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Solid state ^{13}C NMR analysis of syndiotactic copolymers of propene with 1-butene

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Abstract

An analysis of the structure of syndiotactic copolymers of propene with 1-butene prepared with a single-center metallocene-based catalyst in a whole range of comonomer composition, by solid state ^{13}C NMR CPMAS spectroscopy, is presented. The presence of resonances of carbon atoms of butene and propene units in the spectra of all copolymers, with intensities depending on the composition, possibly indicates the inclusion of the comonomeric units in the unit cells of both homopolymers. The splitting of the resonance of methylene carbon atoms in conformational environment *TG·GT* of propene units in propene-rich copolymers has been explained by a conformational effect, assuming that the butene units, included in the crystalline phase of syndiotactic polypropylene, produce a slight distortion of the local conformation close to the comonomeric units. The presence of additional signals at ≈35 and ≈45 ppm, attributed to the resonances of backbone *GT·TG* and *TG·GT* methylene carbon atoms, respectively, located at interfaces between propene (P) and butene (B) units, i.e. belonging to PB sequences, has been explained assuming that also in isolated butene units the lateral ethyl groups assume the "double" *gauche* conformation, typical of the chains of form I of syndiotactic poly(1-butene). © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Solid state ^{13}C NMR; Syndiotactic copolymers; 1-butene

1. Introduction

The structural characterization of syndiotactic copolymers of propene with 1-butene (PPBU), prepared with a single-center metallocene-based catalyst, has been recently reported [1–4]. As outlined in Refs. [1,2,4], the copolymers are crystalline in a whole range of comonomer composition. An increase of *a* and *b* axes of the unit cell from the values of syndiotactic polypropylene (s-PP) to those of syndiotactic poly(1-butene) (s-PB), with increasing the content of 1-butene, has been observed. This indicates that the comonomeric units, propene or 1-butene, are included in the unit cells of both homopolymers.

The copolymers crystallize in modifications having structures intermediate between those of s-PP and s-PB. This is due to the very similar crystal structures of the two homopolymers. We recall that the most stable forms of s-PP and s-PB are both characterized by chains in s(2/1)2 helical conformation, packed in orthorhombic unit cells [5–12]. Two different orthorhombic crystalline forms of s-PP (forms I and II), with chains in s(2/1)2 helical conformation, have been described [6–8]. The most stable form (form I) is characterized, in the limit ordered modification, by a regular alternation of right and left-handed helical chains along both axes of the unit cell (Fig. 1(A)) [6]. The metastable form II can be obtained only in oriented fibers of s-PP [5,8,13] and is characterized, in the limit ordered modification, by an isochiral packing of the helical chains according to the space group $C222_1$ (Fig. 1(B)). Two different crystalline modifications, form I and form II, have been found for s-PB [10]. The structure of the most stable form I [11] is very similar to that of form II of s-PP [5,8]; it is indeed characterized by chains in s(2/1)2 helical conformation packed according to the space group $C222_1$ [11] (Fig. 1(C)). The metastable form II of s-PB is characterized by chains in s(5/3)2 helical conformation [10] packed in a monoclinic unit cell [14].

In Ref. [4], we have shown that syndiotactic poly(propene-*co*-1-butene) (PPBU) samples having small amounts of 1-butene are crystallized in a structure similar to that of form I of s-PP (Fig. 1(A)). 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 [6,7], disordered modifications of form I [15], characterized by statistical disorder in the

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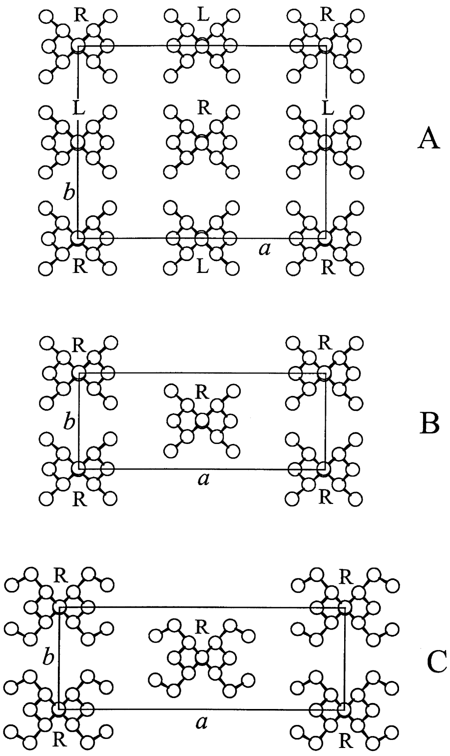

Fig. 1. Models of packing of the limit ordered (A) form I of s-PP, (B) form II of s-PP and (C) form I of s-PB.

alternation of right- and left-handed helices along both axes of the unit cell, are obtained in the as-prepared samples.

