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Structural Characterization of Syndiotactic Copolymers of Propene with 1-Butene

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ABSTRACT: The structural characterization of syndiotactic copolymers of propene with 1-butene, prepared with a single-center metallocene-based catalyst, is reported. The copolymers are crystalline in a whole range of comonomer composition. The increase of *a* and *b* axes of the unit cell from the values of syndiotactic polypropylene to those of syndiotactic poly(1-butene), with increasing content of 1-butene, indicates that the comonomeric units, propene or 1-butene, are included in the unit cells of both homopolymers. As-prepared copolymers having small contents of 1-butene are crystallized in a structure similar to that of form I of syndiotactic polypropylene, although disorder in the alternation of right and left-handed helical chains along both axes of the unit cell and in the stacking of *bc* layers of chains piled along *a* (*b*/4 shifts disorder) is present. With increasing content of 1-butene, the amount of *b*/4 shifts disorder increases and disordered modifications having structures intermediate between the limit-ordered models of form I of syndiotactic polypropylene and form I of syndiotactic poly(1-butene) are obtained. Samples with a content of 1-butene higher than 70−80 mol % crystallize in a structure similar to that of form I of syndiotactic poly(1-butene) (as well as of form II of syndiotactic polypropylene).

Introduction

Syndiotactic polypropylene (s-PP) was originally prepared with vanadium-based catalysts[1] at low polymerization temperature. A poor syndiotactic polymer, having a stereoblock structure with syndiotactic sequences prevailing in respect to isotactic ones and head-to-tail regioirregular defects,[2,3] was obtained. Nevertheless the structural characterization of s-PP was reported early.[4]

Highly stereoregular and regioregular syndiotactic polypropylene has been synthesized with a new single-center metallocene-based catalyst.[5] At variance with the old vanadium-based catalysts, the new syndiospecific metallocene catalytic system for propene polymerization is also able to produce highly syndiotactic polymers of other 1-alkenes.[6]

Thanks to the high stereoregularity and crystallinity, a complete structural characterization of s-PP has been performed and its complex polymorphic behavior has been clarified.[7−19] Four limit-ordered crystalline forms of s-PP have been described. The most stable form I[7−10,15,16] (Figure 1A), and the metastable form II[4,13,19] (Figure 1C) are characterized by chains in the **s**(2/1)2 helical conformation packed in orthorhombic unit cells, whereas forms III[11] and IV[12,17] present chains in trans planar and $(T_6G_2T_2G_2)_n$ conformations, respectively.

The structural characterization of syndiotactic poly(1-butene) (s-PB), prepared with the same metallocene-based catalyst, has been also described.[20−23] Two different crystalline modifications, form I and form II, have been found for s-PB.[20] Form I is characterized by chains in the **s**(2/1)2 helical conformation[20,21] packed in an orthorhombic unit cell,[21] whereas form II is characterized by chains in a **s**(5/3)2 helical conformation[20] packed in a monoclinic unit cell.[23]

It is worth noting that the crystal structure of the most stable form I of s-PB[21] is very similar to the crystal structure of form II of s-PP.[4,13] Both are characterized by chains in the **s**(2/1)2 helical conformation packed in a *C*-centered orthorhombic unit cell[4,13,21] (Figure 1C,D). For the limit-ordered structures of both forms, the space group $C222_1$ has been suggested.[4,13,21] According to this space group, helical chains having the same chirality are included in the unit cell. We recall that form II of

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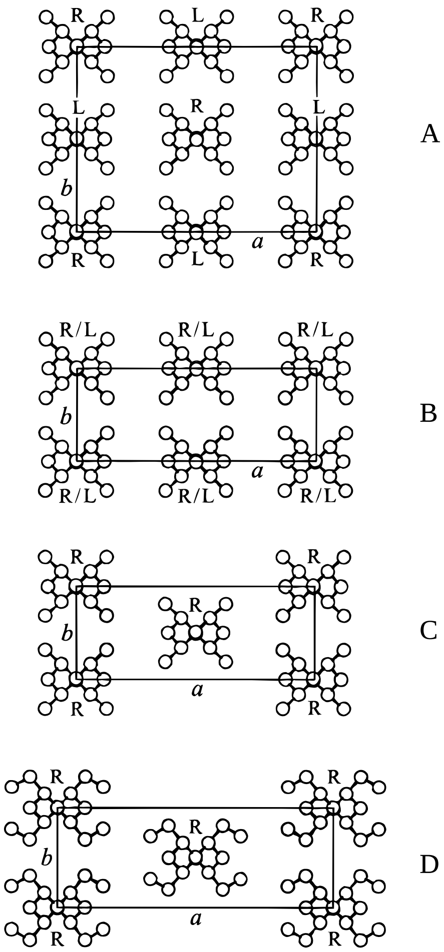

