TEM Studies on Single Crystal Structure of Syndiotactic Poly(Propene-*co*-butene-1)s

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ABSTRACT: Themorphologies and structures of single crystals of syndiotactic poly(propene-*co*-1-butene) (PPBU) with 1-butene contents of 2.6, 4.2, 9.9, 16.2, and 47.9 mol % are studied by transmission electron microscopy and electron diffraction. The electron diffraction results show that the 1-butene units are included in the crystalline phase of the sPP homopolymer. A small amount of 1-butene (<4.2 mol %) has no significant influence on the antichiral chain packing of sPP. With increasing content of 1-butene units, an increasing packing disorder is observed in the PPBU copolymers. The antichiral packing model is, however, always the predominant chain packing structure of the copolymers with the analyzed composition. Bright-field electron microscopy observation shows that the PPBU single crystals exhibit always regular rectangular or lathlike shapes with preferred growth direction along their crystallographic *b*-axes owing to their packing features. The incorporated 1-butene units influence the crystallization behavior of sPP distinctly. With the increase of the 1-butene units, the aspect ratio of the single crystals increases. Furthermore, the typical transverse microcracks and ripples of the highly stereoregular sPP are no more so prominent for the copolymers. The microcracks are occasionally observed in the single crystals of copolymers with low 1-butene content (≤4.2 mol %), while transverse ripples are only seen in the crystals of the copolymer having a 1-butene content of 9.9 mol %. With a further increase in the content of 1-butene units, the copolymers behave like the low stereoregular sPP, where neither cracks nor ripples are observed any more.

Introduction

The development of the new metallocene catalyst systems has made it possible to produce highly syndiotactic polyolefins, such as syndiotactic polypropylene (sPP)[1] and syndiotactic poly(butene-1) (sPB-1).[2] Increasing interest has emerged during the past few years on the structural and morphological studies of new syndiotactic polymers.

The existence of three different chain conformations of sPP, i.e., the trans planar, the s(2/1)2, and the $(T_6G_2T_2G_2)_n$ helical conformations, and the possibility of different modes of packing of the s(2/1)2 helical chains lead to the complex polymorphism of sPP.[3−15] Four different crystalline forms of sPP have been found.[3−6,9,11,12] As illustrated in Figure 1, the stable form (form I) is characterized, in the limit ordered structure, by a regular alternation of right- and left-handed helical chains along both *a* and *b* axes of the unit cell (Figure 1A).[3−6,12,13] The metastable helical form (form II) is obtained in fiber samples and characterized by isochiral s(2/1)2 helical chains packed in a *C*-centered orthorhombic unit cell (Figure 1B).[9,11,14] Forms III[7] and IV[8,15] are characterized by chains in trans-planar and $(T_6G_2T_2G_2)_n$ helical conformations, respectively.

sPB-1 exhibits also pronounced polymorphic behavior. Two different crystalline modifications have been found so far.[16−20] Form I of sPB-1 (following the nomenclature proposed in ref 16) is characterized by the same s(2/1)2 helical conformation of the chains[16] as the dominant forms of sPP, and a chain packing similar to the form

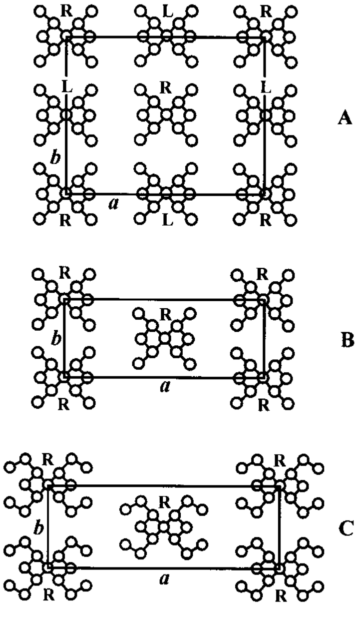

Figure 1. Models of chain packing in form I of sPP (A), form II of sPP (B), and form I of sPB-1 (C).