PPBU samples with a content of 1-butene higher than 70 mol% crystallize in a structure similar to that of form I of s-PB (Fig. 1(C)). Therefore, for these 1-butene rich copolymers, the presence of small amounts of propene (up to 10–20 mol% of propene) does not affect the usual crystallization of s-PB in form I [11] (Fig. 1(C)).

For propene-rich copolymers 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%. Also for 1-butene rich copolymers the value of the *a* axis of form I of s-PB (16.81 Å) [11] remains nearly constant up to a concentration of propene of nearly 10 mol%. Nevertheless, also for propene-rich and 1-butene-rich copolymers it has been assumed that the comonomeric units are included in the unit cells of both homopolymers, although visible changes of the dimensions of the unit cell do not occur.

In this paper the as-prepared PPBU samples are analyzed, in the whole range of comonomer composition, by solid state ^{13}C NMR spectroscopy using cross polarization/magic angle spinning (CPMAS) technique. This technique may be very sensitive to nuclei in rigid environments, and may provide direct information concerning the inclusion of comonomeric units in the crystalline phase of copolymers, as well as the possible changes in the chain conformation of homopolymers as a consequence of the inclusion of comonomeric units in the unit cell.

2. 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 and methylaluminoxane with the method described in Ref. [4]. All samples correspond to those reported in Ref. [4].

The composition of the copolymers were determined by the analysis of the ^{13}C NMR solution spectra, recorded on a Bruker AM300 spectrometer at 120°C in deuterated tetrachloroethane; the copolymers, according to this analysis, are random and homogeneous in the composition. The X-ray powder diffraction patterns of as-prepared PPBU samples are reported in Ref. [4].

Solid state ^{13}C MAS NMR spectra were recorded at room temperature on a Bruker AC-200 spectrometer, equipped with an HP amplifier ^{1}H 200 MHz, 120 W continuous wave, and with a pulse amplifier M3205. The samples (52 mg) were packed into 4 mm zirconia rotors and sealed with Kel-F caps. The spin rate was kept at 8.0 kHz, the 90° pulse was 3.0 μs. For CPMAS spectra the contact time for the Cross Polarization, optimized in order to maximize the signals in the rigid (crystalline) regions of the samples, was 1 ms; the relaxation delay was 4 s. Spectra were obtained with 1024 words in the time domain, zero filled and Fourier transformed with size of 2048 words; 7200 scans were performed for each sample. Crystalline polyethylene was used as external reference at 33.6 ppm from tetramethylsilane (TMS).

The assignment of the resonances observed in the CPMAS spectra was made by comparison with the CPMAS spectra of s-PP [16] and s-PB [12], and by CPMAS experiments performed in the Cross Polarization (CP) mode with a simultaneous phase inversion (PI) [17,18]. This method (CPPI) allows the selective observation of different carbon atoms. The CPPI spectrum was obtained with contact times for the first and second Cross Polarization ($\tau_{CP1} = \tau_{CP2}$) of 1 ms while the lengths of the pulses used for the first and second phase inversion ($\tau_{PI1} = \tau_{PI2}$) were 30 μs. The setup requirement for these experiments was identical to that used in CPMAS experiments.

3. Results and discussion

The ^{13}C NMR CPMAS spectra of PPBU samples are reported in Fig. 2.

The spectra of PPBU copolymers with a small content of 1-butene (2–6 mol%) (Fig. 2(A) and (B)) present the typical resonances of carbon atoms of the chain of s-PP in the s(2/1)2 helical conformation [16], i.e. the methyl carbon resonance at 21.7 ppm, the methine carbon resonance at 27.4 ppm and the resonances at ≈ 40 and 49–50 ppm corresponding to methylene carbon atoms in conformational environments *GT·TG* and *TG·GT*, respectively (the dot indicates the methylene carbon). The spectra of PPBU copolymers with high contents of 1-butene (≈98 mol%) (Fig. 2(I)) present the typical resonances of the carbon atoms of form I of s-PB, with chains in the s(2/1)2 helical conformation [12], i.e. the methyl carbon resonance at ≈10 ppm, the resonance of methylene carbon atoms of the side groups at 26.8 ppm, the methine carbon resonance at 31 ppm, and the resonances at 32.3 and 41 ppm corresponding to the backbone methylene carbon atoms in conformational environments *GT·TG* and *TG·GT*, respectively.