Figure 1. Models of packing of the limit-ordered form I of s-PP (A), the limit-disordered form I of s-PP (B), form II of s-PP (C), and form I of s-PB (D).

s-PP is a metastable modification of s-PP and can be obtained in oriented fibers of s-PP;[13,21] the stable form of s-PP (form I)[7−10] is characterized, in the limit-ordered structure, by a regular alternation of right and left-handed helical chains along the axes of the unit cell (Figure 1A). Form I of s-PP may be characterized by different amounts of disorder,[10,14,16] mostly consisting in departures from the fully antichiral packing,[16] the limit-disordered structural model being represented in Figure 1B.

The characterization of syndiotactic copolymers of propene with 1-butene has been recently reported.[18,24,25] The influence of the presence of small amounts of 1-butene as comonomeric unit on the polymorphic behavior of s-PP has been analyzed in ref 18, whereas Kakugo et al.[24,25] have reported an analysis of syndiotactic poly(propene-*co*-1-butene) (PPBU) in a whole range of 1-butene content. They have shown that PPBU samples maintain crystallinity over the whole range of 1-butene content, and exhibit a depression of the melting temperature lower than that of other poly(propene-*co*-olefins), which do not show crystallinity for samples containing more than 20 mol % of comonomer (ethylene, 1-pentene, 1-hexene, and 4-methyl-1-pentene).[24,25] This has been explained with the inclusion of 1-butene units in the crystalline phase of s-PP, as indicated by the expansion of the axes of the unit cell.[24,25]

In ref 25 a linear expansion of *a* and *b* axes of the unit cell with increasing the 1-butene content has been deduced. It is worth noting, however, that the value of 11.56 Å for the *b* axis of the unit cell of s-PB, reported by Kakugo et al.,[25] is incorrect, the correct one being $b = 6.06$ Å according to the crystal structure.[21] This is due to a misleading indexing of the diffraction peak at Bragg spacing $d = 5.70$ Å ($2\theta = 15.5°$, Cu Kα) of form I of s-PB as the 020 reflection instead of the 110 reflection. Also, all diffraction peaks located at $d = 5.9-5.5$ Å ($2\theta = 15-16°$) in the X-ray powder diffraction patterns of PPBU samples have been interpreted by Kakugo et al.[24,25] as the 020 reflection (as for the s-PP homopolymer),[7,10] because they assume for PPBU samples a structure similar to that of form I of s-PP (Figure 1A). The possibility of occurrence of a packing mode as in s-PB (Figure 1D) or in form II of s-PP (Figure 1C) has not been considered.[25]

In this paper, a more detailed analysis of the crystal structures of PPBU copolymers in a whole range of comonomer composition is reported in order to show the possible changes in the packing mode of s-PP and s-PB as a result of the presence of the comonomeric unit.

Experimental Part

Samples of PPBU copolymers with a content of 1-butene in the range 0−100 mol % were synthesized with a single-center syndiospecific catalyst composed of (isopropylidene)(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (*i*-Pr(Cp)FluZrCl$_2$) and methylaluminoxane (MAO).[5] All copolymerizations were run at 25 °C in a 100 mL Pyrex reactor, agitated with a magnetic stirrer, containing a toluene solution (50 mL) of *i*-Pr-(Cp)FluZrCl$_2$ (with $[\mathrm{Zr}] = 1 \times 10^{-5}$ M) and MAO. The Al/Zr molar ratio was adjusted to 1000. Gas mixtures of 1-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 0.10−0.15 L/min. Under such conditions, total monomer conversions were lower than 10%, thus 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 5−8 g with a 50−150 min reaction time. The conditions of polymerization for all PPBU samples here analyzed are reported in Table 1.

