Stress-Induced Phase Transitions in Syndiotactic Propene−Butene Copolymers

Claudio De Rosa,* Finizia Auriemma, Marco Corradi, Ludovica Caliano, and Giovanni Talarico

Dipartimento di Chimica “Paolo Corradini”, Università di Napoli Federico II, Complesso Monte S.Angelo, Via Cintia, I-80126 Napoli, Italy

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ABSTRACT: A study of the structural transformations occurring during tensile deformation of syndiotactic propylene−butene copolymers (sPPBu) is reported. Melt-crystallized samples of sPPBu copolymers with butene content lower than nearly 70 mol% crystallize in disordered modifications of the helical form I of syndiotactic polypropylene (sPP). The polymorphic transformation of the helical form I into the *trans*-planar form III, typical of sPP, occurs by stretching sPPBu copolymers with butene content lower than 20 mol%. This transformation is inhibited by the presence of higher butene concentrations. The *trans*-planar form III transforms back into the *C*-centered helical form II of sPP by releasing the tension in sPPBu samples with butene contents lower than 4 mol%, and into the helical form I for butene concentrations higher than 4 mol%. For sPPBu copolymers with butene content higher than 20 mol% and lower than 69 mol% only well oriented crystals of the helical form I are obtained by stretching, and no structural transitions occur by releasing the tension. Unoriented samples of copolymers with butene concentration higher than 69 mol% are crystallized in the *C*-centered helical form I of syndiotactic polybutene (sPB), which transforms by stretching at high deformation into the new form I′ of sPB, characterized by the packing of chains in helical conformation similar to the *B*-centered form I of sPP. This new form is metastable and transforms back into the more stable *C*-centered form I of sPB by releasing the tension.

Introduction

It is extensively reported that the occurrence of stress-induced polymorphic transformations during plastic deformation of crystalline polymers may greatly affect the mechanical properties.[1−8] In many polymeric materials the morphological changes occurring during deformation, involving slip processes, mechanical melting and recrystallization in new oriented crystallites, may be accompanied by structural transformations, which involve the destruction of the original lamellae of a crystalline form, followed by recrystallization with formation of fibrils of a new crystalline form, or stress-induced crystal−crystal transformations. Moreover, in some cases, stretching may cause the disruption of lamellar crystals through the pulling out of chains from the crystals, leading to the formation of a mesophase.

In particular, in the case of isotactic polypropylene (iPP)[6] and its copolymers with other olefins[7] it has been shown that crystals of α or γ forms present in the melt-crystallized samples transform by stretching at high deformations into the mesomorphic form of iPP.[6,7]

Furthermore when the crystalline form that develops by stretching is metastable, it may transform back into the more stable form previously present in the unoriented sample, or into another polymorphic form, by removing the tensile stress. In some highly crystalline polymers the polymorphic transition occurring upon releasing the tension is reversible and is associated with a nontrivial recovery of the initial dimensions of the sample.[6−8] The enthalpic gain of the reversible crystal−crystal phase transition occurring upon releasing the tension may play a key role in the elasticity of these materials.

Another interesting example of material with mechanical properties that depend on the structural transformations occurring during deformation is provided by syndiotactic polypropylene (sPP).[8,9] Contrary to iPP, in the case of sPP the structural transformation involves a change of the conformation of the chains.[8] The stable form with chains in 2-fold helical conformation present in the melt-crystallized samples transforms by stretching into form III or into the mesomorphic form, depending on the stereoregularity,[9] both characterized by chains in *trans*-planar conformation. The *trans*-planar form III is metastable and transforms into the more stable helical form II by releasing the tension.[9] Highly crystalline sPP shows unusual elastic properties that are associated with these polymorphic transformations.[8,9]

The polymorphic transformations and the mechanical properties of sPP are strongly affected by the presence of microstructural defects.[8,9] For low stereoregular samples, prepared with suitable metallorganic catalysts,[8,9a] the high concentration of stereodefects prevents the formation of the crystalline *trans*-planar form III by stretching, and only the disordered mesomorphic form is obtained at high deformation.[9a] The mesomorphic form transforms back into the helical form I by releasing the tension, and the samples still show elastic behavior.[8,9a]

The presence of constitutional defects, as comonomeric units, also affects the polymorphic behavior of sPP. The crystallization behavior of syndiotactic propylene−butene copolymers (sPPBu) has been recently studied.[10,11] These copolymers crystallize in the whole range of comonomer composition in disordered modifications[11] intermediate between the *B*-centered form I of sPP,[8,12−17] and the *C*-centered form I of syndiotactic poly(1-butene) (sPB)[18a] (or the *C*-centered form II of sPP),[19] because of the similar crystal structures of sPP[8,12,19] and sPB.[18] Form I of sPP,[12−17] form I of sPB,[18a] and form II of sPP[19] are, indeed, characterized by chains in 2-fold helical conformation packed in orthorhombic unit cells according to similar modes of packing, and propene or butene are included in the unit cells of both homopolymers.[11a,c] In this paper the structure of oriented fibers of sPPBu copolymers is studied in the whole composition range. The effect of the presence of butene units on the stability of helical and *trans*-planar forms of sPP and on polymorphic transitions occurring during stretching is investigated.

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* To whom correspondence should be addressed. Telephone: ++39 081 674346; fax + +39 081 674090; e-mail: claudio.derosa@unina.it.

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Table 1. Composition, Melting Temperature of As-Prepared and Aged Samples (T_m), and Intrinsic Viscosity ([η]) of sPPBu Copolymer Samples[a]

samples	gas composition (mol% of 1-butene)	copolymer composition (mol% of 1-butene)[b]	T_m (°C)[c]	[η] (dL/g)[d]
sPPBu1	1.1	3.2	138	2.6
sPPBu2	2.6	6.1	126	2.0
sPPBu3	4.8	6.7	123	2.5
sPPBu4	6.6	11.2	110	2.3
sPPBu5	7.6	13.6	108	3.0
sPPBu6	11.0	18.2	100	2.1
sPPBu7	16.5	31.5	85	2.0
sPPBu8	22.6	37.9	71	1.50
sPPBu9	34.6	51.7	70	1.46
sPPBu10	45.2	52.1	64	1.35
sPPBu11	65.1	69.9	57	1.10
sPPBu12	84.7	89.0	54	1.65

[a] 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; polymerization time = 2 h; flow rate = 0.3 L/min; yield = 2−5 g. [b] Determined from ^{13}C NMR (Varian XL-200 spectrometer operating at 50.3 MHz) spectra[20] of 10% w/v polymer solutions in deuterated tetrachloroethane (also used as internal standard) at 120 °C. [c] Determined from DSC (Perkin-Elmer DSC-7) curves of as-prepared and aged samples recorded at heating rate 10 °C/min. [d] Measured in 1,2,3,4-tetrahydronaphthalene solutions at 135 °C using standard Ubbelohde viscosimeter.

