

## Structural Analysis of Copolymers of Syndiotactic Polypropylene with $^{13}\text{C}$ -Enriched Ethylene

Claudio De Rosa,<sup>\*,†</sup> Finizia Auriemma,<sup>†</sup> Giovanni Talarico,<sup>†</sup> Vincenzo Busico,<sup>†</sup> Lucia Caporaso,<sup>‡</sup> and Donatella Capitani<sup>§</sup>

Dipartimento di Chimica, Università di Napoli "Federico II", Complesso Monte S. Angelo, Via Cintia, 80126 Napoli, Italy; Dipartimento di Chimica, Università di Salerno, Via S. Allende, 84081 Baronissi (SA), Italy; and Servizio NMR-CNR Area della Ricerca di Roma, Via Salaria, km. 29.300, I-00016 Monterotondo S. R.M. C.P.10, Italy

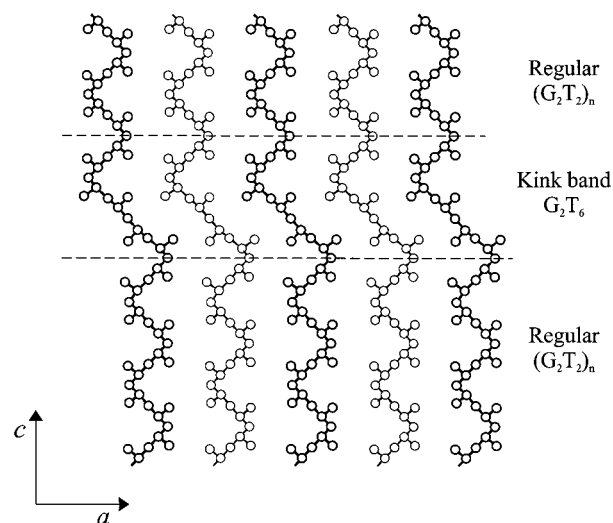
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**ABSTRACT:** A structural analysis of copolymers of syndiotactic polypropylene with small amounts of  $^{13}\text{C}$ -enriched ethylene, in the range 0.4–2.6 mol %, is reported. X-ray diffraction and solid-state  $^{13}\text{C}$  NMR CPMAS data indicate that the as-prepared copolymer samples are crystallized in the conformationally disordered modification of form II of sPP containing kink bands. The disorder corresponds to the presence of portions of chains in the trans-planar conformation in chains having a prevailing 2-fold helical conformation. A direct evidence of the partial inclusion of the ethylene units in the crystalline regions of the copolymers is provided.

### Introduction

Syndiotactic polypropylene (sPP) presents a complex polymorphic behavior,<sup>1–12</sup> complicated by the presence of structural disorder.<sup>6,13–16</sup> Four limit ordered crystalline forms have been described so far. The most stable form I<sup>3–6,10</sup> and the metastable form II<sup>1,9,11</sup> are characterized by chains in a  $s(2/1)2$  helical conformation, packed in orthorhombic unit cells, whereas forms III<sup>2,7</sup> and IV<sup>8</sup> present chains in trans-planar and  $(T_6G_2T_2G_2)_n$  helical conformations, respectively. The limit ordered structure of the stable form I is characterized by a regular alternation of right- and left-handed helical chains along the  $a$  and  $b$  axes of the unit cell.<sup>3</sup> Depending on the conditions of crystallization, different amounts of disorder in the alternation of enantiomorphous chains may be present in the structure.<sup>6,16</sup> Form II of sPP is instead characterized by a fully isochiral packing of the 2-fold helices<sup>1,9</sup> and can be obtained in oriented fibers.<sup>9,11</sup>

The polymorphic behavior of sPP is further complicated by the fact that disorder in the conformation of the chains may be present in low-stereoregular samples of sPP, crystallized in form II by quench precipitation from solutions.<sup>13,14</sup> This disorder has been evidenced by the solid-state  $^{13}\text{C}$  NMR spectra of these samples,<sup>13</sup> which present, besides the main four resonances typical of the nuclei of a chain in the ordered 2-fold helical conformation of s-PP,<sup>17,18</sup> additional resonances in the region of the methyl and methylene carbon atoms.<sup>13</sup> It was argued that these extra resonances are possibly related to the presence of conformational disorder in the crystalline phase, corresponding to the presence of trans-planar portions of chains connecting longer portions in the ordered TTGG 2-fold helical conformation.<sup>13–15</sup> In the resulting structure, shown in Figure 1, trans-planar defects are frozen in the crystals producing the formation of kink bands, while the parallelism of helical portions of chains is preserved. In the ordered regions the chains in helical conformation are packed



