Crystallization of the α and γ Forms of Isotactic Polypropylene as a Tool To Test the Degree of Segregation of Defects in the Polymer Chains

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ABSTRACT: The polymorphic behavior of samples of isotactic polypropylene prepared with unbridged oscillating metallocene catalysts is analyzed and compared with the behavior of samples prepared with a chiral isospecific metallocene catalyst having similar amounts of defects of stereoregularity. In the samples prepared with the unbridged catalysts, the amount of γ form, which develops upon melt-crystallization procedures, turns out to be always lower than that in the samples prepared with the chiral isospecific catalyst. This suggests that, in the samples obtained with the unbridged catalysts, the distribution of defects of stereoregularity is not random, the defects being segregated in more stereoirregular regions of the chains, and confirms that these samples are characterized by a stereoblock structure, with long isotactic sequences alternating to atactic or more stereoirregular sequences. An empirical method to establish the degree of segregation of defects along polypropylene chains is suggested.

Introduction

The γ form of isotactic polypropylene (iPP) has received noticeable attention in the last years.[1−8] The crystal structure is unusual and represents the first example of packing of nonparallel chains.[1−3] Commercial iPP, prepared with the traditional heterogeneous Ziegler−Natta catalytic system, crystallizes, under the most common conditions, in the stable α form.[9] The γ form my be obtained only under special conditions, i.e., by crystallization from the melt at elevated pressures (about 5000 atm),[10,11] or by crystallization at atmospheric pressure of low molecular weight samples,[12] and of copolymers containing small amounts (in the range 5−20 mol %) of other olefins,[13] or also by epitaxial crystallization of iPP over suitable substrates.[14]

iPP samples prepared with homogeneous metallocene catalysts crystallizes more easily in the γ form, even at atmospheric pressure and for high molecular weight samples.[1−8] The different polymorphic behavior of iPP samples prepared with heterogeneous and homogeneous catalysts is related to the different distribution along the chains of defects of stereo- and regioregularity, generated by the different kinds of catalytic systems. The distribution of defects, in turn, influences the average length of the crystallizable (fully isotactic) sequences.

The data published so far,[4−14] indicate that when the fully isotactic sequences are very short, iPP crystallizes in the γ form, whereas very long regular isotactic sequences generally crystallizes only in the α form. In the chains of iPP samples prepared with homogeneous metallocene catalysts (like those studied in refs 4−8) the distribution of defects is random, and the length of fully isotactic sequences is roughly inversely related to the content of errors. As a consequence, even a small amount of defects reduces the length of the regular isotactic sequences and the γ form crystallizes.[5] In the case of iPP samples obtained with heterogeneous Ziegler−Natta catalytic systems, instead, a relatively large amount of defects may be segregated in a small fraction of poorly crystallizable molecules, so that longer fully isotactic sequences can be produced, leading to the crystallization of the α form even for a relatively high overall concentration of defects.[5,10]

It has been reported that for iPP samples prepared with metallocene catalysts, a mixture of the α and γ forms is obtained by isothermal crystallization from the melt, and the content of γ form increases with increasing the content of defects.[5] In the extensive work of Alamo et al.,[5−7] the influence of the molecular weight and of the kind and content of defects on the crystallization of the γ form has been investigated. The relative stability of the γ form seems independent of the molecular weight of the sample (for M_w in the range 40 000−300 000), and depends mainly on the total amount of defects of stereoregularity (mainly *rr* isolated triads) and regioregularity (mainly 2,1 and 3,1 insertions).[5] However, the polymorphic behavior has been studied only for iPP samples obtained with stereorigid metallocene catalysts, which give rise to a random distribution of defects in the polymer chains, although a wide range of concentration of errors has been examined.[4,5,8] For these systems, the higher the content of defects, compatible with the crystallizability of the samples, the higher the maximum amount of the γ form which crystallizes by suitable procedures.[5,8]

In this paper the study of the polymorphic behavior of iPP has been extended to iPP samples with chains having a nonrandom distribution of defects, prepared with unbridged metallocene catalysts.[15−17] These catalytic systems were designed to interconvert between chiral and achiral torsional isomers on the time scale of the polymerization reaction, providing polymer chains with a stereoblock structure, where isotactic sequences alternate to atactic (or more stereoirregular) sequences.[15] The capability of these materials to crystallize in the α or γ forms will be compared to that of samples prepared with stereorigid *ansa*-metallocene catalysts character-

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Table 1. Polymerization Temperatures (T_{pol}), Concentrations of the Pentad [*mmmm*] and the Dyad [*m*], Triads Distribution, Molecular Masses (M_w), Fractions of Steric Errors (ϵ), Average Lengths of Fully Isotactic Sequences ($\langle L_{iso} \rangle$), Melting Temperatures of the As-Prepared Powders (T_m) of the Three IPP Samples Prepared with *rac*-Isopropylidene[bis(3-trimethylsilyl)(indenyl)]zirconium/MAO Catalytic System[18]

samples	T_{pol} (°C)	[*mmmm*] (%)	[*m*] (%)	[*mm*] (%)	[*mr*] (%)	[*rr*] (%)	M_w	ϵ (%)	$\langle L_{iso} \rangle$ (monomeric units)	T_m (°C)
R1	20	89.0	95.5	93.3	4.4	2.3	110 000	2.3	43	144
R2	50	87.4	94.8	92.1	5.2	2.6	75 000	2.6	38	141
R3	60	83.4	93.1	89.7	6.9	3.4	66 000	3.4	29	137

