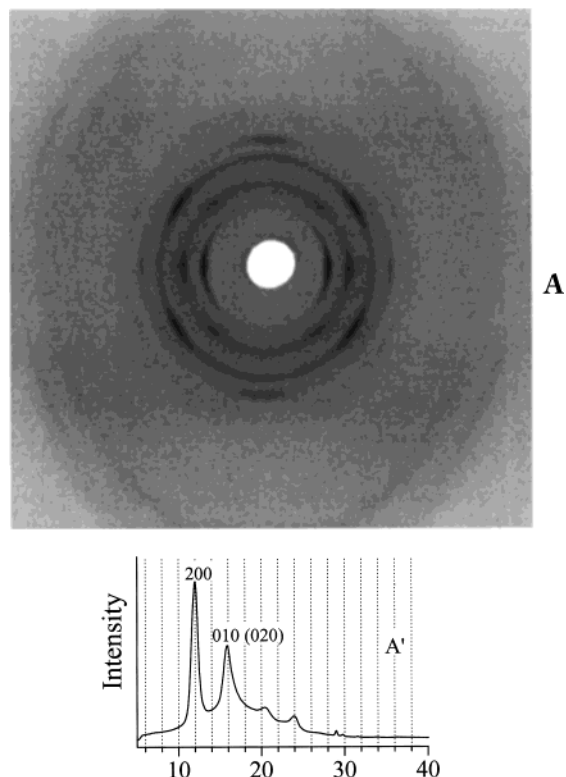
PPBU copolymers having butene contents in the range 5.8–65.3 mol % (samples PPBU(5)–PPBU(10)) present the same behavior as the PPBU(7) sample shown in Figure 10. Stretched fibers, as well as relaxed and annealed fibers, are in the stable helical *B*-centered form I of s-PP, whereas trans planar form III and isochiral helical *C*-centered form II of s-PP are never obtained. The presence of 1-butene comonomeric units for composition higher than 4 mol %, prevents not only the formation in the fiber samples of the trans planar form III of s-PP but even that of the isochiral helical *C*-centered form II of s-PP.

This experimental observation is relevant because indicates that the formation of the isochiral helical *C*-centered form II of s-PP (Figure 1C) is strictly related to that of the trans planar form III of s-PP. As discussed in the Introduction, in the case of the s-PP homopolymer, the pure *C*-centered form II can be obtained in stretched fibers initially in the trans planar form III upon the release of the tension.<sup>12,17</sup> In the PPBU copolymers, only when the trans planar form III forms by stretching (for low butene contents, Figure 8A), can the isochiral helical *C*-centered form II of s-PP be obtained by releasing the tension (Figure 8B). At higher butene content, the trans planar form III cannot be obtained, and as a consequence, the isochiral *C*-centered form II of s-PP does not form any more. The metastable isochiral *C*-centered form II of s-PP can be obtained only starting from the trans planar form III by a spontaneous



**Figure 9.** X-ray fiber diffraction patterns of the PPBU(4) sample with 4.2 mol % of 1-butene (A–C) and corresponding X-ray diffraction profiles read along the equatorial line (A'–C'). Key: (A and A') stretched sample; (B and B') fiber A after the release of the tension; (C and C') fiber A annealed at 80 °C for 20 min. In part A', the Miller indices (020)<sub>t</sub> and (110)<sub>t</sub> indicate reflections of the trans planar form III of s-PP, while the indices 200 indicate the reflection of the helical forms of s-PP. In parts B' and C', the 200 reflection corresponds to both the helical forms I (Figure 1A,B) and II (Figure 1C) of s-PP, while the indices 020 and 010 are given for the unit cells of form I of s-PP of Figure 1, parts A and B, respectively, and the indices 110 for the unit cell of form II of s-PP of Figure 1C.





**Figure 10.** X-ray fiber diffraction patterns of the PPBU(7) stretched sample with 16.2 mol % of 1-butene (A) and corresponding X-ray diffraction profiles read along the equatorial line (A'). The indices of the 020 and 010 reflections are given for the unit cells of form I of s-PP of Figure 1, parts A and B, respectively. The X-ray fiber diffraction patterns of the PPBU(7) fiber sample after the release of the tension or annealing treatments are similar to that in A.

transformation when the tension in stretched fibers is removed.<sup>12</sup> As discussed in a recent paper,<sup>20</sup> this crystal-to-crystal transformation, involving a conformational transition from trans planar to helical conformations, is a cooperative process imposed by steric constraints. The cooperativity induces the formation of helical chains having the same chirality, which pack forming the metastable isochiral *C*-centered form II of s-PP (Figure 1C), even though the antichiral helical form of s-PP (form I, Figure 1A) is more stable. The results on the PPBU copolymers confirm that the metastable *C*-centered form II of s-PP can be obtained only through this cooperative conformational transition. When the trans planar form III is absent, the most stable antichiral form I of s-PP forms in the fiber samples under any conditions.

