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Structure and Morphology of Syndiotactic Poly(propene-*co*-1-butene)s with 1-Butene as a Rich Component

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ABSTRACT: Single crystals of syndiotactic poly(propene-*co*-1-butene) with 1-butene as the rich component have been obtained through ultrathin film growth from the melts. The morphological and structural studies on these single crystals have disclosed the influence of propene units on the crystallization behavior of syndiotactic poly(1-butene) (sPB-1). Bright field electron microscopy shows that incorporating the propene units in the sPB-1 chains influences the crystallization habit of the sPB-1 significantly. For example, the aspect ratio of the single crystals increases with increasing the propene units, resulting in copolymer single crystals more similar to those of the sPP homopolymer. The electron diffraction results indicate that a small amount of propene units, up to 9−10 mol %, does not affect the *C*-centered chain packing of form I of sPB-1. The propene units are most likely included into the crystalline structure of sPB-1. For much higher propene content, around about 30 mol %, the *b*/4 shift disorder takes place. Nevertheless, the *C*-centered chain packing is still the predominant packing scheme in the single crystals of the 1-butene-rich copolymers, even though with substantial amount of disorder.

Introduction

Since the development of the new metallocene catalyst systems, a large amount of work has emerged on producing highly syndiotactic polyolefins, such as syndiotactic polypropylene (sPP),[1] syndiotactic poly(1-butene) (sPB-1),[2] and their corresponding copolymers.[3−8] This has led to an increasing interest in the structural and morphological studies of the new synthetic materials, since they are the important factors for the mechanical properties.

It was well documented that syndiotactic propylene−butene-1 copolymers (sPPBU) are capable to crystallize over the whole composition range with both comonomeric units, included in the unit cells of both homopolymers, due to the very similar crystal structures of sPP and sPB-1 in their stable 2-fold helical forms.[3−6,9,10] A nearly linear expansion of *a*- and *b*-axes of the unit cell from the values of sPP to those of sPB-1 with increasing 1-butene content has been demonstrated by X-ray diffraction, in both powder[4] and oriented fiber samples.[6,10] Moreover, the copolymers can crystallize in modifications having structures intermediate between those of sPP and sPB-1, where disorder in the alternation of right- and left-handed helical chains along the axes of the unit cell and disorder in the stacking of *bc* layers of chains piled along the *a*-axis (*b*/4 shift disorder) are present.[4,6,9,10] 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.[4,6,10]

It should be pointed out that the presence of increasing amount of disorder with high concentration of 1-butene produces a broadening of the X-ray reflection peaks, which prevents an identification of the prevalent mode of packing. A model of the crystallization pattern in powder and fiber samples and of the stress-induced transformations as a function of the 1-butene concentration and of deformation degree has been recently proposed on the basis of X-ray powder and fiber diffraction patterns.[10] However, it is quite difficult for an exact indexing of the broadened X-ray diffractions for the samples with 1-butene concentration in the range 40−60 mol %. Moreover, the X-ray studies tell us nothing about the influence of the propene comonomeric units on the crystallization habit of the copolymers. Electron microscopic observation combined with electron diffraction of the single crystals could give not only a precise indexing of the reflections and therefore more information about the kinds and the amount of structural disorder with respect of the comonomeric composition but also the crystal growth habit of the copolymers. The morphological and electron diffraction analyses are, therefore, of great importance for investigating the influence of comonomeric units on the crystalline structure and the existing defect of the copolymer crystals. This kind of study has, however, rarely been reported yet.