Table 2. Polymerization Temperatures (T_{pol}), Concentrations of the Pentad [*mmmm*] and the Dyad [*m*], Molecular Masses (M_w), Polydispersion Indices (M_w/M_n), Melting Temperatures of the As-Prepared Powders (T_m) of the IPP Samples Prepared with Bis[2-(3,5-di-*tert*-butyl-4-methoxyphenyl)indenyl]zirconium Dichloride/MAO (Samples W1 and W2)[17] and Bis[2-(3,5-di-*tert*-butylphenyl)indenyl]hafnium Dichloride/MAO (sample W3)[19,20] Catalytic Systems. The Concentrations of the Isotactic Pentad [*mmmm*] and the Melting Temperatures (T_m) of the Heptane-Insoluble (Sample W*i*(HI)) and Heptane-Soluble−Ethyl Ether-Insoluble (Samples W*i*(HS)) Fractions of the Three W*i* Samples Are Also Reported

samples	T_{pol} (°C)	[*mmmm*] (%)	[*m*] (%)	M_w	M_w/M_n	T_m (°C)	[*mmmm*] (%) HI fraction	T_m (°C) HI fraction	[*mmmm*] (%) HS fraction	T_m (°C) HS fraction
W1	0	84	95	718 000	4.6	149	90	152	74	145
W2	40	73	91	462 000	3.7	147	84	151	69	145
W3	50	34	73	201 000	2.3	65, 155[a]	76	157	44	65

[a] The DSC scan presents two melting peaks at 65 and 155 °C.

ized by chains having a similar overall concentration of defects, but distributed at random along the chains.

In polymer systems characterized by a nonrandom distribution of defects quantitative direct methods to establish the degree of segregation of the steric errors, like the ^{13}C NMR techniques, generally fail because of the complicated microstructure of the chains and also because the relative amount of stereosequences joining the regular and the defective portions of the chains is often below the limit of detection of the NMR techniques. Information about the microstructure of the chains in these systems have been obtained by indirect methods based, for instance, on the mechanism of polymerization and on the analysis of the physical properties of the polymer. For examples, a stereoblock microstructure has important consequences on the mechanical properties of a polymer; in the case of polypropylene, in fact, an interesting elastomeric behavior has been revealed.[15−17] However, since the crystallization of the γ form depends on the average length of the crystallizable sequences (identifiable with the fully isotactic ...*mmmm*... stereosequences), it is expected that a measure of the relative amount of the crystallized γ form may provide indirect information about the degree of segregation of defects in these samples. In this paper, we suggest a method which allows to find the average length of fully isotactic stereosequences in polypropylene samples having a nonrandom distribution of defects, based on the evaluation of the amount of the crystalline γ form.

Experimental Section

Two different sets of iPP samples, prepared with different classes of metallocene catalysts have been examined.

Three samples, R1, R2, and R3, were synthesized at different temperatures using the single center catalyst composed of *rac*-isopropylidene[bis(3-trimethylsilyl)(indenyl)]zirconium dichloride, activated with methylaluminoxane (MAO), as described in ref 18. This catalytic system is highly regiospecific and produces relatively high molecular weight iPP samples (the polydispersion index of the molecular masses is around 2) with a good stereoregularity and a random distribution of defects, mainly represented by isolated *rr* triads. The molecular weights, the melting temperatures, and the main microstructural characteristics of the three samples are reported in Table 1.

Two samples W1 and W2 were prepared using the unbridged zirconocene catalysts composed of bis[2-(3,5-di-*tert*-butyl-4-methoxyphenyl)indenyl]zirconium dichloride and MAO, as described in ref 17. These catalytic system were designed to interconvert between chiral and achiral torsional isomers on the time scale of the polymerization reaction, to produce polymer chains with an isotactic and atactic stereoblock structure.[17] Usually, they produce a reactor blend of stereoblock polypropylene which can be separated in fractions of different tacticities and melting temperatures. The substituents of the phenyl rings in the catalyst allow to obtain isotactic polypropylene showing, in the unfractioned powder, a relatively high degree of stereoregularity and high molecular weights with a distribution $M_w/M_n > 3$ (see Table 2). These powders have been fractioned with boiling ethyl ether and heptane; fractions soluble in ethyl ether (ES), insoluble in ethyl ether and soluble in heptane (HS) and insoluble in boiling heptane (HI) have been obtained, the relative amount of heptane-insoluble fractions being 63 and 26% for the sample W1 and W2, respectively. The main properties of the various fractions are also reported in Table 2.

Sample W3 was prepared using the unbridged bis[2-(3,5-di-*tert*-butylphenyl)indenyl]hafnium dichloride catalyst,[19,20] activated with MAO, in liquid propylene, as described in ref 19. This system produces polypropylene showing in the unfractioned powder low degree of stereoregularity ([*mmmm*] = 34%) and molecular weight $M_w = 201\,000$.[19,20] Also, this sample has been fractioned with boiling ethyl ether and heptane, the relative amounts of the ether-soluble (ES), heptane-soluble (HS), and heptane-insoluble (HI) fractions are 48, 42, and 10%, respectively. The three fractions present molecular weights M_w of 147 000, 220 000 and 432 000, respectively.[20] The main properties of the unfractioned and fractioned samples are reported in the Table 2. The unfractioned sample W3 presents in the DSC scan two well-separated melting peaks at 65 and 155 °C (Table 2), which indicate that the sample is rather heterogeneous, characterized by fractions having different molecular weights and stereoregularities that melt at low and high temperatures, respectively. The heptane soluble and heptane insoluble fractions of the sample W3 melt, indeed, at 65 and 157 °C, respectively.

