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Influence of the stereoregularity on the crystallization of the *trans* planar mesomorphic form of syndiotactic polypropylene

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Abstract

The crystallization of the *trans*-planar mesomorphic form of syndiotactic polypropylene by quenching the melt at 0°C is investigated as a function of the stereoregularity of the samples. The formation of the *trans*-planar mesomorphic form at 0°C is followed as a function of the permanence times at 0°C by X-ray diffraction and FTIR spectroscopy. Samples kept at 0°C for short time rapidly crystallize into the helical form I at room temperature, whereas longer permanence times at 0°C increase the stability of the *trans*-planar mesomorphic phase which remains stable and inhibits the normal crystallization of the sample into the helical form at room temperature. The stereoregularity of the polymer sample strongly influences the rate of formation of the mesomorphic form at 0°C. Higher the syndiotacticity, easier the formation of *trans*-planar mesomorphic form. Very short permanence times (few hours) at 0°C are enough to form and stabilize the mesomorphic form for highly syndiotactic samples, whereas for stereo-irregular samples the amount of mesomorphic form observed when the sample is removed from the 0°C bath and heated to room temperature, remains always very low, even for very long permanence times (months) at 0°C and the crystallization into the normal helical form is not inhibited. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Syndiotactic polypropylene; Mesomorphic form; Stereoregularity

1. Introduction

The complex polymorphic behavior of syndiotactic polypropylene has been recently described [1–11]. Four different crystalline forms have been found. Forms I and II are characterized by chains in two-fold helical conformation, while forms III and IV present chains in *trans*-planar (8) and $(T_6G_2T_2G_2)_n$ [9,11] conformations, respectively.

Form I is the most stable form of s-PP, it is easily obtained by crystallization from the melt and from solution in powder samples and single crystals of s-PP [2–6]. Form I is characterized by a regular alternation of right- and left-handed helical chains along the *a* and *b* axes of the orthorhombic unit cell [2]. Depending on the conditions of crystallization disorder in the regular alternation of enantiomorphic chains is present [6]. The metastable form II is characterized by an isochiral packing of two-fold helical chains [12]. It can be obtained by stretching, at room temperature, compression molded specimens of s-PP samples having low stereoregularity [7,12], or upon the release of the tension in stretched fibers of s-PP initially in the *trans*-planar form III [7,13]. The transition between the *trans*-planar form III and the helical form II is reversible upon successive stretching and relaxing of s-PP fibers and is responsible of the elastic behavior of s-PP [14].

Discussions have recently appeared in the literature about the crystallization of the *trans*-planar form III [7,15,16]. Originally, form III was obtained by cold drawing procedures of low stereoregular s-PP samples quenched from the melt into ice–water mixtures [17]. Higher stereoregular samples of s-PP, prepared with the homogeneous metallocene catalysts, give fibers in the *trans*-planar form III easily when compression molded specimens are stretched at room temperature [1,7,8]. A transition from the helical form I of the compression molded sample into the *trans*-planar form III is obtained by stretching [7]. The lower the degree of stereoregularity of the sample, the more difficult is the formation of the *trans*-planar form III by stretching [7]. In the limit of stereo-irregular s-PP samples prepared with Vanadium-based Ziegler–Natta catalysts, the helical form II is generally obtained by stretching at room temperature [7,12].

In a recent paper by Nakaoki et al. [15] the crystallization of the *trans*-planar form III is reported to be spontaneously induced by quenching from the melt at 0°C without any mechanical stress. We have shown [16] that this crystalline form of s-PP, obtained by quenching the melt at 0°C, cannot be identified as the known crystalline form III, but it should

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Table 1
Fully syndiotactic pentad contents [*rrrr*], melting temperatures (T_m) and molecular weights (M_w) of the five s-PP samples

Sample	[*rrrr*] (%)	T_m (°C)	M_w
A	95.8	153	2.66×10^5
B	93.4	149	2.13×10^5
C	91.0	146	1.64×10^5
D	81.4	122	5.2×10^4
E	78.0	124	1.9×10^5

be considered as a new phase characterized by chains in *trans*-planar conformation. A lateral disorder in the packing of *trans*-planar chains, probably associated to a rotational disorder around the chain axes and to translational disorder along the chain axes, is present in this phase, which is more properly defined as a mesomorphic, or also a paracrystalline, form of s-PP [16].