**Figure 1.** Possible model of disordered structure of form II of sPP containing kink bands.<sup>13–15</sup> The chains are in a prevailing 2-fold helical conformation with defects characterized by portions in the trans-planar conformation. The defective portions of the chains are clustered in planes, delimited by the dashed lines, and correspond to the conformational sequences  $G_2T_6$ . The chains are packed like in the form II of sPP, the helical portions of the chains being isochiral. The chains drawn with thick and thin lines are at  $b = 0$  and 0.5, respectively.

like in the form II, whereas in the defective regions the chains containing trans-planar sequences are packed like in the form IV of s-PP.<sup>8,12</sup>

The disordered structures presenting kink bands are metastable modifications and could be thought as intermediate between the limit ordered forms II and IV of sPP.

Copolymers of syndiotactic polypropylene with small amounts of ethylene (PPET) have recently received attention. A preliminary structural characterization has shown that the presence of small amounts of comonomeric ethylene units induces, in the as-prepared samples, the crystallization of conformationally disordered modifications of form II of sPP containing kink bands.<sup>19</sup> It

<sup>†</sup> Università di Napoli "Federico II".

<sup>‡</sup> Università di Salerno.

<sup>§</sup> Servizio NMR-CNR Area della Ricerca di Roma.

was argued that these disordered modifications of sPP form more easily in the studied copolymers of sPP because of the inclusion of the ethylene units in the crystalline regions. In fact, while in the case of the sPP homopolymer the formation of the kink-band structures is a rare event occurring only for low stereoregular samples, quench-precipitated from solutions, these disordered structures are observed for any as-prepared samples of the PPET copolymers with low ethylene content. However, as in the sPP homopolymer, also in the case of the PPET copolymers, these disordered modifications are metastable, and their formation is driven by kinetic factors.<sup>19</sup> In ref 19 it was shown that samples of PPET copolymers crystallized from the melt in well-controlled conditions are in the stable form I of sPP with chains in the ordered 2-fold helical conformation, whereas the as-prepared specimens crystallize in these disordered modifications. The ethylene units, included, at least in part, in the crystalline regions, would induce the formation of trans-planar sequences, which makes the formation of the kink-band structures kinetically favored.<sup>19</sup>

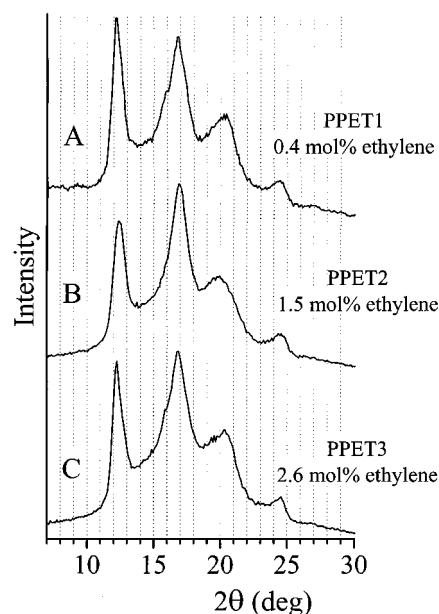
However, direct evidence for the inclusion of the ethylene units in the crystalline regions was not given, since, as expected, no changes of the lattice dimensions were observed. Moreover, although high-resolution <sup>13</sup>C NMR CPMAS techniques for the solid state provide a powerful tool for the study of the conformation of polymer chains in condensed matter, the low content of ethylene units in the copolymers of propylene studied so far has prevented any direct observation of the NMR signals of <sup>13</sup>C nuclei belonging to the ethylene units embedded in the rigid (crystalline) phase of sPP.