In our previous transmission electron microscopy and electron diffraction studies, the morphologies and structures of single crystals of sPB-1 homopolymer and sPPBU copolymers with 1-butene content lower than 50 mol % were presented.[11,12] It was found that the incorporated 1-butene units influence the crystallization behavior and crystalline structure of the sPP remarkably. The antichiral packing model of the most stable form I of sPP[13] is, however, always the predominant chain packing structure of the copolymers, although an increasing packing disorder is observed with increasing 1-butene content in the copolymers. Unfortunately, no morphological and structural details of the copolymers with 1-butene as a rich component were reported there owing to the unsuccessful of producing their single crystals. Recently, we have fulfilled the time-consuming work and were able to obtain the single crystals of sPPBU copolymers with 1-butene concentration higher than 50 mol % up to 98.6 mol %. The electron diffractions on these single crystals clearly indicate that the samples with more than 30 mol % propene exhibit equal intensity (110) and (010) reflections, which indicates that the *C*-centered packing manner of form I of sPB-1,[14] which is similar to that of

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Table 1. Characteristic Data of Poly(propene-*co*-1-butene)s

sample	copolymer composition (mol % of propylene)	melting temp (°C)	crystallization temp (°C)
sPB-1	0	48	RT
sPPBU(1)	1.4	47	RT
sPPBU(2)	9.1	50	RT
sPPBU(3)	34.7	56	52
sPP	100	146	99

form II of sPP,[15] is always predominant for the sPPBU copolymers with 1-butene as a rich component. These reflections contributed a broadened X-ray reflection peak in the 2θ range of 15°−16° and has been indexed simply as the (110) in previous study. Moreover, the bright field electron micrographs demonstrate the morphological change of the copolymers, which reflects the influence of the incorporated propylene comonomeric units on the crystal growth habit of sPB-1. In this paper we present a study of the influence of the propylene component in sPPBU samples on the morphology as well as structure of the sPB-1 single crystals. Understanding the effect of the comonomer composition on the crystallization habit and morphology of sPPBU copolymers may give new insights into the outstanding mechanical properties and elastic behavior of these materials.[16,17]

Experimental Section

Samples of sPPBU copolymers were synthesized with a single center syndiospecific catalyst composed of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane with the method described in ref 4. All the samples used in this work correspond to the samples reported in ref 4.

The melting and crystallization temperatures of the homopolymers and the corresponding copolymers with different composition, which were obtained with a differential scanning calorimeter Perkin-Elmer DSC-7 performing scans in a N_2 atmosphere at heating rate of 10 °C/min, are reported in the Table 1. The composition was determined by the analysis of the ^{13}C NMR solution spectra, recorded on a Bruker AM300 spectrometer at 120 °C in deuterated tetrachloroethane.[4] The copolymers, according to this analysis, are random and homogeneous in composition. It is worth noting that the used catalyst is highly regiospecific and, under the same conditions adopted for the preparation of sPPBU copolymers, produces highly stereoregular sPP and sPB-1 homopolymers, with rrrr pentad concentration higher than 90 mol %.[4−6,10,14,15] In the cases of sPPBU copolymers, no regio-defects have been observed by ^{13}C NMR analysis, whereas the degree of stereoregularity remains constant with the propene concentration and similar to that of sPB-1. This allows for the analysis of the effect of the sole concentration of propene units on the structure and morphology of sPPBU single crystals.

To grow sPPBU single crystals, ultrathin sPPBU films were at first prepared by casting their 0.1 wt % xylene solutions on carbon-coated copper grids at room temperature. After the evaporation of the solvent, the obtained ultrathin sPPBU films were heat-treated at temperatures 80 °C for 5 min to erase completely their previous morphologies, and subsequently cooled to desired temperatures, where isothermal crystallization was allowed for about several weeks to several months due to their lower crystallization rate.

For transmission electron microscopy observations, a JEM 100CX TEM operated at 100 kV was used in this study. While the bright-field (BF) observations were done with platinum shadowed specimens, unshadowed samples were used for the selected area electron diffraction work.