As the formation of the *trans*-planar form III by stretching depends on the degree of stereoregularity [7], it is expected also that the stabilization of the *trans*-planar conformation in the mesomorphic form could depend on the stereoregularity of the s-PP sample. In this paper this issue is investigated by analyzing the crystallization of the mesomorphic form in different s-PP samples having different degrees of stereoregularity.

2. Experimental section

Five different samples of s-PP having different degree of syndiotacticity were analyzed. The samples, supplied by Montell Technology, were synthesized with a single center syndiospecific catalyst composed of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane [18]. The fully syndiotactic pentad contents [*rrrr*], the melting temperatures and the molecular weights of the five samples are listed in Table 1. The different degree of stereoregularity is due to different polymerization temperatures [19].

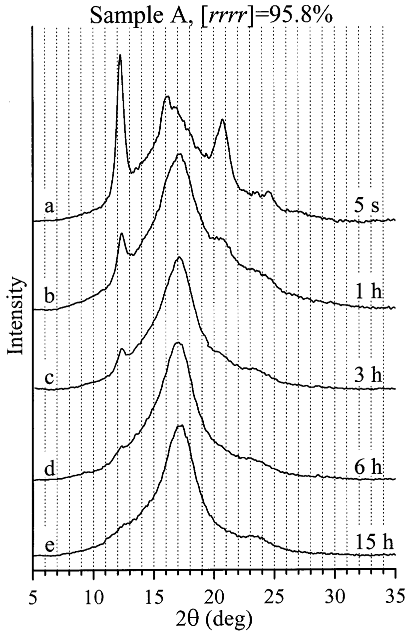

Fig. 1. X-ray powder diffraction patterns of the s-PP sample A ([*rrrr*] = 95.8%) quenched from the melt at 0°C and kept at 0°C for 5 s (a), 1 h (b), 3 h (c), 6 h (d) and 15 h (e).

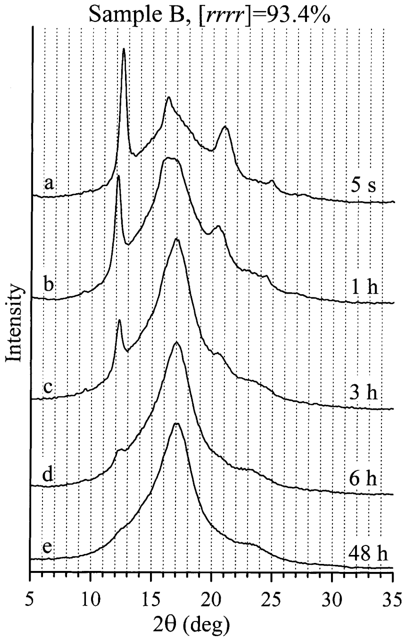

Fig. 2. X-ray powder diffraction patterns of the s-PP sample B ([*rrrr*] = 93.4%) quenched from the melt at 0°C and kept at 0°C for 5 s (a), 1 h (b), 3 h (c), 6 h (d) and 48 h (e).

The melting temperatures were obtained with a differential scanning calorimeter (Perkin–Elmer DSC-7) performing scans in a flowing N_2 atmosphere at a heating rate of 10°C/min.

Powders of the s-PP samples were melted in a hot press at 150°C forming a film 0.20 mm thick, and rapidly quenched at 0°C in an ice–water bath. The X-ray diffraction patterns of small stripes of the film, extracted from the bath at regular interval times, were monitored.

X-ray powder diffraction patterns were obtained with an automatic Philips diffractometer using Ni filtered CuKα radiation.

The Fourier transform infrared (FTIR) spectra were obtained by using a JASCO FT/IR-430 spectrophotometer with a resolution of 0.5 cm^{-1} (32 scans).

