On the Form II of Syndiotactic Polypropylene

Claudio De Rosa,* Finizia Auriemma, and Valeria Vinti

Dipartimento di Chimica, Università di Napoli "Federico II", Via Mezzocannone 4, 80134 Napoli, Italy

Received May 19, 1998; Revised Manuscript Received July 10, 1998

ABSTRACT: The conditions for the crystallization of form II of syndiotactic polypropylene are described. As-prepared, melt-crystallized, and oriented-fiber specimens of different samples of syndiotactic polypropylene having different degrees of stereoregularity, prepared with a metallocene-based catalyst as well as with the traditional Ziegler−Natta vanadium-based catalyst, are analyzed by X-ray diffraction and solid-state ^{13}C NMR CPMAS spectroscopy. According to this analysis, the crystallization of form II is favored in samples having a low degree of stereoregularity. Indeed, as-prepared and melt-crystallized samples of highly stereoregular syndiotactic polypropylene always crystallize in form I, whereas less stereoregular samples present small amounts of crystals of form II and/or a mode of packing of form II occurs as a defect in a prevailing mode of packing of form I. The pure form II has been obtained by stretching compression-molded specimens of samples having low stereoregularity, prepared with the metallocene- or vanadium-based catalysts. By stretching the most stereoregular samples obtained with the metallocene catalyst, fibers in the trans planar form III are obtained. However, also for the higher stereoregular sample, the pure form II can be obtained upon release of the tension in fibers initially in the trans planar form III. Under these conditions a transition from form III into the isochiral helical form II occurs. Annealing fiber samples of form II or form III at high temperatures (100 °C) gives fibers with a mixture of crystals of forms I and II.

Introduction

Syndiotactic polypropylene (s-PP) presents a very complex polymorphic behavior.[1−10] Four limit-ordered crystalline forms of s-PP have been described so far. Forms I and II are characterized by chains in s(2/1)2 helical conformation, whereas forms III and IV present chains in trans planar[3,9] and $(T_6G_2T_2G_2)_n$[10] conformations, respectively. The different crystalline forms are characterized by different kinds and amounts of disorder depending on the degree of stereoregularity and the mechanical and thermal history of the samples.[11−14]

The crystal structures of the limit-ordered form I[4,7,15] and form II[2,8] of s-PP are shown in parts A and B of Figure 1, respectively. Form I was found by Lovinger 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. In this polymorphic form of s-PP, 2-fold helical chains are packed, in the limit-ordered structure, with an alternation of right-handed and left-handed helices along both axes of the unit cell[4,7] (Figure 1A). Electron diffraction patterns and X-ray powder and fiber diffraction patterns of samples in form I are characterized by the presence of the 020 reflection at $d = 5.6$ Å ($2\theta = 15.8°$, Cu Kα),[4−7] typical of the mode of packing of Figure 1A, where the axes of the helices are in the positions $(0, 0, z)$ and $(^1/_2, 0, z)$ of the unit cell. Disorder in the alternation of right- and left-handed helices along both axes of the unit cell is present in powder samples crystallized from the melt at low temperatures[16] or in single crystals grown at low temperatures.[7] This disorder is often associated to the presence of $b/4$ shifts among consecutive bc layers of chains piled along a, leading locally to an arrangement of the chains similar to that of form II.[4,7,16]

Form II is obtained in annealed fiber samples of s-PP.[2,8] For annealed fibers of samples having high degree of stereoregularity, obtained with new homogeneous metallocene-based catalysts,[17] a mixture of crystals of forms II and I have always been observed.[8] Form II corresponds to the C-centered structure deduced by Corradini et al.[1,2] from the X-ray fiber diffraction pattern. In this form chains in s(2/1)2 helical conformation are packed in an orthorhombic unit cell with axes of the helices in the positions $(0, 0, z)$ and $(^1/_2, ^1/_2, z)$ of the unit cell (Figure 1B). The space group proposed for the limit ordered structure of form II was $C222_1$, for which helices of the same chirality are included in the

