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# The Role of the *trans*-Planar Mesophase in the Polymorphic Behavior of Syndiotactic Polypropylene

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**Summary:** The transformations of the *trans*-planar mesophase of syndiotactic polypropylene (sPP) subjected to thermal, mechanical and solvent treatments, were investigated. The unoriented *trans*-planar mesophase, obtained by quenching the melt at 0°C, was annealed at 80°C and the thermal transformation was investigated by X-rays, infrared and dynamic-mechanical analysis. The presence of the helical form II was recognized in the annealed sample. The oriented *trans*-planar mesophase, obtained by drawing at room temperature and releasing the tension, was immersed in liquid dichloromethane for 24 hours. After drying the sample showed the presence of the oriented form II, although it was not possible to exclude a partial transition into form IV. On the basis of the present and literature results we suggested a scheme of the polymorphic transitions of sPP, in which the central role of the *trans*-planar mesophase is enlightened.

**Keywords:** polymorphic transitions; syndiotactic polypropylene; *trans*-planar mesophase

## Introduction

In recent years the complex polymorphic behavior of syndiotactic polypropylene [1-17] is becoming clearer, due to many recent contributions based either on new structural studies or theoretical calculations [18-31]. However a number of questions are not yet resolved in particular with respect to *inter*-conversions between different polymorphs, taking place upon strain, temperature and solvent treatments.

Four crystalline forms of sPP have been described so far, characterized either by different chain conformations or crystalline packing. In forms I and II chains adopt the $(T_2G_2)_n$ helical conformation[1,7,18,32], whereas form III and IV present chains in *trans*-planar and $(T_6G_2T_2G_2)_n$ conformations[5,6], respectively. Form I is the stable form of sPP obtained under the most common crystallization conditions both from the melt and from solution

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as single crystals[1,2,10]. In this form, the helical chains are packed, in the limit-ordered structure (form I), with an alternation of right handed and left-handed helices along both axes of the unit cell. This phase is orthorhombic, *Ibca* being the most plausible space group, with axes $a$ = 14.50 Å, $b$ =11.20 Å, $c$ =7.45 Å. Samples crystallized from the melt at low temperatures present disorder in the described regular alternation, with a lattice where $a$ and $c$ remain the same, while $b$ is halved.

Form II corresponds to a C-centered structure in which the helical chains share the same chirality. In the past it was obtained only by stretching at room temperature compression molded specimens of low stereoregularity[7,11,32], or in mixture with form I for high stereoregular specimens. Recently Zhang *et al.* reported the epitaxial crystallization at low temperature, of a thin layer of sPP in form II on 2-quinoxalinol[27], and Rastogi *et al.* showed that form II can be obtained on cooling the isotropic melt at high pressures[28]. Guadagno et al. found the development of form II either by annealing relaxed fibers of sPP [29], or by solvent induced crystallization of non-oriented samples initially in *trans*-planar conformation [33].

The *trans*-planar form III is a metastable polymorph of sPP, initially recognized only in samples under tension; it crystallizes in an orthorhombic lattice, too[5]. Recently the spontaneous crystallization of an unoriented *trans*-planar form, was obtained by quenching sPP samples from the melt to a 0°C bath and keeping the specimen at that temperature for a long time[23,24,34]. This novel form was interpreted either as the crystalline form III[23], or as a mesophase showing lateral disorder in the packing of the *trans*-planar chains[24]. It was successively found that this mesophase can be described assuming an orthohexagonal unit cell [34] with parameters $a$ = 6.02 Å, $b$ = 10.42 Å, $c$ = 5.05 Å.

Because of the similar stability of different forms, a characteristic of sPP is the tendency to crystallize simultaneously in different modifications. Only in well defined and, in a certain sense, "extreme" conditions a single crystalline polymorph is formed. For the ordered form I high temperature, near the sPP melting is needed; form III requires high draw ratios maintaining the fiber under tension while for "pure" form II cooling the melt at pressures higher than 1.2 kbar[28] appears to be necessary. A mixture of different structures is obtained under most experimental conditions, and this applies even more in *processing* conditions. Due to the different physical properties of the crystalline polymorphs the recognition of the structures obtained in different experimental conditions and the path of the successive phase transformations due to thermal treatments, strain and interaction with different substances, such as interacting vapors or liquids, are of the utmost importance. Although a number of papers deal with the question of interconversion between different sPP polymorphs, a coherent picture is not yet available, in particular for what concerns the crystallization of the helical form II. In this work we present different experimental conditions showing the transformation of the *trans*-planar mesophase into form II. Considering our present results together with the already known transformations between the sPP polymorphs, we suggest a scheme which evidences the key role of the metastable *trans*-planar mesophase, particularly in the formation of the helical form II.