The composition of the copolymers were determined by the analysis of the ^{13}C NMR spectra, recorded on a Brucker AM300 spectrometer at 120 °C in deuterated tetrachloroethane.

X-ray powder diffraction patterns were obtained at room temperature with an automatic Philips diffractometer using Ni-filtered Cu Kα radiation.

Results and Discussion

The X-ray powder diffraction patterns of as-prepared samples of PPBU copolymers are reported in Figure 2. It is apparent that the samples are crystalline in the whole range of comonomer composition. Samples with the highest content of 1-butene (≥80 mol %) behave like s-PB; they are amorphous just after the polymerization but crystallize if kept at room temperature for several days.

The X-ray diffraction profiles of all copolymers present strong analogies with the X-ray patterns of the corresponding homopolymers, i.e., three strong reflection in the 2θ angular ranges (Cu Kα) 10.5−12.2°, 15−16°, and 19−21° (see Figure 2).

The axes of the unit cells of all PPBU samples were determinated by finding values that accounted for the position of these three strong reflections.

Our structural hypotheses are based on the assumption that the unit cell remains orthorhombic whatever the composition of the copolymer, in analogy with the

Table 1. Conditions of the Copolymerizations of Propene and 1-Butene in the Presence of the Metallocene-Based Catalyst Composed of *i*-PrCpFluZrCl$_2$ and MAO[a]

sample	gas composition (mol % of 1-butene)	copolymer composition (mol % of 1-butene[b])	[P] (mol/L)	[B] (mol/L)	catalyst amount (mg)	polymerization time (min)	flow rate (L/min)	activity (g)
PPBU(1)	0.8	1.3	0.663	0.024	3.0	30	0.15	1.0
PPBU(2)	1.5	2.3	0.659	0.03_5	3.1	30	0.15	2.5
PPBU(3)	1.1	2.6	0.662	0.025	3.0	60	0.15	4.3
PPBU(4)	2.1	4.2	0.655	0.05	3.0	50	0.15	4.3
PPBU(5)	3.3	5.8	0.647	0.08	3.2	80	0.15	6.9
PPBU(6)	6.5	9.9	0.626	0.15	3.2	80	0.15	7.0
PPBU(7)	9.6	16.2	0.605	0.23	3.0	150	0.15	7.8
PPBU(8)	25.2	39.6	0.501	0.59	3.4	150	0.1	8.7
PPBU(9)	36.8	47.9	0.423	0.87	2.7	120	0.1	5.8
PPBU(10)	52.8	65.3	0.316	1.25	3.0	130	0.1	8.5
PPBU(11)	72.0	77.0	0.187	1.70	3.0	30	0.15	1.0
PPBU(12)	87.1	90.9	0.086	2.05	6.0	150	0.15	9.8
PPBU(13)	97.8	98.6	0.015	2.30	3.2	80	0.15	7.7

[a] Key: temperature = 25 °C; pressure = 1 atm; solvent = toluene (50 mL); mol ratio Al/Zr = 1000; volume reactor = 100 mL. P = propene; B = 1-butene. [b] The accuracy of monomer percentage is ±0.5.

two homopolymers. Two possible structural models have been considered in order to account for the experimental data, i.e., the packing mode of the disordered form I of s-PP (Figure 1B), and the packing mode of the limit-ordered form I of s-PB (Figure 1D), which is analogous to that of form II of s-PP (Figure 1C). The values of the axes of the unit cell were deduced following in turn the two hypotheses, and only one of them led to reasonable results. Without loss of generality, we assume the value of the *b* axis of form I of s-PP was halved with respect to the axis of the limit-ordered form. We recall that, in s-PP samples not well crystallized in form I, displacements from the fully antichiral packing along the *a* and *b* axes easily occur.[16] The absence in the patterns of Figure 2 of the diffraction maxima around $2\theta = 18.9°$ ($d = 4.70$ Å, corresponding to the 211 reflection for the limit-ordered form I of s-PP, typical of the regular alternation of right- and left-handed helical chains along both axes of the unit cell)[7-10] indicates indeed that disordered modifications of form I are obtained in the as-prepared PPBU samples. In the limit-disordered form, when helices of opposite chirality occupy statistically the lattice positions (Figure 1B), the *b* axis is halved (i.e. $b = 5.6$ Å for s-PP).