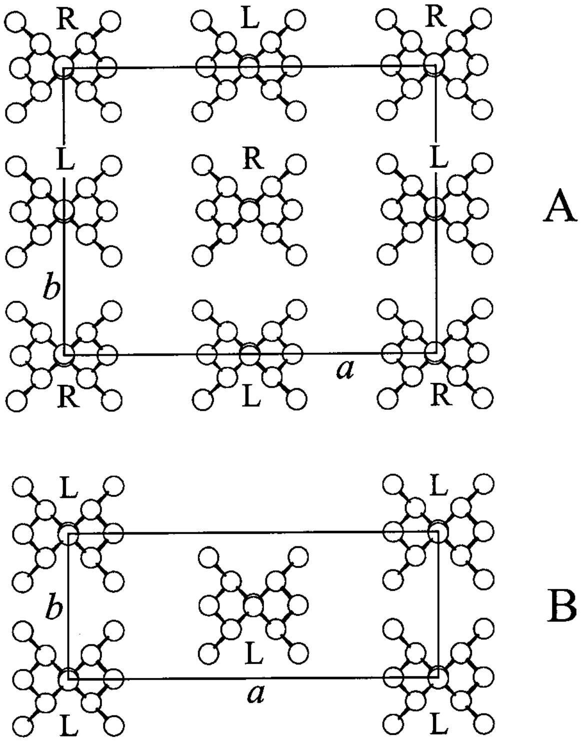

Figure 1. Two polymorphic forms of s-PP with chains in s(2/1)2 helical conformation: (A) form I and (B) form II.

10.1021/ma980789m CCC: $15.00

unit cell.[2] The X-ray fiber diffraction pattern of form II is characterized by the presence of the 110 reflection at $d = 5.22$ Å[2,8] ($2\theta = 17.0°$, Cu Kα; the indices of the 110 reflection are given for the unit cell of Figure 1B with $b = 5.6$ Å).

The conditions which induce the crystallization of the metastable form II are not clear. A sharp 110 reflection at $2\theta = 17.0°$, typical of form II, has been observed only in annealed fiber samples of s-PP up to now.[8] Powder samples of s-PP having a low degree of stereoregularity (fully syndiotactic pentad *rrrr* content 86%), quench precipitated from solutions, show X-ray diffraction features typical of form II, although the reflection at $2\theta = 17.0°$ appears broad, indicating the possible presence of crystals of form I.[8,13] These powder samples are characterized by the presence of conformational disorder,[13] as shown by the analysis of the solid-state ^{13}C NMR spectra.[13,14] The disorder corresponds to the presence of a trans planar portion of chains connecting portions in an s(2/1)2 helical conformations.[13,18] In the resulting structure, the conformational disorder produces the formation of kink bands;[18] the chains would be packed according to an orthorhombic lattice centered on the *ab* face: for the ordered regions such as in form II and for the region comprising the defects such as in form IV.[13,18,19] The modifications presenting kink bands could be thought of as intermediate between the limit-ordered forms II and IV of s-PP. A continuum of structures exists among the limit-ordered ones of forms II and IV. In powder samples of s-PP, only these disordered intermediate modifications of form II have been observed so far.

In a recent paper we have shown that the presence of small amounts of ethylene as comonomeric units, included in the crystalline phase of as-prepared samples of poly(propene-*co*-ethylene), induces the crystallization of conformationally disordered modifications of form II with kink bands.[20]

In this paper the conditions which induce the crystallization of form II are analyzed in order to provide evidence of the existence of the pure limit-ordered form II with chains in an ordered helical conformation and without the occurrence of crystals of form I.

Experimental Section

Three different samples of s-PP were analyzed. Two samples (sPP(A) and sPP(B)), supplied by Montell Technology, were synthesized with a single center syndiospecific catalyst composed of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane.[17] sPP(A) and sPP(B) samples are characterized by fully syndiotactic pentad contents [*rrrr*] of 70 and 96%, respectively, and melting temperatures of 110 and 153 °C, respectively. They have different stereoregularity since they were prepared at different polymerization temperatures.[21] The third sample, sPP(C), was synthesized with the traditional Ziegler–Natta vanadium-based catalyst[22] at very low temperature. The sample sPP(C) is stereoirregular and regioirregular, being characterized by a stereoblock structure with syndiotactic sequences prevailing to isotactic ones and head-to-head/tail-to-tail regioirregular defects[23,24] and melting temperature of 120 °C.