We recall that in the case of form I of s-PB, owing to the particular "double *gauche*" conformation of the lateral ethyl groups found in the crystal structure, the methyl carbon atoms of the side groups are in *gauche* arrangement with respect to both adjacent backbone methylene carbon atoms [10,11]. Hence, methylene carbon atoms in conformational environments *TG·GT* experience two γ-*gauche* shielding effects due to the methyl carbon atoms, whereas methylene carbon atoms in conformational environments *GT·TG* experience four γ-*gauche* shielding effects due to the methine and methyl carbon atoms in the γ position. Therefore, the resonance of the backbone methylene carbon atoms of s-PB is still split into two components separated by ≈10 ppm [12], (as occurs in s-PP), but shifted upfield by nearly 10 ppm with respect to the methylene resonances in s-PP [16]. This shift is also observed in the spectra of 1-butene rich copolymers (Fig. 2(H) and (I)) with respect to those of propene-rich copolymers (Fig. 2(A) and (B)).

The CPMAS spectra of propene-rich copolymers of Fig. 2(A)–(C) present, besides the resonances of carbon atoms belonging to long syndiotactic sequences of propene units, very weak signals at ≈10, ≈30, ≈35 and ≈45 ppm corresponding to the resonances of carbon atoms belonging or adjacent to butene units. The comparison with the spectrum of form I of s-PB [12] and with the spectra of 1-butene rich copolymers (Fig. 2(H) and (I)), allows to assign the signals at ≈10 and ≈30 ppm to the resonances of methyl carbon and methine carbon atoms, respectively, of 1-butene units. This possibly indicates the inclusion of 1-butene units in the crystalline phase of s-PP also for copolymers with low content of 1-butene (<4 mol%), although for these samples visible changes of the dimensions of the unit cell of s-PP do not occur [4]. The intensities of the resonances at ≈10 and ≈30 ppm increase with increasing the 1-butene content (Fig. 2(B)–(F)).

The assignment of the resonances at ≈35 and ≈45 ppm and of the other resonances observed in the CPMAS spectra of Fig. 2(A)–(I) was made by CPMAS experiments performed using cross polarization in combination with polarization inversion (CPPI) [17,18]. Indeed, in a CPPI spectrum obtained with a long CP time (1–2 ms) and a short PI time (30–35 μs), ^{13}CH signals disappear, ^{13}CH$_2$ signals become negative with a relative intensity about 1/3, and methyl signals remain positive and are attenuated by about 62% [17,18]. This allows us to recognize the resonances of methine, methylene and methyl carbon atoms.

The CPPI spectrum of PPBU sample with 65.3 mol% of 1-butene is reported in Fig. 3. The resonance at 30 and 27 ppm present in the CPMAS spectrum of Fig. 2(G), disappear in the CPPI spectrum of Fig. 3, hence they can be attributed to methine carbon atoms. As discussed above, they correspond to the resonances of methine carbon atoms of 1-butene and propene units, respectively. The only positive signals present in the CPPI spectrum of Fig. 3 correspond to the resonances of methyl carbon atoms of propene units at 21.7 ppm, and of 1-butene units at 10–11 ppm.

It is realized from Fig. 3 that the negative signals at 50, 45, 40, 35, 30 and 26 ppm correspond to methylene carbon atoms. As discussed above, the resonances at ≈50 and ≈40 ppm correspond to methylene carbon atoms of long sequences of propene units. Since the resonances of *GT·TG* and *TG·GT* methylene carbon atoms of long sequences of butene units occur at 32 and 41 ppm, respectively (Fig. 2(I)), the resonance of *GT·TG* methylene carbon atoms of long sequences of propene units (40 ppm in Fig. 2(A) and (B)) is overlapped in the spectrum of Fig. 3 to that of *TG·GT* methylene carbon atoms of long sequences of butene units, and a unique signal at 40.6 ppm occurs in the CPPI spectrum of Fig. 3 and in all CPMAS spectra of PPBU samples with nearly equal contents of propene and butene (Fig. 2(E)–(G)). The resonance at 30 ppm in Fig. 3 possibly corresponds to *GT·TG* methylene carbon atoms of long sequences of butene units (as in Fig. 2(I)). The resonance at $\delta = 26$ ppm, overlapped in the CPMAS spectra of Fig. 2 to the methine resonance of propene units at ≈27 ppm (Fig. 2(A)–(G)), and hence often concealed by the latter, becomes evident in Fig. 3 and can be attributed to the resonance of the methylene carbon atoms of the side groups of 1-butene units.

The signals at ≈35 and ≈45 ppm, present in the CPMAS spectra of Fig. 2, become negative signals in the CPPI spectrum of Fig. 3, hence are identified as methylene resonances. They may correspond to the resonances of backbone methylene carbon atoms at interfaces between propene and 1-butene units, i.e. belonging to PB sequences (P: propene, B: 1-butene, Fig. 4). Indeed, the intensities of these resonances increase with increasing the 1-butene content, up to 50–60 mol% (Fig. 2(A)–(G)), then decrease for a further increase of the butene content (Fig. 2(H)), and disappear for the PPBU sample with the highest content of 1-butene (Fig. 2(I)).