The various samples were isothermally crystallized from the melt at different temperatures. Compression molded specimens were melted at 180 °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. The samples were then rapidly cooled to room temperature and analyzed by wide-

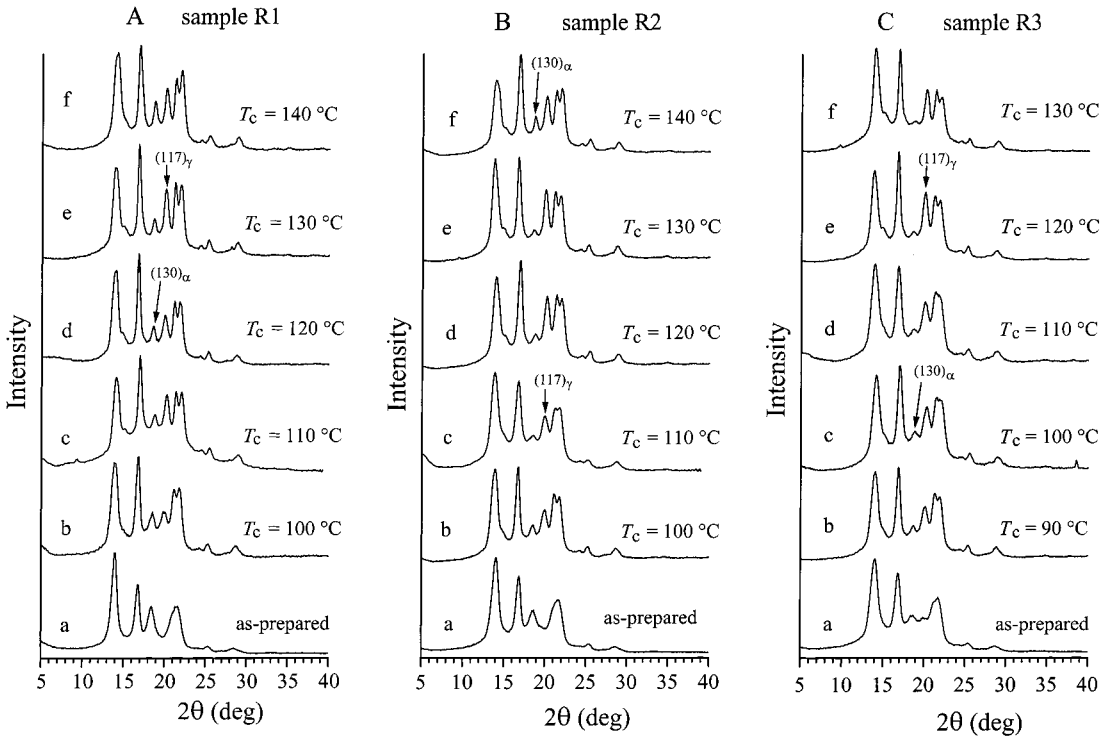

Figure 1. X-ray powder diffraction patterns of the as-prepared iPP samples R*i* and of specimens of the same samples isothermally crystallized form the melt at the indicated temperatures: (A) sample R1; (B) sample R2; (C) sample R3. The $(130)_\alpha$ and $(117)_\gamma$ reflections at $2\theta = 18.6$ and 20.1°, respectively, typical of the α and γ forms of iPP, respectively, are also indicated.

angle X-ray diffraction. In the various isothermal crystallizations, the crystallization time t_c is different depending on the crystallization temperature, the shortest time being 24 h for the lowest crystallization temperatures (for instance, at T_c = 100 and 110 °C for the samples R1, R2, W*i*, and the heptane insoluble fractions W*i*(HI), or at T_c = 90, 80, 70, and 50 °C for the samples R3 and the heptane soluble fractions HS of the samples W1, W2 and W3, respectively). For each sample the crystallization time has been increased with increasing the crystallization temperature, up to 2 weeks for the highest crystallization temperatures (for instance, at T_c = 140 °C for the three samples R*i*, the three samples W*i* and their heptane insoluble fractions W*i*(HI), or at T_c = 110, 100, and 70 °C for the heptane soluble fractions of the samples W1, W2, and W3, respectively). However, as a further check that in any experiment the crystallization time is long enough to complete the crystallization of the crystallizable materials and no appreciable crystallization occurs during the cooling to room temperature, we have verified that the melting temperature of each sample increases regularly with increasing T_c.

X-ray powder diffraction patterns were obtained at room temperature with an automatic Philips diffractometer using Ni-filtered Cu Kα radiation.

The melting temperatures of the various samples were determined by differential scanning calorimetry (DSC), performing scans at a heating rate of 10 °C/min, using a Perkin-Elmer DSC-7 apparatus in a flowing N_2 atmosphere.

