

Polymorphism of syndiotactic polypropylene in copolymers of propylene with ethylene and 1-butene

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The structural characterization, by X-ray diffraction and solid-state ¹³C n.m.r. CPMAS, of copolymers of propylene with small amounts of ethylene and 1-butene, synthesized with a single centre syndiospecific catalyst, is presented. The effect of the presence of comonomeric units on the polymorphic behaviour of syndiotactic polypropylene is discussed. In the as-prepared samples, the presence of small amounts of ethylene induces the crystallization of conformationally disordered modifications of form II, intermediate between the limit ordered forms II and IV. The conformational disorder is characterized by the presence of long *trans*-planar sequences, including the ethylene units, and gives rise a structure with kink bands. In copolymers with 1-butene the usual crystallization in form I occurs. In samples of copolymers crystallized from the melt, the usual crystallization of form I is not affected by the presence of any comonomeric units, although disordered modifications of form I are always obtained. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Syndiotactic polypropylene (s-PP) presents a complex polymorphic behaviour^{1–10}. Four limit ordered crystalline forms of s-PP have been described so far. Different amounts of disorder, depending on the degree of stereoregularity and the mechanical and thermal history of the samples^{11–14}, characterize the crystalline phases of the various forms.

Form I (following the nomenclature proposed in Ref. 15) was found by Lovinger, Lotz *et al.*^{4–7}; it is the stable form of s-PP obtained under the most common conditions of crystallization (melt and solution crystallization) in powder samples and single crystals of s-PP. Form I is characterized by chains in s(2/1)2 helical conformation which are packed, in the ideal limit ordered structure, with an alternation of right handed and left handed helices along both *a* and *b* axes of the unit cell^{4,7}.

The crystal structure of the limit ordered form I has been recently refined¹⁵. Helical s(2/1)2 chains are packed in the monoclinic unit cell with axes *a* = 14.31 Å, *b* = 11.15 Å, *c* = 7.5 Å and γ = 90.3° according to the space group $P2_1/a$ ¹⁵. The main peaks observed in the X-ray powder diffraction profile are at *d* = 7.25, 5.6, 4.70 and 4.31 Å (2θ = 12.2°, 15.8°, 18.8° and 20.7°, CuK α).

Samples of s-PP crystallized in form I present variable amounts of disorder, depending on the crystallization temperatures¹⁶, characterized by defects in the regular alternation of left and right handed helices along the axes of the unit cell¹⁶ as well as by disorder in the stacking of *bc* layers of chains along *a*^{6,7,16}.

Form II is obtained in annealed fibre samples of s-PP (often in mixture with form I). It corresponds to the *C*-centred structure deduced by Corradini *et al.*^{1,2} from X-ray fibre diffraction patterns. This form is characterized by chains in s(2/1)2 helical conformation packed in the orthorhombic unit cell with axes *a* = 14.5 Å, *b* = 5.60 Å, *c* = 7.4 Å. The axes of the helices are in the positions (0,0,*z*) and (1/2,1/2,*z*) of the unit cell and the main peaks in the X-ray powder profile are at *d* = 7.25, 5.22 and 4.31 Å (2θ = 12.2°, 17.0° and 20.6°, CuK α)^{2,8}. The space group proposed for the limit ordered structure of form II was $C222_1$ ² for which helices of the same chirality are included in the unit cell.

Form III is obtained by stretching at room temperature compression moulded samples of s-PP, as found by Natta *et al.*³; it is characterized by chains in *trans*-planar conformation³. The crystal structure of form III has been reported recently by Chatani *et al.*⁹; *trans*-planar chains are packed in an orthorhombic unit cell with axes *a* = 5.22 Å, *b* = 11.17 Å, *c* = 5.06 Å; the space group proposed is $P2_1cn$ ⁹. When the fibre samples of form III are annealed above 100°C (under condition of fixed length), the *trans*-planar form transforms completely into the two-fold helical form; a fibre with a mixture of crystals of form I and form II is generally obtained⁸.

Form IV was obtained by Chatani *et al.*¹⁰ by exposing fibre specimens in the *trans*-planar form (form III) to organic solvents (e.g. benzene at temperature below 50°C). It is characterized by helices in a $(T_6G_2T_2G_2)_n$ conformation, packed in a triclinic unit cell with axes *a* = 5.72 Å, *b* = 7.64 Å, *c* = 11.6 Å, α = 73.1°, β = 88.8° and γ = 112.0°¹⁰. In a recent paper¹⁷ we have shown that form IV can be also

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described by a monoclinic structural model with the unit cell having axes $a = 14.17 \text{ \AA}$, $b = 5.72 \text{ \AA}$, $c = 11.6 \text{ \AA}$ and $\beta = 108.8^\circ$; the chains are packed according to the space group $C2^{17}$. In other words, the structure of s-PP in form IV may be described in the long range according to the average monoclinic C -centred structural model; locally, the symmetry breaks and the packing as in triclinic structural model occurs¹⁷. Form IV is transformed readily into the two-fold helical forms by annealing above 50°C^{10} .

