Structural Characterization of Syndiotactic Propylene–Styrene–Ethylene Terpolymers

Claudio De Rosa,*,† Annamaria Buono,† Lucia Caporaso,‡ and Leone Oliva‡

Dipartimento di Chimica, Università di Napoli "Federico II", Complesso Monte S.Angelo, Via Cintia, 80126 Napoli, Italy, and Dipartimento di Chimica, Università di Salerno, Via S. Allende, 84081 Baronissi (SA), Italy

Received May 8, 2003; Revised Manuscript Received July 11, 2003

ABSTRACT: A structural characterization of a propylene–styrene–ethylene terpolymer sample (sP/(S–E)), prepared with syndiospecific C_s-symmetric metallocene catalyst, is presented. The study of the polymorphic behavior in as-prepared, melt-crystallized, and fiber samples has confirmed that ethylene units are mainly bound to styrene units arising from catalyst reactivation after the secondary insertion of styrene. Styrene–ethylene units are mainly segregated in the amorphous phase. The bulky styrene units, bound to ethylene, prevent the inclusion of ethylene units in the crystals of syndiotactic polypropylene (sPP), as generally occurs for copolymers of sPP with ethylene. This explains the experimental evidence that the influence of the presence of styrene–ethylene units on the polymorphism of sPP is smaller than that observed in copolymers of sPP containing only ethylene or butene comonomeric units.

Introduction

New polymer microstructures have become accessible after the development of metallocene catalysts for the polymerization of olefins and new polymeric materials having interesting physical properties have been prepared.[1–3] In particular, highly syndiotactic poly(α-olefins),[4,5] and copolymers of syndiotactic polypropylene with other α-olefins,[6–19] have been produced. Studies on the synthesis and characterization of copolymers of syndiotactic polypropylene with 1-butene,[6–12,15] ethylene,[6–9,13,14] 4-methyl-1-pentene,[6] and octene[16–19] have recently been reported. It has been demonstrated that smaller comonomeric units, like ethylene[9,13,14] and 1-butene,[10–12] are partially included in the crystals of sPP, strongly affecting the polymorphic behavior of sPP.

ansa-Metallocene based catalysts, including the C_s symmetric catalyst for the synthesis of sPP,[20] generally promote the propylene polymerization through primary insertion of the monomer.[1,21] It is instead generally accepted that the insertion of styrene is prevailingly secondary both with metallocene, as in the case of ethylene–styrene copolymers prepared with the C_s-symmetric catalyst MePhC(cyclopentadienyl)(9-fluorenyl)ZrCl₂[22] and of isotactic polystyrene obtained in the presence of the C_2-symmetric *ansa*-metallocene, *rac*-Me₂C-bis(1-indenyl)ZrCl₂, and with monocyclopentadienyl-based catalysts.[23] These regiospecificities of metallocene catalysts with respect to propylene and styrene insertions can explain the absence in the literature of evidences of propylene–styrene random or alternating copolymerizations, while the ethylene–styrene copolymerization has been widely described.[22–24] In fact, steric hindrance prevents primary propylene insertion into metal–polymer bond when the last inserted unit is secondary styrene. As a consequence, in the propylene–styrene copolymerization, a growing polymer chain should become inactive as soon as styrene is inserted.

However, propylene–styrene copolymers have been recently obtained with both isospecific C_2-symmetric[25,26] and syndiospecific C_s-symmetric catalysts,[26] by adding to the comonomeric mixture a small amount of ethylene as catalyst reactivator. It has been proved that traces of ethylene reactivates the catalyst after secondary insertion of styrene,[25,26] and interesting materials based on copolymers of isotactic[25] and syndiotactic polypropylene,[26] containing styrene–ethylene comonomeric units, have been produced. Incorporating of styrene in isotactic and syndiotactic polypropylene should induce new physical properties in these materials. In this paper, the structural characterization of the syndiotactic propylene–(styrene–ethylene) terpolymer (sP/(S–E)), produced with a syndiospecific C_s-symmetric metallocene catalyst, is presented. The polymorphic behavior of the terpolymer is compared with that of copolymers of sPP with ethylene containing similar ethylene contents, described in the literature.[14]

Experimental Section

The syndiotactic propylene/(styrene–ethylene) sP/(S–E) terpolymer sample has been prepared with the catalyst isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride (Me₂C(Cp)(9-Flu)ZrCl₂) activated with methylalumoxane (MAO), as described in ref 26.

Materials. Ethylene and propylene (Societa' Ossigeno Napoli, polymerization grade) were used without further purification. Toluene was refluxed for 48 h over metallic sodium and distilled under a nitrogen atmosphere. Styrene was purified by distillation under reduced pressure over CaH₂. Commercial methylalumoxane (Witco, 30% toluene solution) was dried in vacuo and added as a powder into the reaction flask. Me₂C(Cp)(9-Flu)ZrCl₂ was prepared according to a published procedure.[20]

Copolymerizations. The terpolymer sample containing 2 mol % of styrene–ethylene comonomeric units was obtained by bubbling (0.10 L/min) the monomers mixture (ethylene–propylene 1/50), prepared with an automatic gas blending device (MKS Instruments, Deutschland GmbH), at atmospheric pressure into a 100 mL Pyrex reactor provided with

* Corresponding author. Telephone: ++39 081 674346. Fax: ++39 081 674090. E-mail: derosa@chemistry.unina.it.
† Università di Napoli "Federico II".
‡ Università di Salerno.

magnetic stirrer, containing toluene (20 mL), styrene (10 mL), MAO (7×10^{-3} mol), and catalyst (7×10^{-6} mol) at 20 °C for 4 h. The sample was coagulated by pouring the reaction mixture into methanol acidified with HCl (aqueous, concentrated) and, then, filtered, washed with fresh methanol, and vacuum-dried. The gas mixtures of the monomers were analyzed by gas chromatography.