The relative amount of crystals in the γ form present in our samples was measured from the X-ray diffraction profiles, as suggested by Turner-Jones et al.,[21] by measuring the ratio between the intensities of the $(117)_\gamma$ reflection at $2\theta = 20.1°$, typical of the γ form, and the $(130)_\alpha$ reflection at $2\theta = 18.6°$, typical of the α form: $f_\gamma = I(117)_\gamma/[I(130)_\alpha + I(117)_\gamma]$. The intensities of the $(117)_\gamma$ and $(130)_\alpha$ reflections were measured from the area of the corresponding diffraction peaks above the diffuse amorphous halo in the X-ray powder diffraction profiles. The amorphous halo has been obtained from the X-ray diffraction profile of an atactic polypropylene, and then it was scaled and subtracted to the X-ray diffraction profiles of the melt-crystallized samples.

Results and Discussion

The X-ray powder diffraction profiles of the as-prepared iPP samples R*i* and W*i* and of the samples isothermally crystallized from the melt at different temperatures, are reported in Figures 1 and 2. We recall that the α and the γ form of iPP present very similar X-ray diffraction profiles, the main difference being the position of the third strong diffraction peak, which occurs at $2\theta = 18.6°$ ($(130)_\alpha$ reflection) in the α form,[9] and at $2\theta = 20.1°$ ($(117)_\gamma$ reflection) in the γ form.[1,2] The presence of the diffraction peak at $2\theta = 18.6°$ and the absence of the reflection at $2\theta = 20.1°$ in the X-ray diffraction patterns of the as-prepared R1, R2, W1, and W2 samples (profiles a in Figures 1A,B and 2A,B, respectively) indicates that these samples are basically in the α form. The X-ray diffraction of the less stereoregular sample of the R*i* set (sample R3) present both reflections of the α and γ forms (profile *a* in Figure 1C), indicating that in the as-prepared sample a mixture of crystals of the two forms of iPP is present. The X-ray diffraction pattern of the as-prepared and unfractioned W3 sample (profile *a* in Figure 2C) indicates a low degree of crystallinity according to the very low degree of stereoregularity (Table 2).

It is apparent from Figures 1 and 2 that the diffraction patterns of the melt-crystallized samples of the R1, R2, R3, W1, and W2 samples present both $(130)_\alpha$ and $(117)_\gamma$ reflections, indicating that the γ form develops by crystallization from the melt. The relative intensity of the $(117)_\gamma$ reflection of the γ form at $2\theta = 20.1°$, with respect to that of the peak of the α form at $2\theta = 18.6°$ ($(130)_\alpha$ reflection), increases with increasing the crystallization temperature, reaches a maximum value and then decreases for a further increase of the crystallization temperature. The relative amount of the γ form with respect to the α form, f_γ, for the various samples is reported in Figure 3 as a function of the crystalliza-

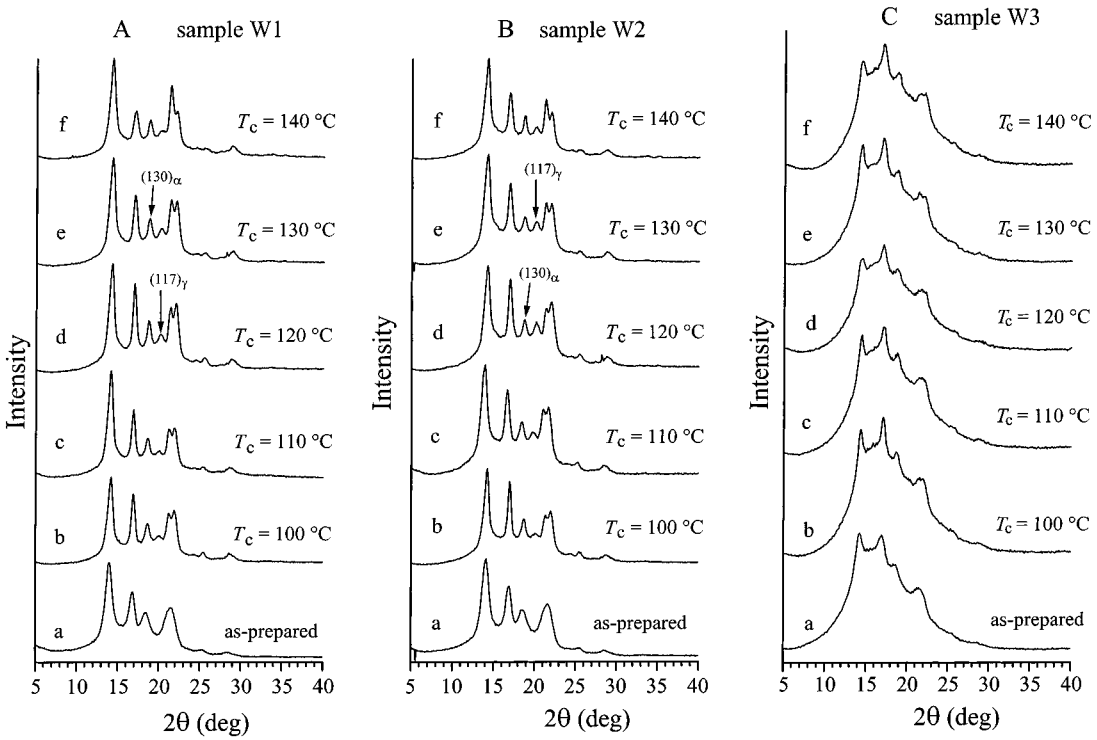

Figure 2. X-ray powder diffraction patterns of the as-prepared iPP samples W*i* and of specimens of the same samples isothermally crystallized form the melt at the indicated temperatures: (A) sample W1; (B) sample W2; (C) sample W3. The $(130)_\alpha$ and $(117)_\gamma$ reflections at $2\theta = 18.6$ and 20.1°, respectively, typical of the α and γ forms of iPP, respectively, are also indicated.