The polymorphism of s-PP is complicated by the fact that, besides the disorder arising from defects in the packing of the two-fold helical chains^{6,7,16}, also a disorder in the conformation of the chains has been evidenced in samples of s-PP of lower stereoregularity¹³. Indeed, extra resonances observed in the solid-state ^{13}C n.m.r. spectra^{13,14} of s-PP samples quench precipitated from solutions, showing X-ray diffraction features typical of form II, have been explained through models characterized by disorder in the conformation of the chains¹³. The disorder corresponds to the presence of *trans*-planar portion of chains connecting portions in a $s(2/1)2$ helical conformations¹³. In the resulting structure, the conformational disorder produces the formation of kink bands¹⁸; the chains would be packed according to an orthorhombic lattice centred on the C face: for the ordered regions like in form II, for the region comprising the defects like in form IV^{13,17,18}. The modifications presenting kink bands could be thought as intermediate between the limit ordered forms II and IV of s-PP. A continuum of structures exists among the limit ordered ones of form II and form IV of s-PP.

In this paper, the effects of the presence of comonomeric units on the polymorphic behaviour of s-PP is analysed. The structural characterization, by X-ray diffraction and solid-state ^{13}C n.m.r., of copolymers of propylene with small amounts of ethylene and 1-butene, is presented.

EXPERIMENTAL SECTION

The samples of copolymers of propylene with ethylene (PPET) and 1-butene (PPBU) were synthesized with a single centre syndiospecific catalyst composed of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminumoxane¹⁹ with the method described in Ref. 20. The used catalytic system should behave with good regio- and stereo-specificity for the propylene comonomer²¹.

Four samples of copolymers were analysed. The compositions of the copolymers and the melting temperatures of the as-prepared samples are reported in Table 1. Melt-crystallized samples were obtained by melting the as-prepared samples at $\approx 200^\circ\text{C}$ and successive rapid cooling to room temperature.

The composition of the copolymers were determined by the analysis of the ^{13}C n.m.r. spectra, recorded on a Bruker

Table 1 Composition (% mol of comonomeric units) of the samples of copolymers of propylene with ethylene and 1-butene

Sample	Comonomer	% Mol comonomer ^a	T_m ($^\circ\text{C}$) ^b
PPET(1)	Ethylene	1.5	114
PPET(2)	Ethylene	1	115
PPBU(1)	1-Butene	2.5	126
PPBU(2)	1-Butene	2	130

^aFrom solution ^{13}C n.m.r. spectra

^bFrom DSC curves recorded at $10^\circ\text{C}/\text{min}$

AC270 spectrometer at 120°C in deuterated tetrachloroethane. These spectra also indicate that the comonomeric units are isolated.

Calorimetric measurements were performed in a differential scanning calorimeter Perkin Elmer DSC-7 in a flowing N_2 atmosphere. The melting temperatures of Table 1 were determined by DSC curves recorded at $10^\circ\text{C}/\text{min}$.

Oriented fibre samples of copolymers were obtained by stretching at room temperature compression moulded samples.

X-ray powder diffraction patterns were obtained at room temperature with an automatic Philips diffractometer using Ni filtered $\text{CuK}\alpha$ radiation. The patterns recorded at different temperatures were obtained with an Hanton-Paar attachment with a temperature control of $\pm 0.5^\circ\text{C}$. The X-ray fibre diffraction patterns were obtained with Ni filtered $\text{CuK}\alpha$ radiation in photographic cylindrical and flat cameras.

An estimation of the crystallinity index, x_c , of the samples was obtained from the X-ray powder diffraction profiles by measuring the intensity of the diffraction of crystalline (i_c) and amorphous (i_a) phases: $x_c = i_c/(i_c + i_a)$.

CPMAS ^{13}C n.m.r. spectra were recorded at room temperature on an AM 250 Bruker spectrometer operating at 62.89 MHz for ^{13}C . The samples (100 mg) were spun in a zirconia rotor at a speed of 4500 Hz. For each spectrum

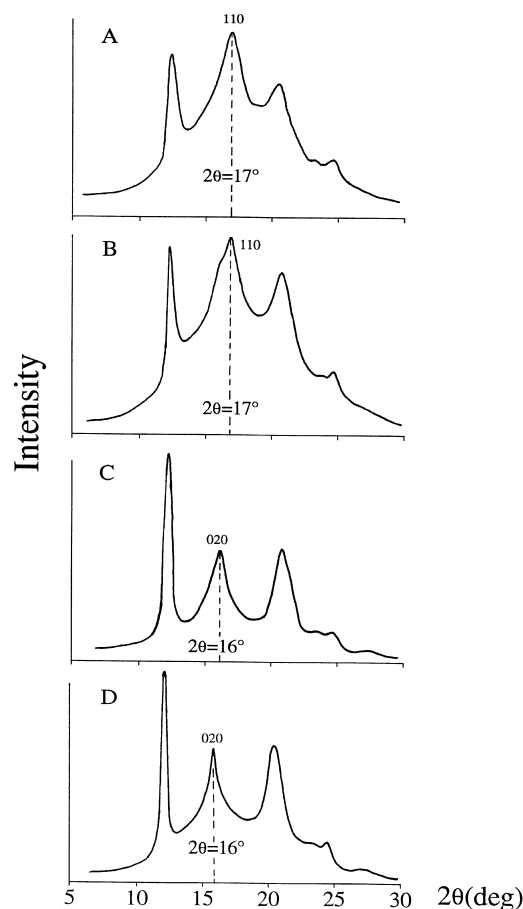


Figure 1 X-ray powder diffraction patterns of the as-prepared samples of copolymers of Table 1. (A) PPET(1) 1.5 mol%ET; (B) PPET(2) 1 mol%ET; (C) PPBU(1) 2.5 mol%BU; (D) PPBU(2) 2 mol%BU. (ET = ethylene, BU = 1-butene). The indices (110) and (020) of the reflections are given for the unit cells with $b = 5.6$ and 11.2 \AA , respectively, corresponding to forms II and I of s-PP, respectively