The values of the *a* axis for all copolymers were deduced straightforward from the position of the first (strongest) peak at $2\theta = 10-12°$ (Cu Kα, $d = 8.84-7.37$ Å), corresponding to the 200 reflection. Then the values of the *b* axis were deduced from the position of the second reflection at $2\theta = 15-16°$ (Cu Kα, $d = 5.91-5.54$ Å), indexed as 010 or 110 depending on the assumed model (Figure 1B or 1C). The position of the diffraction peak at $2\theta = 19-21°$ (Cu Kα, $d = 4.67-4.23$ Å), indexed in all cases as the 111 reflection, can be accounted for only if we assume for the reflection at $2\theta = 15-16°$ indices 010 for the copolymers having a content of 1-butene up to 60-70 mol % (corresponding to the model of packing of Figure 1B) and indices 110 for samples having a higher content of 1-butene (>70%) (corresponding to the model of packing of the limit-ordered form I of s-PB,[21] as well as of form II of s-PP,[4,13] see Figure 1C,D). From the position of the 111 reflection at $2\theta = 19-21°$ the values of the *c* axis were deduced.

The unit cell parameters are reported in Table 2. The increase of the values of *a* and *b* axes from the values of s-PP to those of s-PB indicates that the comonomeric units (propene or 1-butene) are included in the unit cells of both homopolymers.

As already shown in ref 18, the presence of small amount of 1-butene does not affect the usual crystallization of s-PP in the most stable form I. The packing mode of form I of s-PP remains stable when the content of 1-butene increases up to 60-70 mol %, whereas 1-butene-rich copolymers with a content of 1-butene higher than 70 mol % crystallize in a structure similar to that of form I of s-PB (Figure 1D, as well as of form II of s-PP, Figure 1C). Therefore for 1-butene-rich copolymers, the presence of small amounts of propene (up to 10-20 mol %) does not affect the usual crystallization of s-PB in form I (Figure 1D). The presence of higher amounts of propene (30 mol % of propene) avoids the usual crystallization of s-PB, and a different structure, with chains packed prevailingly like in form I of s-PP (Figure 1B), is obtained.

The values of the *a* axis of all PPBU samples are reported in Figure 3 as a function of the composition and, for propene-rich copolymers, in Figure 4 on an enlarged scale. It is apparent from Figure 4 that the *a* axis of the unit cell of s-PP (14.5 Å) remains nearly constant up to a concentration of 1-butene of nearly 4 mol %. The expansion of the unit cell occurs starting from a 1-butene content of 4-5 mol %. Nevertheless, also for copolymers having small amounts of 1-butene (<4 mol %), the comonomeric units would be included in the crystalline phase even though visible changes of the unit cell dimensions do not occur. Indeed, the presence in the solid state ^{13}C NMR CPMAS spectra of these samples of weak signals corresponding to the resonances of carbon atoms of isolated 1-butene units[26] clearly indicates that the comonomeric units are included in the crystalline phase. Moreover, in a recent paper,[18] it was shown by the analysis of the solid state ^{13}C NMR CPMAS spectra of two copolymers containing 2 and 2.5 mol % of 1-butene, that the observed splitting of the resonance of the methylene carbon atoms in conformational environment *TG*·*GT* can be explained assuming the inclusion of 1-butene units in the crystalline phase. The butene units produce a slight distortion of the local conformation close to the comonomeric units (i.e. the trans and the gauche torsion angles slightly deviate from the values they assume in the normal *TTGG* helix of s-PP sequences).[18,26] This hypothesis is confirmed by the slight variations for the copolymer samples of the *c* axis from the value of 7.5 Å, typical of s-PP,[15] to values of 7.6 and 7.7 Å, the latter typical of s-PB[21] (Table 2).