For low content of 1-butene, long sequences of propene units containing isolated butene units (…PBP…) are present (the resonances at 32 and 41 ppm of methylene carbon atoms of sequences of consecutive butene units, are absent in the CPMAS spectra of Fig. 2(A)–(C)). With increasing the content of 1-butene the amount of PB sequences increases and, the amount of sequences of consecutive butene units becomes appreciable when the content of

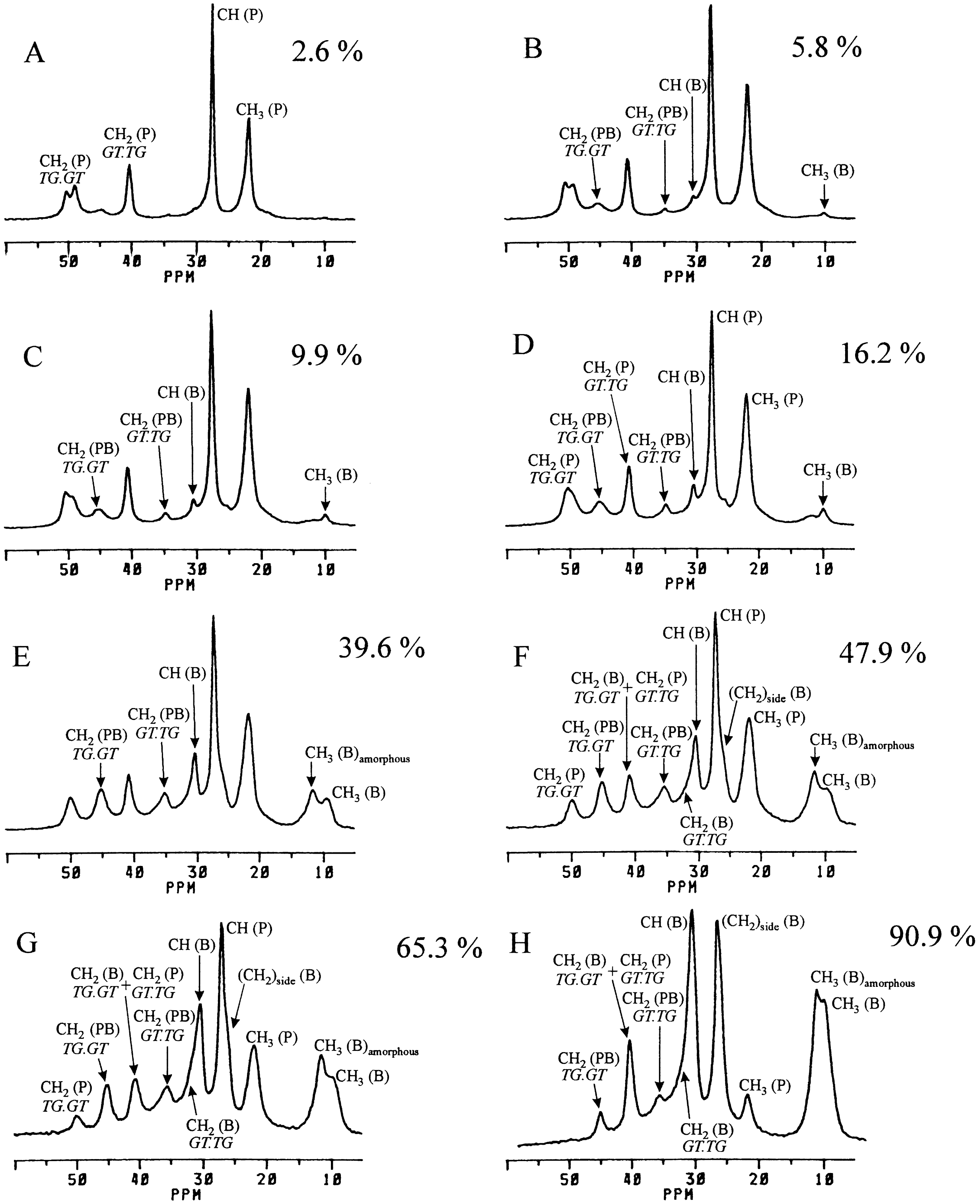

Fig. 2. Solid state ^{13}C NMR CPMAS spectra of PPBU copolymer samples having the indicated content of 1-butene (mol%).