about 1500 transients were collected using the following acquisition parameters: 3 s delay between pulses, 90° pulse of 5.4 μ s and a contact time of 1 ms. Crystalline polyethylene was used as external reference at 33.6 ppm from tetramethylsilane (TMS).

RESULTS AND DISCUSSION

As-prepared samples

The X-ray powder diffraction patterns of the as-prepared samples of copolymers PPET and PPBU of *Table 1* are reported in *Figure 1*. The profiles of the samples of copolymers of propylene with ethylene PPET(1) and PPET(2) (*Figure 1A* and *B*, respectively) are characterized by the presence of the broad reflection at $2\theta = 17^\circ$, typical of form II^{2,8,13,18} (indexed as (110) with the unit cell of form II with axes $a = 14.5 \text{ \AA}$, $b = 5.60 \text{ \AA}$, $c = 7.4 \text{ \AA}$). The copolymers with 1-butene, PPBU(1) and PPBU(2), are instead crystallized in form I as revealed by the presence, in the X-ray diffraction pattern of *Figure 1C* and *D*, of the (020) reflection at $2\theta = 16^\circ$ of form I⁴. The absence of the (211) reflection at $2\theta = 18.8^\circ$, typical of the fully antichiral packing of the chains⁴, indicates that disordered modifications of form I are obtained¹⁶.

We recall that form I is the stable form of s-PP and powder samples of s-PP are generally crystallized in form I under the most common conditions of crystallization (melt and solution crystallization)⁴⁻⁷. Form II is easily obtained only in annealed fibre samples of s-PP (often in mixture with form I)⁸. Modifications of form II presenting conformational disorder¹³, which produces structures with kink-bands¹⁸, crystallize in samples of s-PP of lower stereoregularity quench-precipitated from solutions^{13,14}.

The data of *Figure 1* indicate that the usual crystallization of s-PP in form I in powder samples is affected by the presence of comonomeric units. Indeed, copolymers of propylene with ethylene, for which we can assume at least a partial inclusion of the ethylene units in the crystalline phase of s-PP, are crystallized in form II. Owing to the broadness of the reflection with maximum at $2\theta = 17^\circ$, we cannot exclude the presence in these samples of crystals in form I. In copolymers with 1-butene, the comonomeric unit does not affect the usual crystallization in form I. It is worth noting that in both patterns of *Figure 1C* and *D* the (200) reflection is at the Bragg angle typical of the homopolymer ($2\theta = 12.2^\circ$), indicating that expansions of the a axis of the unit cell of s-PP is not observed for these copolymers. Nevertheless, we cannot exclude that small amounts of 1-butene comonomeric units could be included in the crystalline phase without affecting the usual crystallization in form I and visible changing of the cell dimensions. Indeed, the inclusion of 1-butene comonomeric units in the crystalline phase of s-PP has been recently suggested in the literature^{22,23} for copolymers of higher content of 1-butene (>6 mol%) through the observation of the increase of the a axis of the unit cell.

The solid-state ¹³C n.m.r. CPMAS spectra of the as-prepared samples of the copolymers of *Table 1* are reported in *Figure 2*.

We recall that the solid-state ¹³C n.m.r. CPMAS spectrum of the crystalline syndiotactic polypropylene with chains in the fully helical (TTGG)_n conformation, presents a resonance of the methyl carbon atoms located at $\delta = 21.3$ ppm, a resonance of the methine carbon atoms at 26.7 ppm and two

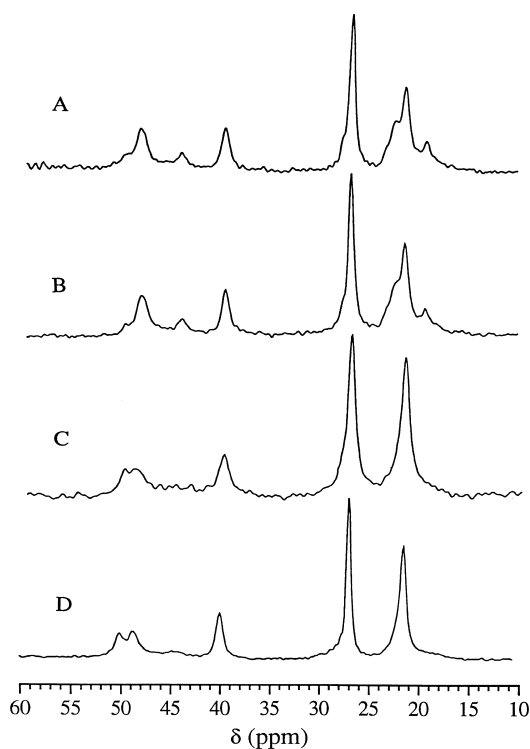


Figure 2 Solid-state ¹³C n.m.r. CPMAS spectra of the as-prepared samples of copolymers of *Table 1*. (A) PPET(1) 1.5 mol% ET; (B) PPET(2) 1 mol % ET; (C) PPBU(1) 2.5 mol% BU; (D) PPBU(2) 2 mol% BU