Experimental Section

Samples of sPPBu copolymers were synthesized with a single center C_s-symmetric syndiospecific catalyst (phenyl)$_2$methylen-(cyclopentadienyl)(9-fluorenyl)zirconium dichloride activated with methylaluminoxane (MAO) with the method described in the literature.[11a]

All copolymerizations were run at 10 °C in a 250 mL Pyrex reactor, agitated with magnetic stirrer, containing toluene (100 mL) and MAO. Gas mixtures of butene 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. The polymerization was started by syringing in a toluene solution of the catalyst (2−3 mg), and the Al/Zr molar ratio was adjusted to 1000. Under such conditions, total monomer conversions were lower than 15%, 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 sPPBu samples are reported in Table 1.

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 $\varepsilon = 100(L_f - L_0)/L_0$) and then removing the tension.

X-ray diffraction patterns have been obtained with Ni-filtered Cu Kα radiation. The powder profiles were obtained with an automatic Philips diffractometer, whereas the fiber diffraction patterns were recorded on a BAS-MS imaging plate (FUJIFILM) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800). The X-ray fiber diffraction patterns have been recorded for stretched fibers soon after the stretching 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.

Results and Discussion

Unoriented Powder Samples. The X-ray powder diffraction profiles of compression-molded samples slowly cooled from the melt of sPPBu samples are shown in Figure 1. It is apparent that the samples are crystalline in the whole range of comonomer composition. Samples with butene content higher than 30 mol % behave like sPB.[18] They are amorphous just after cooling from the melt (curves d′−g′ of Figure 1) but crystallize by aging at room temperature for several days (curves d−g of Figure 1).[11c]

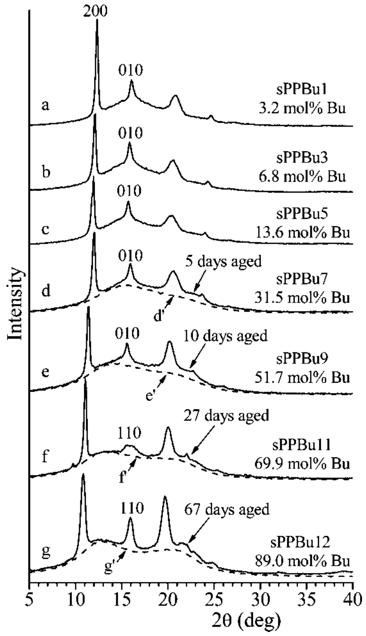

Figure 1. X-ray powder diffraction profiles of compression molded films slowly crystallized from the melt of sPPBu samples of the indicated concentration of butene (Bu). The 200 and 010 reflections of limit disordered *B*-centered form I of sPP (space group *Bmcm*)[8,12,21] and the 110 reflections of the *C*-centered form II of sPP and form I of sPB (space group $C222_1$)[18a,19] are indicated. For the samples sPPBu7-sPPBu12 with butene contents higher than 30 mol%, the dashed lines indicate the diffraction profiles of the amorphous samples obtained immediately after cooling the melt to room temperature (curves d′−g′), whereas the solid lines indicate the diffraction profiles of the samples crystallized by aging the amorphous samples at room temperature for the indicated times (curves d−g).

All copolymer samples present X-ray diffraction profiles similar to those of the corresponding homopolymers, with three strong reflections in the 2θ angular ranges 10.5−12.2°, 15−16°, and 19−21°, the exact position being depending on the composition.[11a,c] Moreover, for each sample the position of the reflections are the same as found in the as-prepared samples,[11a] or in samples isothermally crystallized from the melt at high temperatures.[11c]

The parameters of the orthorhombic unit cells for compression-molded films are therefore the same as those determined in refs 11a,c for as-prepared and isothermally melt-crystallized samples, with values of the *a* and *b* axes that increase with increasing butene content from the values typical of sPP to the values typical of sPB (Table 2 of ref 11a). This indicates that both comonomeric units are included in the unit cells of the two homopolymers and not rejected in the amorphous phase, not only in the fast crystallization from the polymerization solution but even when the samples are slowly crystallized from the melt.

The Bragg spacing of the reflection at 2θ = 10.5−12.2° increases with increasing butene content, whereas that of the reflection at 2θ = 15−16° first increases up to a butene concentration of 60−70 mol% and then decreases for a further increase of the butene content (Figure 1). This indicates that, according to the results of ref 11a,c, sPPBu samples crystallize in different structures, shown in Figure 2, intermediate between those of form I of sPP[8,12−17] and form I of sPB,[18a] depending on the composition.

Samples with butene contents up to 60−70 mol % crystallize from the melt in a structure similar to that of the *B*-centered

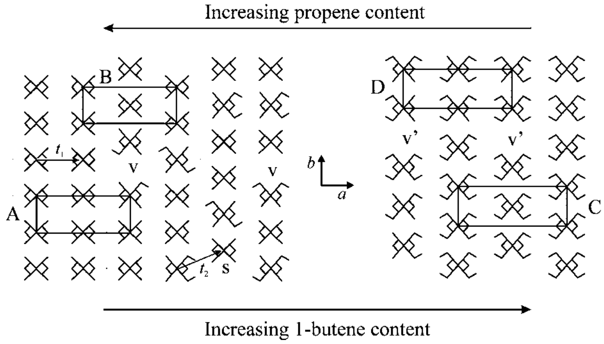

Figure 2. Simplified models of the packing mode of 2-fold $(T_2G_2)_n$ helical chains of sPPBu copolymers in projection parallel to chain axes. The unit cells of the *B*-centered form I of sPP (A), the *C*-centered isochiral form II of sPP (B), and the *C*-centered isochiral form I of sPB (C) are indicated. The unit cell of the new metastable *B*-centered form I′ of sPB, which crystallizes in butene rich sPPBu copolymers, is indicated in D. *b*/2 shift defect (s) and *b*/2 vacancies (v,v′), generated by stacking fault disorder of *bc*-rows of chains, are also indicated. At low butene content, defects v and s produce local arrangements of chains as in the *C*-centered form II of sPP (B) or form I of sPB (C) in a prevailing mode of packing of the *B*-centered form I of sPP (A). At high butene content, defects v′ produce local arrangements of chains as in the *B*-centered form I of sPP (A,D) in a prevailing mode of packing of the *C*-centered form I of sPB (C) and form II of sPP (B).

form I of sPP (Figure 2A),[12] and the diffraction peak at $2\theta = 15-16°$ is interpreted as 010 reflection (curves a−e of Figure 1).[11a,c] Samples with butene content higher than ≈69 mol% crystallize, instead, in a structure similar to that of the isochiral *C*-centered form I of sPB[18a] (space group $C222_1$, Figure 2C) as well as the *C*-centered form II of sPP[8,19,21a] (Figure 2B), and the diffraction peak at $2\theta = 15-16°$ is interpreted as 110 reflection (curves f,g of Figure 1).[11a,c]

In all sPPBu samples a large amount of structural disorder is present in the crystals. In particular, in sPPBu samples with butene content below 60−70 mol%, disorder in the stacking of *bc* layers of chains piled along *a* is present. This disorder implies the presence of defects corresponding to *b*/2 shifts between consecutive *bc* layers[8,12−17,21b] (*b*/2 shift disorder, defect s of Figure 2), and of *b*/2 vacancies[16] (defect v of Figure 2), in a prevailing mode of packing of the *B*-centered form I of sPP (Figure 2A). These stacking faults produce local arrangements of the chains as in the *C*-centered form II of sPP (Figure 2B) or form I of sPB (Figure 2C). The amount of *b*/2 shift (and *b*/2 vacancy) disorder increases with increasing butene content, and a mode of packing intermediate between those of the *B*-centered form I of sPP (Figure 2A) and *C*-centered form I of sPB or form II of sPP (Figure 2B,C) is produced.[11a,c] The presence of this kind of disorder is clearly indicated by the broadening of the 010 reflection at $2\theta \approx 15-16°$ in the X-ray diffraction profiles of these samples (curves a−e of Figure 1).