Results and Discussion

For a better comparison, we presented first the bright-field (BF) electron micrograph and the corresponding diffraction pattern of the sPB-1 single crystal in Figure 1.[11] The BF electron micrograph (Figure 1a) shows that the sPB-1 single crystal exhibits a regular rectangular shape with nonsmooth lateral facets. Also, the surface of the single crystal is not so flat. With careful inspection, some ridges with similar shape of the single crystal can be recognized. They may be associated with the changes in fold period corresponding to the changes in crystallization temperature since it has been grown at ambient temperature for several months. The corresponding electron diffraction pattern (Figure 1b) indicates that the long axis of the single crystal is along its crystallographic *b*-axis. From Figure 1b, sharp (*hk*0) electron reflection spots can be observed, implying a flat-on structure of the crystal with the molecular chains oriented parallel to the lamellar thickness direction since the crystals have not been tilted in the electron microscope. All these reflections can be accounted for by the orthorhombic unit cell with axes a = 1.681 nm, b = 0.606 nm, and c = 0.773 nm proposed by De Rosa et al.[14] Moreover, the appearance of only reflections with $h+k = 2n$ on the diffraction pattern, in particular, the presence of the strong (110) reflection and the absence of the (010) reflection, clearly indicates a *C*-centered packing of isochiral chains according to the space group $C222_1$. This result is in good agreement with the model of packing proposed by De Rosa et al.[14]

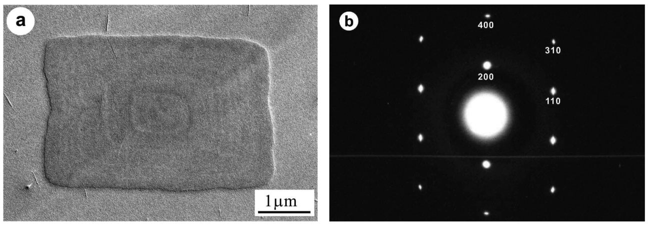

Figure 1. (a) BF electron microscopy image and (b) the corresponding electron diffraction pattern of a sPB-1 single crystal, which was crystallized at room temperature for several months.

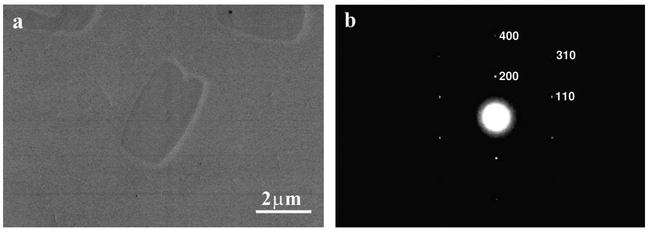

Figure 2. (a) BF electron microscopy image and (b) the corresponding electron diffraction pattern of single crystals of the sPPBU(1) copolymer with 1.4 mol % of propene.

Single crystals of the sPPBU(1) copolymer sample with 1.4 mol % of propene (Table 1) have been obtained by aging the supercooled melt at room temperature for about 6 months. Electron microscopy observation shows that the sPPBU(1) single crystals have a close resemblance with the sPB-1 single crystals shown in Figure 1a. A representative BF electron micrograph of the sPPBU(1) single crystals is shown in Figure 2a. The sPPBU(1) single crystals exhibit also a regular rectangular shape. Unlike the sPB-1 single crystals, they show very smooth top surfaces and regular lateral facets. The reason for the different surface and facet regularity is not clear at the moment. The corresponding electron diffraction pattern of the observed single crystals (Figure 2b) is exactly the same as that of the sPB-1 single crystals (compare Figure 2b with Figure 1b), indicating a *C*-centered packing of isochiral s(2/1)2 helical chains in the orthorhombic unit cell. Similar to the sPB-1 single crystals, the crystallographic *b*-axis is also parallel to the long axis of the rectangular single crystals. These results clearly indicate that a small amount of

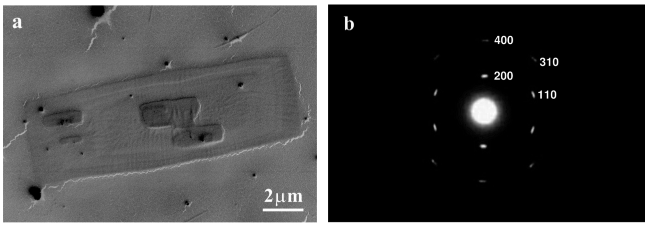

Figure 3. (a) BF electron microscopy image and (b) the corresponding electron diffraction pattern of single crystals of the sPPBU(2) copolymer with 9.1 mol % of propene crystallized at room temperature for ca. 3 months.