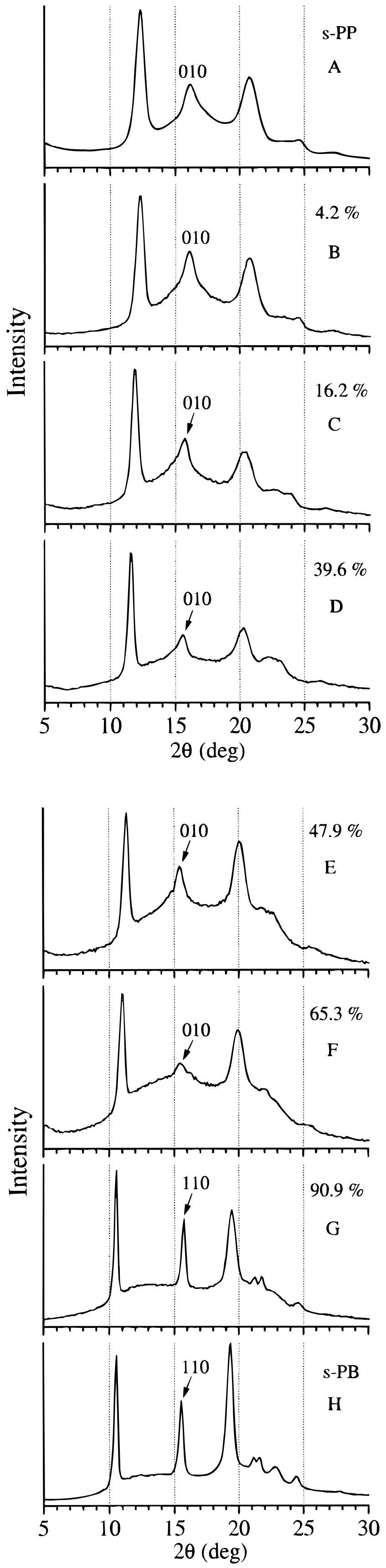

Figure 2. X-ray powder diffraction patterns of as-prepared PPBU samples having the indicated content of 1-butene. The indices of the 010 reflection correspond to the packing mode the limit-disordered form I of s-PP (Figure 1B), whereas those of the 110 reflection correspond to the packing mode of form II of s-PP (Figure 1C) or form I of s-PB (Figure 1D).

Table 2. Values of the Parameters of the Unit Cells of As-Prepared PPBU Copolymers

sample	mol % of 1-butene	*a* (Å)	*b* (Å)	*c* (Å)
s-PP	0	14.50	5.57	7.5
PPBU(1)	1.3	14.50	5.57	7.5
PPBU(2)	2.3	14.50	5.56	7.6
PPBU(3)	2.6	14.50	5.57	7.6
PPBU(4)	4.2	14.52	5.58	7.6
PPBU(5)	5.8	14.68	5.59	7.6
PPBU(6)	9.9	14.77	5.62	7.7
PPBU(7)	16.2	14.87	5.63	7.7
PPBU(8)	39.6	15.32	5.68	7.7
PPBU(9)	47.9	15.63	5.74	7.7
PPBU(10)	65.3	16.12	5.75	7.7
PPBU(11)	77.0	16.52	5.91	7.7
PPBU(12)	90.9	16.80	5.99	7.7
PPBU(13)	98.6	16.80	6.06	7.7
s-PB	100	16.81	6.06	7.73

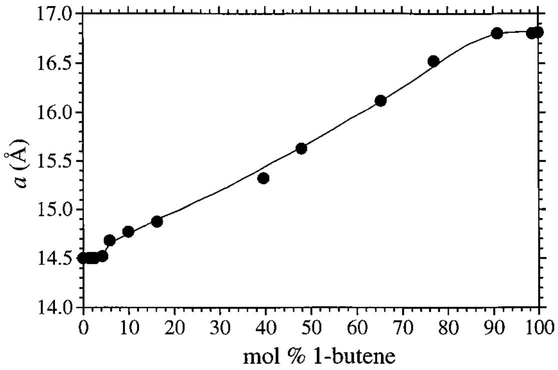

Figure 3. Values of the *a* axis of PPBU samples as a function of the 1-butene content.

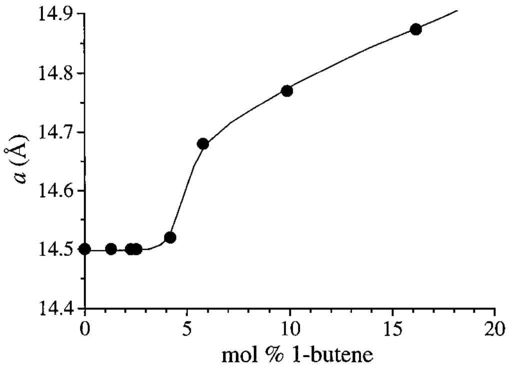

Figure 4. Values of the *a* axis of propene-rich PPBU samples as a function of the 1-butene content on an enlarged scale.