For butene contents higher than ≈60 mol%, the mode of packing of the *C*-centered form I of sPB (Figure 2C) and form II of sPP (Figure 2B) becomes prevalent over that of Figure 2A, and local arrangement of the chains such as in the *B*-centered form I of sPP (Figure 2A) becomes a defect (Figure 2D), due to the presence of *b*/2 shift disorder and *b*/2 vacancy (defect v′ of Figure 2).[11] This kind of disorder is indicated by the broadness and the low intensity of the 110 reflection at $2\theta = 15-16°$ (curve f of Figure 1). The amount of this stacking fault disorder decreases with further increasing butene content, as indicated by the fact that the 110 reflection becomes narrow for the sample sPPBu12 with 89 mol% of butene (curve g of Figure 1).

Oriented Fibers. The X-ray fiber diffraction patterns, and the corresponding profiles read along the equatorial line, of fibers of the sample sPPBu1 with butene content of 3.2 mol%, obtained by stretching at room-temperature compression molded films at different values of strain ε are reported in Figure 3A−D. The disordered modifications similar to the *B*-centered form I of sPP (Figure 2A) with chains in helical conformation, initially present in the unoriented film (profile a of Figure 1), transform by stretching already at 200% deformations into form III with chains in *trans*-planar conformation (Figure 3A and curve a of Figure 3D). This is indicated in Figure 3A by the low intensity of the $(200)_{\mathrm{I}}$ reflection at $2\theta \approx 12°$ of the helical form I of sPP (subscript I standing for form I of sPP) (curve a of Figure 3D) and of the $(111)_{\mathrm{I}}$ reflection on the first layer line,[21a] and the strong intensities of the equatorial $(020)_{\mathrm{III}}$ and $(110)_{\mathrm{III}}$ reflections of form III of sPP (subscript III standing for form III of sPP) at $2\theta \approx 16°$and 18° (curve a of Figure 3D), and of the $(021)_{\mathrm{III}}$ and $(111)_{\mathrm{III}}$ reflections on the first layer line.[22] The intensity of the reflections of form I decrease with increasing deformation and at 600% deformation the sample appears completely crystallized in the *trans*-planar form III (Figure 3B, curve b of Figure 3D).

The X-ray diffraction pattern of fibers of the sample sPPBu1 stretched at 600% deformation after releasing the tension (stress-relaxed fibers) and the corresponding equatorial profile are shown in Figure 3C and Figure 3D (profile c), respectively. It is apparent that form III transforms into the more stable form II of sPP with chains in helical conformation by releasing the tension, as indicated by the presence in the pattern of Figure 3C of the equatorial $(200)_{\mathrm{II}}$ and $(110)_{\mathrm{II}}$ reflections (subscript II standing for form II of sPP) at $2\theta \approx 12$ and 17°, respectively (profile c of Figure 3D), and of the $(111)_{\mathrm{II}}$ reflection on the first layer line, typical of the helical form II of sPP.[19] However, the presence in Figure 3C of reflections on the first layer line corresponding to the chain periodicity of 5.1 Å, typical of *trans*-planar forms of sPP, and the high intensity of the reflection at $2\theta \approx 17°$ with respect to that of the $(200)_{\mathrm{II}}$ reflection at $2\theta \approx 12°$ (profile c of Figure 3D), indicate that a non-negligible portion of crystals of form III of sPP in the stretched sample transforms by releasing the tension into the mesomorphic form of sPP with chains still in *trans*-planar conformation.[23] The transformation of *trans*-planar form III into a mixture of crystals of helical form II and *trans*-planar mesomorphic form by releasing the tension is reversible, i.e. these crystals transform back into the *trans*-planar form III by stretching. This reversible polymorphic transition is associated with a remarkable elastic behavior of fibers of the sample sPPBu1. This behavior is similar to that of sPP.[8,9]

Samples of sPPBu copolymers with butene concentrations in the range 4−20 mol% show a similar behavior, and similar structural transformations occur by stretching. As an example, the X-ray fiber diffraction patterns and the corresponding profiles read along the equatorial line of fibers of the sample sPPBu6 with 18.2 mol% of butene, stretched at different values of strain ε, are shown in Figures 3E−H (see also Supporting Information for other examples). Also these samples are initially crystallized in disordered modifications of form I of sPP, including increased *b*/2 shift and/or *b*/2 vacancy disorder (profiles b,c of Figure 1), which transform into the *trans*-planar form III by stretching at high deformations. This transformation is, however, more gradual than in the sample sPPBu1 with low butene content, and crystals of the *trans*-planar form III of sPP start appearing at values of deformation higher than those observed for samples with butene content lower than 4 mol%. Moreover, these critical values of deformation increase with increasing butene concentration (≈300% deformation for the sample sPPBu3 (see Supporting Information), ≈400% for the sample sPPBu4 with 11.2 mol% of butene and ≈500% for the samples sPPBu5 and sPPBu6 with 13.6 and 18.2 mol% of butene, respectively (Figure