In this paper, a structural characterization, by X-ray diffraction and solid-state <sup>13</sup>C NMR, of some samples of syndiotactic copolymers of propylene containing <sup>13</sup>C-enriched ethylene comonomeric units is presented to provide a direct proof for the inclusion of the ethylene units in the crystalline regions of PPET copolymers. The copolymers used in the present investigation were prepared ad hoc using ethylene-*1-13*C in a content ranging between 0.4 and 2.6 mol %.

## Experimental Section

Three samples of copolymers of propylene with ethylene-*1-13*C (Isotec Inc., 99+% isotopic purity) have been prepared and analyzed. The samples PPET1, PPET2, and PPET3 contain 0.4, 1.5, and 2.6 mol % ethylene-*1-13*C, respectively. All copolymerizations were run according to the method described in ref 20, using the single center catalytic system composed of (methyl)(phenyl)methylen(cyclopentadienyl)(9-fluorenyl)-ZrCl<sub>2</sub> and methylaluminumoxane. The copolymers were coagulated from the reaction medium with excess methanol, acidified with HCl aqueous solution, filtered, washed with additional methanol, and vacuum-dried at 50 °C. The catalyst used has been reported to be syndiotactic specific and highly regioselective (the amount of regioirregularities due to 2,1 insertions of propylene units being less than 0.1%). For the three samples the concentration of the fully syndiotactic pentads [rrrr] is ≈90%, and the amounts of stereodefects [rmmr] and [rmrr] are 1.3% and 1.9%, respectively.

The composition of the copolymers was determined by analysis of the <sup>13</sup>C NMR spectra, recorded with a Varian XL-200 spectrometer operating at 50.3 MHz, on 10% w/v polymer solutions in deuterated tetrachloroethane (also used as internal standard) at 125 °C (see ref 20). These spectra also indicate that the ethylene comonomeric units are isolated, the amount of consecutive ethylene units being negligible (<0.1 mol %).



**Figure 2.** X-ray diffraction patterns of the as-prepared samples of the PPET copolymers having the indicated ethylene contents.

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

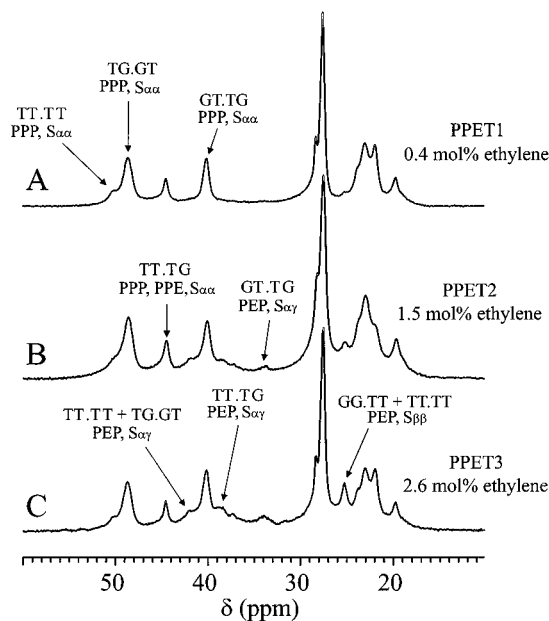
Solid-state <sup>13</sup>C MAS NMR spectra were recorded at room temperature on a Bruker AC-200 spectrometer, equipped with HP amplifier <sup>1</sup>H 200 MHz, 120 W continuous wave and with a pulse amplifier M3205. The samples (50 mg) were packed into 4 mm zirconia rotors and sealed with Kel-F caps. The spin rate was kept at 8.0 kHz, and the 90° pulse was 3.0  $\mu$ s. 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 time was 4 s. Spectra were obtained with 1024 points in the time domain, zero filled, and Fourier transformed with a size of 2048 points; 7200 scans were performed for each sample. Crystalline polyethylene was used as external reference at 32.89 ppm from tetramethylsilane (TMS).<sup>21</sup>

The assignment of the resonances observed in the CPMAS spectra was further checked performing CP-SPI experiments, which combine the standard cross-polarization (CP) with polarization inversion (PI) with a simultaneous phase inversion (SPI).<sup>22,23</sup> The simultaneous phase inversion is used for both CP and PI. The CP is used two times with the same contact time  $\tau_{CP1} = \tau_{CP2}$  but with opposite phases. The PI is also applied two times with the same pulse length  $\tau_{PI1} = \tau_{PI2}$  and opposite phases. The CP-SPI spectra were obtained with contact times  $\tau_{CP1} = \tau_{CP2}$  of 1 ms and pulse lengths  $\tau_{PI1} = \tau_{PI2}$  of 30  $\mu$ s. The CP-SPI method allows for the selective observation of different types of carbon atoms, methyl, methylene, and methine atoms. The setup requirement for these experiments was identical to that used in CPMAS experiments.