3. Results and discussion

The X-ray diffraction patterns recorded at room temperature of the five s-PP samples quenched in ice–water from the melt and kept at 0°C for different times, are shown in Figs. 1–5. It is apparent from the figures that the samples

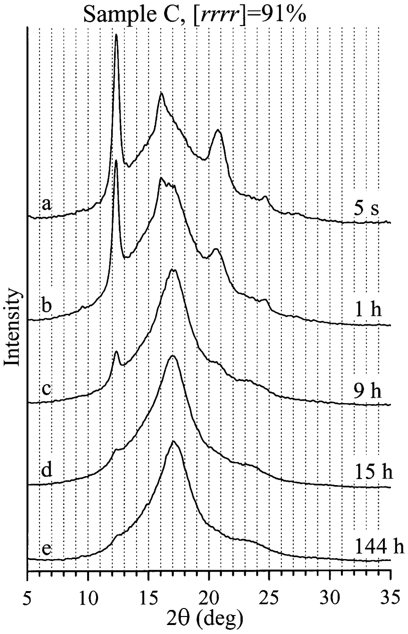

Fig. 3. X-ray powder diffraction patterns of the s-PP sample C ([*rrrr*] = 91.0%) quenched from the melt at 0°C and kept at 0°C for 5 s (a), 1 h (b), 9 h (c), 15 h (d) and 144 h (e).

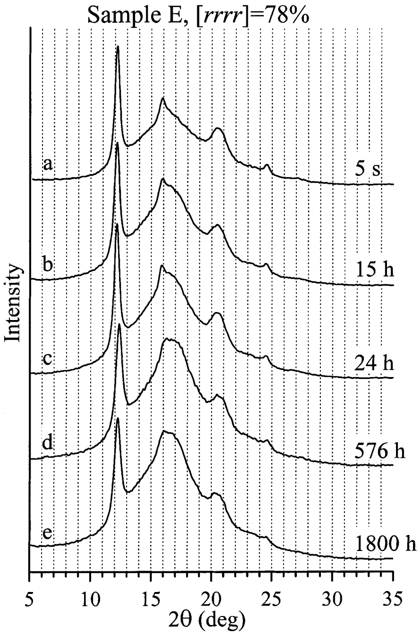

Fig. 5. X-ray powder diffraction patterns of the s-PP sample E ([*rrrr*] = 78.0%) quenched from the melt at 0°C and kept at 0°C for 5 s (a), 15 h (b), 24 h (c), 576 h (d) and 1800 h (e).

immediately taken out from the 0°C bath (curves a in Figs. 1–5), are in all cases crystallized into the normal helical form I of s-PP, as indicated by the presence of the reflections at $d = 7.15$, 5.49 and 4.25 Å (2θ(CuKα) = 12.4, 16.1, 20.9°, respectively) [1,2]. On increasing the permanence time of the films at 0°C, the amount of crystalline form I, which crystallizes at room temperature upon removing the film from the bath at 0°C [20], decreases whereas the amount of *trans*-planar mesomorphic form of s-PP increases. This is indicated by the reduction in the intensities of the reflections typical of form I and in particular of the reflection at $2\theta = 12°$, which is not overlapped by any diagnostic reflection of the mesomorphic form [15], and by the increase in the intensity of the diffraction peak at $2\theta = 17°$ (typical of mesomorphic form) [15,16] with the increase of permanence time in the patterns of Figs. 1–5. The X-ray diffraction patterns of the s-PP samples A, B and C, kept for long time at 0°C (Figs. 1e, 2e and 3e, respectively), exhibit only broad diffraction peaks at $2\theta = 17$ and 24° typical of the *trans*-planar mesomorphic form of s-PP [15,16].

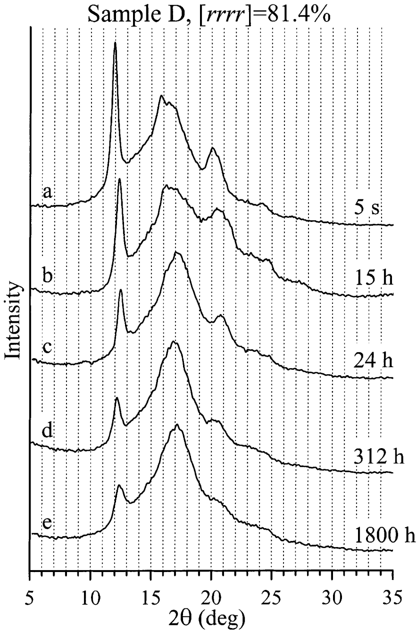

Fig. 4. X-ray powder diffraction patterns of the s-PP sample D ([*rrrr*] = 81.4%) quenched from the melt at 0°C and kept at 0°C for 5 s (a),15 h (b), 24 h (c), 312 h (d) and 1800 h (e).