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II of sPP, i.e., a *C*-centered packing of helical chains having the same chirality (Figure 1C).[17,20] It is worth noting that the *C*-centered packing is the favorable and stable form of sPB-1. Form II is obtained in oriented sPB-1 fibers drawn at high draw ratios and is characterized by chains in an s(5/3)2 helical conformation packed in a monoclinic unit cell.[19]

Recently, the structural characterization of syndiotactic poly(propene-*co*-1-butene) (PPBU) has been reported.[21−26] The PPBU samples maintain crystallinity over the whole range of 1-butene content.[21,23] Thermal analysis of these copolymers has shown a depression of the melting temperature with the increase of the 1-butene content.[21,26] 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 observed by X-ray diffraction.[21,23] This indicates that the comonomeric units, 1-butene or propene, are included in the unit cells of both homopolymers. This is due to the very similar crystal structures of sPP and sPB-1 in their stable 2-fold helical forms (Figure 1). The cocrystallization of the two comonomers has also been confirmed by the solid state ^{13}C NMR spectra of the copolymers, which indeed present resonances of the methylene carbons belonging to propene−butene sequences in the crystalline phase.[25] Moreover, the polymorphic behavior of PPBU copolymers in melt-crystallized samples and oriented fibers has also been analyzed.[26] It has been found that inclusion of 1-butene units in the crystalline phase of sPP occurs also in the melt-crystallized samples and in stretched fibers of the copolymers[26] and affects the polymorphic behavior of sPP. In particular, the copolymers 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 always present.[23,26] With increasing content of 1-butene, the *b*/4 shift disorder increases, and any correlation among the chirality of the chains along the axes of the unit cell is lost at long distances.[23,26]

The crystal morphologies of the copolymers have, however, not been reported yet. Moreover, the presence of an increasing amount of disorder with high concentration of butene produces a broadening of the X-ray reflection peaks, preventing a clear recognition of the prevalent mode of packing.[26] Electron diffraction of single crystals could give a more precise indexing of the reflections and more information about the kinds and the amount of structural disorder present as a function of the butene content. The morphological and electron diffraction analyses are, therefore, of great importance for investigating the influence of 1-butene comonomeric units on the crystalline structure and crystallization behavior of sPP.

In this work, single crystals of the syndiotactic poly(propene-*co*-1-butene)s, with the propene units as the rich component, were produced by ultrathin film growth from their melts, and their morphologies and crystalline structures were investigated by transmission electron microscopy (TEM) and electron diffraction analysis.

Experimental Section

Samples of PPBU 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 23. All the samples correspond to the samples reported in ref 23.

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

sample	copolymer composition (mol % of butene)	melting temp (°C)	crystallization temp (°C)
PPBU(1)	2.6	130	82
PPBU(2)	4.2	123	67
PPBU(3)	9.9	101	45
PPBU(4)	16.2	97	40
PPBU(5)	47.9	64	40

The composition and the melting temperatures of the copolymers are reported in 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.[23] The copolymers, according to this analysis, are random and homogeneous in the composition. The melting and crystallization temperatures were obtained with a differential scanning calorimeter Perkin-Elmer DSC-7 performing scans in a N_2 atmosphere at heating rate of 10 °C/min.

To grow PPBU single crystals, ultrathin PPBU 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 PPBU films were heat-treated at temperatures 50 °C above their measured melting temperatures to erase completely their previous morphologies and subsequently cooled to temperatures a few degrees below their melting temperatures, which were determined by temperature gradient as the highest crystallization temperatures for each copolymers, where isothermal crystallization was allowed under dried nitrogen for about 2 days.

For transmission electron microscopy observations, a Philips CM200 TEM operated at 200 kV was used in this study. While the bright-field (BF) observations were done with platinum shadowed specimens, unshadowed samples were used for the select area electron diffraction work.