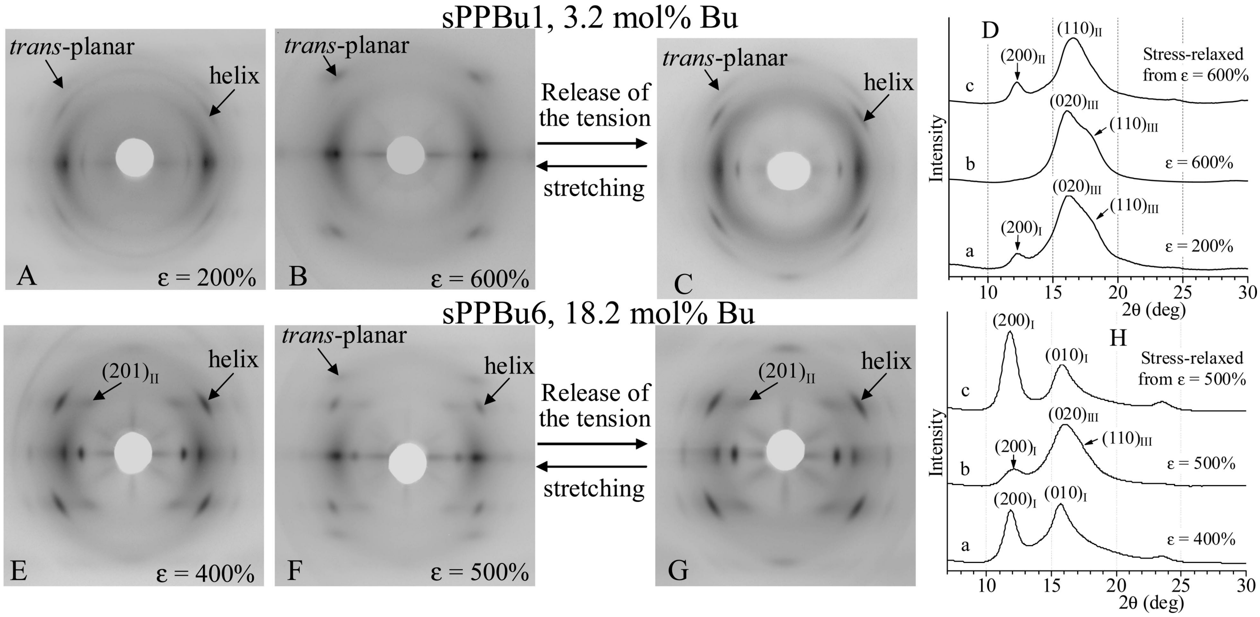

Figure 3. X-ray fiber diffraction patterns (A−C, E−G), and corresponding profiles read along the equatorial lines (D,H), of fibers of the samples sPPBu1 with 3.2 mol% of butene (A−D) and sPPBu6 with 18.2 mol% of butene (E−H), obtained by stretching compression-molded films at the indicated values of the defomation ε, keeping the fibers under tension (A,B,E,F) and after removing the tension from the maximum achieved deformation (C,G). The $(200)_{\mathrm{I}}$ and $(010)_{\mathrm{I}}$ reflections at $2\theta \approx 12$ and 16°, respectively, of the *B*-centered helical form I of sPP,[12,21] the $(200)_{\mathrm{II}}$ and $(110)_{\mathrm{II}}$ reflections at $2\theta \approx 12$ and 17°, respectively, of the *C*-centered helical form II of sPP,[19,21a] and the $(020)_{\mathrm{III}}$ and $(110)_{\mathrm{III}}$ reflections at $2\theta \approx 16$ and 18°, respectively, of the *trans*-planar form III of sPP[22] are indicated in D and H. The reflections on the first layer line relative to helical forms I and/or II and *trans*-planar form III and/or mesophase of sPP are also indicated in A−C and E−G, as "helix" and "*trans*-planar", respectively.

3F)). At low values of deformation fibers with mixtures of crystals of the helical form I and the *trans*-planar form III are obtained for the samples with low butene concentration (see for instance the sample sPPBu3 with 6.7 mol% of butene in the Supporting Information). Well oriented fibers of the pure form I are instead obtained at low deformations for higher butene concentration. In particular, in the X-ray fiber diffraction pattern of fibers of the sample sPPBu6 stretched at 400% deformation the reflections of *trans*-planar form III are still absent, and only the $(200)_{\mathrm{I}}$ and $(010)_{\mathrm{I}}$ equatorial reflections at $2\theta \approx 12$ and 16° and the $(111)_{\mathrm{I}}$ reflection on the first layer line, typical of the helical form I of sPP, are present (Figure 3E, and curve a of Figure 3H). Crystals of the *trans*-planar form III of sPP arise only at 500% deformation, as indicated by the presence of the $(020)_{\mathrm{III}}$ and $(110)_{\mathrm{III}}$ equatorial reflections at $2\theta \approx 16°$ and 18° and the $(021)_{\mathrm{III}}$ and $(111)_{\mathrm{III}}$ reflections on the first layer line in the pattern of Figure 3F and in the profile b of Figure 3H. However, at this high deformation, close to the breaking of the specimen, a large amount of crystals of form I is still present, as indicated by the presence of the equatorial $(200)_{\mathrm{I}}$ reflection and the first layer line $(111)_{\mathrm{I}}$ reflection (Figure 3F and profile b of Figure 3H).

These results indicate that the higher the butene content, the higher the deformation at which form I starts transforming into form III, and that the presence of butene for concentrations higher than 6−7 mol% prevents the complete transformation of form I into form III even by stretching at values of deformation close to the breaking.

Also in these samples form III is metastable and transforms into the more stable helical form by releasing the tension (Figure 3G). However, contrary to the sPPBu samples with butene content lower than 4 mol% (Figure 3B,C), form III transforms back into the helical form I of sPP instead than into form II. This transformation is almost complete, as indicated in Figure 3G by the presence of the $(200)_{\mathrm{I}}$ and $(010)_{\mathrm{I}}$ reflections at $2\theta \approx$ 12° and 16° on the equator (curve c of Figure 3H) and of reflections on the first layer line corresponding to the chain periodicity of the helical conformation, and the absence of reflections typical of the *trans*-planar forms. The formation of crystals of form I is probably nucleated by the crystals of form I that remain present in the stretched fibers up to high deformations. The transformation between form III and form I is reversible (Figure 3F,G) and is associated with an elastic behavior of fibers during mechanical cycles of consecutive stretching and relaxation.

sPPBu samples with butene concentrations in the range 20−60 mol% show a similar behavior. The X-ray fiber diffraction patterns of fibers of the sample sPPBu8 with 37.9 mol% of butene stretched at high deformation ($\varepsilon = 550\%$) and after releasing the tension are reported in Figure 4A−C, as an example (see Supporting Information for other examples). In these samples only oriented fibers of the helical form I of sPP are obtained at any values of the strain, and the *trans*-planar form III is never obtained even by stretching at deformations close to the breaking. In fact, the X-ray fiber diffraction pattern of Figure 4A exhibits the exclusive presence of the $(200)_{\mathrm{I}}$ and $(010)_{\mathrm{I}}$ reflections at $2\theta \approx 11°$ and 16° of the helical form I (see also profiles a of Figure 4C).

Moreover, no structural transformations are observed by releasing the tension regardless of the deformation achieved during the stretching, and the X-ray fiber diffraction patterns of the stress-relaxed fibers are very similar to those of the stretched fibers (Figure 4B and profiles b of Figure 4C). Oriented fibers of these sPPBu samples still show elastic properties.

The structural transformations occurring during stretching of samples sPPBu11 and sPPBu12 with 69.9 and 89 mol% of butene samples are shown in Figure 5, as examples of the similar behavior of samples with butene content higher than 60 mol%. Unoriented films of samples sPPBu11 and sPPBu12 are crystallized in disordered modifications close to the *C*-centered form I of sPB (Figure 2C) or form II of sPP (Figure 2B). The stretching of well crystallized films of these samples induces, already at deformations around 200−300%, orientation of crystals of form I of sPB, as indicated by the presence in the