Characterization. The composition of the terpolymer sample was determined by analysis of the ^{13}C NMR spectra, recorded on an AV 400 Bruker operating at 100 MHz in the Fourier transform mode and at 293 K. The samples (30 mg) were dissolved in 0.5 mL of CDCl$_3$ into a tube with 5 mm outer diameter. Tetramethylsilane (TMS) was used as an internal chemical shift reference. The analysis indicates that 2 mol % of ethylene and 2 mol % of styrene have been incorporated in the terpolymer chains. The terpolymer sample, according to this analysis, is random and homogeneous in the composition.[26]

The intrinsic viscosity was measured in tetrahydronaphthalene at 135 °C. The molecular weight was evaluated from the intrinsic viscosities using the parameters reported for atactic polypropylene.[14] Values of the intrinsic viscosity of 0.60 dL/g and molecular weight M_v of 8.0×10^4 were obtained. This catalytic system produces relatively high molecular weight samples with a polydispersity index of the molecular masses around 2.

The calorimetric measurements and the melting temperatures were obtained with a differential scanning calorimeter Perkin-Elmer DSC-7 performing scans in a N$_2$ atmosphere at heating rate of 2.5 and 10 °C/min.

Samples of sP/(S−E) terpolymer were isothermally crystallized from the melt at various temperatures. The as-prepared sample was melted at 150 °C and kept, for 5 min at this temperature in a N$_2$ atmosphere; they were then rapidly cooled to the crystallization temperature T_c and kept at this temperature, still in a N$_2$ atmosphere, for a time t_c long enough to allow complete crystallization at T_c. In the various isothermal crystallizations, the crystallization time t_c is different depending on the crystallization temperature. The shortest time is 24 h for the lowest crystallization temperature and increases with increasing the crystallization temperature, up to 2 weeks for the highest crystallization temperature. The samples were then cooled to room temperature and analyzed by wide-angle X-ray diffraction and DSC.

Oriented fibers of sP/(S−E) terpolymer sample were obtained by stretching at room-temperature compression molded samples.

X-ray diffraction patterns were obtained with Ni-filtered Cu Kα radiation. The powder profiles were obtained with an automatic Philips diffractometer, whereas the fiber diffraction patterns were recorded on a BAS-MS imaging plate (FUJIF-ILM) using a cylindrical camera and processed with a digital imaging reader (FUJIBAS 1800).

For sP/(S−E) samples crystallized from the melt in the form I of sPP, an evaluation of the degree of order present in the structure was obtained from the X-ray diffraction profiles following the method used for the sPP homopolymer and described in ref 27. Precisely, the ratio between the intensities of the 211 and 020 reflections, at $2\theta = 18.8$ and 15.8°, respectively, $R = I(211)/I(020)$, was used as a measure of the degree of order in the alternation of right and left-handed helical chains. The intensities of the 211 and 020 reflections were measured from the area of the corresponding diffraction peaks arising above the diffuse halo in the X-ray powder diffraction profiles.[27]

Results and Discussion

The structure and the polymorphic behavior of the terpolymer sP/(S−E) sample, containing 2 mol % of styrene−ethylene units, have been studied in various crystallization conditions, in powder melt-crystallized samples and oriented fibers, and compared with the polymorphic behavior of the sPP homopolymer.
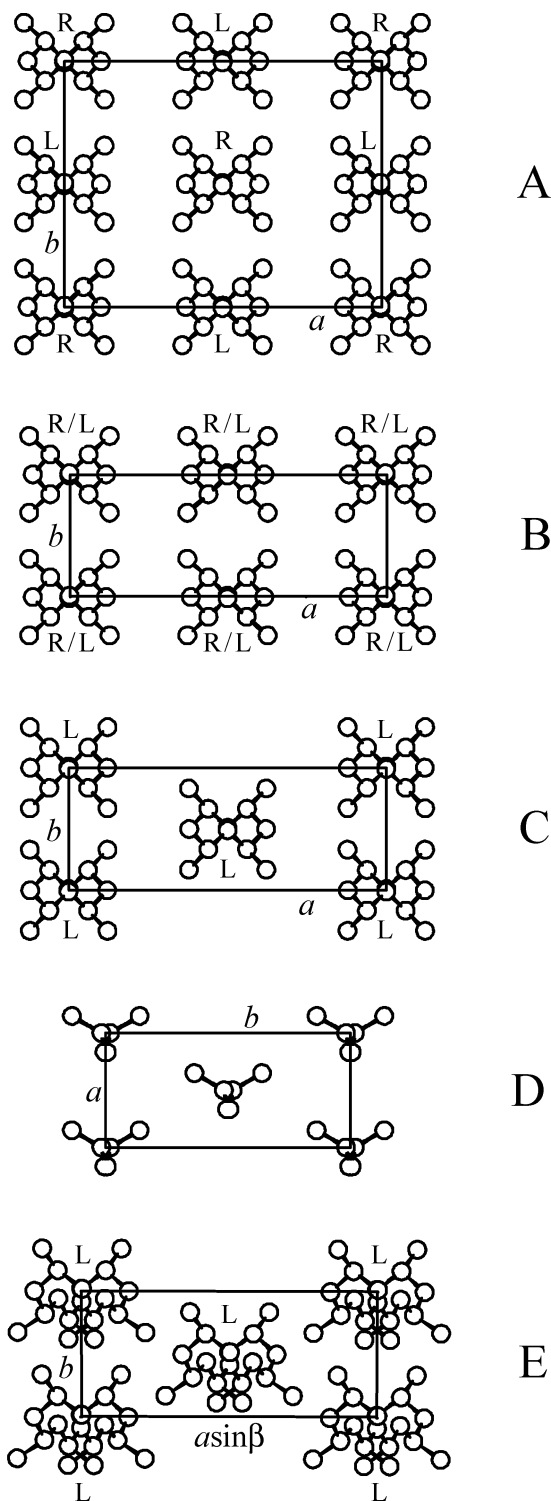