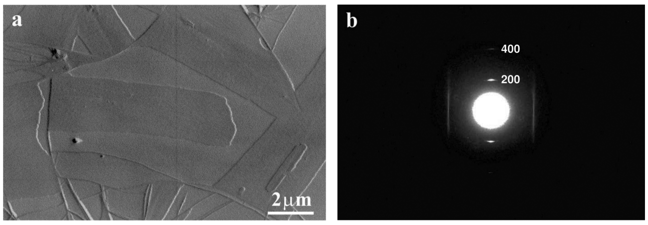

Figure 4. (a) BF electron microscopy image and (b) corresponding electron diffraction pattern of single crystals of the sPPBU(3) copolymer with 34.7 mol % of propene. The sample has subjected a thermal treatment at 100 °C for 5 min and then isothermally crystallized at 52 °C for about 15 days.

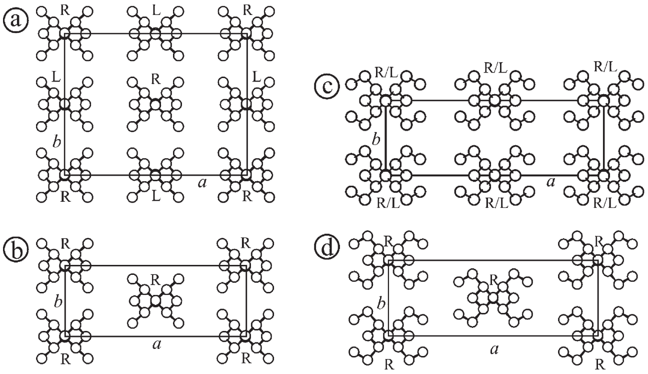

Figure 5. Models of chain packing in form I of sPP (a), form II of sPP (b), form I′ of sPB-1 (c), and form I of sPB-1 (d). The metastable form I′ of sPB-1 (c) has been found in oriented fibers of sPPBU copolymers with low concentration of propene units (lower than 30 mol %) stretched at high deformation.[9,10] In part c the symbol R/L indicates that in the structure of form I′ of sPB-1 disorder in the packing of right (R)- and left (L)-handed helices is present;[9] that is, in each site of the lattice right- and left-handed chains can be found with the same probability.

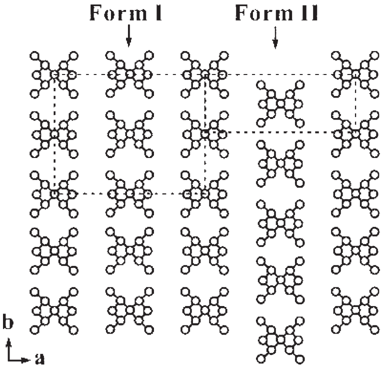

Figure 6. A sketch showing the packing defect that produces the streaks along the *h*20 (or *h*10) layer around the 020 (or 010) reflection along *a*-axis direction in the electron diffraction patterns of single crystals of sPP and of propene-rich sPPBU copolymers (see Figure 8).

propene comonomeric unit (e.g., 1.4 mol %) has no detectable effect on the intermolecular chain packing of sPB-1.