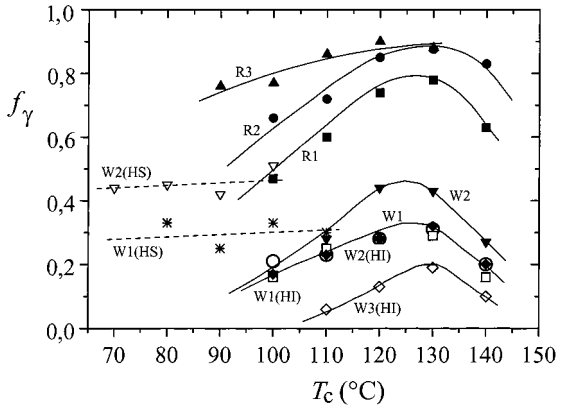

Figure 3. Amount of the crystallized γ form of iPP, f_γ, in the samples R*i* and W*i* isothermally crystallized from the melt, as a function of the crystallization temperature, T_c: (■) sample R1; (●) sample R2; (▲) sample R3; (○) sample W1; (□) HI fraction of the sample W1 (sample W1(HI)); (∗) HS fraction of the sample W1 (sample W1(HS)); (▼) sample W2; (◆) HI fraction of the sample W2 (sample W2(HI)); (▽) HS fraction of the sample W2 (sample W2(HS)); (◇) HI fraction of the sample W3 (sample W3(HI)).

tion temperature. The content of the γ form increases with increasing the crystallization temperatures and a maximum amount of the γ form is obtained, for each samples, at temperatures in the range 120−130 °C. Similar curves have been already reported and discussed in refs 5 and 8 for different samples of iPP prepared with different metallocene catalysts.

We observe that for a given value of the crystallization temperature T_c, within the same series, the content of γ form increases with increasing the concentration of defects of stereoregularity. The lower the degree of isotacticity the higher the maximum amount of the crystallized γ form (f_γ(max)). In particular, for the R*i* samples, f_γ(max) ≈ 78% for the sample R1 ([*mmmm*] = 89.0%) and f_γ(max) ≈ 90% for the less stereoregular R2 and R3 samples ([*mmmm*] = 87.4 and 83.4%, respectively). For the W*i* samples, f_γ(max) ≈ 30% for the sample W1 ([*mmmm*] = 84.0%) and f_γ(max) ≈ 40% for the sample W2 ([*mmmm*] = 73.0%). For the less stereoregular sample W3 ([*mmmm*] = 34%), neither the degree of crystallinity nor the content of the γ form are improved by the melt-crystallizations (Figure 2C). Apparently, this sample does not show crystallization of the γ form in the as-prepared sample as well as in the melt-crystallizations. This is probably due to the fact that the sample is very heterogeneous containing a large amount of amorphous or poorly crystalline fractions (Table 2).

These data confirm that the crystallization of the γ form is favored when the regular isotactic sequences are shortened by the presence of defects.[5] The increase of the content of γ form with increasing the crystallization temperature and the successive decrease (Figure 3) may be explained considering that for these samples, containing an appreciable amount of defects of stereoregularity, the formation of the γ form is thermodynamically favored,[5,22,23] and, as a consequence, a high amount of the γ form develops in the slow crystallizations at high temperatures. At lower temperatures, the fast crystallization of the α form is instead kinetically favored, giving a low amount of γ form. With increasing crystallization temperature, the amount of γ form increases, but at very high crystallization temperatures (higher than 130 °C) the crystallization of the γ form is too slow because of its lower melting temperature,[5,23] and the α form becomes again kinetically favored, so that the amount of γ form decreases.

It is also apparent from Figure 3 that the content of the γ form present in the samples R1−R3 is always higher than that in the samples W1 and W2, whichever the crystallization temperature, even though the amount

of defects of stereoregularity present in the samples is similar. For instance, the samples W1 and R3 have nearly the same concentration of the fully isotactic pentads [*mmmm*], but while sample R3 is basically in the γ form at any crystallization temperature (the maximum amount of the γ form being 90%), the sample W1 crystallizes mainly in the α form (the maximum amount of the γ form which develops by melt-crystallization being only 30%). For sample W2, which is apparently less stereoregular ([*mmmm*] = 73.0%) than the sample R3 ([*mmmm*] = 83.4%), the maximum amount of the γ form is only 40%.

These data clearly indicate that the relative stability of α and γ forms of iPP is related to the average length of the fully isotactic sequences in the chains comprised between two successive interruptions, the γ form being favored when the regular isotactic sequences are short. The number of interruptions depends, in turn, on the content of defects and the degree of segregation of the defects along the polymer chain.