## Results and Discussion

The X-ray powder diffraction patterns of the as-prepared samples of the PPET copolymers, reported in Figure 2, are characterized by the presence of reflections at  $d = 7.25$ , 5.22, and 4.35 Å ( $2\theta = 12.2^\circ$ ,  $17.0^\circ$ , and  $20.4^\circ$ , Cu K $\alpha$ ). The position of the second reflection at  $2\theta = 17^\circ$  indicates that these samples are crystallized in modifications close to the form II of sPP.<sup>9,15</sup> However, since this reflection is rather broad, we cannot exclude the presence of some amount of crystals of the form I.

The solid-state <sup>13</sup>C NMR CPMAS spectra of the three PPET samples are reported in Figure 3. The spectra are



**Figure 3.** Solid-state  $^{13}\text{C}$  NMR CPMAS spectra of the as-prepared samples of the PPET copolymers having the indicated ethylene contents.

similar to those of the quench-precipitated sPP samples of refs 13 and 14 and of the as-prepared PPET samples of ref 19, containing chains in a disordered conformation. Most of the resonances observed in the spectra of Figure 3 do not scale with the ethylene concentration and are indicative of a nonordered conformation of the chains. We will first analyze these spectral features and, then, analyze the resonances related to the ethylene units. The spectra of Figure 3 are characterized by the usual resonances of the methyl, methine, and methylene carbon atoms at  $\delta = 21.9$ ,  $27.4$  and at  $40.2$  and  $49.1$  ppm, respectively, typical of the  $(\text{T}_2\text{G}_2)_n$  helical conformation, and by additional resonances at  $\delta = 19.6$  and  $22.8$  ppm for the methyl carbon atoms, and at  $\delta = 44.5$  and  $50.2$  ppm for the methylene carbon atoms. Moreover, the resonances of the methyl carbon atoms at  $\delta = 22.8$  ppm and of the methine carbon atoms at  $\delta = 27.4$  ppm present shoulders at  $\delta = 23.4$  and  $28.2$  ppm, respectively. As suggested in refs 13 and 14, these additional resonances could be attributed to the presence of conformational disorder in the crystalline phase, which originates from the presence of trans-planar sequences in chains having a prevailing 2-fold helical  $(\text{TTGG})_n$  conformation. In particular, the resonance at  $\delta = 44.5$  ppm was assigned to  $\text{CH}_2$  groups in a TT.TG or GT.TT conformational environment (the dots indicate the methylene carbon atoms which experience one  $\gamma$ -gauche effect), whereas the resonance at  $18.9$  ppm was assigned to methyl carbon atoms in portions of chains in the trans-planar TTTT conformation,<sup>13</sup> according to the resonance found by Sozzani et al. for the form III of s-PP.<sup>24</sup>

The spectra of Figure 3 indicate that the as-prepared samples of the PPET copolymers are crystallized in disordered modifications like that shown in the model of Figure 1. It is worth noting that the intensities of the resonances at  $18.9$  and  $44.5$  ppm, indicative of the presence of trans-planar sequences, do not depend on the ethylene concentration of the copolymers. In fact, these resonances have relative intensities similar to those observed in the sPP homopolymer (see Figure 3 of ref 13). This indicates that the resonances at  $18.9$  and