resonances of the methylene carbon atoms at 40.2 and 49.1 ppm^{24,25} attributed to the methylene carbons in the two conformational environments *GT.TG* and *TG.GT*, respectively (the dot indicates the methylene carbon atom). In Ref. 13 we have shown that samples of s-PP, identified by X-ray diffraction as in form I of s-PP, exhibits solid-state ¹³C n.m.r. CPMAS spectra analogous to those already described in the literature. In contrast, spectra of some quench precipitated s-PP samples, which shows X-ray diffraction features of form II, present, in addition to the main four peaks listed above, two additional peaks in the region of the methyl groups at $\delta = 18.9$ and 22.4 ppm and one additional peak at 44.9 ppm in the region of methylene groups. Moreover, the methyl group resonance with the maximum at $\delta = 22.4$ ppm exhibits a shoulder at 23.4 ppm and the methine group resonance shows a shoulder at 27.6 ppm¹³. These resonances belong to nuclei in well-defined conformational environment fixed in rigid structures placed at the interface of the crystallites and within the strained or disordered area of the crystallites themselves: the resonance at $\delta = 44.9$ ppm in particular, was assigned to CH₂ groups in a *TX.YG* conformation¹³, whereas, in analogy with literature data^{26,27}, the resonance at 18.9 ppm was assigned to methyl groups in portion of chains in *trans*-planar conformation¹³. We argued that the extra-resonances in the methyl and methylene regions are possibly connected to the presence of conformational disorder in the crystalline phase, which seems to originate from the presence of *trans*-planar portions in chains in a prevailing (TTGG)_n conformation¹³. This disorder produces the formation of kink bands in the structure of form II¹⁸.

It is apparent from the spectra of *Figure 2* that also the two samples of the copolymers with ethylene PPET, which are mainly crystallized in form II (*Figure 1A* and *B*), present ¹³C n.m.r. CPMAS spectra similar to that of the

quench-precipitated sample of s-PP of low stereoregularity of Ref. 13. Indeed, these spectra (Figure 2A and B) are characterized by the usual resonances of the methyl carbons at $\delta = 21.8$ ppm, of the methine carbons at $\delta = 27.3$ ppm and of the two methylene carbon atoms at $\delta = 40.1$ and 48.7 ppm, typical of the helical $(TTGG)_n$ conformation, and by additional resonances at $\delta = 20$ ppm for the methyl carbons and at $\delta = 45$ and 50.2 ppm for the methylene carbon atoms. Moreover, the resonances of the methyl carbons at $\delta = 21.8$ ppm and of the methine carbons at $\delta = 27.3$ ppm present shoulders at $\delta = 23$ and 28.2 ppm, respectively. As suggested for the homopolymer¹³, these additional resonances could be attributed to the presence of conformational disorder in the crystalline phase, which seems to originate from the presence of *trans*-planar portions in chains in a prevailing helical $(TTGG)_n$ conformation¹³.

Samples of copolymers PPBU(1) and PPBU(2) which are crystallized in form I (Figure 1C and D, respectively), present usual ¹³C n.m.r. CPMAS spectra characteristics of s-PP in the regular helical $TTGG$ conformation (Figure 2C and D), except for the resonance at $\delta = 50.2$ ppm, which is generally assigned to methylene carbon atoms in conformational sequences $TT.TT$ ²⁶. This resonance is evident in the spectra of Figure 2C and D, but the absence in these spectra of the corresponding resonance of the methyl carbon atoms in conformational sequences $TT|TT$ (the vertical bar indicates the carbon bounded to the methyl) at $\delta \approx 19$ – 20 ppm²⁶ allows us to exclude that *trans*-planar sequences belong to the crystalline phase. Assuming that 1-butene units are included in the crystalline regions^{22,23}, the local conformation close to these units is expected to be slightly distorted (i.e. the *trans* and the *gauche* torsion angles slightly deviate from the values they assume in the normal $TTGG$ helix of s-PP). These distortions make the CH₂ carbons close to 1-butene units not equivalent to the methylene carbons in the usual conformational environment $TG.GT$ of long propene sequences. It is worth noting that the measured $T_{1\rho}$ (spin-lattice relaxation time in the rotating

frame) of the nuclei corresponding to the resonances at 40.1, 48.7 and 50.2 ppm in the spectra of Figure 2C and D are all higher than 70 s. This indicates that all these nuclei belong, indeed, to the crystalline regions.