It is apparent from Figure 3 that also for 1-butene-rich copolymers (≥90 mol % of 1-butene) the values of the *a* axis are very close to that of the homopolymer. Indeed the *a* axis of form I of s-PB (16.81 Å)[21] remains nearly constant up to a concentration of propene of nearly 10 mol %. Nevertheless, the propene units would be included in the crystalline phase of s-PB, as shown by the presence in the ^{13}C NMR CPMAS spectra of these samples of resonances of carbon atoms belonging to propene units.[26]

The values of the Bragg spacing of the reflection at $2\theta = 15-16°$ and of the *b* axis for all PPBU copolymers are reported in Figure 5 as a function of the composition. Compared to the *a* axis expansion, the *b* axis shows a little variation. This could be accounted for by the *double* gauche conformation of the lateral ethyl group in butene units[20-22] and the model of packing of s-PP. Indeed, owing to the double gauche conformation,[20-22] the methyl groups of 1-butene units, included in the unit

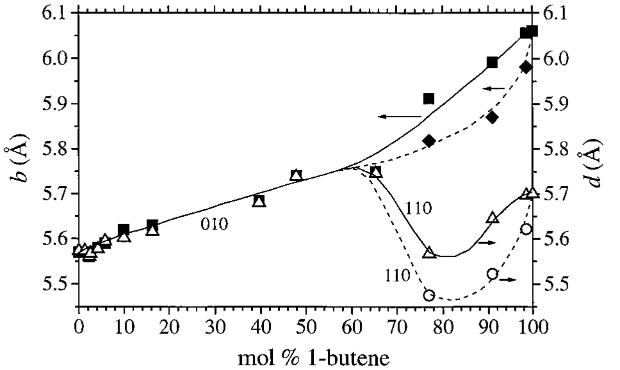

Figure 5. Values of the Bragg spacing *d* of the reflection at $2\theta = 15-16°$ (△) and of the *b* axis (■) of PPBU samples as a function of the 1-butene content. The Bragg distances (○) and the values of the *b* axis (◆) for PPBU(11), PPBU(12), and PPBU(13) samples at the beginning of the crystallization at room temperature are also shown (see Figure 6).

cell, are directed along the *a* axis (Figure 1D); hence, an increase of the value of the *b* axis much lower than that of the *a* axis is required for the accommodation of butene units in the unit cell. It is apparent from Figure 5 that the Bragg spacing increases with increasing 1-butene content up to a concentration of 60−70 mol % and decreases for a further increase of the 1-butene content. The reduction of the Bragg spacing for these compositions is a clear indication of the change of the packing mode, from the model of form I of s-PP (Figure 1B) to the model of form I of s-PB and of form II of s-PP (Figure 1C,D), when the content of 1-butene exceeds 70 mol %. The Bragg spacings of Figure 5 correspond to the 010 reflection, up to 60−70 mol % of 1-butene, and to the 110 reflection from 70 to 100 mol % of 1-butene. The *b* axis, calculated from these different indexing, shows a normal increase with the 1-butene content (Figure 5).

It is worth noting that although for PPBU samples having 1-butene contents up to 60−70 mol % the reflections at $2\theta = 15-16°$ have been indexed as 010 reflection, typical of the mode of packing of Figure 1B, disorder in the stacking of *bc* layers of chains piled along *a*, implying *b*/4 shifts among consecutive *bc* layers (*b*/4 shifts disorder), should be present. This disorder produces local arrangements of the chains such as in form II of s-PP (Figure 1C) or form I of s-PB (Figure 1D). As a matter of fact, this kind of disorder is probably present in all the as-prepared PPBU samples; for rich propene copolymer the *b*/4 shift disorder is present only as defects in a prevailing mode of packing of form I of s-PP (Figure 1B), whereas for PPBU samples with 1-butene contents in the range 50−70 mol % the amount of *b*/4 shifts increases and a mode of packing intermediate between those of parts B and C of Figure 1 occurs. The presence of this kind of disorder is clearly indicated by the broadening of the 010 reflection in the X-ray diffraction patterns of these samples (see for instance the Figure 2F). For 1-butene contents higher than 70 mol %, the mode of packing of s-PB (Figure 1D) and form II of s-PP (Figure 1C) prevails over that of Figure 1A,B, as indicated by the reduction of the Bragg spacing of the reflection at $2\theta = 15-16°$ (hence indexed as the 110 reflection).