## Experimental

Syndiotactic polypropylene was synthesized according to established procedures [21]. The polymer was analyzed by $^{13}$C-NMR spectroscopy at 120°C on an AM 250 Bruker spectrometer operating in the FT mode at 62.89 MHz, by dissolving 30 mg of sample in 0.5 ml of $C_2D_2Cl_4$. Hexamethyl-disiloxane was used as internal chemical shift reference. The sample showed 91% syndotactic pentads.

### Preparation of the samples

**Sample Q0**: polymer powders were molded in a hot press (CARVER Inc.), at 150°C, forming a film 0.2 mm thick, and rapidly quenched to 0°C in an ice-water bath. The sample was left in the cold bath for 3 days.

**Sample Q80:** sample **Q0** was progressively annealed, in successive 1 hour steps, at 40°, 50°, 60°, 70° and 80°C.

**Sample FR**: polymer powders were molded in a hot press at 150°C, forming a film 0.2 mm thick, and rapidly quenched to 0°C in an ice-water bath. The sample was directly drawn in the cold bath at 0°C up to draw ratio of 6, defined as $\lambda = l/l_0$, where l an $l_0$ are the final and the initial length, respectively. The drawn sample was left fixed in the bath for 10 days. Then it was removed and analyzed by X-ray diffraction and FTIR.

**Sample FRD**: sample FR was immersed in dichloromethane for 24 hours, then it was extracted and dried under vacuum for 24 hours.

### Methods

Wide-angle X-ray patterns were obtained using a Philips PW 1710 Powder diffractometer (CuKα-Ni filtered radiation). The scan rate was 2°θ/min.

The FR fiber was obtained using a dynamometric INSTRON 4301 apparatus. The deformation rate was 10 mm/min, and the initial length of the samples was 10 mm.

Fiber diffraction spectra were all recorded at room temperature, under vacuum by means of a cylindrical camera with a radius of 57.3 mm and the X-ray beam direction perpendicular to the fiber axis (Ni-filtered Cu-Kα radiation). A Fuji BAS-1800 imaging plate system was used to record the diffraction patterns.

The infrared spectra were obtained in absorbance mode using a Bruker IFS66 FTIR-spectrophotometer with a 2 $cm^{-1}$ resolution (64 scans collected).

Dynamic-mechanical properties were performed using a Rheometric Dynamic Mechanical Thermal Analyzer. The spectra were recorded in the tensile mode obtaining the loss factor, tangδ, at a frequency of 1 Hz , as a function of temperature. The heating rate was 3° C/min in the range of -50 , 150°C.

## Results

### Thermal Treatments of the *trans*-Planar Mesophase

In Figure 1 the X-ray diffraction patterns of the sPP samples Q0 and Q80 are compared. For sample Q0 a peak centered at $2\vartheta = 17°$ (CuKα) together with a weak one centered around $2\vartheta = 24°$ is apparent. These peaks correspond to the *trans*-planar mesophase already described with an orthohexagonal unit cell [34] with parameters $a = 6.02$ Å, $b = 10.42$ Å, $c = 5.05$ Å. Another weak maximum around $2\vartheta = 12.3°$ is present, due to the helical crystalline form probably resulting upon removing the sample from the bath at 0°C and bringing it to room temperature. Sample Q80, annealed at 80°C, also shows the maximum at $2\vartheta = 17°$ together with the sharp peaks at $2\vartheta$ equal to 12.3° and 20.6°, characteristic of helical sPP forms.

To better understand the transformation of the *trans*-planar mesophase at 80°C, in Figure 2 we show the FTIR spectra in absorbance (1300-1700 $cm^{-1}$) of samples Q0 and Q80. Infrared analysis is a very powerful tool to recognize the molecular conformations of sPP: helical and *trans*-planar bands have been evidenced since the first preparation of the syndiotactic isomer of polypropylene[32] and confirmed in many recent studies [14,15,34]. Sample Q0 shows the *trans*-planar bands, appearing at 831, 963, and 1132 $cm^{-1}$ very evident and well developed. Some helical bands are present too, due to a minor component possibly formed manipulating the sample at room temperature. In sample Q80 we observe that the *trans*-planar bands are strongly reduced, although they are still present, whereas the helical bands at 810, 868, 977, and 1005 $cm^{-1}$ have developed as compared to their intensity in Q0. The combined X-ray and infrared analysis allows us to deduce that a transition from the *trans*-planar mesophase to a helical form, as already reported in many studies[24-26], occurred. However it is more difficult to discriminate between the helical forms I and II. The presence of the peak at $2\vartheta = 17°$ , together with the other helical peaks at $2\vartheta = 12.3$ and 20.6°, seems to indicate that prevalently form II was obtained.