**Table 1.** Comparison between the Calculated (According to Grant and Paul Empirical Rules)<sup>25</sup> and the Observed (Spectra of Figure 3) Chemical Shifts for the Methylene Carbon Atoms in the Proper Constitutional Sequence, in All the Possible Conformational Environments Compatible with the Crystalline State,<sup>8</sup> i.e. Corresponding to Sequences  $\dots\text{T}_2\text{G}_2\text{T}_{4n+2}\text{G}_2\text{T}_2\dots$ <sup>a</sup>

methylene nucleus	constitutional sequence	conformational environment	chemical shift (ppm)		
			calcd	obsd	
$\text{S}_{\alpha\alpha}$	PPP and/or PPE	TT.TT	51.2	50.2	
		TG.GT	51.2	49.1	
		GT.TG	41.2	40.2	
		GT.TT	46.2	44.5	
$\text{S}_{\alpha\gamma}$	PEP	TT.TG	46.2	44.5	
		TT.TT	43.8	41.8	
		TG.GT	43.8	41.8	
		GT.TG	33.8	33.8	
$\text{S}_{\beta\beta}$	PEP	GT.TT	38.8	38.5	
		TT.TG	38.8	38.5	
		TT.TT	25.9	25.2	
		GG.TT	25.9	25.2	
			TT.GG	25.9	25.2

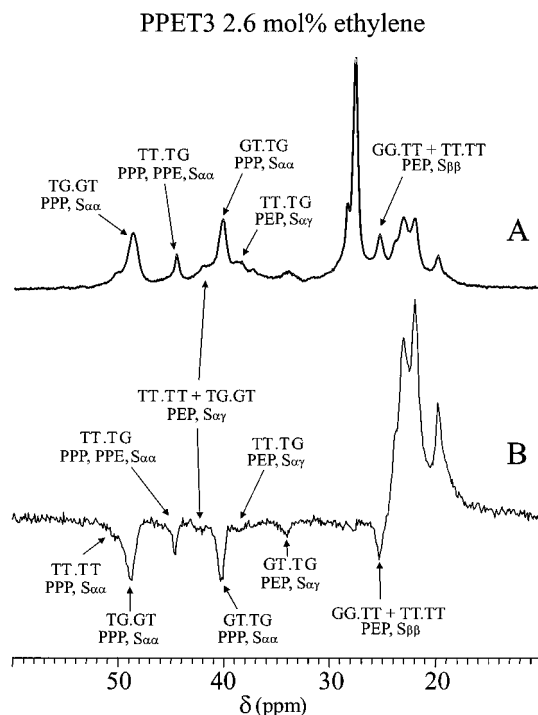
<sup>a</sup> In the calculation of the chemical shifts an additional empirical term of  $-5$  ppm for each  $\gamma$ -gauche effect is also used.

$44.5$  ppm are mostly due to methyl and methylene carbon atoms, respectively, belonging to propylene  $\dots\text{PPP}\dots$  sequences. Therefore, the relative amount of trans-planar portions of chains and kink bands does not scale with the ethylene concentration.

However, the presence of ethylene comonomeric units in the crystalline regions of the PPET copolymers probably favors, locally, the formation of trans-planar sequences, which, in turn, induce the crystallization of the samples in disordered modifications of the form II containing kink bands (Figure 1). The kinetically favored clustering of  $\text{T}_6\text{G}_2$  sequences, like in the model of Figure 1, induces the crystallization in these disordered modifications, where the trans-planar sequences (TTTT or TTTG) do not necessarily occur in correspondence of the ethylene comonomeric units.

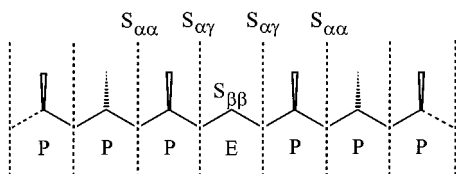
A direct proof of the partial inclusion of the ethylene units in the crystalline regions is given by the presence in the spectra of Figure 3 of the resonances of small intensity at  $\delta = 25.2$ ,  $33.8$ ,  $38.5$ , and  $41.8$  ppm, all consistent with the presence of isolated ethylene comonomeric units (E) in fully syndiotactic propylene (P) sequences ( $\dots\text{PEP}\dots$ ) and hence relative to secondary carbon atoms in suitable conformational environments. A comparison between the chemical shifts of the methylene carbon atoms observed in the spectra of Figure 3 and those calculated according to the Grant and Paul rules,<sup>25</sup> for methylene carbon atoms in the proper constitutional sequence and in different conformational environments, is reported in Table 1. In the calculations of the chemical shifts an additional empirical term of  $-5$  ppm for each  $\gamma$ -gauche effect was also used. It is apparent that the signal at  $25.2$  ppm may be assigned to secondary carbon atoms belonging to PEP sequences symmetrically placed between two tertiary carbon atoms in the  $\beta$  positions (atoms  $\text{S}_{\beta\beta}$ , the symbol S standing for secondary carbon atoms; see Scheme 1), which always experience two  $\gamma$ -gauche effects regardless of the conformational environment. The signals at  $33.8$ ,  $38.5$ , and  $41.8$  may be assigned instead to methylene carbon atoms in PEP sequences, placed between two methine groups in the  $\alpha$  and  $\gamma$  positions (atoms  $\text{S}_{\alpha\gamma}$ , see Scheme 1), in the conformational environments GT.TG (two  $\gamma$ -gauche effects), TT.TG or GT.TT (a single  $\gamma$ -gauche