For the samples of the R*i* set, the distribution of configurational errors (mainly isolated *rr* triads) is random and the average length of the fully isotactic sequences, $\langle L_{iso} \rangle$, is inversely proportional to the content of errors ($\langle L_{iso} \rangle \approx 1/[rr]$; see Table 1). As a consequence, the amount of γ form at a given crystallization temperature turns out to be higher for the less stereoregular sample R3 (with $\langle L_{iso} \rangle \approx 29$ monomeric units) than for the samples R2 ($\langle L_{iso} \rangle \approx 38$ monomeric units) and R1 ($\langle L_{iso} \rangle \approx 43$ monomeric units). The samples W1 and W2 present a content of γ form much lower than that of the samples R*i*; they, therefore, behave as if the average length of the fully isotactic sequences was longer than that in the sample R*i*, even though their overall amounts of the fully isotactic pentads [*mmmm*] are nearly the same as in the samples R*i*. This indicates that in the samples W*i*, prepared with the unbridged catalysts, the defects of stereoregularity are segregated in poorly crystallizable chain fractions or also in atactic sequences alternating to long isotactic ones, giving rise to polymer chains with a stereoblock structure.[15]

Since the as-prepared samples W*i* are mixtures of different fractions having different stereoregularities and molecular weights,[16,17,19,20] in order to confirm that the single homogeneous fractions are made by polymer chains having a stereoblock structure, the polymorphic behavior of the heptane-insoluble (HI) and heptane-soluble (HS) fractions of the samples W1, W2, and W3 (samples W*i*(HI) and W*i*(HS)) has also been investigated. The ether-soluble fractions (ES) of the three samples did not present evident X-ray crystallinity and were not further analyzed. The heptane-insoluble fraction of the sample W3 is much more stereoregular than the whole sample (Table 2), indicating that this sample is characterized by very heterogeneous fractions.

The X-ray diffraction patterns of the melt-crystallized samples of the HI and HS fractions of the W*i* samples are reported in Figures 4−6. It is apparent that the HI and HS fractions of the samples W1 and W2 (Figures 4 and 5) have a same behavior as the unfractioned samples. The as-fractioned HS and HI samples are basically in the α form, as indicated by the absence of the $(117)_\gamma$ at $2\theta = 20.1°$ in patterns a of Figures 4A,B and 5A,B, whereas a certain amount of γ form develops by the melt-crystallization procedures, as indicated by the presence of both $(130)_\alpha$ and $(117)_\gamma$ reflections at $2\theta = 18.6$ and 20.1° in the X-ray patterns of the melt-crystallized samples (Figures 4 and 5). The low stereoregular HS fraction of the sample W3 (sample W3(HS), [*mmmm*] = 44%) has a same behavior as the unfractioned sample (Figure 6A), whereas the more stereoregular and crystalline HI fraction (sample W3(HI), [*mmmm*] = 76%) (Figure 6B) behaves like the HI fractions of the samples W1 and W2 (Figures 4B and 5B). A small amount of γ form is obtained in the melt-crystallized samples, whereas the as-fractioned sample is basically in the α form (Figure 6B).

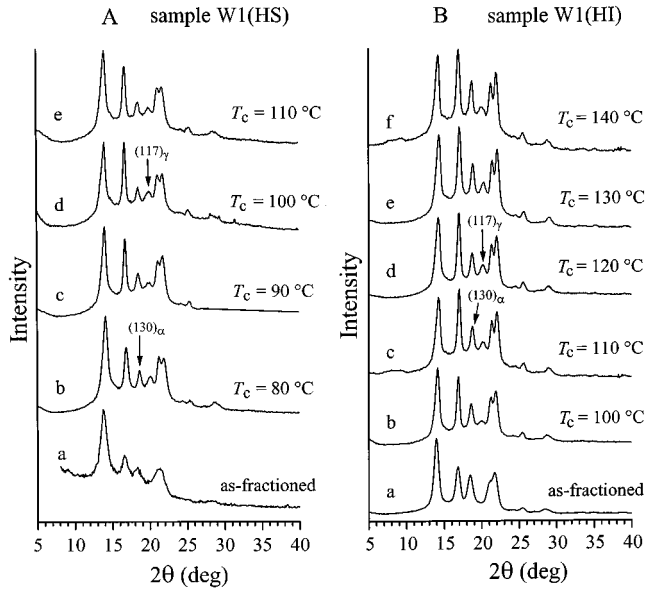

Figure 4. X-ray powder diffraction patterns of the heptane-soluble (A) and heptane-insoluble (B) fractions of the sample W1 (samples W1(HS) and W1(HI), respectively) and of specimens of both fractions isothermally crystallized form the melt at the indicated temperatures. The $(130)_\alpha$ and $(117)_\gamma$ reflections at $2\theta = 18.6$ and 20.1°, respectively, typical of the α and γ forms of iPP, respectively, are also indicated.

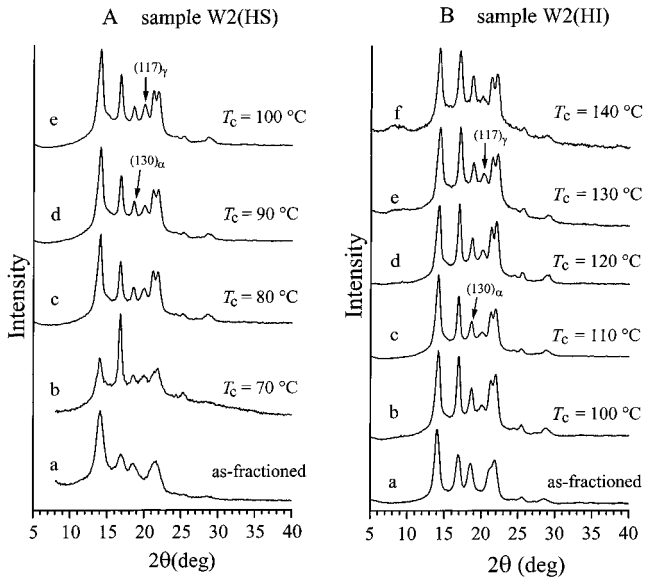

Figure 5. X-ray powder diffraction patterns of the heptane-soluble (A) and heptane-insoluble (B) fractions of the sample W2 (samples W2(HS) and W2(HI), respectively) and of specimens of both fractions isothermally crystallized form the melt at the indicated temperatures. The $(130)_\alpha$ and $(117)_\gamma$ reflections at $2\theta = 18.6$ and 20.1°, respectively, typical of the α and γ forms of iPP, respectively, are also indicated.