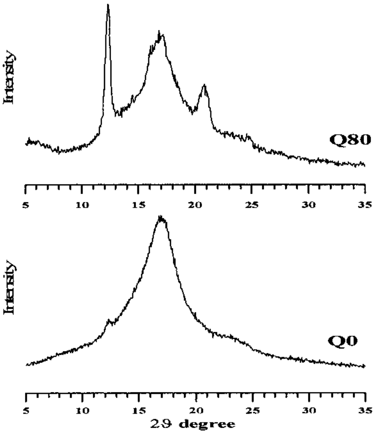


Fig. 1. X-ray diffraction patterns of the sSPP samples Q0 and Q80.

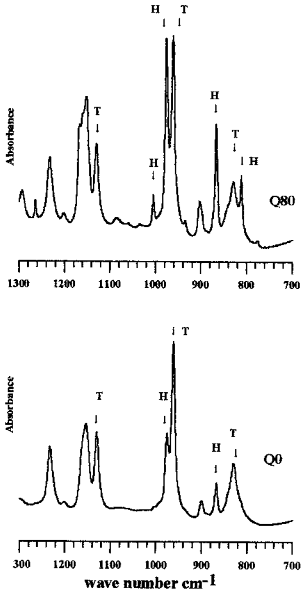


Fig. 2. FT-IR spectra of the sPP samples Q0 and Q80.

However a non-negligible fraction of chains in *trans*-planar conformation is still present, and this fraction can also contribute to the peak at $2\vartheta = 17°$. Ohira et al.[25] found a partial transformation, quantified in 16%, of the *trans*-planar phase into form II by annealing. In a previous paper, on the basis of X-ray, infrared and solid state NMR analysis[24], we indicated a transition to form I without excluding a partial transformation to form II. In successive studies we analyzed the structure and the dynamic-mechanical behavior of different sPP polymorphs[35].

We correlated the thermal transitions of the different sPP polymorphs with the dissipation peaks observed in the dynamic mechanical analysis, and found that each dissipation peak is distinctive of a different polymorph. In particular the helical form II shows a very sharp and intense dissipation peak centered at 100°C, never appearing with form I samples. This result makes dynamic-mechanical analysis an effective tool to recognize the presence of the different sPP polymorphs, even in the cases in which X-ray analysis is not able to discriminate. We are at this point able to detect the presence of form II in sample Q80, and in Figure 3 we show the dynamic-mechanical dissipation peaks of sample Q0 and Q80.

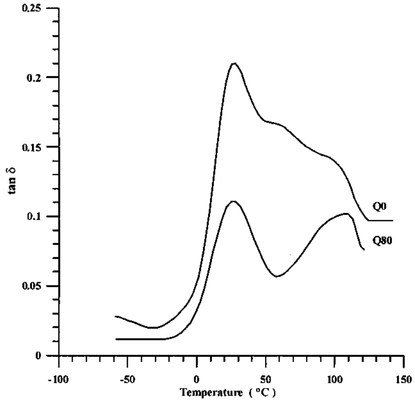


Fig. 3. Dynamic-mechanical dissipation peaks (tanδ) of the sPP samples Q0 and Q80.

The starting sample Q0, which is in the *trans*-planar mesophase, shows an intense peak centered at 20°C, due to the amorphous glass transition, a peak at 70°C ascribable to the *trans*-planar phase and a shoulder at 100°C. The annealed sample Q80 shows, besides the peak at 20°C due to the amorphous glass transition, an intense peak at 100°C. It is worth recalling that form I shows, in the dynamic-mechanical spectrum, only the peak at 20°C. Therefore we can deduce the presence of form II in sample Q80, confirming that the *trans*-planar mesophase is mainly transformed at 80°C into the helical form II.