As discussed above, as-prepared and melt-crystallized PPBU samples with a content of 1-butene higher than 70 mol % (PPBU(11–13)) crystallize in a structure similar to that of the isochiral *C*-centered form I of s-PB (Figure 1D) and behave like the s-PB homopolymer. Indeed they do not crystallize from the melt, and oriented crystalline fibers of these samples can be obtained, as in the case of s-PB,<sup>13,14</sup> by stretching amorphous samples and keeping the fiber samples under tension at room temperature to allow crystallization. These fiber samples result crystallized in a structure similar to that of the *C*-centered form I of s-PB (Figure 1D).<sup>14</sup> No change of the X-ray fiber diffraction pattern is observed by releasing the tension or annealing treatments of the fiber samples.

## Conclusions

The presence of 1-butene comonomeric units affects the polymorphic behavior of s-PP in the melt-crystallized and fiber samples of PPBU copolymers.

Melt-crystallized samples of PPBU samples are crystallized in the *B*-centered form I of s-PP up to a content of 1-butene of 60–70 mol %. Disorder in the alternation of right- and left-handed helical chains along both axes of the unit cell and disorder in the stacking of *bc* layers of chains piled along *a* (*b*/4 shift disorder), are present. More ordered modifications, close to the limit ordered, fully antichiral, form I of s-PP are obtained only for samples containing small contents of 1-butene (1–2 mol %) by crystallization from the melt at high temperatures. The presence of 1-butene prevents that the order in the alternation of right- and left-handed helical chains develops at high crystallization temperatures, as instead occurs for the s-PP homopolymer. With increasing the content of 1-butene the *b*/4 shifts disorder increases and any correlation among the chirality of the chains along the axes of the unit cell is lost at long distances. Structures intermediate between those of the *B*-centered form I of s-PP and the *C*-centered form I of s-PB are obtained in the composition range 40–70 mol % of 1-butene, although the packing mode of the *B*-centered form I of s-PP (Figure 1B) is still prevalent. Samples with contents of 1-butene higher than 70 mol % do not crystallize from the melt but slowly crystallize at room temperature in structures similar to that of the *C*-centered form I of s-PB.

Fiber samples of copolymers with small content of 1-butene (1–2 mol %) present the same behavior of s-PP. Stretched fibers are in the trans planar form III of s-PP, which transforms into the helical isochiral *C*-centered form II of s-PP upon the release of the tension. Mixtures of crystals in forms I and II of s-PP are obtained by annealing. With increasing 1-butene content, only the antichiral helical form I of s-PP is observed in the stretched fibers of the copolymers, as well as upon the release of the tension. The presence of 1-butene units, for content higher than 4 mol %, prevents the formation of the trans planar form III of s-PP by stretching and stabilizes the helical form. This result has given new insights into the understanding of the formation of the isochiral helical form II of s-PP. When the formation of the trans planar form III in the PPBU copolymers is prevented, the isochiral helical *C*-centered form II of s-PP does not form any more in the fiber samples. This is a further evidence that the isochiral helical form II of s-PP can be obtained only from fibers initially in the trans planar form III. The transformation of the trans planar form into the helical form is a cooperative process, imposed by steric constraints, which induces the formation of helical chains having the same chirality. When the trans planar form is absent, the most stable antichiral helical form I of s-PP forms in the fiber samples in any conditions.

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- (21) For sake of simplicity, here and in the following we define the form I of s-PP (Figure 1A,B) as *B*-centered form I, where the centering of the *B* face is referred to the positioning of the chain axes, regardless of the chirality of the chains. As a matter of fact, the ordered fully antichiral form I (Figure 1A) is basically a *I*-centered structure, while the limit statistically disordered form I (Figure 1B) is really *B*-centered. The isochiral form II of s-PP (Figure 1C) and form I of s-PB (Figure 1D) are *C*-centered structures.

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