Results

Figure 2 shows a BF electron micrograph and the corresponding electron diffraction pattern of the single crystals of the PPBU(1) copolymer with 2.6 mol % of butene, isothermally crystallized at 125 °C for 2 days. The BF electron micrograph (Figure 2a), shows large regular rectangular shaped lamellar single crystals. These single crystals contain multilayer overgrowths with very smooth top surfaces and relative regular end facets. The corresponding electron diffraction pattern of the observed single crystals (Figure 2b) has a close resemblance with the electron diffraction pattern of the sPP single crystals in its stable form I.[3] The sharp electron diffraction spots correspond to the equatorial *hk*0 reflections, with sharp and well-defined 200 and 020 reflections. Therefore, the electron diffraction pattern indicates a packing of the s(2/1)2 helical chains in the orthorhombic unit cell similar to that of form I of sPP (Figure 1A). Similar to the sPP single crystals, the crystallographic *b* axis is parallel to the long axis of the rectangular single crystals as deduced from the electron diffraction pattern. These results clearly indicate that a small amount of 1-butene comonomeric unit (e.g., 2.6 mol %) has no significant effect on the intermolecular chain packing as well as on the crystalline morphology of sPP.

The BF electron micrograph and the corresponding electron diffraction pattern of ultrathin films of the PPBU(2) copolymer with 4.2 mol % of 1-butene, isothermally crystallized at 120 °C for 2 days, are shown in Figure 3. In the BF image (Figure 3a), the appearance of the PPBU(2) single crystal is quite similar as those observed in Figure 2a. It should be pointed out that the

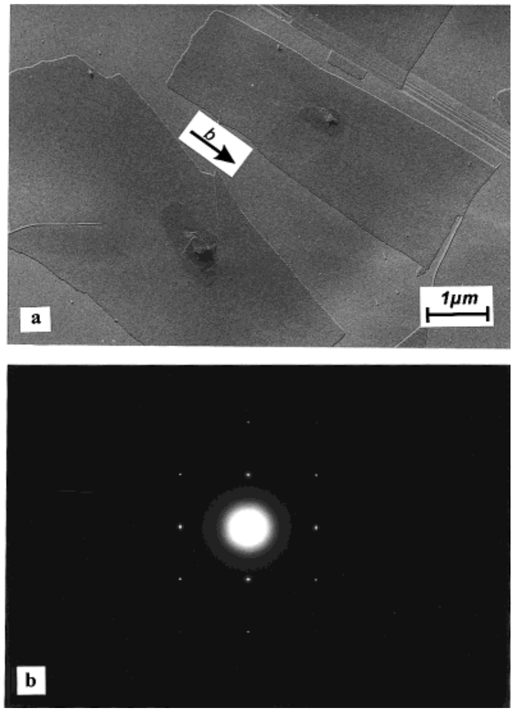

Figure 2. BF electron microscopy image, shadowed with platinum, of single crystals of the PPBU(1) copolymer with 2.6 mol % of 1-butene (a) and the corresponding electron diffraction pattern (b). The sample was annealed at 180 °C for 5 min and then isothermally crystallized at 125 °C for 2 days. The crystallographic *b* axis is along the long dimension of the crystal as indicated by an arrow.

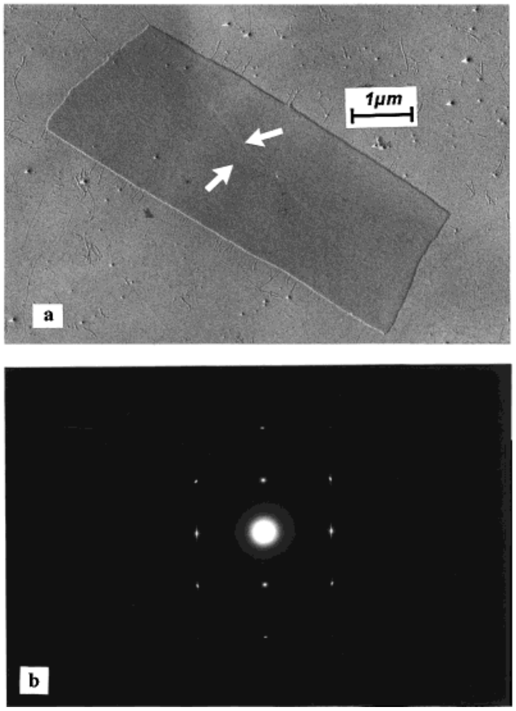

Figure 3. BF electron microscopy image, shadowed with platinum, of single crystals of the PPBU(2) copolymer with 4.2 mol % of 1-butene (a) and the corresponding electron diffraction pattern (b). The sample has subjected to a thermal treatment at 170 °C for 5 min and then isothermally crystallized at 120 °C for 2 days. The arrows in the picture indicate the two sector lines of the single crystal.