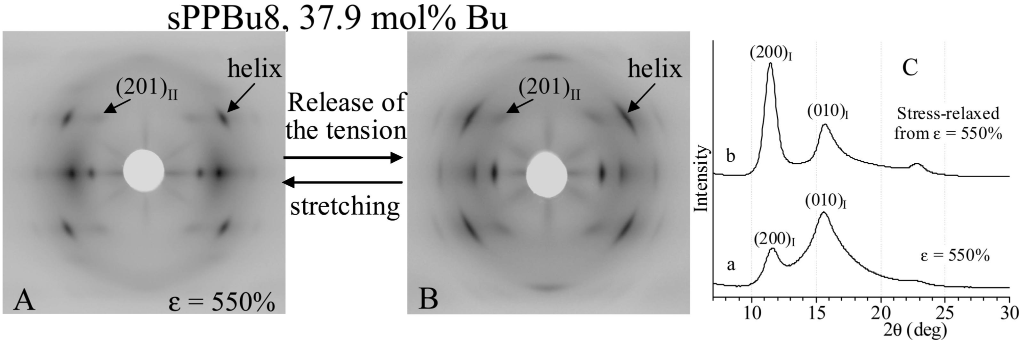

Figure 4. X-ray fiber diffraction patterns (A,B), and corresponding profiles read along the equatorial lines (C), of fibers of the samples sPPBu8 with 37.9 mol% of butene, obtained by stretching compression-molded films at 550% strain, keeping the fibers under tension (A) and after removing the tension (B). The $(200)_I$ and $(010)_I$ reflections at $2\theta \approx 12$ and 16°, respectively, of the *B*-centered helical form I of sPP,[12,21] are indicated. On the first layer line the weak $(201)_{II}$ reflection of form II of sPP and the strong 111 reflection of both helical forms I and II of sPP (indicated as "helix") are also indicated.

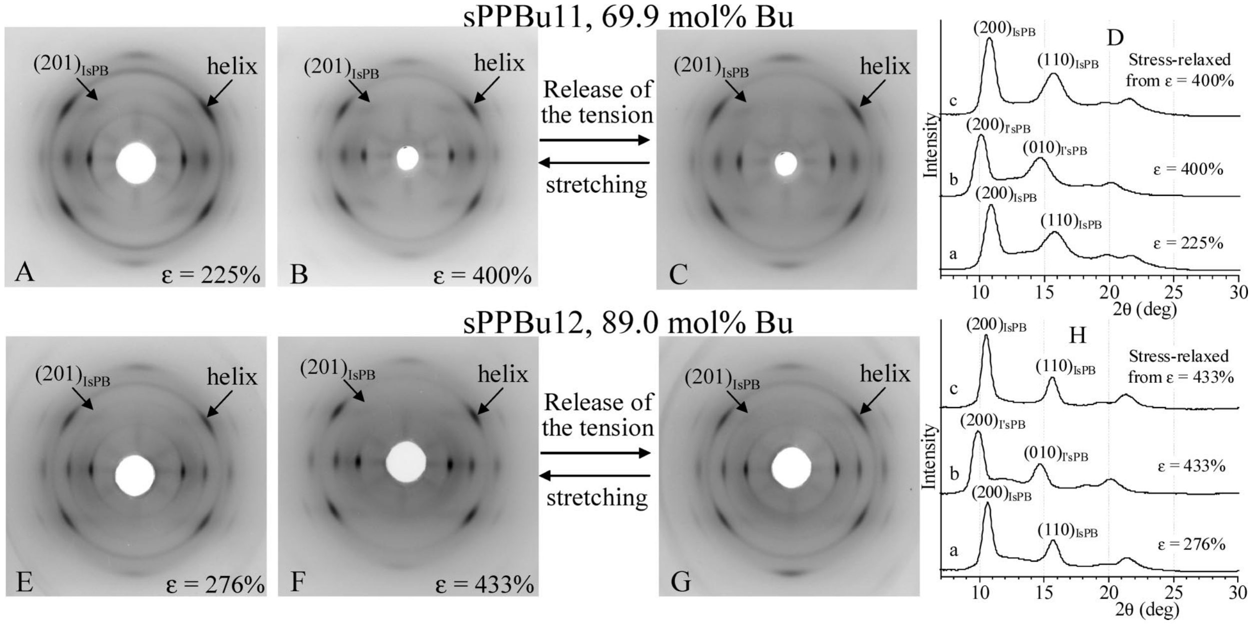

Figure 5. X-ray fiber diffraction patterns (A−C, E−G) and corresponding profiles read along the equatorial lines (D,H), of fibers of the samples sPPBu11 with 69.9 mol% of butene (A−D) and sPPBu12 with 89 mol% of butene (E−H) stretched at different values of the strain ε keeping the fiber under tension (A,B,E,F) and after releasing the tension from the maximum achieved deformation (C,G). The $(200)_{IsPB}$ and $(110)_{IsPB}$ reflections at $2\theta \approx 11$ and 16°, respectively, and the first layer line $(201)_{IsPB}$ reflection of form I of sPB (Figure 2C), and the $(200)_{I'sPB}$ and $(010)_{I'sPB}$ at $2\theta \approx$ 10 and 15°, respectively, of the new *B*-centered form I′ of sPB (Figure 2D) are indicated. The strong 111 reflection on the first layer line relative to the helical form I and form I′ of sPB is also indicated as "helix".

patterns of Figure 5A,E and in the profiles a of Figure 5D,H of well polarized equatorial $(200)_{IsPB}$ and $(110)_{IsPB}$ reflections at $2\theta \approx 11°$ and 16° (subscript IsPB standing for form I of sPB) and of reflections corresponding to the chain periodicity of helical conformation on the first layer line.

With increasing deformation at ≈400%, a shift of the equatorial reflections at $2\theta \approx 11°$ and 16° (profiles a of Figure 5D,H) toward lower 2θ values of ≈10 and 15°, respectively, is observed (Figure 5B,F and profiles b of Figure 5D,H). This indicates that a distortion of the orthorhombic unit cell of form I of sPB (Figure 2C), corresponding to an increase of the *a*-axis, occurs, whereas the value of the *b* axis remains substantially unaltered if the diffraction peak at $2\theta \approx 15°$ is interpreted as 010 reflection. This distortion corresponds to a phase transition from form I of sPB (Figure 2C), where the chains are packed in a *C*-centered orthorhombic unit cell, into a new form, defined form I′,[24] characterized by a mode of packing more similar to form I of sPP, where the chains are packed in a *B*-centered orthorhombic unit cell, as shown in Figure 2D.[24] Therefore, the reflections at $2\theta \approx 10$ and 15° in the diffraction patterns of Figure 5B,F (profiles b of Figure 5D,H) correspond to the $(200)_{I'sPB}$ and $(010)_{I'sPB}$ of form I′ of sPB. In the form I′ *b*/2-shift is still present (defect v′ of Figure 2), producing local facing situations of close neighboring chains faced along *a* as in the *C*-centered form I of sPB (form II of sPP).