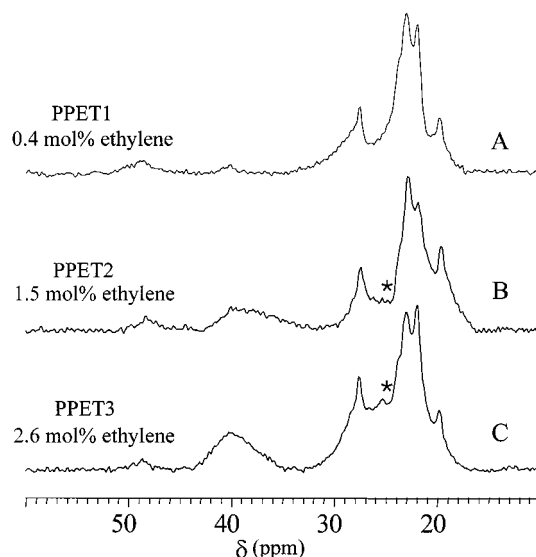
**Figure 4.** Solid-state  $^{13}\text{C}$  NMR CPMAS (A) and CP-SPI (B) spectra of the as-prepared PPET3 sample with 2.6 mol % of ethylene. Spectrum B has been amplified in order to make visible the weak resonances of the methylene carbon atoms.

#### Scheme 1



effect), and TT.TT or TG.GT (zero  $\gamma$ -gauche effect), respectively (see Figure 3).

To confirm these assignments, CPMAS experiments were performed in the cross-polarization (CP) mode in combination with polarization inversion (PI) with a simultaneous phase inversion (CP-SPI method).<sup>22,23</sup> In a CP-SPI spectrum obtained with long CP time (1–2 ms) and short PI times (30–35  $\mu\text{s}$ ),  $^{13}\text{CH}$  signals disappear,  $^{13}\text{CH}_2$  signals become negative with an intensity reduced to  $1/3$  and methyl signals remain positive and are attenuated by about 62%,<sup>22,23</sup> provided the crystal lattice is relatively rigid. This allows us to recognize the resonances of methine, methylene, and methyl carbon atoms. The CPMAS and the CP-SPI spectra of the sample PPET3 containing 2.6 mol % ethylene units are compared in Figure 4 as an example. The resonance at 27.4 ppm (with the shoulder at 28.2 ppm) present in the CPMAS spectrum of Figure 4A disappears in the CP-SPI spectrum of Figure 4B, confirming the assignment to methine carbon atoms. The positive resonances present in the spectrum of Figure 4B correspond only to the signals of the methyl carbon atoms. The complex multiplet structure of Figure 4A is preserved. The strong signals at  $\delta = 40.2$ , 44.5, and 49.1 ppm and the weak signals at  $\delta = 25.2$ , 33.8, 38.5, 41.8, and 50.2 ppm in Figure 4A all become negative in Figure 4B, indicating that they correspond to methylene carbon atoms.



**Figure 5.** Single-pulse  $^{13}\text{C}$  NMR MAS spectra, obtained with a short recycle time (1 s), of the as-prepared samples of the PPET copolymers having the indicated ethylene contents.