sectorization of the PPBU single crystal has also been recognized here despite of the quite smooth top surface of the single crystal. As indicated by arrows in the picture, two sector lines are found along the diagonal directions of the regular single crystal and divide the crystal into four sectors. The two sectors having the short edge (the *a* axis) are slightly thinner than those with the long edge (the *b* axis). This has a close analogue with the sPP homopolymer.[27] On the boundary of the single crystals, few short edge-on lamellae, grown transverse to the end facets of the lamellar single crystal, are observed. These may originate from rejected material, which is crystallized after cooling the sample to room temperature. The rejected material may be associated with (i) chemically disordered molecules due to the incorporation of the 1-butene comonomeric units in the polymer chain or (ii) low molecular weight molecules fractionated during high-temperature growth.

The electron diffraction pattern of Figure 3b presents, besides the sharp reflection spots located at the same positions as those in Figure 2b, weak streaks around the (*h*20) reflections along *h*. At the same time, the (020) reflection is now slightly broadened while the (200) and (400) reflection spots remain sharp. As already well documented by Lotz and Lovinger et al.,[6] these streaks indicate the presence of disorder in the stacking of *bc* layers of chains piled along the *a* axis. This disorder implies shifts along the *b* axis of *b*/4 among consecutive *bc* layers (*b*/4 shifts disorder),[6,13] and produces local arrangements of the chains like in the *C*-centered form II of sPP (Figure 1B) or form I of sPB-1 (Figure 1C). We recall that the *b*/4 shifts disorder occurs for the sPP homopolymer in the case, for instance, of single crystals grown at low temperatures[6] and for powder samples crystallized from the melt at low temperatures.[13] As discussed in the Introduction, the presence of this kind of disorder has also been suggested for the PPBU copolymers,[23,26] because of the broadening of the 020 reflection at $2\theta = 16°$ in the X-ray powder diffraction profiles, the amount of disorder being dependent on the butene content. The presence of streaks in the electron diffraction pattern of Figure 3b confirms the occurrence of this kind of disorder.

The electron diffraction results indicate that in single crystals of the PPBU(2) copolymer the *b*/4 shifts disorder is present only as defects in a prevailing mode of packing of form I of sPP (Figure 1A). Since the sample has been crystallized at the highest temperature, the observed disorder cannot be attributed to the temperature influence, but only to the influence of the 1-butene comonomeric units, confirming the inclusion of butene in the crystalline phase of sPP. This is in agreement with the results reported in the ref 26 on the melt-crystallized samples of the PPBU copolymers, which have indicated that, even though the copolymer with 4.2 mol % of 1-butene crystallizes in the *B*-centered form I (Figure 1A), 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 sPP homopolymer. More ordered modifications, close to the limit ordered, fully antichiral form I of sPP (Figure 1A), are obtained only for samples containing small amounts of 1-butene (1−2 mol %) by crystallization from the melt at high temperatures.[26] With increasing content of 1-butene, the *b*/4 shifts disorder increases, as shown by the electron diffraction pattern of Figure 3b, and this prevents the formation of any correlation among the chirality of the chains along the axes of the unit cell.

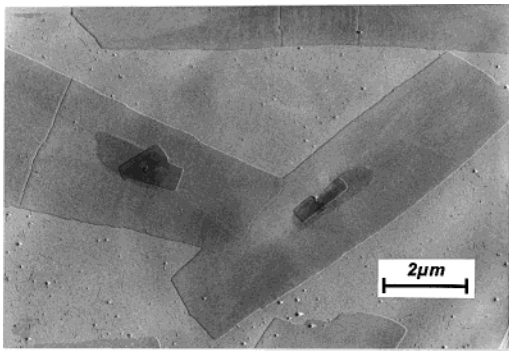

Figure 4. BF electron micrograph of single crystals of the PPBU(2) copolymer with 4.2 mol % of 1-butene, showing the microcracks formed in the single crystals isothermally grown at 120 °C for 2 days. The sample was shadowed with platinum at shallow angle.