Isothermal crystallizations from the melt of the sample sPP(A) were performed with the following procedure. The as-prepared sample was melted at 200 °C and kept for 5 min at this temperature in a N_2 atmosphere; it was 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. The sample was then cooled to room temperature and analyzed by wide-angle X-ray diffraction.

Oriented-fiber samples of s-PP were obtained by stretching, at room-temperature, compression-molded samples.

X-ray powder diffraction patterns were obtained with an automatic Philips diffractometer using Ni filtered Cu Kα radiation. X-ray fiber diffraction patterns were obtained with Ni-filtered Cu Kα radiation in photographic cylindrical camera.

^{13}C NMR CPMAS spectra were recorder at room temperature on a AM 250 Brucker 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 about 1500 transients were collected using the following acquisition parameters: 3 s delay between pulses, 90° pulse of 5.4 μs and a contact time of 1 ms. Crystalline polyethylene was used as external reference at 33.6 ppm from tetramethylsilane (TMS).

Results and Discussion

Powder Samples. As shown in the literature, as-prepared and melt-crystallized samples of s-PP having a high degree of stereoregularity (with fully syndiotactic pentad *rrrr* content higher than 90%) always crystallize in the most stable form I.[5−8,15,16] Also, in single crystals of s-PP, only form I has been observed.[4−7] In these samples, form II has been obtained in annealed fibers[8] but always in mixture with crystals of forms I.

As discussed in the Introduction as-prepared samples of s-PP having lower stereoregularity ([*rrrr*] = 86−88%) can crystallize in conformationally disordered modifications of form II.[13,18] However, these samples give rise the most stable form I by crystallization from the melt[8,13] or in single crystals.[4]

The X-ray powder diffraction patterns of the as-prepared sample s-PP(A) having a low degree of stereoregularity ([*rrrr*] = 70%), and of samples of s-PP(A) obtained by isothermal crystallization from the melt at various temperatures T_c are reported in Figure 2. The pattern of the as-prepared sample presents both 020 and 110 reflection at 16° and 17°, typical of forms I and II, respectively. The patterns of the melt-crystallized samples indicate that, at each temperature, crystallization in form I mostly occurs, as indicated by the presence of the 020 reflection at $2\theta = 16°$. The absence or the low intensity of the 211 reflection at $2\theta = 18.8°$ in the patterns of Figure 2 indicates that, for this sample of s-PP, disordered modifications of form I are always obtained by crystallization from the melt, even at high crystallization temperatures. The limit-ordered form I, characterized by a regular alternation of right- and left-handed helices along both axes of the unit cell,[4] obtained in samples of s-PP having high stereoregularity and crystallized at high temperatures,[7,16] is never obtained for the less stereoregular s-PP sample. As shown in a previous paper,[16] the disorder corresponds to defects in the alternation of right- and left-handed helices along both axes of the unit cell. The broadening and the low intensity of the 020 reflection at $2\theta = 16°$, and the presence of shoulders or peaks of low intensity at $2\theta = 17°$ in the X-ray patterns of Figure 2 indicate that small amounts of crystals of form II are present in the melt-crystallized samples and/or a mode of packing of form II (Figure 1B) occurs as a defect in a prevailing mode of packing, form I (Figure 1A). This kind of defect corresponds to a disorder in the stacking of *bc* layers of chains, implying *b*/4 shifts among consecutive *bc* layers piled along *a*.[6,7] It also occurs in samples of s-PP having a high degree of stereoregularity in the case, for instance, of single crystals of s-PP grown at low temperatures[7] (≤120 °C) and of powder samples of s-PP crystallized from the melt at temperatures lower than 120 °C.[16] It produces a broadening of the 020 reflection