The BF electron micrograph and corresponding electron diffraction pattern of ultrathin films of the sPPBU(2) copolymer with 9.1 mol % of propene, isothermally crystallized at room temperature for ca. 3 months, are shown in Figure 3. From the BF image (Figure 3a), one can see that there are several different morphological features of the sPPBU(2) single crystals as compared with the sPPBU(1) and sPB-1 ones. First of all, even though the sPPBU(2) single crystals exhibit still a rectangular shape, they are evidently elongated. The sPPBU(2) single crystals appear now as lathlike single crystals. The aspect ratio for the underlying lath (ca. 3) is larger than those of both the sPPBU(1) and sPB-1 single crystals, which is about 1.5 for both cases. Second, screw dislocation is observed in Figure 3a, which induces the multilayer overgrowth of the single crystals. Third, in the boundary area, especially along the long axis direction, the single crystal is somewhat thicker than the center part of it. Moreover, another interesting feature of the sPPBU(2) single crystals is the appearance of the ripples or undulations, which have been reported by Lovinger and Lotz et al.[18] to be one of the exceptional characteristics of sPP single crystals. All these features indicate that incorporating 9.1 mol % of propene comonomeric units in the sPB-1 leads to the crystal growth habit of the copolymer more or less similar to that of the sPP homopolymer. The corresponding electron diffraction pattern (Figure 3b) shows, however, the same *C*-centered packing of isochiral s(2/1)2 helical chains in the orthorhombic unit cell, even though the reflection spots are not as sharp as those shown in Figures 1b and 2b. This indicates that the presence of 9.1% propene comonomeric units in the copolymer changes the morphology remarkably and the crystal perfection slightly but does not change the packing manner of the sPB-1.

When crystallizing the sPPBU(3) with 34.7 mol % of propene at 52 °C for 15 days, as shown in Figure 4a, abundant long lath flat-on crystals with quite smooth top surface, which have to some extent a close analogue with the sPP homopolymer,[19] have been observed. The electron diffraction pattern of the flat-on crystals is shown in Figure 4b. It is apparent from Figure 4b the presence of the broadened 200 and 400 reflection spots located at the same positions as those in Figures 1b−3b, and of clear streaks along the *h*10 layer, connecting the 110 reflections of the sPB-1 or the copolymers with lower propene content along the *a*-axis direction. This kinds of streaks has also been observed for the sPP homopolymer in the case, for instance, of single crystals grown at low temperatures,[20] and is analogous to the broadening of the 010 reflection of form I of sPP observed in powder samples crystallized from the melt at low temperatures.[21] These features of electron and X-ray diffractions indicate the presence of structural disorder and are related to the complex polymorphism of sPP, which crystallize in at least four different crystalline forms.[13,15,20−29] As illustrated in Figure 5, the stable helical form I of sPP is characterized, in the limit ordered structure, by a regular alternation of right- and left-handed s(2/1)2 helical chains along both *a*- and *b*-axes of the unit cell (Figure 5a).[13,20,21,23] The metastable helical form II is characterized by isochiral s(2/1)2 helical chains packed in a *C*-centered orthorhombic unit cell (Figure 5b).[15,24,28] As well explained by Lotz and Lovinger et al.,[20] the observed streaks indicate the presence of disorder in the stacking of *bc* layers of chains in form I crystals, which is caused by a *b*/4 shift of consecutive *bc* layers along the *b*-axis (*b*/4 shifts disorder, see Figure 6).[20,21] This disorder produces local arrangements of the s(2/1)2 helical chains like in the *C*-centered form II of sPP (Figure 5b). These streaks have also been observed in the electron diffraction patterns of single crystals of propylene-rich sPPBU copolymers when the concentration of 1-butene units is higher than about 4−5 mol %,[12] indicating the occurrence of