It should be pointed out that, as reported by Lovinger et al.,[28] the formation of transverse microcracks and ripples or undulations are two exceptional characteristics of sPP single crystals. These microcracks have not at all been observed in copolymers of sPP with octene,[29] but are occasionally observed for the PPBU(1) and PPBU(2) single crystals, as shown in Figure 4. This unambiguously indicates a different impact of 1-butene and octene units on the crystallization behavior of sPP. The transverse ripples or undulations have, however, not been detected in the PPBU(1) and PPBU(2) single crystals as prepared under the present condition, even in the areas with multilamellar overlaps. This illustrates a different crystallization behavior of sPP and PPBU copolymers and reflects the influence of the 1-butene units on the crystallization behavior of the sPP.

With further increases in the content of the 1-butene comonomeric units, their effect on the crystallization behavior as well as on the crystalline structure of sPP becomes more apparent. The BF electron micrograph of the single crystals of the PPBU(3) copolymer with 9.9 mol % of 1-butene, isothermally grown at 100 °C for 2 days, is presented in Figure 5a. There are several different morphological features of the PPBU(3) single crystals as compared with the PPBU(1) and PPBU(2) ones. First of all, PPBU(3) single crystals are evidently elongated. They appear now as lathlike single crystals. The aspect ratio for the underlying lath (>7) is much larger than that for the crystal shown in Figure 3a (~2.6). Second, the lathlike single crystals are delineated by heavy irregular transverse edge-on lamellar aggregates. These transverse aggregates are found in every layer of the profuse overgrowths. This confirms that the transverse grown crystals on the sides of the single crystals are originated from the rejected materials. The fact that the amount of rejected materials increases with the increase of the 1-butene content indicates that they are most likely characterized by the chemically disordered molecules due to the incorporation of the 1-butene units in the polymer chains. Third, screw dislocation and twinning are observed in Figure 5a. As indicated by arrows in Figure 5a, the twinned underlying lamellar crystals are 52° apart from each other. This has been observed also for the sPP homopolymer and corresponds to a rotation twin with the *b* axis of the second crystal superposed along the [110] direction of the first one.[28]

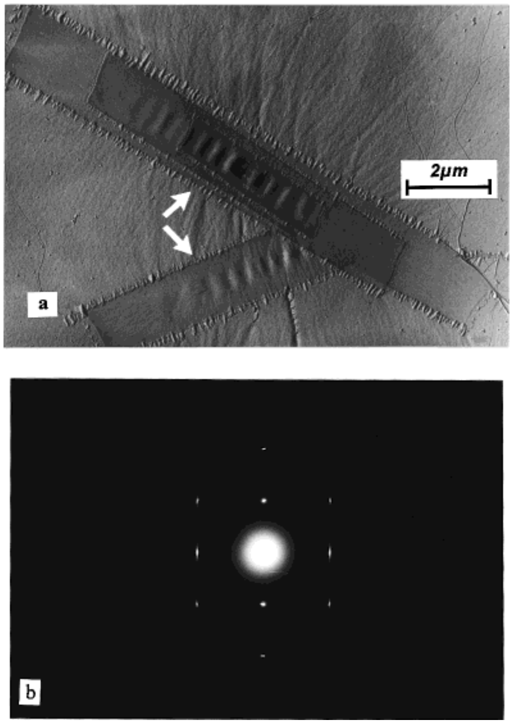

Figure 5. BF electron micrograph, shadowed with platinum, of single crystals of the PPBU(3) copolymer with 9.9 mol % of 1-butene (a) and the corresponding electron diffraction pattern (b). The sample has been isothermally crystallized at 98 °C for 2 days. The arrows in the picture indicate the twinned crystalline lamellae.