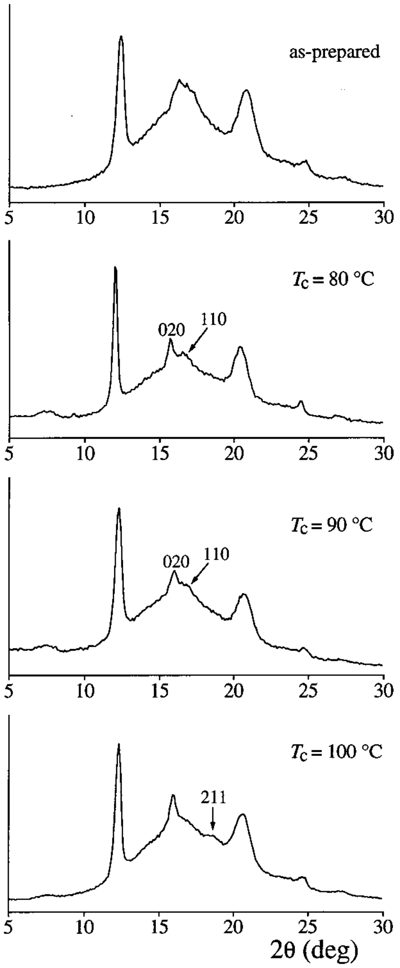

Figure 2. X-ray powder diffraction patterns of the as-prepared sPP(A) sample and of samples of sPP(A) isothermally crystallized from the melt at the indicated crystallization temperatures, T_c. The indices of the 020 and 211 reflections are given for the unit cell of forms I of Figure 1A (with b = 11.2 Å), while those of the 110 reflection are given for the unit cell of form II of Figure 1B (with b = 5.6 Å).

in the X-ray powder diffraction patterns[16] and streaks along the h20 line in the electron diffraction patterns.[7,11]

For samples of s-PP of Figure 2, the disorder which produces a local arrangement of the chains such as in form II occurs at every crystallization temperature. This indicates that samples of s-PP having low stereoregularity are not able to crystallize from the melt in the ordered form I, owing to the tendency to form local arrangements of the chains such as in form II.

Oriented Samples. Oriented fibers of s-PP samples were obtained by stretching, at room-temperature compression-molded specimens.

The X-ray fiber diffraction pattern of the oriented sample sPP(A) is shown in Figure 3. Although a low degree of orientation is achieved, the pure form II is obtained after stretching, as indicated by the presence in the pattern of Figure 3 of a broad reflection centered at $2\theta = 17°$, indexed as the 110 reflection, and the absence of the 020 reflection at $2\theta = 16°$. The X-ray fiber diffraction pattern of the oriented sample sPP(C), obtained with the vanadium-based catalyst, is shown in Figure 4. A well-oriented, pure form II is obtained, as indicated by the presence in the pattern of Figure 4 of the 110 reflection at $2\theta = 17°$. Therefore, less stereoregular samples of s-PP, prepared with the new metallocene-based catalyst, behave like the irregular samples prepared with the traditional Ziegler–Natta vanadium-based catalyst; the stretching of compression-molded specimens of these samples gives rise to fibers in the pure form II. This is in agreement with the results of Corradini et al.,[2] who found form II of s-PP by the analysis of the X-ray pattern of fibers obtained by stretching regioirregular and stereoirregular s-PP samples prepared with vanadium-based catalysts.

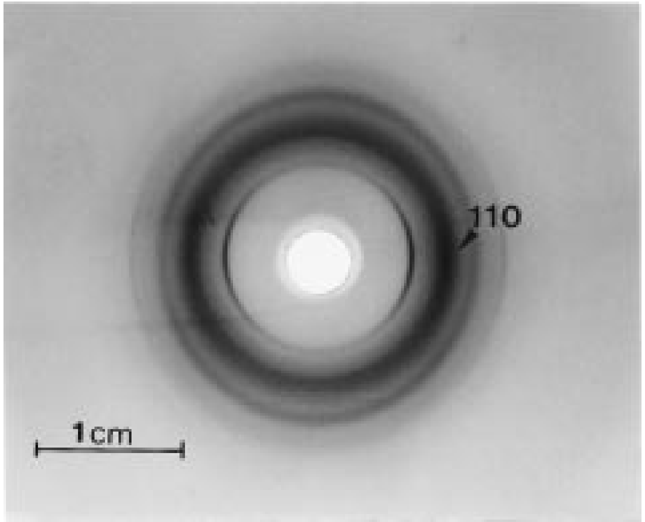

Figure 3. X-ray fiber diffraction pattern of the stretched sPP(A) sample (form II). The indices of the 110 reflection are given for the unit cell of Figure 1B with b = 5.6 Å. Notice that on the equator the scale in mm gives directly the diffraction angle 2θ.