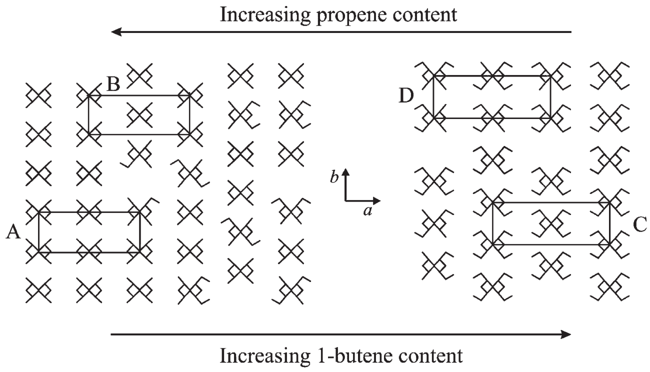

Figure 7. Models of packing of s(2/1)2 helical chains of sPPBU copolymers as a function of butene concentration. The unit cells of the *B*-centered form I of sPP (A), the *C*-centered isochiral form II of sPP (B), the *C*-centered isochiral form I of sPB-1 (C), and *B*-centered form I′ of sPB-1 (D) are indicated. For propene-rich copolymers $b/4$ shift defects produce local arrangements of chains as in the *C*-centered form II of sPP (B) or form I sPB (C) in a prevailing mode of packing of the *B*-centered form I of sPP (A). At high butene content, $b/4$ shift defects 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-1 (C) and form II of sPP (B).

the same $b/4$ shift defects as in Figure 6, in a prevailing mode of packing of the *B*-centered form I of sPP.[12]

On the other hand, the stable form I of sPB-1 with same s(2/1)2 helical chain conformation is characterized by a isochiral *C*-centered packing of the helical chains (Figure 5d),[14,30,31] i.e., a chain packing similar to that of form II of sPP. Moreover, it has been recently shown that butene-rich sPPBU copolymers with concentration of propylene comonomeric units lower than 30 mol % may show the same polymorphism as sPP; that is, they may crystallize in oriented fibers into the stable *C*-centered isochiral form I (Figure 5d) and into the metastable form I′ (Figure 5c) that presents a chain packing similar to that of form I of sPP (Figure 5a) but with statistical positioning of right- and left-handed helical chains on the sites of the lattice.[9,10]

Taking all these into account, the appearance of the streaks in electron diffraction patterns of single crystals of both propylene-rich and butene-rich sPPBU copolymers demonstrates the mutual influence of the butene and propylene components on the crystallization of these copolymers. Accordingly, sPPBU copolymers crystallize in different structures, shown in Figure 7, intermediate between those of form I of sPP and form I of sPB-1, depending on the composition.[10] In sPPBU samples with butene content below 60−70 mol % the presence of $b/4$ shift defects implies the presence of local arrangements of the chains as in the *C*-centered form II of sPP (Figure 7B) or form I of sPB-1 (Figure 7C) in a prevailing mode of packing of the *B*-centered form I of sPP (Figure 7A). The amount of $b/4$ shift disorder increases with increasing butene content. For butene-rich copolymers (butene contents higher than $\approx$60 mol %), the mode of packing of the *C*-centered form I of sPB-1 (Figure 7C) and form II of sPP (Figure 7B) becomes prevalent over that of Figure 7A, and local arrangement of the chains such as in the *B*-centered form I of sPP (Figure 7A) becomes a defect (Figure 7D) due to the presence of $b/4$ shift disorder.[10] The amount of this stacking fault disorder increases with increasing propylene content.

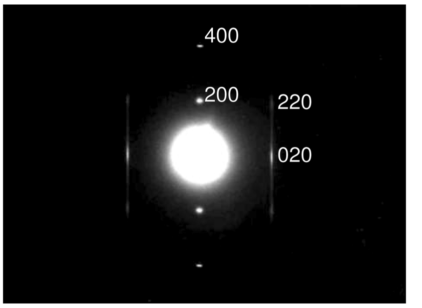

Figure 8. An electron diffraction pattern of the single crystals of a sPPBU copolymer with 52.1 mol % of propylene, which has been heated to 100 °C for 5 min and then isothermally crystallized at 63 °C for 2 days.[12] The streaks around the *h*20 reflections, along the *a*-axis direction, show clearly the intensity maxima at the positions of 020 and 220 reflections.