Figure 1. Models of packing of the limit ordered form I (A), limit disordered form I (B), form II (C), form III (D), and form IV (E) of sPP. R = right-handed helix; L = left-handed helix.

sPP presents a complex polymorphic behavior,[27−38] complicated by the presence of structural disorder.[27,32,40−43] Four different crystalline forms[28,29,33−37] and a mesomorphic form[44] have been found (Figure 1). The most stable form I (Figure 1A,B) and the metastable form II (Figure 1C) are characterized by chains in **s**(2/1)2 helical conformation, packed in orthorhombic unit cells.[27−29,35,36] In the limit-ordered structure of the stable form I right- and left-handed helical chains alternate along the a and b axes of the unit cell (Figure 1A),[29] whereas a fully isochiral packing of the 2-fold helices
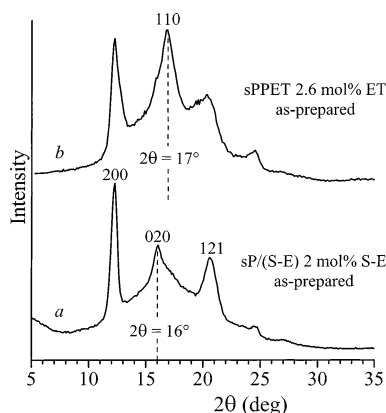
Figure 2. X-ray powder diffraction profiles of as-prepared samples of the sP/(S−E) terpolymer with 2 mol % of styrene−ethylene units (a) and of the sPPET copolymer with 2.6 mol % of ethylene (b).[14] The 200 and 121 reflections at $2\theta = 12.2$ and 20.6°, respectively, of the helical forms of sPP, the 020 reflection at $2\theta = 15.9°$ of form I and the 110 reflection at $2\theta = 17°$ of form II of sPP, are indicated.

characterizes the structure of form II (Figure 1C).[28,35,37] The two metastable modifications, form III (Figure 1D) and form IV (Figure 1E) present chains in trans-planar[33] and $(T_6G_2T_2G_2)_n$[34,39] helical conformations, respectively.

The polymorphic behavior of sPP is affected by the presence of constitutional defects. It has been reported that the presence of 1-butene or ethylene comonomeric units prevents the formation of the ordered form I by crystallization from the melt.[12,14] Only disordered modifications of form I, characterized by disorder in the alternation of right- and left-handed helical chains along the axes of the unit cell (Figure 1B), have been obtained even by crystallization at high temperatures. Moreover, it has been shown that the presence of 1-butene, for concentration higher than 4 mol %, prevents the formation of the trans planar form III by stretching,[12] whereas the presence of ethylene induces the crystallization of disordered modifications of form II,[9,13,14] characterized by disorder in the conformation of the chains (kink-bands disorder).[41−43]

Changes of the polymorphic behavior of sPP, in turn, strongly influence the physical properties. For instance, oriented fibers of sPP show elastic behavior,[45−47] which is related to the structural organization. For this reason, studies of the variation of the polymorphism of sPP as a consequence of incorporation of bulky comonomeric units, as in sP/(S−E) terpolymers, are quite important.

The X-ray powder diffraction profile of the as-prepared sample of the sP/(S−E) terpolymer containing 2 mol % of styrene−ethylene units is reported in Figure 2 (profile a) and compared with the diffraction profile of the as-prepared sample of the copolymer of sPP with 2.6 mol % of ethylene (sPPET), taken from ref 14 (profile b).

It is apparent that the as-prepared samples of sP/(S−E) terpolymer and sPPET copolymer, having similar ethylene contents, present different X-ray diffraction profiles. The sP/(S−E) terpolymer is in the helical form I (Figure 1A,B), as indicated by the presence of the 200, 020, and 121 reflections at $2\theta = 12.2$, 15.9, and 20.6°, respectively, in the diffraction profile of Figure 2a. The Bragg angles of 200, 020, and 121 reflections are the same as in the diffraction pattern of sPP homopolymer samples in form I,[29,36] indicating that the values of the unit cell parameters in sP/(S−E) crystals are the same

as in form I of sPP ($a = 14.5$ Å, $b = 11.2$ Å, $c = 7.4$ Å),[29] and hence, styrene units are excluded from crystals of sPP.