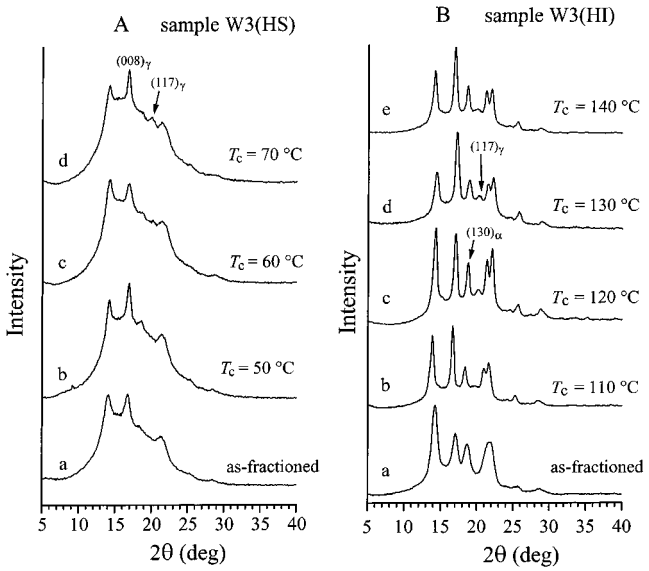

Figure 6. X-ray powder diffraction patterns of the heptane-soluble (A) and heptane-insoluble (B) fractions of the sample W3 (samples W3(HS) and W3(HI), respectively) and of specimens of both fractions isothermally crystallized form the melt at the indicated temperatures. The $(130)_\alpha$ and $(117)_\gamma$ reflections at $2\theta = 18.6$ and 20.1°, respectively, typical of the α and γ forms of iPP, respectively, and the $(004)_\alpha = (008)_\gamma$ reflection at $2\theta = 16.7°$, common in the α and γ forms, are also indicated.

The relative amounts of the γ form, f_γ, for the HI and HS fractions of the samples W1 and W2 and the HI fraction of the sample W3 are also reported in Figure 3 as a function of the crystallization temperature. It is apparent that the HI fraction of the sample W2 (sample W2(HI)), presents a content of γ form slightly lower than that in the unfractioned sample at any crystallization temperature, due to the slightly higher degree of stereoregularity ([*mmmm*] = 84%). The amount of the γ form for the sample W2(HI) is similar to that in the unfractioned W1 sample, according to their similar degrees of isotacticity (Table 2). The sample W1 and its HI fraction (sample W1(HI)) present a similar content of γ form, probably because the whole W1 sample contains a high percentage of the HI fraction (63%) and their degrees of stereoregularity are not very different ([*mmmm*] = 84 and 90%, respectively). In Figure 3, the data of γ form content for the samples W1, W1(HI), and W2(HI) are fitted by the same curve.

The content of γ form is instead increased in the less stereoregular HS fractions (samples W1(HS) and W2-(HS)), which present an amount of γ form nearly constant with the crystallization temperature and nearly corresponding to the maximum amount, f_γ(max), obtained for the corresponding unfractioned samples (Figure 3).

Also for these homogeneous fractions of the samples W1 and W2, obtained with the same catalytic system, the content of γ form increases with increasing the concentration of defects of stereoregularity. The maximum amount of γ form which develops by melt-crystallization, f_γ(max), is nearly 50% for the sample W2(HS), having a fully isotactic pentads concentration [*mmmm*] = 69%, and only 30% for the sample W1(HI), having [*mmmm*] = 90%.

The comparison with the behavior of the samples R*i*, reported in Figure 3, indicates that the samples W2-(HI) and R3 have the same concentration of the fully isotactic pentads ([*mmmm*] ≈ 84%), but while the sample R3 crystallizes basically in the γ form at any crystallization temperature (f_γ(max) = 90%), the maximum amount of the γ form in sample W2(HI) is only f_γ(max) = 30%. The samples R1 and W1(HI) have the same content of the fully isotactic pentads ([*mmmm*] = 89−90%), but f_γ(max) = 78% for the sample R1 and only about 30% for the sample W1(HI). The sample W2(HS) is the less stereoregular sample, apparently less stereoregular than the sample R3, but the content of γ form in this sample is always lower than that obtained in the sample R3.

These data confirm that in the samples W*i* the average length of the fully isotactic sequences is longer than that in the sample R*i* and indicate that for the W*i* samples, obtained with the unbridged metallocene catalysts, and their homogeneous fractions, the distribution of defects along the polymer chains is not random. The defects would be segregated in more stereoirregular regions of the chains. Therefore, all fractions of the samples W*i* have probably a stereoblock structure characterized by long regular isotactic sequences alternating to more stereoirregular sequences. The length of the fully isotactic sequences is longer the higher the boiling point of the extracting solvent. These sequences tend to crystallize in the α form and the amount of the γ form turns out to be low even though the overall degrees of stereoregularity, as evaluated by the ^{13}C NMR spectra, are apparently very low.