Another interesting feature in the PPBU(3) single crystals is the presence of ripples or undulations, which have not been observed for the PPBU(1) and PPBU(2) samples, as mentioned above. These ripples are clearly detected in both the monolayer and multilayer regions. Like in the case of sPP homopolymer, the ripples existing in the multilayer overgrowth region are more prominent than those in the monolayer region. This may implies the relative ease of deformation of lamellae in contact with each other with respect to those in contact to the carbon support film. On the other hand, it should be pointed out that the ripples observed for the PPBU(3) single crystal lamellae differ significantly from those observed for the sPP homopolymer.[28] While those for sPP homopolymer are seen almost always in association with the characteristic microcracks, the ripples for the PPBU(3) single crystals are formed without any microcracks, which are indeed not observed at all for the PPBU(3) single crystals prepared under the present conditions. Furthermore, the ripples are clearly more concentrated in the center regions than at the edges of the lathlike crystalline lamellae. All these aforementioned features together indicate the existence of the influence of 1-butene units on the crystallization habit of sPP.

The corresponding electron diffraction pattern of the PPBU(3) single crystals is presented in Figure 5b. Except for an increasing intensity of the streaks of the (h20) reflections along h, Figure 5b shows no distinct difference with respect to the pattern of Figure 3b. This indicates that the mode of packing of form I (Figure 1A) is still prevalent for the PPBU(3) sample but the amount of $b/4$ shift disorder is increased, in agreement with the results obtained for the powder samples.[23,26]

With higher 1-butene content in the PPBU copolymer, long regular lathlike crystals with densely, parallel, aligned edge-on lamellae, grown transversely to their

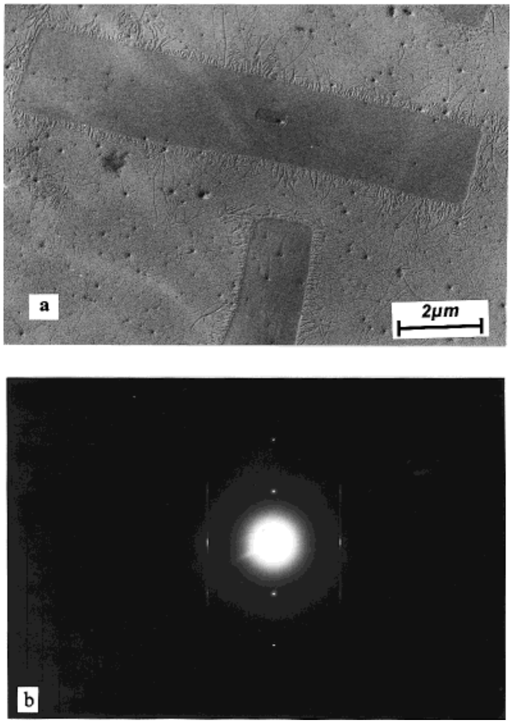

Figure 6. BF electron microscopy image, shadowed with platinum, of single crystals of the PPBU(4) copolymer with 16.2 mol % of 1-butene (a) and the corresponding electron diffraction pattern (b). The single crystals have been obtained by isothermal crystallization at 95 °C for 2 days.

long edges are the dominant morphologies. As an example, Figure 6a shows a BF electron microscopy image of the single crystals of the PPBU(4) copolymer with 16.2 mol % of 1-butene grown at 95 °C. Neither the microcracks nor the ripples are detected for these single crystals. The corresponding electron diffraction pattern (Figure 6b) present streaks around the (*h*20) reflections with maxima located still at the positions of the (020) and (220) reflections, typical of the regular *B*-centered chain packing (Figure 1A). This indicates for the PPBU(4) single crystals still a predominant packing in form I (Figure 1A) but with a high amount of *b*/4 shift disorder.