¹³C n.m.r. CPMAS spectra of samples PPET (Figure 2A and B) are also similar to the spectrum of form IV of s-PP reported in the literature²⁷. This could indicate that the above as-prepared samples of copolymers are in form IV rather than in a conformationally disordered modification of form II. The Bragg distances of the reflections observed in the corresponding X-ray powder diffraction patterns (Figure 1A and B) are nearer to those of the form II^{2,8} than those of form IV¹⁰. Indeed, although X-ray powder profiles of the limit ordered forms II and IV are not available, we have shown that the calculated powder profile of form IV presents strong reflections at $2\theta = 13.1^\circ$, 17.4° , 19.6° , 21.9° and 25.0° ¹⁸, whereas the patterns of Figure 1A and B present reflections at $2\theta = 12.4^\circ$, 17.0° , 20.7° and 24.7° nearer to that present in the calculated pattern of the limit ordered form II ($2\theta = 12.2^\circ$, 17.1° , 20.8° and 24.4°)¹⁸.

The hypothesis that the copolymers PPET are crystallized in form IV could be definitely ruled out by a comparison between the thermal behaviours of the copolymers and s-PP in form IV. We recall that form IV of s-PP transforms in the helical $TTGG$ forms (I or II) by heating at temperatures $T \geq 50^\circ\text{C}$ ¹⁰.

We have performed thermal treatments of the samples PPET(1) and PPET(2) and recorded the X-ray powder diffraction patterns at various temperatures. Since the behaviour of the copolymers PPET is the same, we report in Figure 3 the X-ray powder diffraction profiles, at the indicated temperatures, only for the sample PPET(1).

It is apparent, from Figure 3, that the reflection at $2\theta = 17^\circ$ is present also at temperatures greater than 50°C , indicating that this peak arises from the diffraction of crystals of s-PP in form II and not in form IV. The (020) reflection at $2\theta = 16^\circ$, typical of form I⁴ appears only at temperatures of 80 – 90°C . The sample initially crystallized

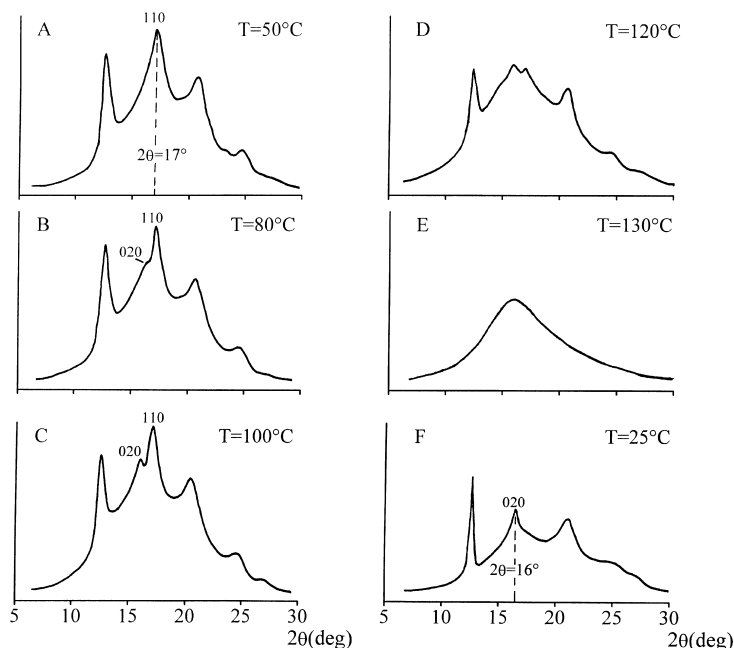


Figure 3 X-ray powder diffraction patterns of the as-prepared copolymer PPET(1) recorded at different temperatures. (A) 50°C ; (B) 80°C ; (C) 100°C ; (D) 120°C ; (E) 130°C ; (F) 25°C after melting at 130°C

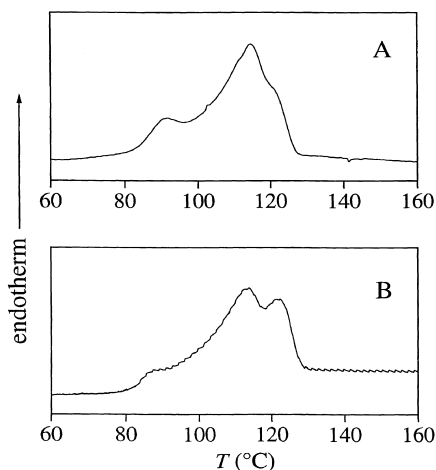


Figure 4 DSC curves of the as-prepared sample of the copolymer PPET(1) at heating rates of 10 (A) and 2.5°C/min (B)

in a conformationally disordered modification of form II (Figure 3A) starts to transform into form I at 80–90°C. The relative intensity of the peak at $2\theta = 16^\circ$ increases with increasing the temperature with respect to the intensity of the peak at $2\theta = 17^\circ$. At 130°C the sample is in the melt state (Figure 3E); after the cooling to room temperature, crystallization in form I occurs (Figure 3F). It is worth noting that the degree of crystallinity decreases already at 110–120°C (Figure 3D) indicating a partial melting of the sample.