From the above results, it is clear that incorporation of propylene units in the sPB-1 chains influence the crystallization behavior of sPB-1. The influence of the propene units on the crystallization behavior of sPB-1 presented in this work is, however, different from the influence of 1-butene units on the crystallization behavior of sPP as reported in ref 12. First of all, for the propylene-rich sPPBU copolymers the effect of 1-butene on the chain packing of sPP in its stable form I is evident when the content of 1-butene is higher than 4−5 mol %. On the contrary, for the 1-butene-rich sPPBU copolymers no detectable influence of propene units on the chain packing of sPB-1 has been recognized even when the concentration of propene component reaches 9.1 mol %. This is reasonable when the $b/4$ shifts disorder as a characteristic feature of the sPP homopolymer crystallized at relatively low temperature is considered.[20,21] For these copolymers, even though it was confirmed that chain sequences of one comonomeric unit can be included into the crystalline phase of the other homopolymer, the crystallization of the polymorphic form of the majority component is expected. Therefore, the propene-rich sPPBU copolymers exhibit mainly the crystallization habit of sPP.[4,12] As a result, the $b/4$ shifts disorder, which is revealed as the broadening of the (020) reflection at $2\theta = 16°$ in the X-ray powder diffraction profiles and the streaks in the electron diffraction patterns, could be easily observed.[4,12] Moreover, the increase of this disorder with 1-butene content also indicates that the 1-butene units play an important role in producing the $b/4$ shifts disorder of sPP. Consequently, a small amount of 1-butene units in the copolymer already encourage the formation of the disorder. On the other hand, for the 1-butene-rich copolymers, the crystallization of sPB-1 sequences is the key factor governing the crystallization of the copolymers. The minor propene component is most likely incorporated into the sPB-1 crystalline phase, which can be deduced by the slight reduction of both *a* and *b* values with increasing propene content as calculated from the electron diffractions. In this way, it will not produce the $b/4$ shift at all. As a result, for low propylene concentrations, up to nearly 9−10 mol %, the $b/4$ shifts disorder is almost absent or too small to be detected under electron diffraction.

Moreover, the electron diffraction data indicate that the predominant packing models of the propene-rich and 1-butene-rich copolymers are different, confirming the hypothesis of Figure 7.[4,10] The streaks in the electron diffraction patterns of propene-rich copolymers, as shown in Figure 8 as an example, exhibit always clear intensity maxima at the locations of 220 and 020 reflection spots for the form I unit cell of Figure 5a. This indicates that the *B*-centered packing of form I of sPP of Figure 5a, with substantial amount of the $b/4$ shifts disorder, is always the predominant packing scheme in the single crystals of the copolymers with 1-butene content up to 50 mol %. For the 1-butene-rich copolymers, even though the streaks appear at the usual position (Figure 4b), the intensity distribution is quite different from that observed in propene-rich copolymers; compare Figure 4b with Figure 8. One can see that the intensity of the streaks at the center *b*-axis positions, i.e., the 020 reflection of form I sPP (or 010 reflection of form I sPB-1) in Figure 8, is about the same as that at the 110 reflection of the form II sPP in

Figure 4b. At the same time, in the pattern of Figure 4b the 220 reflection (or 210 reflection) of the stable form I sPP can be hardly recognized. This unambiguously indicates that the 1-butene-rich sPPBU copolymers crystallize predominantly in a *C*-centered packing way of form I of sPB-1 or the form II of sPP.

As a final remark, we point out that the changes in the crystal structure of the sPPBU copolymers produced by the increase of propene concentration induce large change in the crystal morphology. In particular, the rectangular shape of single crystals of sPB-1 homopolymer[11] and sPPBU copolymers with propene concentration lower than 2 mol % (Figures 1 and 2) and the lathlike shape of single crystals of sPP homopolymer[13,18,20,22] and sPPBU copolymers with propene concentration higher than 9 mol % (Figures 3 and 4) are a variant of a same basic habit reflecting the orthorhombic space group symmetry of the corresponding unit cells. In all cases the long axis of the basal face of single crystals is parallel to the crystallographic *b*-axis, whereas the short axis is parallel to the *a*-axis.

