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Recognition of the Syndiotactic Polypropylene Polymorphs *via* Dynamic-mechanical Analysis

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Summary: Three syndiotactic polypropylene samples were crystallized under different conditions in order to obtain different polymorphs. A first sample was crystallized at high temperature, obtaining the helical form I; a second was crystallized from the melt at 0°C for many days obtaining the trans-planar mesophase; a third sample was obtained by solvent induced crystallization followed by annaeling of the trans-planar mesophase, leading to a mixture of both the helical forms I and II. In the dynamic-mechanical analysis the helical form I showed only one peak of tan δ corresponding to the amorphous glass transition. The other polymorphs also showed this transition centered at about the same temperature. Beside the peak corresponding to the Tg, the trans-planar mesophase was characterized by a peak appearing at 70°C, and the helical form II by a peak at 100°C. These peaks, unambiguously associated to transitions of the different forms, can be considered a distinctive evidence for the polymorphs obtained in different processing conditions.

Keywords: polymorphism; polypropylene; syndiotactic; trans-planar mesophase

Introduction

Although the complex polymorphic behavior of syndiotactic polypropylene[1-14] is becoming clearer and clearer, due to many recent contributions,[15-24] based either on new structural studies or theoretical calculations, some questions are not yet resolved and the problem is still in debate.

Four crystalline forms of sPP have been described so far, characterized by different either chain conformations or crystalline cells. In forms I and II chains adopt $(T_2G_2)_n$ helical conformation,[1-3,9-12] whereas form III and IV present chains in *trans*-planar and $(T_6G_2T_2G_2)_n$

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conformations,[5-6] respectively.

Actually, due to the closeness of the energy of different forms,[23] characteristic of sPP is the attitude to contemporaneously crystallize in different structures. Only in well defined and, in a certain sense, “extreme” conditions a pure polymorph is formed. For example, the ordered form I is crystallized only at very high temperature, near the sPP melting; form III only at very high draw ratios maintaining the fiber under tension; and form II on cooling the melt at pressures higher than 1.2 kbar. A mixture of different structures is obtained in the major part of the experimental conditions, and even more in processing conditions. The recognition of the different polymorphs is mainly based on X-ray analysis, being well established the structural parameters of the different forms. However the peaks exclusive of a particular polymorph are few, and often they appear superimposed along the equatorial line, making the recognition of the polymorph very uncertain, as in the case of form II and trans-planar mesophase that are both characterized on the equator by the peak at 17° of 2ϑ. Moreover in non-oriented samples the attribution of the peak at 17° cannot be supported by the periodicity determined on the first layer.

In a previous paper, analyzing the X-ray patterns, we have shown that the helical form II undergoes between 100°C and 130°C a melting and re-crystallization phenomenon, clearly associated to a strong dissipation peak in the dynamic-mechanical analysis.[25]

In this paper we have analyzed the structure and the dynamic-mechanical behavior of different sPP polymorphs. We have correlated the thermal transitions of the different sPP polymorphs with the dissipation peaks observed in the dynamic mechanical analysis, and have found that there are dissipation peaks distinctive of a particular polymorph. This result makes the 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 completely satisfactory.

Experimental

The syndiotactic polypropylene was synthesized according to a previously reported procedure. 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, and resulted as containing 86% of syndiotactic pentads. The molecular weight M_w, evaluated by GPC, was 157000.

A sample crystallized in the helical form I was obtained by molding the sPP powders at 150°C in a hot press, and rapid cooling in a bath at 100°C for 2 hours (Sample FI).

A sample crystallized in the trans-planar mesophase was obtained by molding the polymer powders in a hot press, at 150°C, and rapidly quenching in a bath at 0°C. The film was left in the cold bath for seven days (Sample Q).

A sample in the helical form II, mixed to form I, was obtained immersing sample Q in dichloromethane for 24 hours, drying under vacuum up to the recovery of the initial weight and annealing at 80°C for 2 hours (Sample FII).

Wide angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer (Cu Kα + Ni filtered radiation). The scan rate was 2ϑ°/min.

The infrared spectra were obtained at room temperature by using a FTIR-Bruker IFS66 spectrophotometer with a resolution of 2 cm^{-1} (32 scans collected). The absorbances of the trans-planar conformational bands were associated to the wavenumbers 831 cm^{-1}, 963 cm^{-1}, and 1132 cm^{-1}, whereas the absorbances of the helical bands fall at 810 cm^{-1}, 977 cm^{-1} and 1005 cm^{-1}.