To establish whether the above weak signals belong to nuclei embedded in rigid (crystalline) or mobile (amorphous) regions, single-pulse  $^{13}\text{C}$  NMR MAS experiments with a short recycle time (1 s) were performed. In these spectra only the resonances of nuclear species belonging to the most mobile phase generally appear. The single-pulse spectra of the three PPET samples are reported in Figure 5. It is apparent that the most prominent resonances are those of the methyl carbon atoms, which preserve the multiplet structure observed in Figure 3. This is expected because methyl carbon atoms in solid polypropylenes always exhibit short spin–lattice relaxation times  $T_1$  due to the fast methyl rotation around the C–C bonds, irrespective of the mobility of the guest phase. In the spectra of Figure 5 the resonances of the methine groups at 27.4 ppm are noticeably reduced with respect to those in the CPMAS experiments. Since the relaxation times of the methine carbon atoms are substantially shortened by the influence of the close rotating methyl groups, also the crystalline methine groups are evident in the spectra of Figure 5, even though they are attenuated relative to the noncrystalline methine atoms. Finally, two broad bands at  $\delta \approx 49$  and 40 ppm are present in the spectra of Figure 5, due to the noncrystalline methylene carbon atoms. These signals are hardly evident in Figure 5A as a result of a very broad noncrystalline methylene lines. The resonances at 44.5 and 33.8 ppm, present in the CPMAS spectra of Figure 3, disappear in Figure 5, and the resonance at  $\delta = 25.2$  ppm (indicated with an asterisk in Figure 5) is strongly reduced in intensity. This confirms that the additional resonances at  $\delta = 44.5$ , 33.8, and 25.2 ppm (and most likely also the small intensity resonances at 38.5 and 41.8 ppm) are due, at least in part, to nuclei embedded in the rigid portions of the material, placed at the interface of the crystallites and/or within the area of the crystallites themselves.

Therefore, the presence of the narrow resonance at 25.2 ppm and of the resonances at 33.8, 38.5, and 41.8 ppm, in the CPMAS spectra of Figure 3, and the absence of the same narrow signals in the single-pulse experiments of Figure 5, are evidence of inclusion of the ethylene units in the crystalline phase. However, the presence of the weak signal at 25.2 ppm in the spectra

of Figure 5 (indicated by an asterisk) is also evidence that an appreciable amount of ethylene units are also contained in the noncrystalline phase.

### Conclusions

The ethylene units are partially included in the crystalline regions of the PPET copolymers. As-prepared samples of these copolymers crystallize in disordered modifications of form II of sPP. The disorder corresponds to the presence, in the crystalline phase, of portions of chains in trans-planar conformations in chains having a prevailing 2-fold helical conformation and packed like in the isochiral form II of sPP (Figure 1). The presence of the trans-planar defects is indicated by the resonances at 44.5 and 50.2 ppm in the  $^{13}\text{C}$  NMR CPMAS spectra, relative to  $^{13}\text{CH}_2$  nuclei in PPP and/or PPE sequences and by the resonance at 18.9 ppm, due to the methyl carbon atoms (Figure 3). The amount of trans-planar portions of chains does not scale with the ethylene concentration, since the resonance at 44.5 and 18.9 ppm are mostly due to the methylene and methyl carbon atoms belonging to propene sequences. However, the trans-planar defects may be also pinned to the ethylene units, as clearly indicated by the presence of the signals at 25.2, 38.5, and 41.8 ppm relative to PEP sequences (see Table 1 and Figure 3). Moreover, a nonnegligible portion of  $^{13}\text{CH}_2$  nuclei in the PEP sequences is also included in the ordered regions with chains in the TTGG 2-fold helical conformation, as indicated by the presence of the resonance at 33.8 ppm in the spectra of Figure 3. Finally, an appreciable amount of ethylene units is also included in the noncrystalline phase of the copolymers as indicated by the narrow resonance at 25 ppm in the spectra of Figure 5.

In the PPET copolymers the disordered modifications with kink bands form more easily than in the case of the sPP homopolymer because they are kinetically favored by the easier local formation of trans-planar sequences in the presence of ethylene units. These kink-band structures are, however, metastable also for the copolymers and transform into the more stable form I of sPP with chains in the ordered 2-fold helical conformation by thermal treatments or melt crystallization.<sup>19</sup>

It is worth noting that the inclusion of ethylene comonomeric units in the crystalline lattice of isotactic polypropylene has been also recently proved by NMR CPMAS experiments.<sup>26</sup>

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