The FTIR spectra of the sample A kept at 0°C for different times (Fig. 6) confirm the formation of long portions of chain in *trans*-planar conformation on increasing the permanence time at 0°C. The bands at 810, 868, 977 and 1005 cm^{-1}, typical of the helical form of s-PP [21], are present in the spectra of the samples kept at 0°C for short time (Figs. 6a–c) and are strongly reduced for longer permanence time (Fig. 6d). At variance, the intensity of bands corresponding to the long polymer portions in a *trans*-planar conformation [17] at 831, 963 and 1130 cm^{-1} increases with the increase in the permanence time at 0°C.

It is also apparent from Figs. 1–5 that higher the degree of stereoregularity, shorter the permanence time at 0°C necessary to stabilize the *trans*-planar mesomorphic form. For the highest syndiotactic sample A ([*rrrr*] = 95.8%), only 6 h are sufficient for the mesomorphic form to be stable and to prevent the crystallization of the helical crystalline

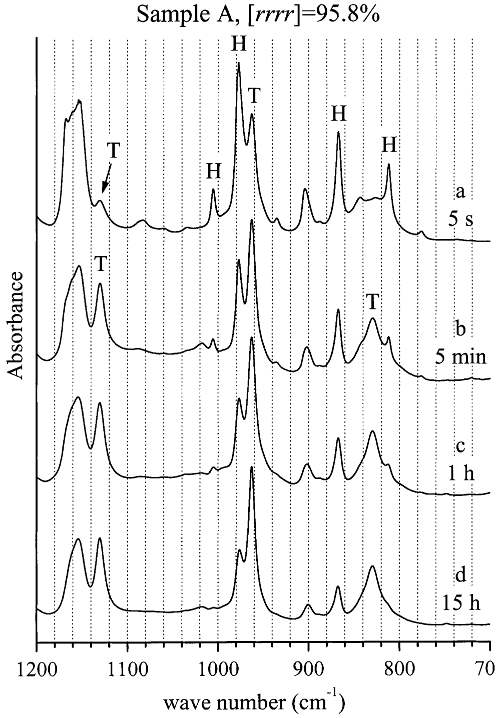

Fig. 6. FTIR spectra of the s-PP sample A ([*rrrr*] = 95.8%) quenched from the melt at 0°C and kept at 0°C for 5 s (a), 5 min (b), 1 h (c) and 15 h (d). The FTIR bands relative to the long strands of chains in the two-fold helical (H) and in the *trans*-planar (T) conformations are indicated.

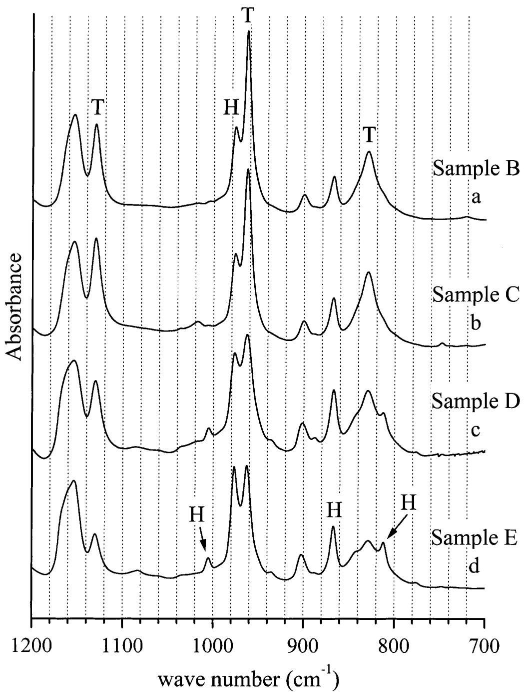

Fig. 7. FTIR spectra of the s-PP samples B (a), C (b), D (c) and E (d), corresponding to the samples of Figs. 2e–5e, quenched from the melt and kept at 0°C for the longest permanence time.

form at room temperature. For lower stereoregular B and C samples longer permanence times are needed to form a pure *trans*-planar mesomorphic form (Figs. 2e and 3e), whereas for samples D and E the pure mesomorphic form is never obtained even for a very long time, as indicated by the presence of the reflection at $2\theta = 12°$ of the helical crystalline form in Figs. 4e and 5e.