The as-prepared sample of the copolymer sPPET with 2.6 mol % of ethylene is instead in a disordered modification of form II,[14] as indicated by the presence of the 110 reflection at $2\theta = 17°$ in the diffraction profile of Figure 2b. As demonstrated in the literature,[14] in these copolymers of sPP with ethylene, ethylene units are, at least in part, included in the crystals of sPP. In the as-prepared samples, the presence of ethylene induces the crystallization of conformationally disordered modifications of form II of sPP (kink-bands disordered modifications), characterized by portion of chains in trans-planar conformation in chains having a prevailing helical conformation.[14]

The data of Figure 2 indicate that in the as-prepared sP/(S−E) terpolymer sample the presence of ethylene comonomeric units does not induce the crystallization of kink-bands conformationally disordered modifications of form II, as instead occurs for the propylene−ethylene copolymers containing similar ethylene concentration,[14] but the usual disordered modification of form I (Figure 1B) is obtained. This suggests that in this terpolymer sample the ethylene units are not included in the crystals of sPP and confirms that the bulky styrene units are mainly bound to ethylene units,[25,26] preventing the inclusion of ethylene in the crystals and, hence, not affecting the usual crystallization of sPP in form I.

The X-ray powder diffraction profiles of samples of the sP/(S−E) terpolymer containing 2 mol % of styrene−ethylene units obtained by crystallization from the melt at various crystallization temperature T_c are reported in Figure 3.

It is apparent that also melt-crystallized samples are in the helical form I (Figure 1A,B), as indicated by the presence of the 200, 020, and 121 reflections at $2\theta = 12.2$, 15.9, and 20.6°, respectively, in the diffraction profiles of Figure 3.

The data of Figure 3 also show that the width of the 200 and 020 reflections is smaller in the melt-crystallized samples (Figure 3b−e) than in the as-prepared sample (Figure 3a), and decreases with increasing the crystallization temperature, indicating an increase of the crystal size with increasing the crystallization temperature. From the width of the 200 reflection at $2\theta = 12.2°$, values of the size of crystals of form I along the a axis direction of nearly 100 Å for crystals of the as-prepared sample, and of 170, 200, 250, and 270 Å, for crystals of samples crystallized at 90, 100, 110, and 120 °C, respectively, have been estimated.

The diffraction profiles of Figure 3 indicate that the as-prepared sP/(S−E) sample, or samples crystallized from the melt at low temperatures, crystallize in disordered modifications of form I of sPP, characterized by a statistical disorder in the positioning of right and left-handed helical chains (Figure 1B, space group *Bmcm*),[27,29] as demonstrated by the absence of the 211 reflection at $2\theta = 18.8°$ in the X-ray powder diffraction profiles of Figure 3a−c. We recall that for the sPP homopolymer, the 211 reflection at $2\theta = 18.8°$ is typical of the packing characterized by the regular alternation of 2-fold helices of opposite chirality along the a and b axes (Figure 1A).[29] This reflection is present only in the X-ray diffraction profiles of sP/(S−E) samples crystallized from the melt at higher temperatures and its intensity increases with increasing the crystallization
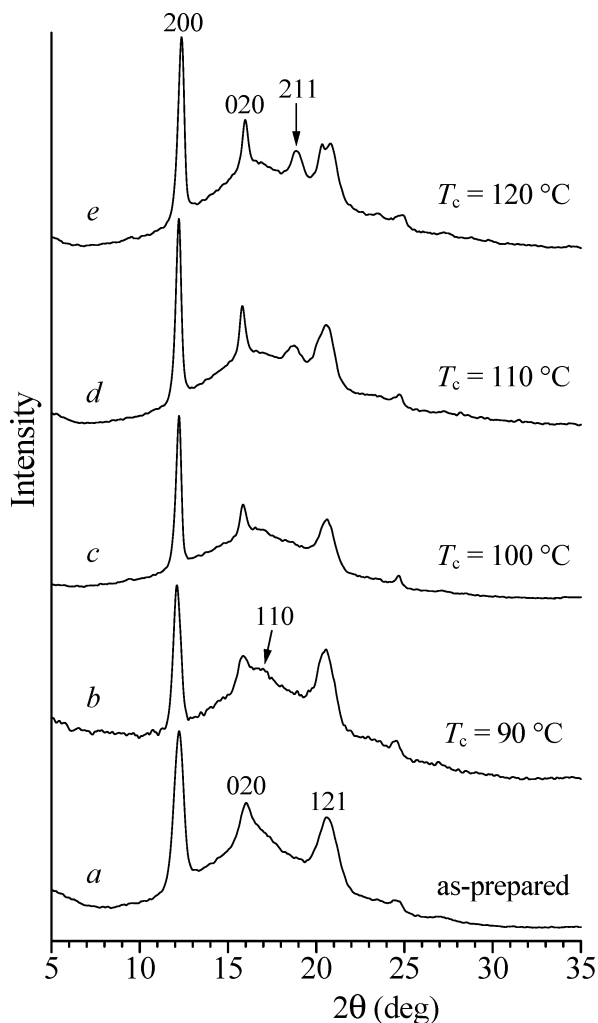
Figure 3. X-ray powder diffraction profiles of the as-prepared sample of the sP/(S−E) terpolymer with 2 mol % of styrene−ethylene units, and of samples isothermally crystallized from the melt at the indicated crystallization temperatures T_c. The 200 and 121 reflections at $2\theta = 12.2$ and 20.6°, respectively, of the helical forms, the 020 and 211 reflections at $2\theta = 15.9$ and 18.8°, respectively, of form I, and the 110 reflection at $2\theta = 17°$ of form II of sPP are indicated.