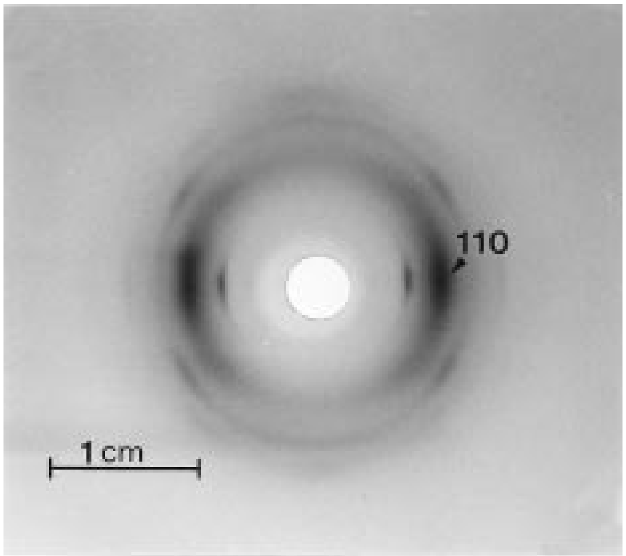

Figure 4. X-ray fiber diffraction pattern of the stretched sPP(C) sample (form II). The indices of the 110 reflection are given for the unit cell of Figure 1B with b = 5.6 Å. Notice that on the equator the scale in mm gives directly the diffraction angle 2θ.

The X-ray fiber diffraction pattern of the oriented sample sPP(B), having higher stereoregularity, is shown in Figure 5. It is apparent from Figure 5 that the trans planar form III is obtained.[8,9] While less stereoregular samples of s-PP give, by stretching, fibers in form II, samples having higher stereoregularity give, by stretching, the trans planar form III, as already reported in the literature.[8]

It is worth noting that the pattern of Figure 5 is obtained by holding the fiber sample under tension. The

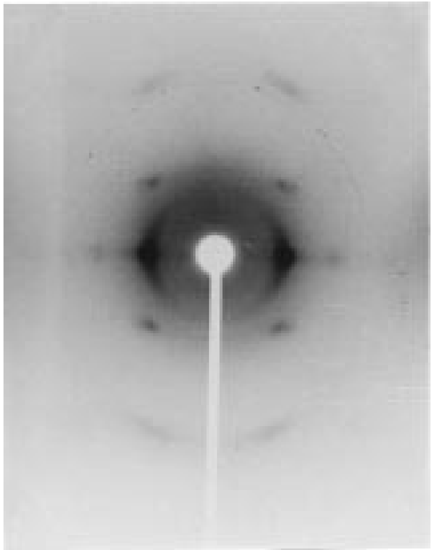

Figure 5. X-ray fiber diffraction pattern of the stretched sPP(B) sample (form III).