The FTIR spectra of samples B, C, D and E kept at 0°C for the longest permanence time in our experiment (corresponding X-ray diffraction profiles reported in Figs. 2e–5e), are shown in Fig. 7. It is apparent that the amount of long portions of chain in *trans*-planar conformation, indicated by the intensity of the bands at 831, 963 and 1130 cm^{-1}, decreases with the decrease in the stereoregularity of the sample. Conversely, the intensity of the FTIR band at 977 cm^{-1}, typical of the helical conformation, increases with the decrease in the syndiotacticity; indeed for the less stereoregular s-PP samples D and E, the crystallization in the normal helical form I of s-PP at room temperature is not inhibited, even after 1800 h of permanence time of the samples in the 0°C bath.

The amount of the *trans*-planar mesomorphic form in the samples having different stereoregularity kept at 0°C for different times can be obtained from the X-ray diffraction patterns of Figs. 1–5. The presence of the reflection at $2\theta = 16°$ in the X-ray pattern of Figs. 1a–5a indicates that the crystalline helical form which is produced at room temperature upon removing the film from the bath at 0°C [20] is basically, in all cases, the form I of s-PP. The X-ray diffraction patterns of the curves of Figs. 1–5 arise, in general, from the contributions of the mesomorphic phase, the amorphous phase and the crystalline helical form I, which can be easily separated knowing the patterns of the three single phases. Hence, the values indicative of the relative amounts of the three phases present in the samples may be evaluated by the ratio of the area subtending the diffraction profile of a given contributing phase to the total area subtending the whole diffraction patterns of Figs. 1–5. It is worth noting that the total fraction of crystalline phase, evaluated as the sum of the fractions of the mesomorphic and the helical forms so estimated, is nearly constant for all the samples (of the order of 27–28%), and quite independent on the amount of time the sample is maintained in the 0°C bath. In other words, the maximum crystalline fraction achievable at room temperature is always obtained: for short permanence times of the sample in the 0°C bath, the sample fully crystallizes in the helical form in a fractional amount of 27–28%; for long permanence time the sample is partially crystallized in the mesomorphic form and partially in the helical form I, the sum of mesomorphic and helical fractional amounts being still of the order of 27–28%. The crystallization of the helical form I is almost completely inhibited for highly stereoregular s-PP samples for longer permanence times and the fractional amount of mesomorphic form achieved still corresponds to 27–28%.

The fraction of the mesomorphic form, with respect to the

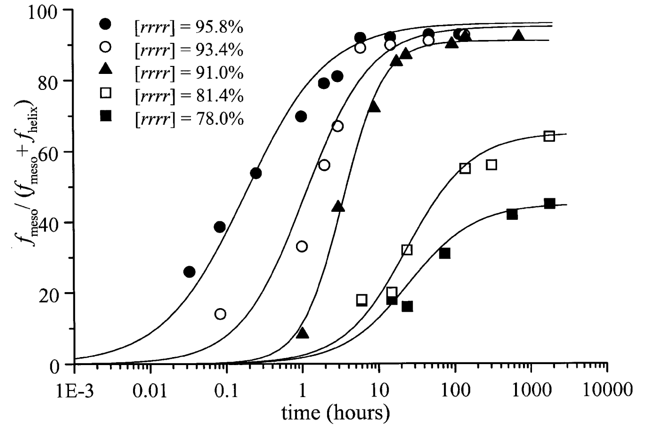

Fig. 8. Fraction of the *trans*-planar mesomorphic form, with respect to the crystalline phase, as a function of permanence time (logarithmic scale) at 0°C for the samples A (●), B (○), C (▲), D (□), and E (■).

total fraction of crystalline phase, in the different samples is reported in Fig. 8 as a function of permanence time at 0°C. It is apparent that higher the degree of stereoregularity, faster the formation of the *trans*-planar mesomorphic form. For the most stereoregular s-PP sample A, appreciable amounts of the *trans*-planar mesomorphic phase are observed already for the permanence times in the 0°C bath of a few minutes. For the less stereoregular s-PP samples B and C, the fractional amount of mesomorphic form becomes not negligible for permanence times of the order of 1 h. At least 8–10 h are necessary to achieve an appreciable fraction of mesomorphic form for the poorly stereoregular s-PP samples D and E. After this 'induction' time, a steep increase in the relative amount of mesomorphic form with the time is followed by a rather slow rate zone of formation of the mesomorphic form. Probably the relative amount of mesomorphic form, with respect to the total fraction of crystalline phases present in our samples, tends asymptotically to a limiting value, which is 100% of the crystalline phases (i.e. 28% of the total, crystalline plus amorphous fractions) for the samples A, B and C, ≈ 63% (i.e. 18% of the total, crystalline plus amorphous fractions) for the sample D and ≈ 43% (i.e. 12% of the total, crystalline plus amorphous fractions) for the sample E.