1-butene exceeds 40–50 mol%. Correspondingly the resonances of methylene carbon atoms at 32.3 and 41 ppm, typical of long sequences of butene units (as in s-PB), appear (Fig. 2(F)), and their intensities increase with increasing the 1-butene content (Fig. 2(G)–(I)). For butene rich copolymers having 1-butene content higher than 80–90 mol% the resonances at ≈35 and ≈45 ppm are still present, although of low intensities (Fig. 2(H)). In this case, they correspond to the resonances of methylene carbon atoms of propene or butene units in long sequences of

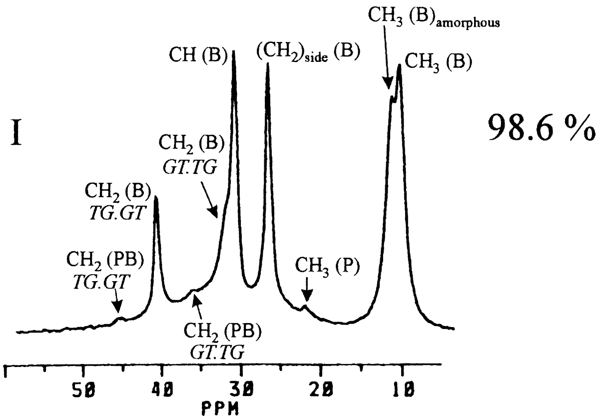

Fig. 2. (*continued*)

butene units containing isolated propene units (…BPB… sequences; the resonances at 40 and 49 ppm of methylene carbon atoms of sequences of consecutive propene units, are absent in the CPMAS spectrum of Fig. 2(H)). The presence in the spectrum of Fig. 2(H) of these resonances, along with the methyl resonance of propene units at 21.7 ppm, is a possible evidence of the inclusion of the propene units in the crystalline phase of s-PB also for low content of propene (<10 mol%), although changes of the dimensions of the unit cell of form I of s-PB do not occur up to nearly 10 mol% of propene [4].

The presence of different resonances for the backbone methylene carbon atoms belonging to PB sequences (signals at ≈35 and ≈45 ppm), consecutive propene units sequences (signals at 40 and 49 ppm, as in s-PP) and consecutive butene units sequences (signals at 32.3 and 41 ppm, as in s-PB) indicate that these methylene carbon atoms are not equivalent, hence have different conformational environments. This can be explained assuming that the particular “double *gauche*” conformation of the lateral ethyl groups, found for the chains of form I of s-PB in the s(2/1)2 conformation [10,11], is maintained by ethyl groups in the butene units of PB sequences. The methyl carbon atom of the butene unit is in *gauche* arrangement to both adjacent backbone methylene carbon atoms. Therefore, with reference to Fig. 4, the methylene carbon atom 1 in conformational environment *GT·TG* experiences three γ-*gauche* shielding effects due to backbone methine carbon atoms and to the methyl carbon atom of the butene unit. Its resonance should

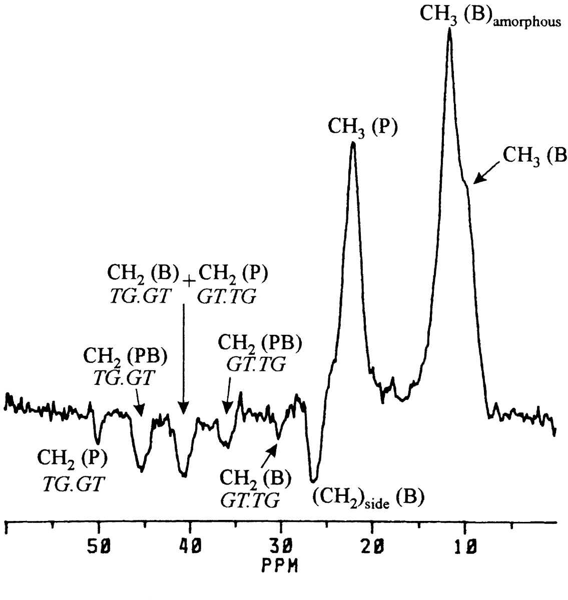

Fig. 3. Solid state ^{13}C NMR CPPI spectrum of the PPBU sample with 65.3 mol% of 1-butene obtained using CP in combination with PI.

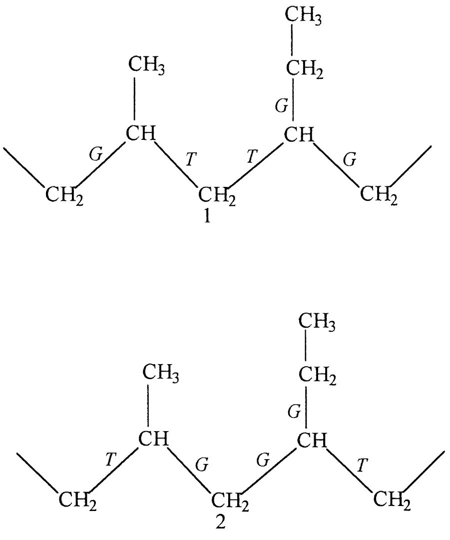

Fig. 4. Sequences of consecutive propene and 1-butene units (PB sequences, P: propene and B: 1-butene) with the methylene carbon atom in conformational environments *GT·TG* and *TG·GT*.