Dynamic-mechanical properties were performed using a Rheometric Dynamic Mechanical Thermal Analyzer. The spectra were recorded in the tensile mode, obtaining the logarithm of the modulus E', and the loss factor, tanδ, at a frequency of 1Hz, as a function of temperature. The heating rate was 3°C/min in the range of –100-160°C.

Results and Discussion

In Figure 1 we report the X-ray diffractograms (WAXD) of sample FI (a), sample Q (b) and sample FII (c).

The WAXD of sample FI (a) is characterized by the peaks appearing at 12.3°, 15.9°, 20.6°, and 23.4° of 2ϑ, typical of form I of syndiotactic polypropylene.[9]

Sample Q (b) shows a broad halo centered around $2\vartheta = 17°$ together with a smaller one centered at $2\vartheta = 24°$; this pattern corresponds to the mesophase with chains in trans-planar conformation;[22,24] also a small maximum around $2\vartheta = 12.3°$ is present, probably due to a very small fraction of a helical form produced at room temperature upon removing the sample from the bath at 0°C.

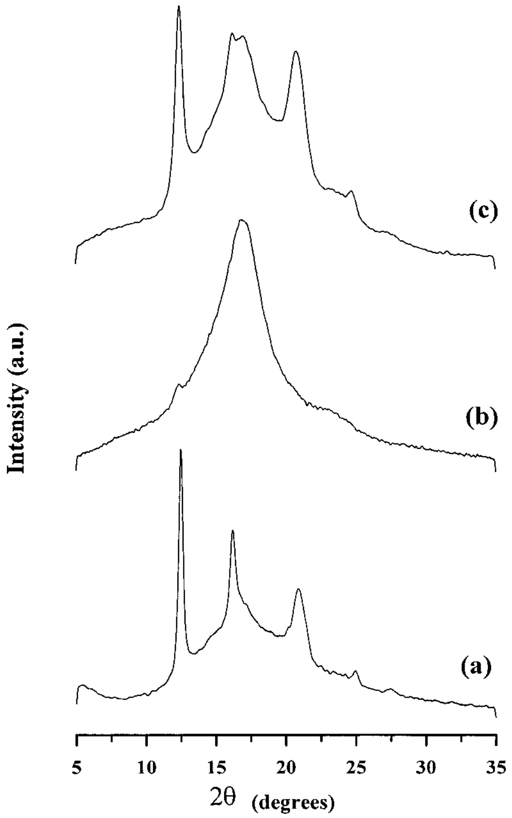

Fig. 1. X-ray diffractograms of sample FI (a), sample Q (b), and sample FII (c).

The diffractogram of sample FII, kept in dichloromethane 24 h and annealed (c) shows the presence of both the helical forms I and II, as already reported.[26] As a matter of fact it was shown that the trans-planar mesophase (sample Q) transforms, between 50 and 70°C, in a mixture of helical forms. Actually we observe the peaks at $2\vartheta = 12.3°$ and 20.8°, common to either the helical forms I and II, the peak at 15.9° of 2ϑ, typical of form I, and the peak at 17° of 2ϑ, typical of form II, demonstrating the presence of both the forms.

To check the chain conformation, thus confirming the X-ray analysis, in Figure 2 we report the FTIR spectra of sample FI (a), sample Q (b), and sample FII (c). Infrared analysis is very sensitive for the chain conformation determination: as a matter of fact helical and trans planar bands have been evidenced since the first preparation of the syndiotactic isomer of polypropylene.[27-28] In sample FI, crystallized at 100°C in form I, all the helical bands, appearing at 810, 868, 977, and 1005 cm^{-1}, are well evident and developed, whereas in sample Q they are strongly reduced or completely absent. At variance, sample Q shows all the trans-planar bands appearing at 831, 963 and 1132 cm^{-1}, not present in the sample crystallized at 100°C.

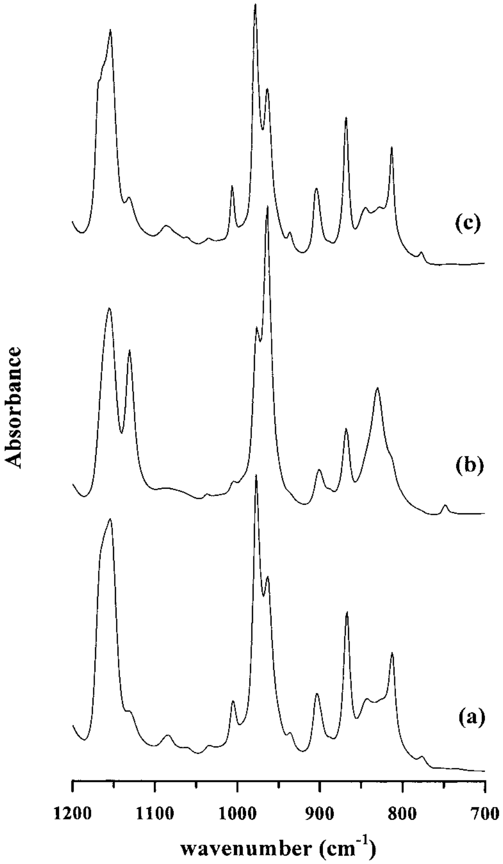

Fig. 2. FTIR spectra in absorbance (1300-700 cm^{-1}) of sample FI (a), sample Q (b), and sample FII (c).