Figure 4. Values of the order parameter R of sP/(S−E) terpolymer samples with 2 mol % of styrene−ethylene units, crystallized from the melt reported as a function of the crystallization temperature T_c (○), and compared with the values of R for s-PP homopolymer samples taken from ref 27 (●), and for copolymer samples of sPP with 2.6 mol % of ethylene (sPPET) (□), taken from ref 14.

values of R of sPP homopolymer samples, taken from ref 27, and of samples of the sPPET copolymer with 2.6 mol % of ethylene, taken from ref 14. It is apparent that, while for the homopolymer the order parameter R increases with T_c from $R = 0$, corresponding to the limit disordered structure of form I, characterized by a statistical positioning of right and left-handed helical chains in each site of the lattice (Figure 1B), to a constant value $R \approx 1$, corresponding to the limit ordered structure of form I of Figure 1A,[27] for the sP/(S−E) terpolymer the limit value of R is lower than 1 (nearly 0.7), but higher than the limit value obtained for the copolymers of sPP containing nearly the same ethylene content ($R \approx 0.5$),[14] despite the presence of the bulkier styrene units.

These data clearly indicate that the presence of styrene−ethylene units does not affect the usual crystallization of sPP in the most stable *B*-centered form I, but prevents the formation of the ordered antichiral packing (Figure 1A) even at high crystallization temperatures. However, the degree of order in the alternation of antichiral helices along the axes of the unit cell is higher than that achieved in copolymers containing only ethylene comonomeric units.

In the case of copolymers of sPP with ethylene the presence of low degree of order has been explained considering that ethylene units are, at least in part, included in the crystals of sPP both in as-prepared and in melt-crystallized samples.[14] As discussed above, in the as-prepared samples the presence of ethylene induces the crystallization of kink-bands disordered modifications of form II of sPP (Figure 2b).[14] These modifications are metastable and transform into the stable helical form I by crystallization from the melt.[14] The presence of ethylene, however, prevents the formation of ordered modification of form I (Figure 1A) since it produces the development of disorder in the stacking of *bc* layers of chains piled along *a*, characterized by shift of *bc* layers of *b*/4 along *b* (*b*/4 shifts disorder),[32,27] which in turn produces local arrangements of the chains as in the *C*-centered form II of sPP (Figure 1C).[14] This kind of disorder, observed also in sPP homopolymer samples crystallized at low temperature,[32,27] destroys any correlation at long distances between the chirality of the helices along the *a* and *b* axes of the unit cell. Antichiral packing of first neighboring chains may still be preserved locally and lost in the long range because of the occurrence of the *b*/4 shifts disorder.

temperature T_c (Figure 3d,e). The diffraction profiles of Figure 3 indicate that more ordered crystals of form I of sPP, characterized by a certain degree of order in the alternation of right- and left-handed helices along the axes of the unit cell, are obtained with increasing the crystallization temperature. However, even at the highest crystallization temperature, the intensity of the 211 reflection is still lower than that expected for the limit ordered structure of form I of sPP.[27,29]

The intensity of the 211 reflection at $2\theta = 18.8°$ can be used as a measure of the degree of order present in the crystals of form I. As reported for sPP homopolymer[27] and for copolymers with 1-butene and ethylene,[12,14] since the intensity of the 020 reflection is constant with T_c, we use the ratio between the intensities of 211 and 020 reflections, at $2\theta = 18.8$ and 16°, respectively, $R = I(211)/I(020)$, to eliminate any dependence of the intensity on the crystallinity and the thickness of the samples.

The values of R of the sP/(S−E) terpolymer samples with 2 mol % of styrene−ethylene units, crystallized from the melt, are reported in Figure 4 as a function of the crystallization temperature and compared with the
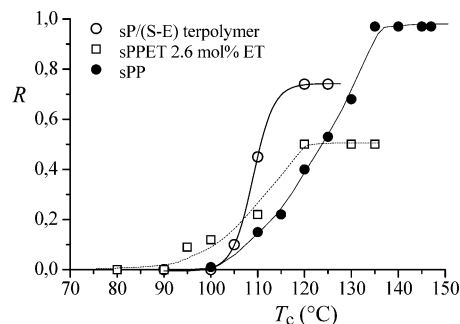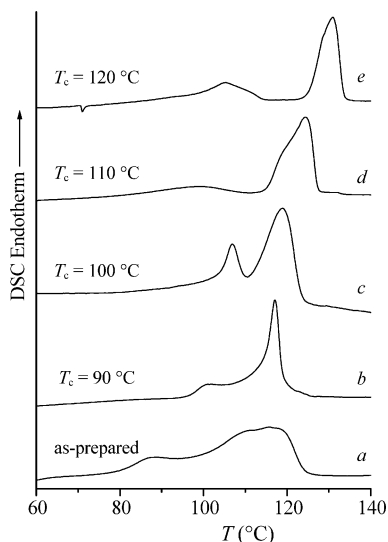
Figure 5. DSC heating scans, recorded at 10 °C/min, of the as-prepared sP/(S−E) terpolymer sample with 2 mol % of styrene−ethylene, and of samples crystallized from the melt at the indicated temperatures.