Table 1

Ranges of values of the chemical shifts (ppm from TMS) of the resonances observed in the ^{13}C NMR CPMAS spectra of PPBU copolymer samples of Fig. 2 (P: propene comonomeric unit, B: 1-butene comonomeric unit. The symbol CH_2 *GT·TG* (B) indicates methylene carbon atoms in conformational environment *GT·TG* belonging to consecutive butene units sequences. The other symbols have analogous meaning)

	δ
CH_3 (B)[a]	9.5–10.3
CH_3 (P)	21.7–21.9
CH (P)	27.2–27.5
$(CH_2)_{side}$ (B)	26.0–26.8
CH (B)	30.2–30.8
CH_2 *GT·TG* (B)	32.0–32.2
CH_2 *TG·GT* (B)[b]	40.6–41.0
CH_2 *GT·TG* (PB)	34.5–35.5
CH_2 *TG·GT* (PB)	45.0–45.4
CH_2 *GT·TG* (P)[b]	40.2–40.7
CH_2 *TG·GT* (P)	48.7–49.2, 50.0–50.3

[a] In the CPMAS spectra of Fig. 2A resonance at 11.6 ppm, attributed to methyl carbon atoms of the amorphous phase, is also present.

[b] The resonances of *TG·GT* methylene carbon atoms of 1-butene units and *GT·TG* methylene carbon atoms of propene units are overlapped and a unique signal at values of the chemical shift in the range 40.2–41 ppm appear in the spectra of Fig. 2.

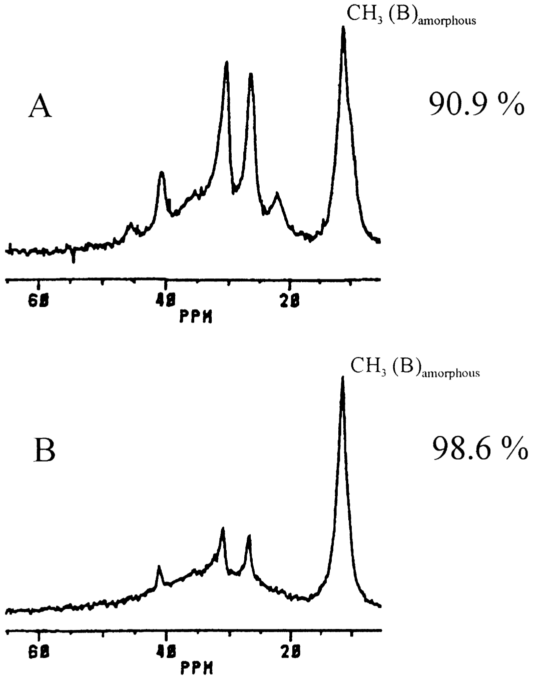

Fig. 5. Solid state ^{13}C NMR CPMAS spectra of nearly amorphous PPBU samples having the indicated content of 1-butene (mol%) at the beginning of the crystallization.

be shifted upfield by 4–5 ppm from the typical signal of *GT·TG* methylene of consecutive propene units sequences (two γ-*gauche* effects, 40 ppm) and downfield by 4–5 ppm from the typical signal of *GT·TG* methylene carbon atoms of consecutive butene units sequences (four γ-*gauche* effects, 32 ppm), and should occur at ≈35 ppm, as actually found (Fig. 2(A)–(H)). The methylene carbon atom 2 (Fig. 4), in conformational environment *TG·GT*, experience one γ-*gauche* shielding effect due to the methyl carbon atom of the butene unit. Its resonance should be shifted upfield by 4–5 ppm from the typical signal of *TG·GT* methylene of consecutive propene units sequences (49 ppm), and downfield by 4–5 ppm from the typical signal of *TG·GT* methylene carbon atoms of consecutive butene units sequences (two γ-*gauche* effects, 41 ppm) and should occur at ≈45 ppm, as actually found (Fig. 2(A)–(H)).

The assignment of all resonances in the spectra of Fig. 2 is shown in Table 1.