In the sample kept in dichloromethane (FII) the helical bands at 810, 868, 977, and 1005 cm^{-1}, are all very well evident and developed, whereas the trans-planar bands at 831, 963, 1132 cm^{-1} although still present, show a very much reduced intensity, indicating only a small residual presence of the trans-planar phase in the sample crystallized from the solvent. The prevalent presence of the helical bands in sample FII strongly indicates that the peak at $2\vartheta = 17°$ in the WAXD must be attributed to the helical form II, and not to the trans-planar mesophase.

In Figure 3 we report the change of the elastic modulus E' and the loss factor tan δ as a function of temperature for sample FI, crystallized in the helical form I. The elastic modulus, E' (MPa) is almost constant in the glass region, between –60°C and 10°C, then it shows a sharp drop due to the glass transition and a slightly decreasing value up to the melting. In the temperature interval corresponding to the modulus drop, an intense dissipation peak appears in the tan δ curve, unambiguously ascribable to the glass-rubber transition of the amorphous phase. It is centered at 20°C and is almost symmetric around the maximum. We will call it a γ peak. No other dissipation peak is present in the dynamic-mechanical spectrum of the helical form I.

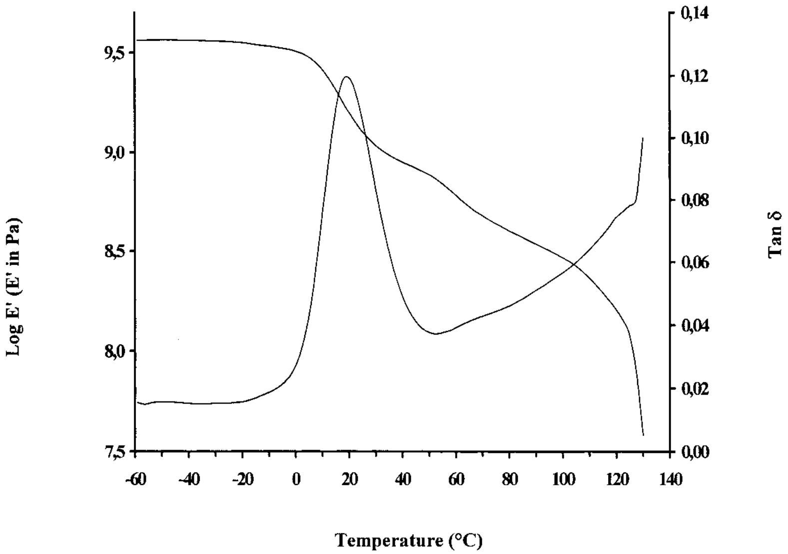

Fig. 3. The dynamic-mechanical modulus and the loss factor, tan δ, of sample FI as a function of temperature.

In Figure 4 the dynamic-mechanical spectrum of the trans-planar mesophase (sample Q) is shown. The elastic modulus, E', is almost constant in the glassy region, up to 10°C and then a drop is observable. But, at variance with the previous case of form I, the drop is not very intense. After it, an almost constant course and a second strong drop are well observable.

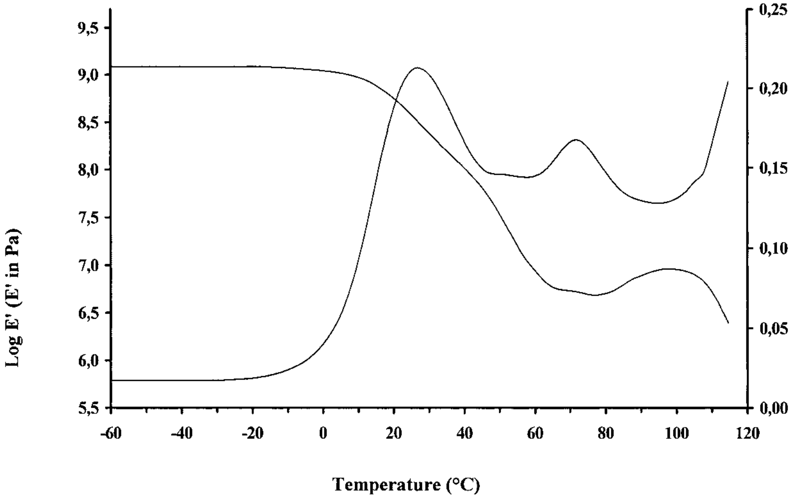

Fig. 4. The dynamic-mechanical modulus and the loss factor, tan δ, of sample Q as a function of temperature.