The crystallization of the *trans*-planar mesomorphic form of s-PP at 0°C could be explained considering that portions of s-PP chains in the *trans*-planar and two-fold helical conformations are in equilibrium in the amorphous state at 0°C. If the sample is kept at 0°C for a sufficient amount of time, the slight mobility of the chains, still present at 0°C, allows the *trans*-planar portions of the chains to organize in small crystalline bundles, characterized by lateral disorder in the packing, forming the mesomorphic form [20]. The formation of such mesomorphic bundles produces an increase in the fraction of C–C bonds in the *trans*-planar conformation. According to ^{13}C NMR results of Ref. [20], indeed the fraction of backbone C–C bonds in the *trans* state, f_{trans}, measured at 0°C, keeping the quenched s-PP sample in an ice–water bath for 10 min corresponds to ≈80% and increases with the increase in the permanence time of the sample in the 0°C bath, while the mesomorphic phase forms. Such high value for f_{trans} is not surprising since the equilibrium fractional amount of C–C bonds in the *trans* state expected at 0°C for a fully syndiotactic chain, evaluated in the isomerical rotational state model approximation, using for instance the approach suggested by Suter and Flory in Ref. [22], is 67%. Hence, the mechanism of formation of the mesomorphic form of s-PP is close to the mechanism underlying the normal crystallization in polymer systems: the formation of stable mesomorphic aggregates with chains in *trans*-planar conformation, probably controlled by diffusion, alters the normal distribution of conformational states typical of an amorphous sample, because the longer *trans*-planar strands of chains result in segregation in the more ordered mesomorphic zones.

When the permanence time at 0°C is long enough, the crystalline *trans*-planar mesomorphic bundles are well-formed and stable and prevent the crystallization at room temperature of the stable crystalline helical form I when the sample is removed from the bath at 0°C.

The experimental observation, reported in this paper, that the pure *trans*-planar mesomorphic form can be obtained only for high stereoregular s-PP samples, may be explained by considering that the long polymer strands in *trans*-planar conformation are less stable in the presence of configurational defects characterized by *mm* triads or isolated *m* diads, typical of s-PP samples prepared with syndiospecific C_s metallocene catalysts. These defects, which are randomly distributed along the chains of s-PP, are probably more easily tolerated in the two-fold helical conformation than in the *trans*-planar conformation of s-PP. In the presence of configurational defects long portions of the s-PP chains are able to crystallize only if they assume the helical conformation. The same reasons can be invoked to explain the formation of crystalline *trans*-planar form III by stretching only for high stereoregular s-PP samples, and the helical form II for very low stereoregular samples [7].

4. Conclusions

The crystallization of the mesomorphic form of s-PP depends on the stereoregularity of the polymer sample.

The mesomorphic form of s-PP is obtained by quenching the melt at 0°C and keeping the samples at 0°C for a long time. Samples kept at 0°C for a short time rapidly crystallize into the helical form I at room temperature, whereas longer permanence time at 0°C increases the stability of the *trans*-planar mesomorphic form, which remains stable and inhibits the normal crystallization of the sample into the helical form at room temperature. The higher the degree of stereoregularity of the sample, the shorter the permanence time at 0°C necessary to stabilize the *trans*-planar mesomorphic form. For stereoirregular s-PP samples the pure *trans*-planar mesomorphic form is never obtained even for long permanence time at 0°C and the crystallization of the stable helical form is not inhibited. The formation of the pure *trans*-planar mesomorphic form only for highly stereoregular s-PP samples can be explained by considering that the configurational defects are probably more easily tolerated in the two-fold helical conformation than in the *trans*-planar conformation of s-PP. In the presence of large amounts of configurational defects, long portions of s-PP chain are able to crystallize only if they assume the helical conformation.

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