In the sP/(S−E) terpolymer samples, we observe that a higher degree of order in the alternation of antichiral helices in the crystals of form I is achieved in the melt-crystallized samples, with respect to copolymers containing only ethylene comonomeric units (Figure 4). This confirms that the bulkier styrene−ethylene units are mainly excluded from the crystals of form I, affecting in a lower amount the ordering process of form I with increasing the crystallization temperature. However, also for the sP/(S−E) terpolymer a certain amount of $b/4$ shifts disorder, and/or local arrangements of the chains as in the C-centered form II, are present in the as-prepared sample and in samples crystallized from the melt at low temperatures. This is clearly indicated by the presence of the shoulder at $2\theta = 17°$ of the 020 reflection at $2\theta = 16°$ in the X-ray diffraction profile of the as-prepared sample (Figure 3a), and the small diffraction peak at $2\theta = 17°$ in the profiles of samples crystallized at low temperatures (Figure 3b,c), corresponding to the 110 reflection typical of form II of sPP (Figure 1C).

The DSC heating scans of the as-prepared and melt-crystallized samples of the sP/(S−E) terpolymer are reported in Figure 5.

A steep increase of the melting temperature with increasing the crystallization temperature is apparent. This is in part linked to the increase of the lamellar thickness and crystal size (as discussed above, the latter increases from nearly 100 Å for crystals of the as-prepared sample, to 270 Å for crystals of the sample crystallized from the melt at the highest temperature) and also to the increase of the structural order in the crystals of form I (Figure 4).

It is apparent that the DSC curves of the as-prepared sample and of samples crystallized at low temperatures present broad endotherms with multiple peaks, which indicates the occurrence of recrystallization phenomena during heating. This is confirmed by the DSC scans recorded at different heating rates, shown in Figure 6 for the sample crystallized from the melt at 100 °C. The area of the peak at low temperature decreases with decreasing heating rate, demonstrating that recrystallization occurs during melting. It is also worth noting
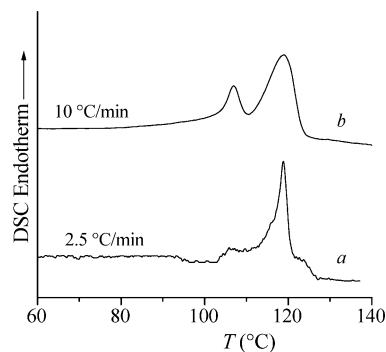

Figure 6. DSC heating scans, recorded at the indicated heating rates, of the sP/(S−E) terpolymer sample with 2 mol % of styrene−ethylene, crystallized from the melt at 100 °C.
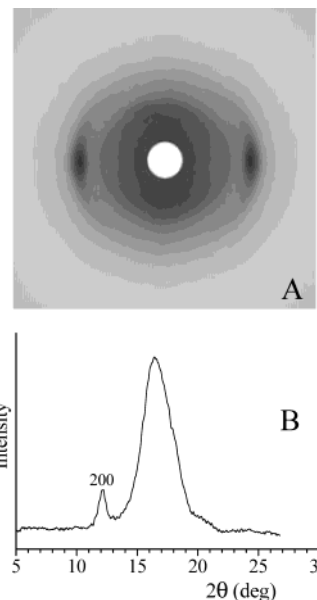

Figure 7. X-ray fiber diffraction pattern (A), and corresponding X-ray diffraction profile read along the equatorial line (B), of fibers of the sP/(S−E) terpolymer sample with 2 mol % of styrene−ethylene. The 200 reflection at $2\theta = 12°$ of the helical form of sPP is indicated in part B.

that the melting temperature of the as-prepared sample of the sP/(S−E) terpolymer (nearly 116 °C) is much lower than that of the copolymer of sPP containing the same concentration of ethylene comonomeric units (nearly 130 °C),[14] indicating the strong effect of the presence of styrene units on the melting temperature of sPP.