We recall that the *b*/4 shifts disorder also occurs for the s-PP homopolymer in the case, for instance, of as-prepared samples and powder samples crystallized from the melt at temperatures lower than 120 °C,[16] for single crystals grown at low temperatures[10] (≤120 °C), and for low stereoregular samples crystallized at any temperatures.[19] It is worth noting that Lovinger, Lotz, et al.[10] proposed a model of the s-PP lattice incorporating *b*/4 point vacancies, produced by *b*/4 shifts defects, to explain electron diffraction patterns of single crystals grown at low temperatures (see Figure 9 of ref 10). This model could be suitable to explain the broadening of the 010 reflection also for PPBU samples (Figure 2F). Indeed these vacancies could occur also in a large amount to better accommodate the butene units without lowering the density.

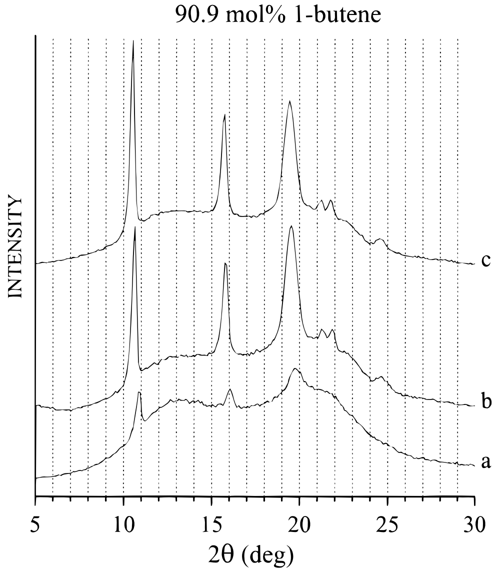

Figure 6. X-ray powder diffraction patterns of the PPBU(12) sample (90.8 mol % 1-butene) registered during the crystallization at room temperature, after 3 months (a), 6 months (b), and 10 months (c) from the polymerization. It is worth noting that at temperatures lower than the room temperature (3−4 °C) the crystallization rate is higher and the crystallization is complete within 2−3 weeks.

As discussed above, PPBU samples with high contents of 1-butene (≥80 mol %) behave like s-PB; they are amorphous just after the polymerization but crystallize if kept at room temperature for several days. The X-ray diffraction patterns of the PPBU(12) sample, with 90.9 mol % of 1-butene, registered at different crystallization times, are reported in Figure 6 as an example. Similar behavior were observed for PPBU(11) and PPBU(13) samples. It is apparent from Figure 6 that with increasing the degree of crystallinity the 200 and 110 reflections move to lower values of the diffraction angle 2θ, corresponding to higher values of the *a* and *b* axes. For the fully crystallized sample the values of the *a* axis (reported in Table 2 and Figure 3) approach to that of form I of s-PB. Indeed, as shown in Figure 3, the *a* axis of the unit cell of form I of s-PB (16.81 Å) remains nearly constant up to a concentration of propene of nearly 10 mol %.

The values of the *a* axis for 1-butene-rich copolymers, calculated from X-ray diffraction patterns such as those of the Figure 6 for different crystallization times, are reported in Figure 7. It is apparent that for samples with a low degree of crystallinity (not fully crystallized) a reduction of the *a* axis of s-PB is observed with increasing content of propene. This reduction becomes smaller with the proceeding of the crystallization and negligible (up to 10 mol % of propene) when the crystallization is complete. Of course for higher content