This new form I′ has never been observed in sPB homopolymer samples and in powder samples of sPPBu copolymers with high butene concentration. Copolymer samples, indeed, crystallize by precipitation from the polymerization solution or by slow crystallization from the melt,[11] into the stable *C*-centered form I of sPB (Figure 2C)[18a,b] or form II of sPP (Figure 2B).[19]

The *B*-centered form I′ obtained by stretching at high deformation is metastable, and transforms back into the more stable *C*-centered form I of sPB by releasing the tension. In fact the $(200)_{I'sPB}$ and $(010)_{I'sPB}$ reflections at $2\theta \approx 10°$ and 15° of form I′ present in the diffraction patterns of stretched fibers of Figure 5B,F come back to values of $2\theta \approx 11°$ and 16° in the diffraction patterns of Figure 5C,G obtained after removing the tension (profiles c of Figure 5D,H), as in the unstretched compression-molded film (profiles f and g of Figure

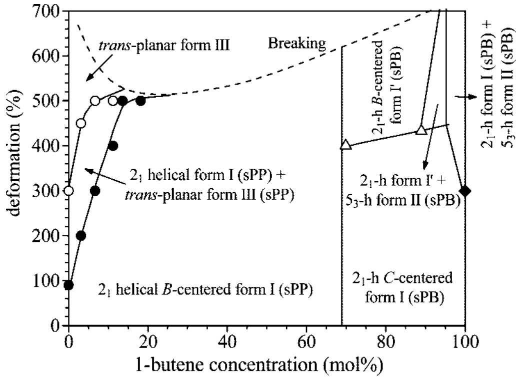

Figure 6. Phase diagram of sPPBu copolymers showing the region of stability of the different polymorphic forms as a function of strain and copolymer composition. (The abbreviated symbols 2_1-h and 5_3-h stand for "2_1 helical" and "5_3 helical", respectively). Form II of sPB with chains in 5_3 helical conformation is obtained in samples of sPB stretched at high strains.[18c] Small amounts of form II are also obtained in the sample sPPBu12 stretched at high strains (Figure 5F, see Supporting Information).

1) or in fibers stretched at low deformations (Figure 5A,E and profiles a of Figure 5D,H). The transformation of form I into form I′ is reversible and is associated with elastic properties of fibers of the samples sPPBu11 and sPPBu12.

Also in oriented fibers of sPPBu copolymers crystallized in form I of sPP structural disorder is present (see Supporting Information). The diffraction patterns of Figure 3−5 always show a broad and weak $(201)_{II}$ (or $(201)_{IsPB}$) reflection at $2\theta \approx 15-16°$ on the first layer line, which is typical of the *C*-centered isochiral helical form II of sPP (Figure 2B) and form I of sPB (Figure 2C). This reflection should be absent in the *B*-centered form I of sPP and form I′ of sPB.[21a,24] The simultaneous presence of the $(201)_{II}$ (or $(201)_{IsPB}$) and $(010)_{I}$ (or $(010)_{I'sPB}$) equatorial reflections is due to the presence of *b*/2 shift and/or *b*/2 vacancy disorder as defects in a prevailing mode of packing of form I of sPP (or form I′ of sPB, Figure 2A,D). This stacking fault disorder produces local arrangements of the chains as in the *C*-centered form II of sPP (Figure 2B) or form I of sPB (Figure 2C).[16,21b] Calculations of structure factors (see Supporting Information) have indicated that disordered domains of form I of sPP contain ≈30−35% of consecutive *bc* layers facing as in form II of sPP or form I of sPB (Figure 2B,C), and the probability of *b*/2 shift disorder increases up to 40−45% with increasing butene concentration.

The data of Figures 3−5 have allowed building a phase diagram of the sPPBu copolymers where the region of stability of the different polymorphic forms of sPP and sPB in oriented fibers are defined as a function of copolymer composition and degree of deformation (Figure 6).

The boundary lines in the phase diagram define the transformations of the helical form I into the *trans*-planar form III of sPP, at butene concentration lower than 69 mol%, and of the helical form I of sPB into the helical form I′ at higher butene content. The boundary lines have been determined by the emergence during deformation of reflections typical of the polymorphic forms of sPP and sPB in the X-ray fiber diffraction patterns. It is apparent that the values of the critical strain at which the polymorphic transitions start and at which the transformation is complete depend on the copolymer composition.

Unit Cell Parameters of Stretched and Stress-Relaxed Fibers. The X-ray diffraction patterns of fibers of the samples sPPBu1-sPPBu6 (as in Figure 3) stretched at the maximum possible deformation, containing crystals of the *trans*-planar form III, show that the equatorial $(020)_{III}$ and $(110)_{III}$ reflections, typical of the form III,[22] are on average at nearly the same values of the Bragg angles $2\theta \approx 16$ and 17.5−18°, respectively, regardless of the composition, that is at values similar to those in the diffraction pattern of form III of sPP homopolymer.[22] This indicates that, regardless of the butene content, the unit cell parameters of crystals of form III formed in the copolymer samples sPPBu1-sPPBu6 at high deformations are similar to those of form III of sPP ($a = 5.22$ Å, $b = 11.17$ Å, and $c = 5.1$ Å),[22] and only a slight increase of the *a* axis is observed (see Supporting Information). This strongly supports the hypothesis that butene units are practically rejected from the crystals of the *trans*-planar form III. The rejection of butene units can be easily explained in term of high conformational energy required for a sPP chain including high concentration of butene units to assume a *trans*-planar conformation.[18b] Therefore, only propylene sequences free from butene units are able to crystallize in the *trans*-planar form III. This also explains the fact that the presence of butene units at concentration higher than 20 mol% (samples sPPBu7-sPPBu12) prevents the crystallization of form III, even by stretching at deformation close to the breaking (Figure 4), and induces stabilization of the helical forms.

In previous papers it has been shown that in powder samples of sPPBu copolymers butene and propylene units are instead able to cocrystallize in the helical forms of sPP and sPB,[10,11] so that butene and propene units are easily included in the crystals of form I of sPP and form I of sPB, respectively. This was clearly demonstrated by the increase of the unit cell parameters with increasing butene concentration from the values of form I of sPP to those of the *C*-centered form I of sPB.[11a,c]

The values of the axes of the unit cells of the helical forms in fibers of sPPBu copolymers stretched up to deformations close to the breaking and in stress-relaxed fibers, evaluated from the X-ray fiber diffraction patterns as those of Figure 3−5 are reported in Figure 7 as a function of copolymer composition (see also Supporting Information), in comparison with those evaluated for powder as-prepared and melt-crystallized samples.[11a,c] The values of the *a* and *b* axes of the helical forms for all samples have been deduced from the positions of the equatorial diffraction peaks at $2\theta \approx 10-12°$ ($d = 8.84-7.37$ Å), corresponding to the 200 reflection of forms I and II of sPP,[12,19,21a] and of forms I and I′ of sPB,[18a,24] and at $2\theta \approx 15-16°$ ($d \approx 5.91-5.54$ Å), respectively.

Contrary to the powder, as-prepared, or melt-crystallized samples of sPPBu copolymers,[11a,c] in the case of fibers stretched at maximum deformation the diffraction peak at $2\theta \approx 15-16°$ has been interpreted as 010 reflection for any comonomer composition, indicating that all samples with butene content higher than 3−4 mol% are crystallized in *B*-centered modifications (form I of sPP or form I′ of sPB). In the case of stress-relaxed fibers, the peak at $2\theta \approx 15-16°$ has been interpreted as 010 reflection (*B*-centered mode of packing) for the sPPBu samples with butene content comprised in the range 4−69 mol% (samples sPPBu2-sPPBu10) and 110 reflection (*C*-centered mode of packing) for the samples with butene content lower than 4 mol% (sample sPPBu1) and higher than 69 mol% (samples sPPBu11 and sPPBu12). The unit cell parameters evaluated with these assumptions (see Supporting Information) account for the position of all other diffraction peaks observed in the fiber diffraction patterns of Figure 3−5.