It is worth noting that in the spectra of PPBU copolymers with small amounts of 1-butene, up to 16.2 mol% (Fig. 2(A)–(D)), the resonance at ≈49 ppm of methylene carbon atoms of propene units in conformational environments *TG·GT*, is split into a doublet at 49 and 50 ppm. The intensity of the component at 50 ppm is lower than that at 49 ppm in the spectra of PPBU samples having low content of 1-butene (Fig. 2(A)) and increases with increasing the 1-butene content (Fig. 2(B)–(D)). For 1-butene content higher than 20–30 mol% (Fig. 2(E)–(G)) the component at 49 ppm disappears and only the component at ≈50 ppm is present (Fig. 2(E)). This splitting is present also for very low concentration of 1-butene (2.6 mol%) (Fig. 2(A)) and, as already discussed in Ref. [3], may be taken as a further evidence of the inclusion of the butene units in the unit cell of s-PP also for low content of the comonomeric units, although for these samples visible changes of the dimension of the unit cell of s-PP do not occur [4]. Indeed the presence of butene units produces 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 …PPP… sequences. Since the γ-*gauche* shielding effect depends on the exact values of the torsion angles [19,20], methylene carbon atoms in conformational environment *TG·GT* close to the comonomeric units are no longer equivalent to those belonging to long propene sequences. This hypothesis may account for the splitting of the *TG·GT* methylene resonance and may be confirmed by the observation, reported in Ref. [4], of the slight variation for the copolymer samples of the *c*-axis from the value of 7.5 Å, typical of s-PP [8,9], to values of 7.6 and 7.7 Å, the latter typical of s-PB [11]. Splittings of nearly 1 ppm due to this kind of conformational effect has been recently observed in CPMAS spectra of form I of isotactic poly(4-methyl-1-pentene) [19] and syndiotactic poly(4-methyl-1-pentene) [20].

It is worth noting that two different resonances for methyl carbon atoms of 1-butene units at ≈10 and 11.6 ppm are present in the spectra of PPBU samples with contents of 1-butene higher than 16 mol% (Fig. 2(E)–(I)). For very low 1-butene content only the resonance at ≈10 ppm is present (Fig. 2(A)–(C)); with increasing the 1-butene content, starting from ≈16 mol%, the resonance at 11.6 ppm appears (Fig. 2(D)). The intensities of both resonances increase with increasing the butene content (Fig. 2(E)–(I)).

In Ref. [12] it was shown that the resonance of methyl carbon atoms of amorphous s-PB occurs at 11.9 ppm, i.e. at a chemical shift higher than that of the crystalline methyl carbon atoms in the rigid double *gauche* conformation. Also for PPBU copolymer samples of Fig. 2 the resonance at 11.6 ppm may be attributed to methyl carbon atoms in mobile regions. This is evidenced by the ^{13}C NMR CPMAS spectra of nearly amorphous samples of PPBU copolymers with 90.9 and 98.6 mol% of 1-butene, as soon as prepared, reported in Fig. 5. These samples present a very low crystallinity, as shown by the X-ray powder diffraction patterns reported in Fig. 6 (curves a) of Ref. [4]. Indeed, as shown in Ref. [4], PPBU samples with very high 1-butene content are amorphous just after the polymerization but slowly crystallize if kept at room temperature for several months. The ^{13}C NMR CPMAS spectra of Fig. 2(H) and (I) correspond indeed to the spectra of well crystallized samples.

It is apparent that only the resonance at 11.6 ppm is present in the spectra of Fig. 5, whereas also the resonance at ≈10 ppm is present in the spectra of well crystallized