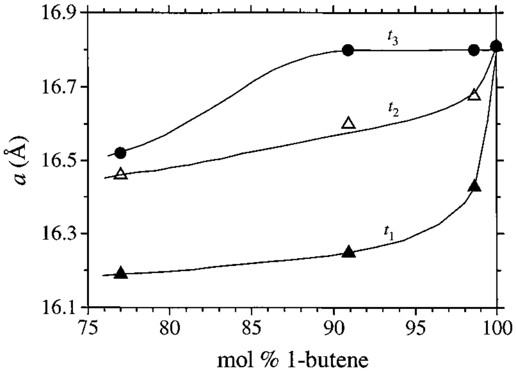

Figure 7. Values of the *a* axis of 1-butene-rich PPBU copolymers, from X-ray patterns such as those of Figure 6, as a function of the 1-butene content at different crystallization times: (▲) $t_1 = 3$ months; (△) $t_2 = 6$ months; (●) $t_3 = 10$ months.

of propene (≈20 mol %) the value of the *a* axis is lower than that of s-PB also for the fully crystallized sample. Also the Bragg spacings of the 110 reflections and the values of the *b* axis of these copolymers are lower than those of s-PB at the beginning of the crystallization (dashed lines in Figure 5); then they increase as the crystallization proceeds (Figure 5) and, for samples with content of 1-butene higher than 90 mol %, approach those of s-PB. This behavior could be explained by assuming that at the beginning of the crystallization small amounts of crystals, containing most of the comonomer propene units and having unit cell dimensions smaller than those of s-PB, are formed. The presence of point defects such as vacancies, produced by the occurrence of *b*/4 shifts defects, would possibly determine a nearly constant density value of the crystalline regions, at any stage of the crystallization, despite the contraction of the average unit cell volume. For fully crystallized samples with propene contents up to ≈10 mol %, the volume of the unit cell is determined by the predominant butene units and the *a* axis approaches the value of form I of s-PB (Figure 7).

Conclusions

Syndiotactic copolymers of propene with 1-butene have been prepared with a single-center metallocene-based catalyst. They are crystalline in a whole range of comonomer composition. The values of the parameters of the unit cells of all samples have been calculated from the position of the main reflections observed in the X-ray powder diffraction patterns. The increase of *a* and *b* axes from the values of s-PP to those of s-PB, with increasing content of 1-butene, indicates that the comonomeric units, propene or 1-butene, are included in the unit cells of both homopolymers. A continuum of modifications having structures intermediate between those of s-PP and s-PB exists. This is due to the very similar crystal structures of s-PP and s-PB.[7,13,21]

Copolymers having small contents of 1-butene are crystallized in a structure similar to that of form I of s-PP[7,10,15] (Figure 1B). Moreover, the usual crystallization of s-PP in the most stable form I is not affected by the presence of the comonomeric units also for high amounts of 1-butene, up to 50−60 mol %. However, as occurs for the homopolymer,[7,16] disordered modifications of form I,[16] characterized by statistical disorder in the alternation of right and left-handed helices along both axes of the unit cell and disorder in the stacking of *bc* layers of chains piled along *a*, implying *b*/4 shifts among consecutive *bc* layers (*b*/4 shifts disorder), are obtained in the as-prepared sample. The *b*/4 shifts disorder produces local arrangements of the chains such as in form II of s-PP (Figure 1C) or form I of s-PB (Figure 1D). Its amount increases with increasing 1-butene content and is no longer negligible for samples containing 50−60 mol % of 1-butene.

Copolymers with a content of 1-butene higher than 70 mol % crystallize in a structure similar to that of form I of s-PB (Figure 1D), as well as form II of s-PP (Figure 1C). For these 1-butene-rich copolymers, the presence of small amount of propene (up to 10−20 mol % of propene) does not affect the usual crystallization of s-PB in form I[21] (Figure 1D). The presence of a higher amount of propene (30 mol % of propene) avoids the usual crystallization of s-PB in form I and a new structure, with chains packed prevailingly like in form I of s-PP (Figure 1 A,B), is obtained.

The *b*/4 shifts disorder is probably present in all the as-prepared PPBU samples; for propene-rich copolymers it is present only as defects in a prevailing mode of packing of form I of s-PP (Figure 1A,B). For PPBU samples with 1-butene contents in the range 50−70 mol %, the amount of *b*/4 shifts increases and a mode of packing intermediate between those of parts B and C of Figure 1 occurs. For 1-butene contents higher than 70 mol % the mode of packing of s-PB (Figure 1D) and form II of s-PP (Figure 1C) prevails over that of Figure 1A,B.

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