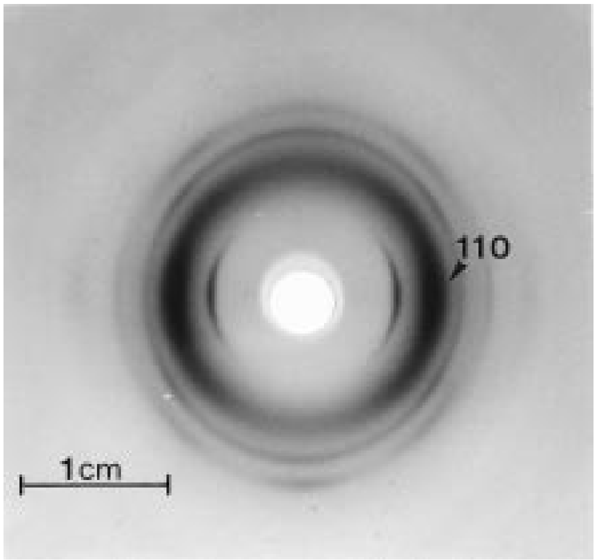

Figure 6. X-ray fiber diffraction pattern of the stretched sPP(B) sample of Figure 5 after the release of the tension (form II). The indices of the 110 reflection are given for the unit cell of Figure 1B with $b = 5.6$ Å. Notice that on the equator the scale in mm gives directly the diffraction angle 2θ.

X-ray fiber diffraction pattern of the sample of Figure 5 after the release of the applied tension is reported in Figure 6. A transition from the trans planar form III into the helical form of s-PP occurs. It is apparent from Figure 6 that, after the release of the tension, although some orientation is lost, the pure form II of s-PP is obtained, as indicated by the presence of the broad 110 reflection centered at $2\theta = 17°$, typical of form II, and the absence of the reflection of $2\theta = 16°$, typical of form I.

The X-ray fiber diffraction pattern of the oriented sample in form III of Figure 5 after annealing at 100 °C (holding the fiber sample under tension) is reported in Figure 7. The presence, in the pattern of Figure 7, of both 020 and 110 reflections at $2\theta = 16°$ and 17°, respectively, is apparent. Fibers with a mixture of crystals of forms I and II are obtained by annealing fibers of form III.[8] The same result is obtained by annealing the fiber samples in form II of Figures 3, 4, and 6.

The solid-state ^{13}C NMR CPMAS spectrum of the fiber sample in form II, corresponding to the X-ray pattern of Figure 3, is reported in Figure 8. Similar spectra are obtained for the fiber samples of Figures 4 and 6. It is apparent that these samples present the usual spectrum of s-PP typical of the ordered s(2/1)2 helical conformation.[25] This indicates that, at variance with powder samples of s-PP crystallized in form II, which may be characterized by conformational disorder,[13,18] fiber samples of s-PP crystallized in form II are characterized by chains in the ordered 2-fold helical conformation.

We recall that in a previous paper[8] a kind of disorder present in oriented-fiber samples in form II was outlined. It was revealed by the observation that the X-ray diffraction intensity of the 201 reflection is weaker than that one calculated according to the space group $C222_1$.[8,11] Correspondingly, some diffuse scattering appears close to the 201 reflection along the first layer line[8,11] (see also Figure 4). As shown in ref 11, the disorder giving rise to such diffraction phenomenon can be ascribed to departures from the fully isochiral packing of the helices. Such departures may occur correspondingly to configurational defects of kind ...*rrrmrrr*..., as shown in Figure 2B of ref 11, or to a vacancy of one monomeric unit, as shown in Figure 2C of ref 11 and Figure 7 of ref 13. The less stereoregular s-PP samples of this paper present indeed isolated *m* defects in a nonnegligible amount. The inclusion of such kind of defects in the crystals of s-PP is probably more tolerated in form II than in form I. This could explain the favored crystallization of form II in less stereoregular s-PP samples. Furthermore, the onset of form II in highly stereoregular samples of s-PP, upon release of the tension starting from the form III, may be ascribed to a cooperative isochiral wrapping of the helices (for geometrical reasons), as discussed in a forthcoming paper.[26]

Conclusions

Form I is the most stable polymorphic form of s-PP; it is generally obtained in powder as-prepared or melt-crystallized samples.