The change of aspect ratio of the single crystals with increasing propene concentration, and, in particular, the fact that the habit of single crystals of sPPBU(1) with 1.4 mol % propene is similar to that of sPB-1 homopolymer, whereas the habit of single crystals of sPPBU(2) and sPPBU(3) with 9 and 34.7 mol % propene, respectively, becomes similar to that of sPP, while the chain packing keeps more similar to that of sPB-1, may be explained considering that, in general, single crystals are bounded by the crystallographic faces of closest packing, which also correspond to the planes of slowest growth rate at a given temperature. Overall, the shape of single crystals depends on the relative growth rate of the lowest energy (closest packing) crystallographic faces. In the case of sPP the chains are closely packed along *b* and more loosely packed along *a*.[13,18,20] Therefore, the planes {100} are those of closest packing, and the growth rate of crystals along the *a*-axis direction is remarkably lower than that along the *b*-axis. As a consequence the crystal habit assumes the characteristic lathlike shape with typical dimensions along *b* higher than those along *a*.[19]

Also in the case of sPB-1 the {100} planes corresponds to the planes of closest packing.[10,14,17] However, in this case, owing to the double gauche conformation of lateral ethyl groups, the methyl groups are directed along the *a*-axis (Figure 5d),[14] producing a more effective interlocking of adjacent chains along *a* than in sPP. At the same time in the crystals of sPB-1 the outside envelope of the chains along *b* is smoother than that in sPP crystals. The rectangular shape of single crystals of sPB-1 is therefore characterized by a low aspect ratio probably because the growth rates along *a* and *b* are more similar than in the case of sPP. In sPPBU copolymers for low propene concentrations both the crystal habit and the packing of chains are namely driven by the close interlocking of lateral ethyl groups along both *a*- and *b*-axes and the methyl groups of propene units act only as a small disturbance. This explains the similar crystal habit of single crystals of sPB-1 homopolymer and sPPBU(1) copolymer with 1.4 mol % propene. For propene concentration higher than 9 mol % the disturbance effect of propene counits increases, producing a neat increment of *b*/4 shift disorder and less interlocking of chains, especially along *a* (see Figure 7). As a result, single crystals grown from sPPBU(2) and sPPBU(3) samples with 9 and 34.7 mol % propene (Figures 3 and 4), respectively, become more similar to that of sPP, even though the chains are still packed in disordered modification more similar to the *C*-centered packing scheme of form I sPB-1.

Conclusions

Single crystals of syndiotactic poly(propene-*co*-1-butene) (sPPBU) copolymers with 1-butene as the rich component were produced by time-consuming ultrathin film growth from their melts and studied by transmission electron microscopy combined with electron diffraction. Bright field electron microscopy observation shows that the sPPBU single crystals exhibit rectangular or lathlike shapes with their long axes along their crystallographic *b*-axis. Incorporating propene units in the sPB-1 chains influences the crystallization behavior of the sPB-1 significantly. The aspect ratio of the single crystals increases with increasing the propene units, resulting in copolymer single crystals more similar to those of the sPP homopolymer. However, only one of the characteristic features of the highly stereoregular sPP, i.e., the presence of irregular ripples or surface undulations, is occasionally observed. The electron diffraction results indicate that a small amount of propene units, up to 9−10 mol %, shows no detectable effect on the *C*-centered chain packing of form I of sPB-1. The propene units are most likely included into the crystalline structure of sPB-1. For much higher propene content, around about 30 mol %, the *b*/4 shift disorder takes place, as deduced from the presence of streaks around the *h*10 layer, connecting the 110 reflections, along the *a*-axis direction in the electron diffraction patterns. According to the intensity distribution of the streaks, the *C*-centered chain packing with substantial amount of disorder is still the predominant packing scheme in the single crystals of the 1-butene-rich copolymers.

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References and Notes

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