In the case of the PPBU(5) copolymer with higher 1-butene content (47.9 mol %), due to the high content of the rejected material, the formed edge-on lamellar stacks are sometimes observed even on the top surface of the underlying crystal lamellae. Figure 7a gives an example of the crystal morphology of this kind of PPBU(5) single lamella. Electron diffraction analysis shows an overall decrease of the intensity and a shortening of the lifetime (under electron beam) of the reflection spots. This implies a reduced stability of the crystals under the electron beam. Anyway, as shown in Figure 7b, the accompanying streaks on the (*h*20) layer of the reciprocal lattice with maxima on the 020 reflection can still be clearly seen.

Discussion

According to the obtained experimental results, two aspects should be addressed. The first one concerns the chain packing models of the copolymers. As already mentioned in the Introduction part, while the *C*-centered isochiral packing (Figure 1B) is the less common and stable packing model of sPP, the one shown in Figure 1C describes the most stable and favorable packing of sPB-1. As described in refs 23 and 26, powder samples of PPBU copolymers are crystallized in the *B*-centered form I (Figure 1A) of sPP up to a content of 1-butene of 60−70 mol %. Owing to the presence of the *b*/4 shift disorder, which increases with increasing butene content, structures intermediate between those of the *B*-centered form I of sPP (Figure 1A) and the *C*-centered form I of sPB-1 (Figure 1C) are obtained in the composition range 40−70 mol % of 1-butene, although the packing mode of the *B*-centered form I of sPP (Figure 1A) is still prevalent. This has been confirmed by the electron diffraction analysis of single crystals of the copolymers, since a regular *C*-centered packing has not been observed for the copolymers with the content of 1-butene ranges from 2.6 to 47.9 mol %.

The values of the unit cell parameters, evaluated from the electron diffraction patterns of single crystals, are reported in Table 2. The values of *b* axis are halved for comparison with the values evaluated from the X-ray diffraction profiles reported in refs 23 and 26. The values obtained from electron diffraction are in reasonable agreement with those obtained from the X-ray diffraction analysis.[23] With a small amount of 1-butene units, e.g., ≤4.2 mol %, no changes of the unit cell

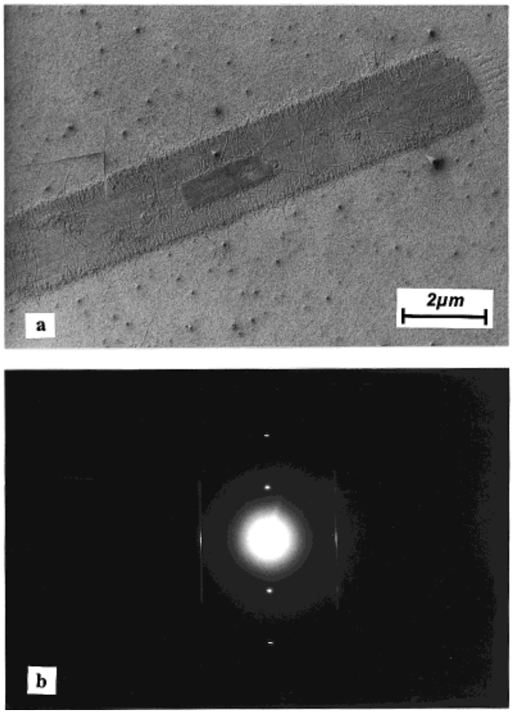

Figure 7. BF electron microscopy image, shadowed with platinum, of single crystals of the PPBU(5) copolymer with 47.9 mol % of 1-butene (a) and the corresponding electron diffraction pattern (b). Profuse edge-on lamellar stacks are evident even on the top surface of the crystal. The sample has been heated to 100 °C for 5 min and then isothermally crystallized at 63 °C for 2 days.

Table 2. Values of the *a* and *b* Axes of the Orthorhombic Unit Cells of Poly(propene-*co*-1-butene)s Obtained from Single-Crystal Electron Diffraction Patterns and X-ray Diffraction Profiles Reported in Ref 23

sample	mol % of 1-butene	*a* (nm)		*b* (nm)	
		TEM	X-ray[23]	TEM	X-ray[23]
PPBU(1)	2.6	1.446	1.450	0.558	0.557
PPBU(2)	4.2	1.446	1.452	0.557	0.558
PPBU(3)	9.9	1.470	1.477	0.561	0.562
PPBU(4)	16.2	1.467	1.487	0.568	0.563
PPBU(5)	47.9	1.546	1.563	0.573	0.574

parameters along both *a* and *b* directions are detected. When the 1-butene content exceeds 9.9 mol %, a slight expansion of both *a* and *b* axes are clearly observed. This undoubtedly implies an inclusion of the 1-butene units in the crystalline phase of the sPP.