Oriented Fibers. Oriented fibers of sP/(S−E) terpolymer have been obtained by stretching at room-temperature compression molded films crystallized in form I. The X-ray fiber diffraction pattern, and the corresponding intensity profile read along the equatorial line, of sP/(S−E) fibers are reported in Figure 7, parts A and B, respectively. It is apparent that the disordered trans-planar mesomorphic form of sPP has been obtained by stretching, as indicated by the presence of the broad equatorial reflection at $2\theta \approx 17°$ in the pattern of Figure 6. The helical form I in the unoriented film transforms into the trans-planar mesophase by stretching. A small amount of the helical form is still present as indicated by the presence of the 200 reflection of low intensity at $2\theta = 12°$, in the pattern of Figure 7. These data indicate that for these terpolymers the ordered trans-planar form III does not form by stretching, as instead occurs for sPP homopolymer.[33,35]
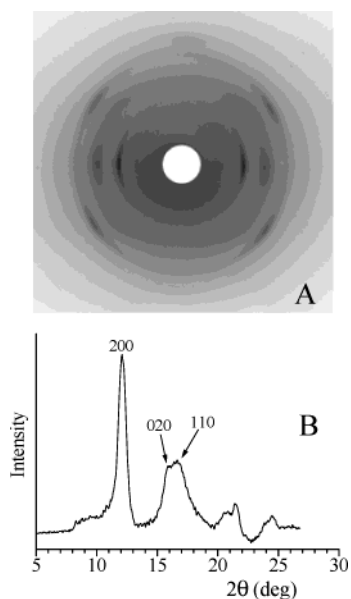
Figure 8. X-ray fiber diffraction pattern (A), and corresponding X-ray diffraction profile read along the equatorial line (B), of the sP/(S−E) fiber sample of Figure 7 after annealing at 70 °C for 20 min. The 200 reflection at $2\theta = 12.2°$ of the helical forms of sPP and the 020 and 110 reflections at $2\theta = 16$ and 17°, respectively, typical of forms I and II of sPP, respectively, are indicated in part B.

It is worth noting that in the case of copolymers of sPP with 1-butene, having a similar comonomer concentration (nearly 2 mol %), stretched fibers are in the ordered trans-planar form III,[12] and only at high concentration (higher than 5−6 mol %) is the formation of the trans-planar form III prevented by the presence of the bulky constitutional defects, and the stable form I is obtained by stretching.[12] In the case of sP/(S−E) terpolymer sample, instead, the formation of the trans-planar form III is prevented already for lower amounts of the bulkier styrene−ethylene units. However, the presence of styrene−ethylene units does not prevent the formation of the trans-planar conformation, as in the case of copolymers with 1-butene but only prevents the packing of the trans-planar chains in the ordered lattice of form III, and the disordered mesomorphic form is obtained (Figure 7). This gives a further experimental evidence that the styrene−ethylene units are basically segregated in the amorphous phase and do not affect the usual formation of the trans-planar conformation of sPP by stretching.[33,35] The formation of the disordered mesomorphic form instead of the ordered trans-planar form III is probably due to the high degree of disorder produced by the presence of constitutional defects.

The X-ray fiber diffraction pattern and the corresponding intensity profile read along the equatorial line, of the fiber of the sP/(S−E) terpolymer in the mesomorphic form annealed at 70 °C for 20 min, are reported in Figure 8, parts A and B, respectively.

It is apparent that fibers in mixtures of crystals of the helical form I and form II of sPP are obtained by annealing, as indicated by the increase of the intensity of the 200 reflection at $2\theta = 12°$, typical of the helical forms, and the presence of both 020 and 110 reflections at $2\theta = 16$ and 17°, respectively, typical of forms I and II, respectively, in the diffraction pattern of Figure 8. This behavior upon annealing treatments is similar to that observed for the sPP homopolymer.[35,46]

Conclusions

The structural characterization of a propylene−styrene−ethylene terpolymer sample (sP/(S−E)), prepared with syndiospecific C_s-symmetric metallocene catalyst, has confirmed that ethylene units are mainly bound to the styrene units, arising from catalyst reactivation after the secondary insertion of styrene.

The presence of ethylene comonomeric units does not induce the crystallization, in the as-prepared sample, of kink-bands conformationally disordered modifications of form II, as instead occurs for the propylene−ethylene copolymers,[14] but disordered modifications of form I crystallizes. This indicates that in this terpolymer the bulky styrene units are bound to the ethylene units,[25,26] preventing the inclusion of ethylene in the crystals and, hence, not affecting the usual crystallization of sPP.

The terpolymer sP/(S−E) sample crystallizes from the melt in the stable form I, characterized by a degree of order in the alternation of antichiral helices along the axes of the unit cell higher than that achieved in copolymers containing only ethylene comonomeric units. This also confirms that the bulkier styrene−ethylene units are mainly excluded from the crystals of form I, affecting in a lower amount the ordering process of form I with increasing the crystallization temperature.

Stretching of sP/(S−E) terpolymer compression molded films produces transformation of the form I into the trans-planar mesomorphic form. The presence of styrene−ethylene units does not prevent the formation of the trans-planar conformation, as instead occurs in the case of copolymers of sPP with 1-butene,[12] but only prevents the packing of the trans-planar chains in the ordered lattice of form III. This also indicates that the styrene−ethylene units are basically segregated in the amorphous phase and do not affect the usual formation of the trans-planar conformation of sPP by stretching.[33,35]