The second drop is followed by an increase of modulus, typical of a thermally induced crystallization, and by the final drop due to the melting. Corresponding to the two drops of modulus, the tan δ curve shows two dissipation peaks, that we will call γ and β peaks. The first peak (γ peak) having its maximum at 26°C is correspondent to the amorphous glass transition, as shown before in the case of form I. The second peak (β peak), extending between 50 and 80°C, corresponds to the transition of the trans-planar mesophase into the helical crystalline form, as already reported. As a matter of fact the thermal transformation of the chains in trans-planar conformation into chains in helical conformation in the interval of temperature 50-80°C was already described.[16,18,22] We can observe that in the sample crystallized in the trans-planar mesophase (Sample Q) this transition prevalently determines the drop of the elastic modulus and is followed by the increase of modulus due to the crystallization of the helical form. Therefore the β peak, not present in samples crystallized in the helical form I, is specific of the trans-planar mesophase. In Figure 5 the dynamic-mechanical spectrum of sample FII, containing both the helical forms I and II is shown. Also in this case, the elastic modulus is almost constant in the glassy region up to 10°C, then a first drop occurs between 10 and 35°C, followed by a less intense decrease up to 80°C. A second drop is observable between 80°C and 120°C. Correspondently, two dissipation peaks are evident in the tan δ curve, and we will call them γ and α peaks.

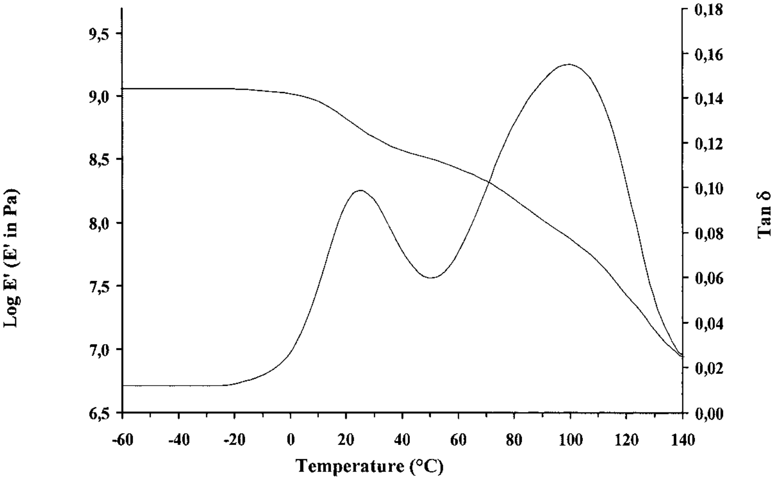

Fig. 5. The dynamic-mechanical modulus and the loss factor, tan δ, of sample FII as a function of temperature.

The first, centered at 24°C is due to the amorphous glass transition and it corresponds to the first drop of the elastic modulus (γ peak). The second, very strong peak, centered at 100°C corresponds to a transition of the helical form II (α peak). Using X-ray analysis in temperature we already showed that the oriented helical form II undergoes around 100°C a melting and re-crystallization phenomenon, leading to the ordered form I.[25] In correspondence of this structural change the dynamic-mechanical analysis showed a strong dissipation peak, that could be unambiguously associated to the structural transition. In the present case we obtained a non-oriented form II and it shows a similar and very intense dissipation peak of tan δ at the same temperature. It is therefore confirmed that this peak is typical of the helical form II and does not appear either in the helical form I or in the trans-planar mesophase.

In Table 1 the temperature of the peaks of tan δ, present in the different samples, is reported.

Table 1. The temperature of the peaks of tan δ present in the dynamic-mechanical spectra of the different samples.

Sample	**γ (°C)**	**β (°C)**	**α (°C)**
FI	20	-	-
Q	26	71	-
FII	24	-	100

It is also intersting to note that in samples crystallized in form I the drop of the elastic modulus sharply occurs in the amorphous glass transition region, whereas in the sample having the chains in trans-planar conformation the drop partly occurs at Tg and partly in correspondence of the conformational transition. In the case of the sample crystallized in form II the modulus drop is observed both at Tg and in correspondence of the form II transition.

Acknowledgements

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