The second aspect concerns the crystallization nature of the copolymers. We recall that the incidence of the transverse cracks and ripples is a typical characteristic of the highly syndiotactic polypropylene. Detailed studies on these two phenomena have been performed by Lovinger et al.[28] and by Tsukruk et al.[30] The cracks (originated from cleavage of the lamellae) and ripples were found to be introduced transversely during cooling by buildup stresses, as a result of the anisotropic thermal properties of the sPP crystals, namely, an order-of-magnitude greater contraction along the *b* axis (longitudinal direction of the single crystals) than along the *a* axis (transverse direction of the crystals). Taking this into account, our observed morphological features may be explained as follow. When the buildup stresses exceed a certain critical value, the microcracks occur in an attempt to release these stresses. If the stresses are too great to be released completely by the cracks solely, ripples generate to release the remaining stresses. Considering that the stresses should be concentrated at the locus where cracks are initiated, it is reasonable that the ripples are almost always observed in association with the preformed cracks. In the case of copolymers, the inclusion of 1-butene units in the crystalline phase of the sPP may reduce the buildup stresses in the same way as the effect of lowering the syndiotacticity of the polypropylene. If this hypothesis is valid, a small amount of incorporated 1-butene units may reduce the stresses to a critical value that can be released completely by the formation of the cracks. An increase of the 1-butene units, for example up to 9.9 mol %, may lead to a further reduction of the stresses to a value which is small enough to be released only by ripples, while no cracks are needed. As a consequence, ripples having no association with the cracks are produced. When the content of 1-butene units is further increased, for instance $\geq$16.2 mol %, the copolymers behave just like the low syndiotactic polypropylenes, where neither cracks nor ripples are produced.

Conclusions

Single crystals of syndiotactic poly(propene-*co*-1-butene) (PPBU) were produced by ultrathin film growth from the melts and studied by transmission electron microscopy and electron diffraction.

The electron diffraction analysis clearly indicates that the 1-butene units are included in the crystalline structure of sPP. With a small content of 1-butene (e.g., 2.6 mol %), no detectable effect of 1-butene on the chain packing of sPP in the stable form I has been recognized. With an increase in the 1-butene content, the disorder in the stacking of *bc* layers of chains piled along the *a* axis (*b*/4 shifts disorder) increases, as deduced from the presence of streaks around the (*h*20) reflection in the electron diffraction patterns. According to the results obtained for powder samples of the copolymers, the *B*-centered packing of form I of sPP, with substantial amount of disorder in the perfect alternation of right- and left-handed helical chains along the axes of the unit cell and of the *b*/4 shifts disorder, is always the predominant packing scheme in the single crystals of the copolymers up to 40−50 mol % of 1-butene. The regular isochiral *C*-centered packing of form II of sPP is not obtained in the single crystals of the copolymers for the analyzed composition and under the present conditions.

Bright field electron microscopy observation shows that the PPBU single crystals exhibit regular rectangular or lathlike shapes with their long axes along their crystallographic *b*-axes. The incorporated 1-butene units have significant influence on the crystallization behavior of sPP. First of all, with the increase of the 1-butene units, the aspect ratio of the single crystals increases remarkably. Moreover, the characteristic transverse microcracks and ripples of the highly stereoregular sPP are no longer so prominent for the copolymers. The microcracks are only occasionally observed in the single crystals of the copolymers with low 1-butene content ($\leq$4.2 mol %), while transverse ripples are solely seen in the crystals having a 1-butene content of 9.9 mol %. Copolymers with higher 1-butene content (higher than 16.2 mol %) exhibits a similar crystallization behavior as that of the low syndiotactic polypropylene. Neither transverse microcracks nor ripples are observed any more.

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