References and Notes

(1) Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143.
(2) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3907.
(3) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2586.
(4) Ewen, J. A.; Jones, R.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.
(5) Albizzati, E.; Resconi, L.; Zambelli, A. Eur. Pat. Appl. 387609 (Himont Inc.), 1991; *Chem. Abstr.* **1991**, *114*, 62980a.
(6) Galimberti, M.; Albizzati, E.; Mazzocchi, R.; U.S. Patent 5196496, 1993.
(7) Kakugo, M. *Macromol. Symp.* **1995**, *89*, 545.
(8) Naga, N.; Mizunuma, K.; Sadatoshi, H.; Kakugo, M. *Macromolecules* **1997**, *30*, 2197; *Polymer* **2000**, *41*, 203.
(9) De Rosa, C.; Auriemma, F.; Vinti, V.; Grassi, A.; Galimberti, M. *Polymer* **1998**, *39*, 6219.
(10) De Rosa, C.; Talarico, G.; Caporaso, L.; Auriemma, F.; Fusco, O.; Galimberti, M. *Macromolecules* **1998**, *31*, 9109.
(11) De Rosa, C.; Auriemma, F.; Caporaso, L.; Talarico, G.; Capitani, D. *Polymer* **2000**, *41*, 2141.
(12) De Rosa, C.; Auriemma, F.; Orlando, I.; Talarico, G.; Caporaso, L. *Macromolecules* **2001**, *34*, 1663.
(13) De Rosa, C.; Auriemma, F.; Talarico, G.; Busico, V.; Caporaso, L.; Capitani, D. *Macromolecules* **2001**, *35*, 1314.
(14) De Rosa, C.; Auriemma, F.; Fanelli, E.; Talarico, G.; Capitani, D. *Macromolecules* **2003**, *36*, 1850.

(15) Zhang, B.; Yang, D.; De Rosa, C.; Yan, S. *Macromolecules* **2002**, *35*, 4646.

(16) Jungling, S.; Mulhaupt, R.; Fisher, D.; Langhauser, F. *Angew. Makromol. Chem.* **1995**, *229*, 93.

(17) Thomann, R.; Kressler, J.; Mulhaupt, R. *Macromol. Chem. Phys.* **1997**, *198,* 1271.

(18) Thomann, R.; Kressler, J.; Mulhaupt, R. *Polymer* **1998**, *39*, 1907.

(19) Hauser, G.; Schmidtke, J.; Strobl, G. *Macromolecules* **1998**, *31*, 6250.

(20) Ewen, J. A.; Jones, R.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255.

(21) Longo, P.; Grassi, A.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1987**, *20*, 1015.

(22) Oliva, L.; Caporaso, L.; Pellecchia, C.; Zambelli, A. *Macromolecules* **1995**, *28*, 4665.

(23) Pellecchia, C.; Pappalardo, D.; D'Arco, M.; Zambelli, A. *Macromolecules* **1996**, *29*, 1158.

(24) Pellecchia, C.; Oliva, L. *Rubber Chem. Technol.* **1999**, *72*, 553.

(25) Caporaso, L.; Izzo, L.; Oliva, L. *Macromolecules* **1999**, *32*, 7329.

(26) Caporaso, L.; Izzo, L.; Zappile, S.; Oliva, L. *Macromolecules* **2000**, *33*, 7275.

(27) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1997**, *30*, 4137.

(28) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C* **1967**, *16*, 2477.

(29) Lotz, B.; Lovinger, A. J.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.

(30) Lovinger, A. J.; Lotz, B.; Davis, D. D. *Polymer* **1990**, *31*, 2253.

(31) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552.

(32) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J. *Macromolecules* **1993**, *26*, 3494.

(33) Chatani, Y.; Maruyama, H.; Noguchi, K.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Part C* **1990**, *28*, 393.

(34) Chatani, Y.; Maruyama, H.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Polym. Phys.* **1991**, *29*, 1649.

(35) De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5711.

(36) De Rosa, C.; Auriemma, F.; Corradini, P. *Macromolecules* **1996**, *29*, 7452.

(37) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1998**, *31*, 7430.

(38) De Rosa, C.; Auriemma, F.; Vinti, V.; Galimberti, M. *Macromolecules* **1998**, *31*, 6206.

(39) Auriemma, F.; De Rosa, C.; Ruiz de Ballesteros, O.; Vinti, V.; Corradini, P. *J. Polym. Sci., Polym. Phys. Ed.* **1998**, *36*, 395.

(40) Auriemma, F.; De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5719.

(41) Auriemma, F.; Born, R.; Spiess, H. W.; De Rosa, C.; Corradini, P. *Macromolecules* **1995**, *28*, 6902.

(42) Auriemma, F.; Lewis, R. H.; Spiess, H. W.; De Rosa, C. *Macromol. Chem.* **1995**, *196*, 4011.

(43) Auriemma, F.; De Rosa, C.; Ruiz de Ballesteros, O.; Corradini, P. *Macromolecules* **1997**, *30*, 6586.

(44) Nakaoki, T.; Ohira, Y.; Hayashi, H.; Horii, F. *Macromolecules* **1998**, *31*, 2705.

(45) Auriemma, F.; Ruiz de Ballesteros, O.; De Rosa, C. *Macromolecules* **2001**, *34*, 4485.

(46) De Rosa, C.; Gargiulo, M. C.; Auriemma, F.; Ruiz de Ballesteros, O.; Razavi, A. *Macromolecules* **2002**, *35*, 9083.

(47) D'Aniello, C.; Guadagno, L.; Naddeo, C.; Vittoria, V. *Macromol. Chem. Rapid Commun.* **2001**, *22*, 104. Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V. *Macromolecules* **2001**, *34*, 2512. Guadagno, L.; D'Aniello, C.; Naddeo, C.; Vittoria, V.; Meille, S. V. *Macromolecules* **2002**, *35*, 3921.