The DSC curves of the sample PPET(1), recorded at different heating rates are reported in Figure 4. The endotherms are very broad and show a multiple peak shape. Melting starts at 90–100°C; the area of the high temperature peak, which is present as a shoulder at $T = 121^\circ\text{C}$ in the curve at 10°C/min (Figure 4A), increases with the decrease of the heating rate (Figure 4B). This indicates the occurrence of recrystallization phenomena. In other terms, crystals of form II start to melt at 90–100°C and recrystallize at temperature below 120°C. Then, the more ordered crystals melt at higher temperature.

The calorimetric data of Figure 4 and the X-ray powder diffraction profiles of Figure 3 indicate that the transition of form II into form I occurs through a recrystallization; with increasing the temperature above 90–100°C, crystallites of the copolymers initially in form II melt and readily recrystallize in form I. Moreover, the thermal behaviour of the copolymers PPET confirms that the as-prepared samples are in a conformationally disordered modification of form II and not in form IV.

A possible example of a model structure comprising kink-bands for copolymers of propylene with ethylene is shown in Figure 5. Correspondingly to the ethylene comonomeric units, the dihedral angles are expected to assume preferably a *trans* conformation. The ethylene comonomeric units are hence included in the long *trans*-planar regions of the crystals (see Figure 5, as an example) at a low cost of conformational energy. Probably, the presence of ethylene as comonomeric units in s-PP and the inclusion of these units in the crystalline regions induce crystallization in the metastable form II of s-PP, rather than in the more stable form I.

Melt-crystallized samples

The X-ray powder diffraction patterns of the samples of copolymers of Table 1 crystallized from the melt by rapid

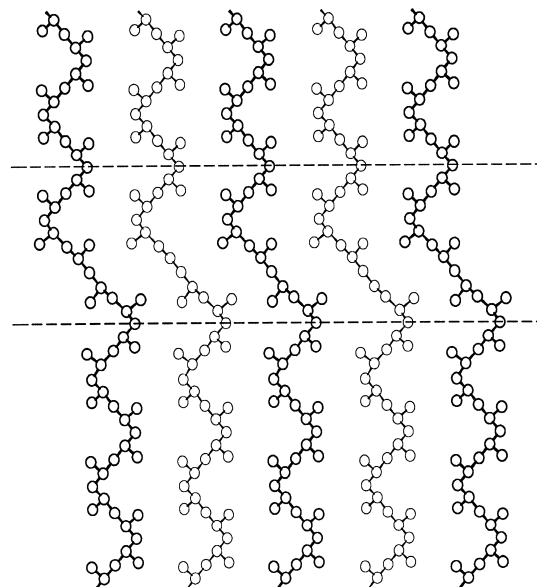


Figure 5 Possible example of disordered structural model of form II of s-PP comprising kink bands in the copolymers PPET. Chain drawn with thin and bold lines are at 0 and 1/2 along b (perpendicular to the plane of drawing). The 'defective' portions of the chains (delimited by the dashed lines) correspond to the conformational sequences $G_2T_{2(2n+1)}$ with $n = 1$, and include ethylene units

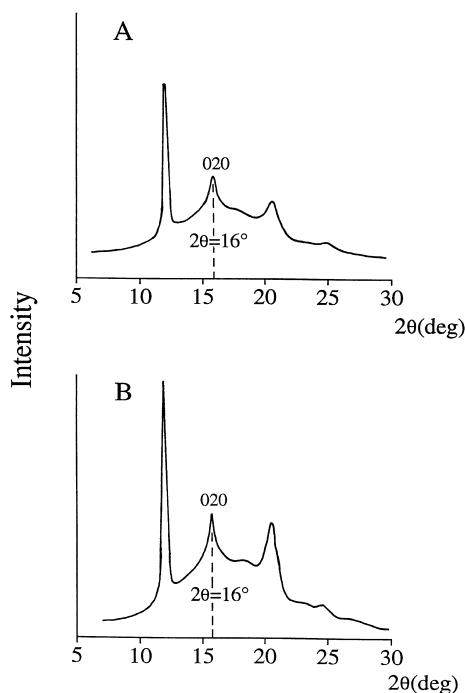


Figure 6 X-ray powder diffraction patterns of samples of copolymers rapidly crystallized from the melt: (A) PPET(1) 1.5 mol% ET; (B) PPBU(1) 2.5 mol% BU

cooling of the melted state to room temperature, present only the (020) reflection at $2\theta = 16^\circ$ indicating that all samples are crystallized in form I⁴. The patterns are very similar, therefore only those of samples PPET(1) and PPBU(1) are shown in Figure 6. The absence of the (211) reflection at $2\theta = 18.8^\circ$, typical of the fully antichiral packing of the chains⁴, indicates that disordered modifications of form I are formed^{4,16}.