It is apparent that, with the only exception of the samples sPPBu11 and sPPBu12 with butene content higher than 69 mol%, the values of *a*, *b*, and *c* axes of the helical forms that develop in oriented fibers increase with increasing butene concentration from the values typical of sPP up to the values typical of sPB (Figure 7). This indicates that the comonomeric units, propene or butene, are included in the unit cells of both homopolymers, as in the case of as-prepared or melt-crystallized

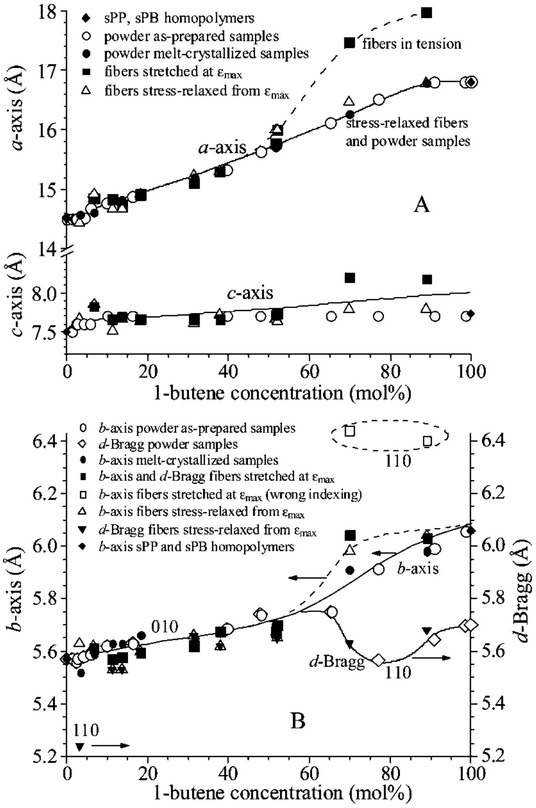

Figure 7. Values of the *a*, *c* (A) and *b* (B) axes of the unit cells of helical forms that develop in oriented fibers of sPPBu copolymer samples as a function of the butene content. The fibers have been obtained by stretching unoriented films up to the maximum possible deformations, close to the breaking (ε_{max}), keeping the fiber in tension (■) and after removing the tension (△). The values of *a*, *c* (A) and *b* (B) axes of the unit cells of powder as-prepared (○) and melt-crystallized compression-molded (●) samples of copolymers[11a,c] and of sPP and sPB homopolymers (◆) are reported for comparison. In part B, the values of the Bragg spacing d_{110} or d_{010} of the equatorial reflection at $2\theta \approx 15-16°$ in powder as-prepared samples (◇) and stress-relaxed fibers (▼) are also reported. Wrong too high values of the *b*-axis for fibers of the samples sPPB11 and sPPBu12 with 69.9 and 89.0 mol% of butene, stretched at the maximum deformation ε_{max}, calculated from a wrong indexing of the equatorial reflection at $2\theta \approx 15-16°$ as 110 reflection, like in the *C*-centered form I of sPB (Figure 2C), instead of 010 reflection as in the *B*-centered form I′ of sPB (Figure 2A and D), are also reported in B (□).

powder samples. The values of axes of the unit cell for oriented fibers are practically coincident with those of as-prepared or melt-crystallized powder samples.[11a,c]

As shown in Figure 5B,F, in the case of samples sPPBu11 and sPPBu12 with butene content of 69.9 and 89.0 mol%, the stretching at high deformations of samples crystallized in the *C*-centered form I of sPB (Figure 2C) produces transformation into the *B*-centered form I′ (Figure 2D). This structural transformation is evidenced by the shift of the equatorial reflections at $2\theta \approx 11°$ and 16° (profiles a of Figure 5D,H) toward lower values of $2\theta \approx 10$ and 15°, respectively (profiles b of Figure 5D,H). The values of axes of the unit cell of the *B*-centered form I′ are $a = 17.98$ Å, $b = 6.03$ Å, $c = 8.18$ Å for the sample sPPBu12 with 89 mol% of butene, and $a = 17.48$ Å, $b = 6.04$ Å, $c = 8.2$ Å for the sample sPPBu11 with 69.9 mol% of butene.[24] Therefore, as shown in Figure 7A, the transformation of form I into form I′ implies a remarkable increase of the *a* axis, so that the values of the *a* axis of the new form I′ is ≈7% higher than the value of the *a* axis of form I obtained at lower deformations and in the powder samples ($a = 16.78$ Å and 16.26 Å for the powder samples sPPBu12 and sPPBu11, respectively)[11a] and even higher than the value of the *a* axis of form I of sPB homopolymer ($a = 16.81$ Å).[18a] The values of *b* and *c* axes remain, instead, substantially the same as in the form I of the powder samples (Figure 7). The constancy of the *b* axis is clearly indicated by the fact that the equatorial diffraction peak at $2\theta \approx 15°$ of Figure 5B,F (profiles b of Figure 5D,H) can be interpreted only as 010 reflection, as in the *B*-centered form I of sPP. The indexing of this diffraction peak as 110 reflection, as in the *C*-centered form I of sPB, would lead to a too high value of the *b* axis ($b = 6.44$ Å and 6.40 Å for the samples sPPBu11 and sPPBu12, respectively, encircled points of Figure 7B), and therefore a too low value of the density of the crystals (10% lower than that of form I crystals).

The *B*-centered form I′ of sPB obtained in the samples sPPBu11 and sPPBu12 stretched at high deformation transforms back into the more stable *C*-centered form I of sPB by releasing the tension, and, correspondingly, the values of the *a* axes for the stress-relaxed fibers come back to values similar to those of the powder samples (Figure 7A). The axes of the unit cells for the stress-relaxed fibers of the sample sPPBu12 with 89 mol% of butene are, indeed, $a = 16.78$ Å, $b = 6.04$ Å, $c = 7.79$ Å, whereas those for the sample sPPBu11 with 69.9 mol% of butene are $a = 16.46$ Å, $b = 5.98$ Å, $c = 7.79$ Å.