### Mechanical and Solvent Treatments

In Figure 4 we report the X-ray patterns of sample FR and FRD. Sample FR is drawn in the bath at 0°C to a draw ratio 6, removed from the bath after 10 days, and relaxed after 18 hours. Upon releasing the tension the sample underwent a 33% shrinkage, contracting from a draw ratio 6 to 4. The pattern is typical of the oriented *trans*-planar mesophase: three reflections are evident on the equator, namely a very intense one, overlapped with the

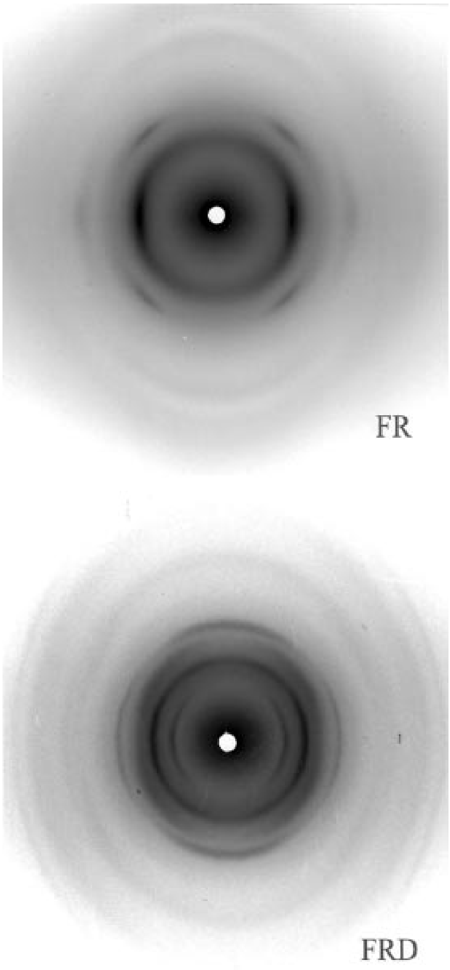


Fig. 4. X-ray diffraction patterns of the sPP samples FR and FRD.

amorphous halo, at $2\vartheta = 17.0°$, a weak reflection and a very weak one respectively at $2\vartheta = 29.7°$ and at $2\vartheta = 34.4°$. On the first layer, corresponding to a fiber periodicity of 5.05 Å, we observe the reflection at $2\vartheta = 23.7°$. All the observed reflections allow us to conclude that the drawing of the glassy sPP at 0°C and releasing at room temperature, produces the trans-planar mesophase, as already reported.[34] From the diffraction pattern of sample

FRD it is evident that this sample, after solvent treatment and drying, underwent a transformation with a partial loss of orientation.

On the equator we observe three intense reflections: The first centered at $2\vartheta \approx 12.6°$ corresponds to a helical form; the second very strong, centered at $2\vartheta \approx 17.0°$ is a reflection observable in the X-ray pattern of both the helical form II, and the *trans*-planar mesophase. However the non-negligible polarization of this reflection, with the simultaneous absence of the reflections on the layer with periodicity of 5.05Å, excludes the presence of the *trans*-planar mesophase. The third weaker equatorial reflection is observed at $2\vartheta = 24.8°$, and is due to the helical forms.

With respect to other non-equatorial reflections we observe the maximum at $2\vartheta = 20.8°$, corresponding to a fiber periodicity of 7.45 Å, typical of the helical forms. The simultaneous presence of the peak at $2\vartheta = 17°$ on the equator and the helical periodicity of the first layer is a clear evidence of the presence of form II, also considering and the absence of the reflection at $2\theta=16.0°$ characteristic of form I. On the other hand from the non-equatorial maxima we cannot exclude the presence of form IV. The presence of this crystalline form is not easily detectable when also form II is present, due to the closeness of the peaks on the equator. As matter of fact form IV shows the equatorial reflections at $2\vartheta = 12.9°$ and 16.8° very near to those of form II. Therefore the presence of form IV could be hidden by the presence of form II, at least in the present case. Work is in progress to verify the possibility to obtain clearer evidence with respect of form IV by exposing the *trans*-planar mesophase to different liquid solvents.

In conclusion the diffraction pattern of sample FRD indicates that the solvent treatment of the FR fiber induced a phase transition from *trans*-planar mesophase to the helical form II. This result has already been reported for unoriented films of sPP in *trans*-planar modification[33], in which, after solvent treatment with dichloromethane, a transition to the helix conformation in form II was observed. In Figure 5 we compare the FTIR spectra of the two samples FR and FRD. The appearance of the helical bands in the sample after solvent treatment confirms the conformational transition to a helical structure.