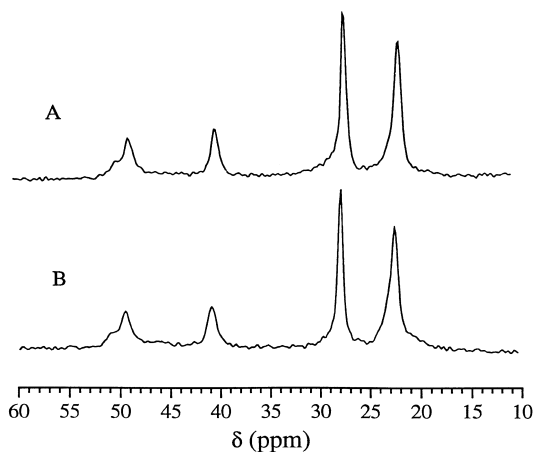


Figure 7 Solid-state ^{13}C n.m.r. CPMAS spectra of samples of copolymers rapidly crystallized from the melt: (A) PPET(1) 1.5 mol% ET; (B) PPBU(1) 2.5 mol% BU

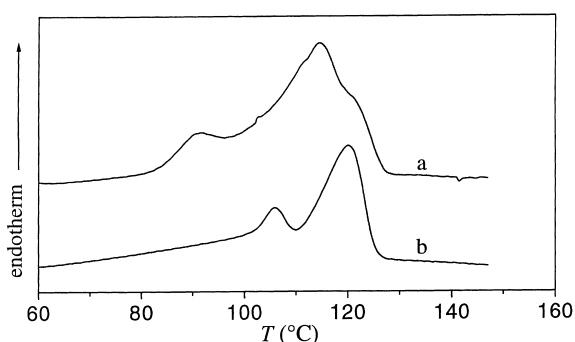


Figure 8 DSC curves of samples of the copolymer PPET(1) at heating rate of $10^\circ\text{C}/\text{min}$. (a) As-prepared sample (first run); (b) melt-crystallized sample (second run after the run (a) and cooling to room temperature)

The solid-state ^{13}C n.m.r. CPMAS spectra of the samples of copolymers of *Table 1* crystallized from the melt are similar. Only the spectra of the samples of *Figure 6* are reported in *Figure 7*. It is apparent that all samples crystallized in form I, present the usual ^{13}C n.m.r. CPMAS spectrum characteristic of s-PP in the regular helical *TTGG* conformation.

The X-ray diffraction patterns and the solid-state ^{13}C n.m.r. CPMAS spectra indicate that the usual crystallization from the melt of form I of s-PP¹⁶ is not affected by the presence of these comonomeric units.

A comparison between the X-ray diffraction patterns of the as-prepared samples of copolymers (*Figure 1*) and those of the melt-crystallized samples (*Figure 6*) shows a reduction of the degree of crystallinity for the melt-crystallized

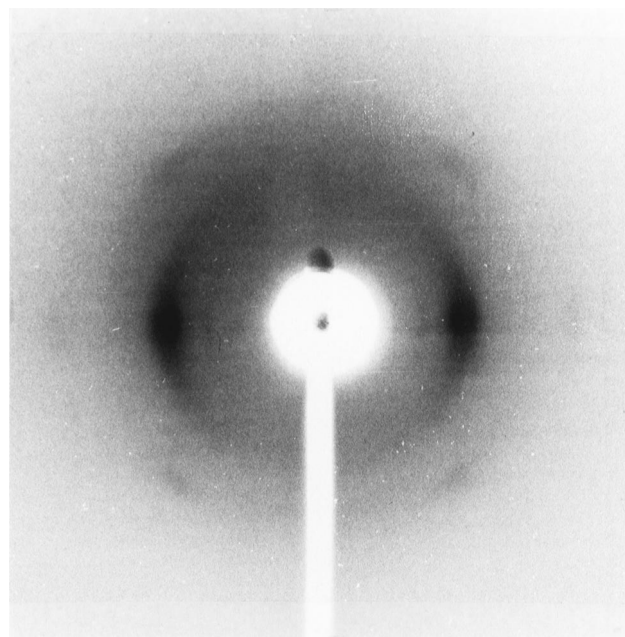


Figure 9 X-ray fibre diffraction pattern, on a cylindrical film, of an oriented sample of the copolymer PPET(1) (form III)

samples. A similar conclusion can be drawn from the comparison between the DSC curves of the as-prepared and melt-crystallized samples. In *Figure 8* are reported, as an example, the DSC curves at a heating rate of $10^\circ\text{C}/\text{min}$, of the sample PPET(1), corresponding to the melting of the as-prepared sample (curve *a*) and to the second melting (curve *b*), performed after curve *a* and cooling to room temperature. It is apparent that the enthalpy of melting of the sample crystallized from the melt is lower than that of the as-prepared sample; moreover, recrystallization phenomena occur also for the melt crystallized sample. The enthalpies of melting and the degrees of crystallinity, evaluated from the X-ray diffraction profiles, of as-prepared and rapidly melt-crystallized samples of all copolymers are reported in *Table 2*.

In melt-crystallized samples the comonomeric units do not affect the usual crystallization of s-PP although low crystallinity degrees and disordered modifications of form I¹⁶ are always obtained.

Oriented samples

Oriented fibres of copolymers were obtained by stretching at room temperature compression moulded samples.