The remarkable increase of the *a* axis during transformation of form I of sPB (Figure 2C) into form I′ (Figure 2D) by stretching indicates a distortion of the unit cell of crystals of form I in a direction perpendicular instead than parallel to the stretching direction. This nonstandard mode of distortion of the crystals reflects conformational energy barriers and crystallographic restraints on the slip processes involved at high deformations. It is well-known that the stretching at high deformations of sPB homopolymer samples produces transformation of the crystals of the *C*-centered form I with chains in the 2-fold helical conformation into form II, characterized by chains in a complex **s**(5/3)2 helical conformation.[18b,c] This conformational transition is at low cost of internal energy and corresponds only to a small distortion of the backbone torsion angles from the *trans* and *gauche* states of the $(TTGG)_n$ sequences.[18b] It is also well-known that in the case of sPP the stable 2-fold helical conformation transforms by stretching into the metastable fully extended *trans*-planar conformation,[8,22] which corresponds to a relative minimum of the conformational energy.[8] In the case of sPB the formation of the *trans*-planar conformation is prevented by a too high energy barrier.[18b]

In the copolymer samples sPPBu11 and sPPBu12 with 69.9 and 89 mol% of butene, the formation of form I′ by stretching is due to the fact that both the *trans*-planar form III of sPP and form II of sPB cannot be obtained. In fact, in these samples the sequences of propene units are too short to transform into the *trans*-planar conformation. Moreover, the inclusion of propene units in the crystals of form I of sPB prevents the distortions of the torsion angles from the values characteristics of the **s**(2/1)2 helices to those of the **s**(5/3)2 helical conformation and prevents the formation of form II of sPB, because for chains containing propene sequences the 5_3 conformation corresponds to a too high internal energy. Therefore, the structural transformation of the most stable *C*-centered form I of sPB into the metastable *B*-centered form I′ at high deformation is driven by the impossibility of butene-rich chains of sPPBu copolymers, with butene content in the range 69−90 mol%, to adopt both the *trans*-planar and the 5_3 helical conformations. The mechanical energy stored by the sample at high deformation before the final rupture of the specimen, is, instead, used to induce mechanical melting of the crystals of form I of sPB, immediately followed by recrystallization into the new form I′, with preservation of the 2-fold helical conformation of the chains.

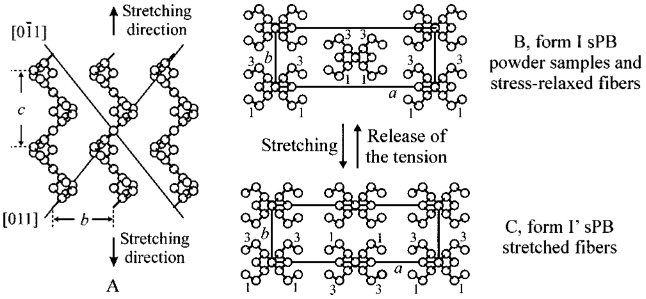

Figure 8. Scheme of the polymorphic transition occurring during stretching and relaxation of fibers of sPPBu copolymers with butene concentrations higher than 69 mol%. Structural models of a *bc* layer of sPB chains in **s**(2/1)2 helical conformation (A), and of the *C*-centered form I of sPB (B) and the *B*-centered form I′ of sPB (C). The transformation of the form I of sPB (B) into the form I′ of sPB (C) by stretching involves slipping of *bc*-layers of chains along the [011] or $[0\bar{1}1]$ lattice directions (A) according to slip vectors $\mathbf{t} = \pm\mathbf{b}/2 \pm \mathbf{c}/2$. The relative heights of the ethyl groups are indicated in *c*/4 units.

Mechanical melting of form I crystals probably involves slip of the (200) planes of maximum packing along directions parallel to the [011] or $[0\bar{1}1]$ crystallographic directions, which correspond to directions in form I crystals where the atoms are at the closest contact distance (Figure 8A,B). The slipping of close neighboring *bc* layers facing as in the *C*-centered form I of sPB (Figure 8B) of $b/2+c/2$ produces local facing situations of helices as in the *B*-centered form I of sPP (Figure 2A,D). This shift is accompanied by a slight increase of the interplanar distance of the (200) planes in order to reduce the steric interactions between atoms along the *a* axis. As a consequence, recrystallization into the form I′ (Figure 8C) occurs while maintaining the periodicities along the *c* and *b* axes but with a slight increase of the dimension of the *a* axis (Figures 7A and 8B,C). In other words the transition of form I into form I′ occurs because the crystals "prefer to shear" rather than to extend parallel to the stretching direction during deformation. In the hypothesis of complete inclusion of the comonomeric units in the crystals of fibers of samples sPPBu11 and sPPBu12 the density decreases from the value of $\approx$0.92 g/cm^3 of form I of sPB (Figure 8B) to a value of $\approx$0.82 g/cm^3 of the *B*-centered form I′ of sPB (Figure 8C).

Conclusions

Syndiotactic propylene−butene copolymers crystallize in the whole range of comonomer composition, and propene or butene comonomers are included in the unit cells of both homopolymers. Melt-crystallized samples of sPPBu copolymers are crystallized in disordered modifications of the *B*-centered form I of sPP for butene contents lower than 69 mol% (Figure 9) and in disordered modifications of the *C*-centered form I of sPB for higher butene concentration (Figure 8B). The structural transformations occurring by stretching sPPBu samples are summarized in Figures 9 and 8 for butene concentrations lower and higher than 69 mol%, respectively.

The helical form I sPP transforms into the *trans*-planar form III by stretching only sPPBu samples with butene content lower than 20 mol% (Figure 9). Butene units are rejected from crystals of form III, but easily included in crystals of the helical forms of sPP. This may explain the experimental observation that the presence of butene for concentration higher than 20 mol% prevents the formation of the *trans*-planar form III even by stretching at a high degree of deformations, close to the breaking of the sample.

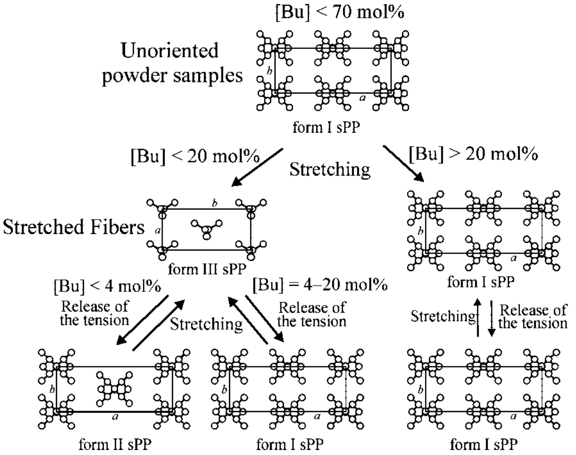

Figure 9. Scheme of the polymorphic transitions occurring during stretching and relaxation of fibers of sPPBu copolymers with butene (Bu) concentrations up to 70 mol%.

The *trans*-planar form III transforms back into the *C*-centered helical form II of sPP by releasing the tension in sPPBu samples with butene contents lower than 4 mol% and into the helical form I for butene concentrations higher than 4 mol% (Figure 9). For sPPBu copolymers with butene content higher than 20 mol% and lower than 69 mol%, only fibers in the helical form I are obtained by stretching and no structural transitions occur by releasing the tension.

Melt-crystallized sPPBu samples with butene concentration higher than 69 mol% crystallize in the *C*-centered helical form I of sPB, which transforms by stretching at high deformations into the form I′ of sPB, characterized by a packing of the chains in 2-fold helical conformation similar to the *B*-centered form I of sPP (Figure 8). This transformation occurs through a non standard distortion of the crystalline lattice of the *C*-centered form I of sPB in a direction transverse to the applied tensile force, with remarkable increase of the *a* axis of the orthorhombic unit cell. The *B*-centered form I′ of sPB is metastable and transforms back into the more stable form I of sPB by releasing the tension.

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Supporting Information Available: Text giving X-ray fiber diffraction patterns of various copolymer samples and analysis of the structural disorder present in both stretched and stress-relaxed fibers. This material is available free of charge via the Internet at http://pubs.acs.org.

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