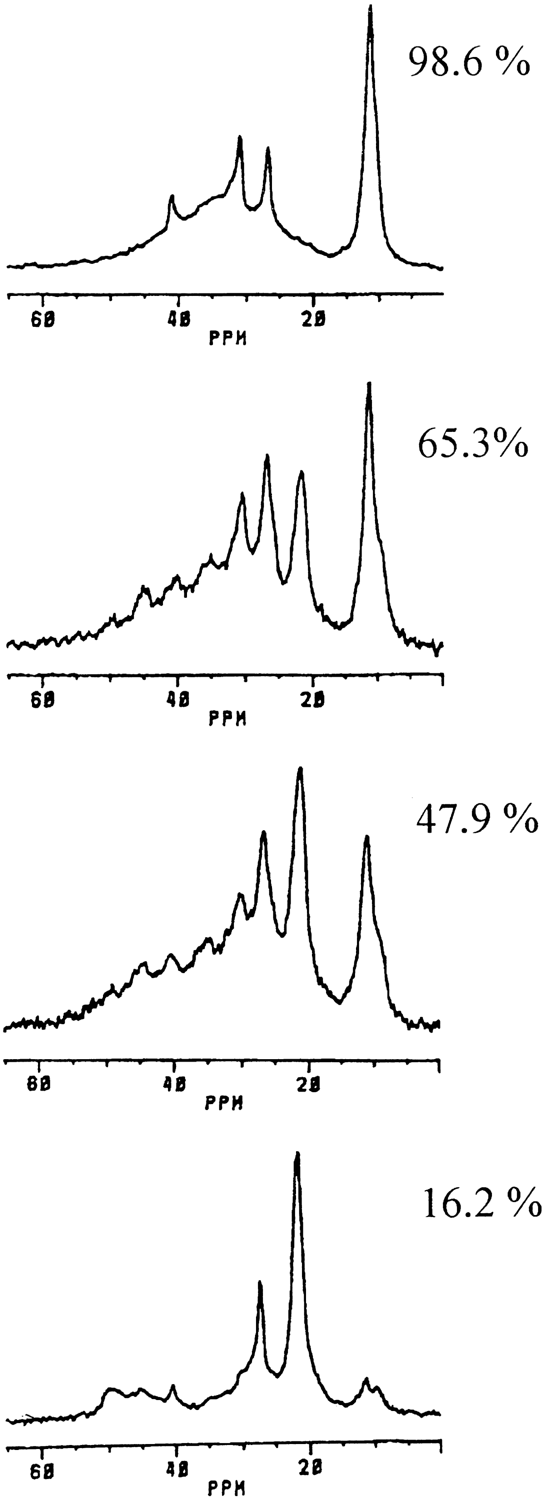

Fig. 6. Solid state ^{13}C NMR MAS spectra of PPBU copolymer samples having the indicated content of 1-butene (mol%) with 1 s recycle time.

samples of Fig. 2(H) and (I); this confirms the assignment of the resonance at 11.6 ppm to amorphous methyl carbon atoms.

As a further check, single pulse ^{13}C NMR MAS experiments with short recycle time (1 s) were performed. These spectra are shown in Fig. 6 for four PPBU samples. Generally, in the spectra obtained with short recycle times only the resonances of nuclear species belonging to the most mobile phase appear. In Fig. 6 only the resonance for the methyl carbon atoms at 11.6 ppm is present, although with a shoulder at upfield due to the methyl groups belonging to the crystalline regions. The presence of this shoulder can be explained considering that the methyl groups have short spin–lattice relaxation time T_1 due to the fast methyl rotation irrespective of the mobility of the guest phase. Nevertheless, above the glass transition, the T_1 time of these nuclei in the amorphous regions should be lower than that in the crystalline phase. Also these data confirm that the resonance at 11.6 ppm in the CPMAS spectra of Fig. 2 correspond to methyl carbon atoms placed in the amorphous regions.

4. Conclusions

Syndiotactic copolymers of propene with 1-butene prepared with a single-center metallocene-based catalyst, have been studied by solid state ^{13}C NMR CPMAS spectroscopy. The assignment of the resonances in the ^{13}C NMR CPMAS spectra was made by comparison with the spectra of s-PP [16] and s-PB [12] and by CPMAS experiments performed using Cross Polarization in combination with Polarization Inversion (CPPI) [17,18].

The spectra of propene rich copolymers present, besides the typical resonances of carbon atoms of the chain of s-PP in the s(2/1)2 helical conformation [16], additional signals with weak intensities at ≈10, ≈30, ≈35 and ≈45 ppm corresponding to the resonances of carbon atoms belonging or adjacent to butene units. This possibly indicates the inclusion of the 1-butene units in the crystalline phase of s-PP also for low content of 1-butene (<4 mol%), although visible changes of the dimensions of the unit cell of s-PP do not occur [4] The resonances at ≈10 and ≈30 ppm have been assigned to methyl and methine carbon atoms, respectively. The signals at 35 and 45 ppm correspond to the resonances of backbone methylene carbon atoms in conformational environments *GT·TG* and *TG·GT*, respectively, belonging to PB sequences. These resonances are also present in CPMAS spectra of butene rich copolymers. This may be taken as a further evidence of the inclusion of propene units in the unit cell of s-PB, although visible changes of the dimensions of the unit cell of form I of s-PB do not occur up to a concentration of propene of nearly 10 mol% [4].

These data indicate that the methylene carbon atoms in PB sequences are not equivalent to those in consecutive propene or butene units sequences and this can be explained assuming that also in isolated butene units the lateral ethyl groups assume the double *gauche* conformation, typical of s-PB [10–12].

In the spectra of PPBU copolymers having small amounts of 1-butene the resonance at ≈ 49 ppm of methylene carbon atoms of propene units, in conformational environments

TG·GT, is split in a doublet at 49 and 50 ppm. This splitting may be taken as a further evidence of the inclusion of the butene units in the unit cell of s-PP also for low content of the comonomeric units [3,4]. Indeed the presence of butene units in the unit cell produces 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. The methylene carbon atoms in conformational environment *TG·GT* close to the comonomeric units are no longer equivalent to those belonging to long propene sequences.

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