The X-ray fibre diffraction patterns of oriented samples of the copolymers of *Table 1* are very similar. In *Figure 9* only the X-ray fibre diffraction pattern of the sample PPET(1) is shown, as an example. It is apparent from *Figure 9* that, as

Table 2 Enthalpies of melting, ΔH_m , and X-ray crystallinities, X_c , of the as-prepared and melt-crystallized samples of copolymers of propylene with ethylene and 1-butene

Sample	ΔH_m (J/g) ^a		X_c^b	
	As-prepared	Melt-crystallized	As-prepared	Melt-crystallized
PPET(1)	54	37	0.50	0.30
PPET(2)	47	32	0.50	0.31
PPBU(1)	53	28	0.53	0.38
PPBU(2)	67	30	0.53	10.40

^aFrom DSC curves recorded at $10^\circ\text{C}/\text{min}$

^bFrom X-ray diffraction profiles

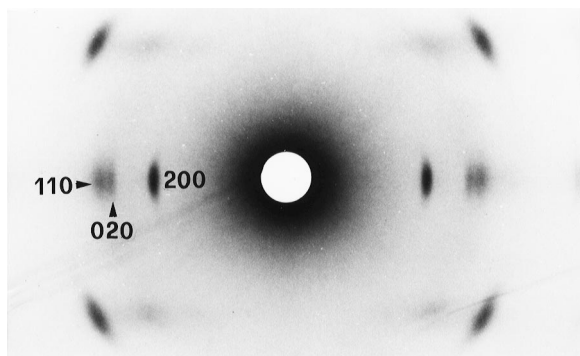


Figure 10 X-ray fibre diffraction pattern, on a flat plate, of the oriented sample of the copolymer PPET(1) of Figure 9 after annealing at 90°C (form I + form II). The indices (110) and (020) of the reflections are given for the unit cells with $b = 5.6$ and 11.2 Å, respectively, corresponding to forms II and I of s-PP, respectively

occurs for the homopolymer^{8,9}, the *trans*-planar form III is obtained by stretching.

Annealing of the fibres (under tension) at temperatures of 90–100°C produces a transition of form III into the two-fold helical modification⁸. The X-ray fibre diffraction pattern of the annealed fibre of the copolymer PPET(1) is reported in Figure 10. It is apparent the presence, in the pattern of Figure 10, of both (020) and (110) reflections at $2\theta = 16^\circ$ and 17° , respectively. As observed for the homopolymer⁸, also for the copolymer samples, fibres with a mixture of crystals of form I and form II are obtained by annealing fibres of form III.

CONCLUSIONS

The complex polymorphic behaviour of s-PP is affected by the presence of comonomeric units.

As for prepared samples of copolymer of propylene with small amounts of comonomer units, like ethylene or 1-butene, a partial inclusion of the comonomeric units in the crystalline phase of s-PP, may be assumed. Copolymers with ethylene are crystallized in form II whereas in copolymers with 1-butene, the comonomeric unit does not affect the usual crystallization in form I, although disordered modification of form I are obtained¹⁶.

¹³C n.m.r. CPMAS spectra of samples of copolymers crystallized in form II indicate the occurrence of conformational disorder characterized by the presence of *trans*-planar sequences in chains in prevailing helical (*TTGG*)_n conformation. As already observed for homopolymer s-PP samples^{13,18}, when the as-prepared samples of copolymers crystallize in form II, conformationally disordered modifications of form II, intermediate between the limit ordered forms II and IV, are obtained. The presence of ethylene as comonomeric units in s-PP and the inclusion of these units in the crystalline phase make easier the formation of long *trans*-planar crystalline regions and, hence, induce crystallization in metastable, conformationally disordered modifications of form II, presenting kink bands, rather than in the more stable form I. The analysis of the thermal behaviours of these samples allows us to exclude the hypothesis that these samples are crystallized in form IV rather than in a disordered modification of form II. Moreover, the calorimetric measurements and the X-ray diffraction patterns recorded at different temperatures up to the melting, have shown the occurrence of recrystallization

phenomena during the heating; crystallites of the copolymers initially in form II melt when the temperature increases above 90–100°C, and rapidly recrystallize in form I below 120°C. Then, the so obtained more ordered crystals of form I melt at higher temperatures.

The as-prepared samples of the copolymers with 1-butene, crystallized in form I, present the usual solid-state ¹³C n.m.r. CPMAS spectra, characteristic of s-PP in the regular helical *TTGG* conformation, but for the presence of an extra resonance at 50.2 ppm. This resonance is related to methylene carbons belonging to crystalline regions, placed close to 1-butene comonomeric units. The local conformation close to these units is expected to be slightly distorted from the usual conformation of propene sequences. These distortions make the CH₂ carbons close to 1-butene units not equivalent to the methylene carbons in the usual conformational environment *TG.GT* of long propene sequences.

The presence of comonomeric units does not affect the usual crystallization of form I of s-PP in samples of copolymers crystallized from the melt. Indeed, for all samples crystallized from the melt, form I is always formed and the usual solid-state ¹³C n.m.r. CPMAS spectra, characteristic of the regular helical *TTGG* conformation, are obtained. The absence of the (211) reflection at $2\theta = 18.8^\circ$, typical of the fully antichiral packing of the chains⁴, indicates that disordered modifications of form I are formed^{4,16}.

Oriented fibres of copolymers show a polymorphic behaviour very similar to that of the homopolymer⁸. Usual form III is obtained by stretching at room temperature compression moulded samples of all copolymers. Annealing at temperatures of 90–100°C produces a transition of form III into the stable two-fold helical modifications; fibres with a mixture of crystals of forms I and II are obtained.

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