The crystallization of form II is favored in samples of s-PP having a low degree of stereoregularity. Samples obtained by isothermal crystallization from the melt of the less stereoregular sPP(A) sample ([*rrrr*] = 70%) crystallize essentially in form I, but the broadening and the low intensity of the 020 reflection at $2\theta = 16°$, and the absence or the low intensity of the 211 reflection at $2\theta = 18.8°$, indicate that disordered modifications of form I[16] are always obtained, even at high crystallization temperature. Moreover, the presence of shoulders or peaks of low intensity at $2\theta = 17°$, already present in the as-prepared sample, indicates that small amounts of crystals of form II are present and/or a mode of packing of form II occurs as a defect in a prevailing mode of packing of form I. This kind of defect corresponds to a disorder in the stacking of *bc* layers of chains, implying *b*/4 shifts among consecutive *bc* layers piled along *a*.[6,7] It also occurs in samples of s-PP having a high degree of stereoregularity in the case, for instance, of single crystals of s-PP grown at low temperatures[7] (≤120 °C) and of powder samples of s-PP crystallized from the melt at temperatures lower than 120 °C.[16] This disorder is present in low stereoregular

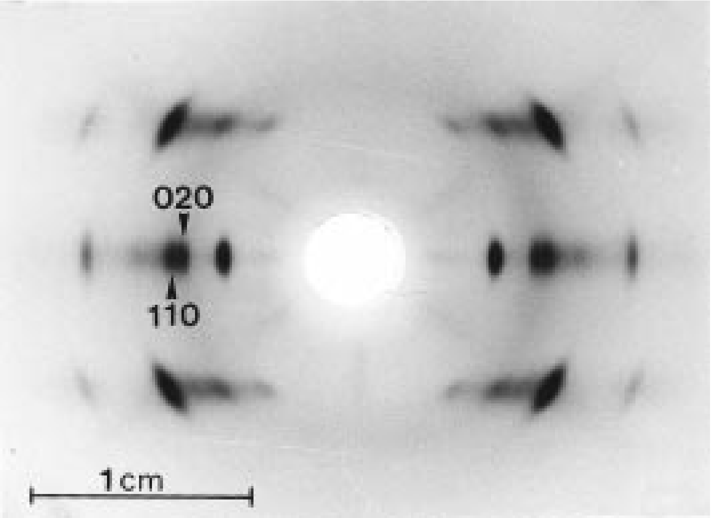

Figure 7. X-ray fiber diffraction pattern of the stretched sPP(B) sample of Figure 5 after annealing at 100 °C (form I + form II). The indices of the 020 and 110 reflections are given for the unit cells of parts A and B of Figure 1, with $b = 11.2$ and 5.6 Å, respectively, corresponding to forms I and II of s-PP, respectively. Notice that on the equator the scale in mm gives directly the diffraction angle 2θ.

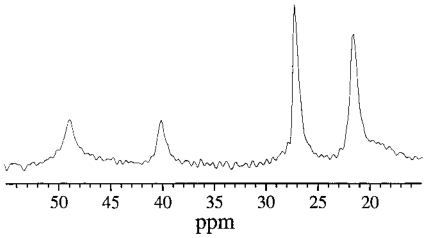

Figure 8. Solid-state ^{13}C NMR CPMAS spectrum of the stretched sPP(B) sample after the release of the tension (form II).

s-PP in the as-prepared samples as well as in the melt-crystallized samples obtained at every crystallization temperature.

Samples of s-PP having low stereoregularity are not able to crystallize from the melt in the ordered form I owing to the tendency to form local arrangements of the chains such as in form II.

The pure form II is obtained in stretched samples of s-PP having low stereoregularity (sPP(A) and sPP(C) samples). The less stereoregular sample, prepared with the new metallocene catalyst (sPP(A)) behaves like the irregular samples prepared with the traditional Ziegler−Natta vanadium-based catalyst; the stretching of compression-molded specimens of these samples gives fibers in the pure form II. By stretching the most stereoregular sPP(B) sample the trans planar form III is obtained.[8] However, also for the sPP(B) sample, the pure form II can be obtained upon release of the applied tension in fibers initially in the trans planar form III. Under these conditions a transition from form III into the helical form II occurs. These fibers in form II present chains in the ordered 2-fold helical conformation and do not present the conformational disorder of kink bands typical of powder samples of s-PP crystallized in form II.[13,18]

The annealing of fiber samples in form III, as well as in form II, at high temperatures (100 °C) gives fibers with a mixture of crystals of forms I and II.[8]