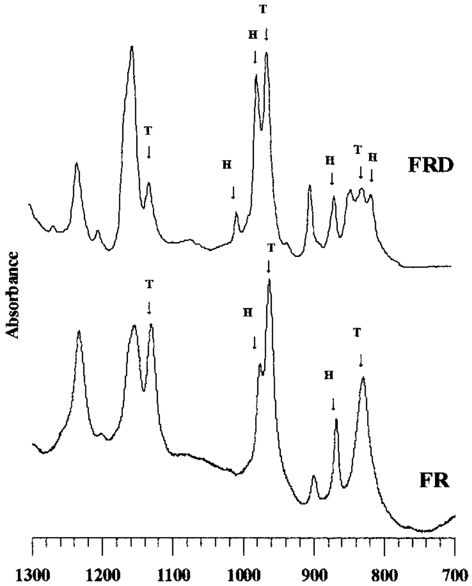
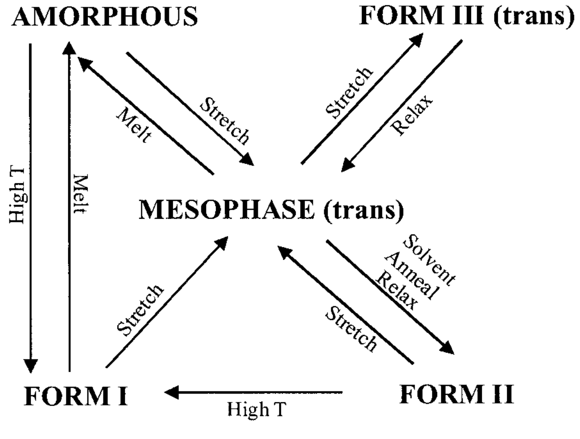


Fig. 5. FT-IR spectra of the sPP samples FR and FRD.

## Discussion and Conclusions

The experimental results of the present paper represent strong evidence that, in order for form II to develop, the *trans*-planar mesophase has to be present, either in oriented or in unoriented samples. This is consistent with a role played by the mesophase in the nucleation and growth of form II. Packing energy calculations and experimental melting behavior are consistent with the idea that this form is less stable than form I. It is noteworthy that form II irrespective of the non-chiral nature of the sPP chain, adopts a chiral space group implying that crystallites consist of isochiral helices. This arrangement appears less probable than that of racemic form I crystals consisting of alternated left and right handed helices. Therefore crystallization into form II rather than form I appears to be favored by kinetic factors. We recall that helices packing in the chiral form II is close to *pseudo*-hexagonal while a *quasi*-fourfold coordination is found in form consistent with suggestions in the paper on chiral crystallization of helical polymers by Allegra *et al.*[36] The proposal is that *pseudo*-hexagonal packing in the pre-crystallization state (nuclei, mesophase, possibly also other crystalline phases) favors, if preserved during crystallization, adoption of isochiral helical conformations in crystals of nontrivial helical molecules.

In the case of sPP there is a remarkable additional feature resulting from experiment, namely that crystallization of chains in the achiral *trans* planar conformation occurs with, or close to, a *pseudo*-hexagonal arrangement. This leads to speculate that *pseudo*-hexagonal arrangements, expected to some degree also in amorphous sPP, are likely to be particularly compatible and thus favor the *trans* conformations. With appropriate annealing, releasing the stress, or solvent treatments, favoring the mobility of the chains, the *trans* chains will adopt the more stable helical conformation. If this occurs at low enough temperatures and rapidly enough to maintain the local memory of the pseudo-hexagonal chain packing, then the chiral form II will be favored, since its packing is closer to hexagonal. On the other hand we must consider that the fraction of ordered phase in samples containing the trans planar mesophase is low, ranging between 20 and 30%, as reported in previous papers[24-25]. It is therefore expected that annealing or solvent treatments of samples containing the *trans* planar mesophase can induce the crystallization the thermodynamically stable, twofold helical, racemic form I, from the amorphous phase. In these cases we will have the simultaneous presence of both the helical form I and II, proceeding from the amorphous and from the *trans*- planar mesophase respectively, as observed in many reported cases.



Scheme 1. Summary of phase transitions for stereoregular sPP at ambient pressure.

The role of the metastable trans planar mesophase could be therefore central in the crystallization of sPP as we suggest in Scheme 1. In this scheme we actually did not consider form IV, characterized by chains in $(T_6G_2T_2G_2)_n$ conformations, although its presence in the oriented, solvent treated samples is plausible. Work is in progress to clarify also this issue of the complex polymorphic behavior of syndiotactic polypropylene.

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