From the present analysis and from the results already reported in the literature,[13,18,19] we can conclude that the limit-ordered forms II and IV of s-PP crystallize in fiber samples of s-PP,[2,8] whereas all modifications crystallized in powder samples, presenting conformational kink bands disorder and X-ray features typical of form II,[13,18] represent intermediate disordered modifications between the two limit-ordered forms II and IV.[18,19]

Acknowledgment. We thank Dr. M. Galimberti of Montell (Ferrara) for supplying the polymer samples synthesized with the homogeneous metallocene catalyst, Prof. A. Zambelli of University of Salerno for supplying the polymer sample prepared with the vanadium-based catalyst, and Prof.A. Grassi of University of Salerno for collecting the solid-state ^{13}C NMR CPMAS spectrum. Financial support from the “Ministero dell’ Università e della Ricerca Scientifica e Tecnologica”, is gratefully acknowledged.

References and Notes

(1) Natta, G.; Corradini, P.; Ganis, P. *Makromol. Chem.* **1960**, *39*, 238.
(2) Corradini, P.; Natta, G.; Ganis, P.; Temussi, P. A. *J. Polym. Sci., Part C* **1967**, *16*, 2477.
(3) Natta, G.; Peraldo, M.; Allegra, G. *Makromol. Chem.* **1964**, *75*, 215.
(4) Lotz, B.; Lovinger, A. J.; Cais, R. E. *Macromolecules* **1988**, *21*, 2375.
(5) Lovinger, A. J.; Lotz, B.; Davis, P. D. *Polymer* **1990**, *31*, 2253.
(6) Lovinger, A. J.; Davis, D. D.; Lotz, B. *Macromolecules* **1991**, *24*, 552.
(7) Lovinger, A. J.; Lotz, B.; Davis, D. D.; Padden, F. J. *Macromolecules* **1993**, *26*, 3494.
(8) De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5711.
(9) Chatani, Y.; Maruyama, H.; Noguchi, K.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Part C* **1990**, *28*, 393.
(10) Chatani, Y.; Maruyama, H.; Asanuma, T.; Shiomura, T. *J. Polym. Sci., Polym. Phys.* **1991**, *29*, 1649.
(11) Auriemma, F.; De Rosa, C.; Corradini, P. *Macromolecules* **1993**, *26*, 5719.
(12) Auriemma, F.; De Rosa, C.; Corradini, P. *Rend. Fis. Acc. Lincei* **1993**, *4*, 287.
(13) Auriemma, F.; Born, R.; Spiess, H. W.; De Rosa, C.; Corradini, P. *Macromolecules* **1995**, *28*, 6902.
(14) Auriemma; F. Lewis, R. H.; Spiess, H. W.; De Rosa, C. *Macromol. Chem.* **1995**, *196*, 4011.
(15) De Rosa, C., Auriemma, F., Corradini, P., *Macromolecules* **1996**, *29*, 7452.
(16) De Rosa, C.; Auriemma, F.; Vinti, V. *Macromolecules* **1997**, *30*, 4137.

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

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

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

(20) De Rosa, C.; Auriemma, F.; Vinti, V.; Grassi, A.; Galimberti M. *Polymer* **1998**, *39*, 6219.

(21) Balbontin, G.; Dainelli, D.; Galimberti, M.; Paganetto, G. *Macromol. Chem.* **1992**, *193*, 693.

(22) Natta, G.; Pasquon, P.; Zambelli, A. *J. Am. Chem. Soc.* **1962**, *84*, 1488.

(23) Zambelli, A.; Locatelli, P.; Rovasoli, A.; Ferro, D. R. *Macromolecules* **1980**, *13*, 267.

(24) Ammendola, P.; Shijing, X.; Grassi, A.; Zambelli, A. *Gazz. Chim. Ital.* **1988**, *118*, 769.

(25) Bunn, A.; Cudby, E. A.; Harris, R. K.; Packer, K. J.; Say, B. J. *J. Chem. Soc., Chem. Commun.* **1981**, *15*.

(26) Lotz, B.; Mathieu, C.; Thierry, A.; Lovinger A. J.; De Rosa, C.; Ruiz de Ballesteros, O.; Auriemma, F. Submitted to *Macromolecules*.

MA980789M