The sample W3 presents a similar stereoblock structure but shows a slightly different behavior, compared to the samples W1 and W2, because it has been prepared with a different unbridged catalyst.[19,20] The unfractioned sample W3 and the corresponding HS fraction (sample W3(HS)) are poorly crystalline, according to the very low stereoregularities ([*mmmm*] = 34% and 44%, respectively), and do not show development of appreciable amount of γ form in the melt-crystallizations (Figures 2C and 6A, respectively). The X-ray diffraction patterns are nearly the same at any crystallization temperature, and only a broad peak at 2θ = 20.1° of the γ form, with very small intensity, is apparent over the broad diffuse scattering in the patterns of the sample W3(HS) crystallized at high temperatures (Figure 6A). The HI fraction is much more stereoregular than the whole sample ([*mmmm*] = 76%) and presents a higher degree of crystallinity. The as-fractioned sample is in the α form, and a small amount of the γ form develops by melt-crystallizations (Figure 6B). The content of γ form, also reported in Figure 3, is however very low, f_γ(max) being only 20%. Although the stereoregularity of the sample W3(HI) ([*mmmm*] = 76%) is lower than those of the samples W2(HI) ([*mmmm*] = 84%) and W1(HI) ([*mmmm*] = 90%), and similar to that of the sample W1(HS) ([*mmmm*] = 74%), the content of γ form in the sample W3(HI) is much lower than that of the samples W2(HI), W1(HI), and W1(HS) (Figure 3). Moreover, despite the similar stereoregularities, the melting temperature of the sample W3(HI) (157 °C) is much higher than that of the sample W1(HS) (145 °C) (Table 2). This indicates that the sample W3(HI) is characterized by a stereoblock structure with long isotactic and atactic alternating sequences, longer than those in the samples W1 and W2 and their fractions. This is also in agreement with the high molecular weight (M_w = 432 000) of the sample W3(HI).

These data indicate that the sample W3 is quite heterogeneous, being characterized by a poorly crystalline and stereoirregular HS fraction and higher molecular weight HI fraction having very long isotactic sequences.

It is worth noting that the absence of the $(117)_\gamma$ reflection at $2\theta = 20.1°$ of the γ form in the X-ray diffraction patterns of some of the samples analyzed, for instance the samples W3 and W3(HS) (Figures 2C and 6A, respectively), does not necessarily indicate that the γ form is completely absent. We have recently shown[22,23] that in samples of iPP crystallized in the γ form or in mixtures of α and γ forms, in oriented fibers[22] or powder specimens,[23] disordered modifications intermediate between the α and γ forms are generally obtained.[22] The disorder corresponds to the statistical succession of bilayers of chains packed with chains parallel, like in the α form, or nearly perpendicular, like in the γ form (see Figure 5 in ref 22). In the X-ray diffraction patterns of these crystalline disordered modifications, the intensities of both the $(130)_\alpha$ and $(117)_\gamma$ reflection, typical of the α and γ forms, respectively, are reduced with respect to those arising from crystals in the pure α and γ forms.[22] The intensities of the diffraction peaks at $2\theta = 16.7°$, corresponding to the $(040)_\alpha$ and $(008)_\gamma$ reflections of the α and γ forms, respectively, and at $2\theta = 21.2°$, corresponding to the $(111)_\alpha$ and $(202)_\gamma$ reflections are instead not influenced by the presence of disorder. In the X-ray diffraction patterns of the samples W3 (Figure 2C) and W3(HS) (Figure 6A), both $(130)_\alpha$ and $(117)_\gamma$ at $2\theta = 18.6$ and 20.1°, respectively, are practically absent, or are present with very low intensities, at every crystallization temperature, whereas the reflection at $2\theta = 16.7°$ is always sharp. Moreover, in the samples W1 and W2 crystallized at 140 °C (Figure 2, parts A and B, respectively), the intensity of the $(117)_\gamma$ reflection is very low, while the $(202)_\gamma$ reflection at $2\theta = 21.2°$ is sharp and with a strong intensity. This indicates that in these samples, disordered modifications, with high degree of $\alpha-\gamma$ disorder, are always obtained. All the analyzed samples show this behavior, as evidenced by the fact that in samples apparently crystallized in the pure α form, like for instance the as-prepared samples R1, R2, W1, and W2, the relative intensities of the reflections in the X-ray diffraction patterns (profiles a in Figures 1A,B and 2A,B, respectively), do not correspond to those expected for the pure α crystals of iPP.[22,23]

The different polymorphic behaviors of the R*i* and W*i* samples (evidenced in Figure 3), related to the different distribution of defects along the chains of the different samples, suggests that the data relative to the crystallization of the γ form in iPP samples having a random distribution of defects, may be used as a practical tool to establish a parameter closely related to the average length of the fully isotactic sequences in iPP samples having a nonrandom distribution of defects, $\langle L_{iso}\rangle$. The maximum amount of the γ form which crystallizes upon the melt-crystallization procedures, f_γ(max), for various iPP samples is reported in Figure 7 as a function of the average length of the fully isotactic ...*mmmm*... sequences $\langle L_{iso}\rangle$. The data relative to the samples R*i*, obtained in this paper, are reported in Figure 7 (open squares) along with literature data relative to other samples prepared with different metallocene catalysts, taken from refs 4 (open triangles), 5 (full circles) and 8 (full triangles). Some data obtained in our laboratories

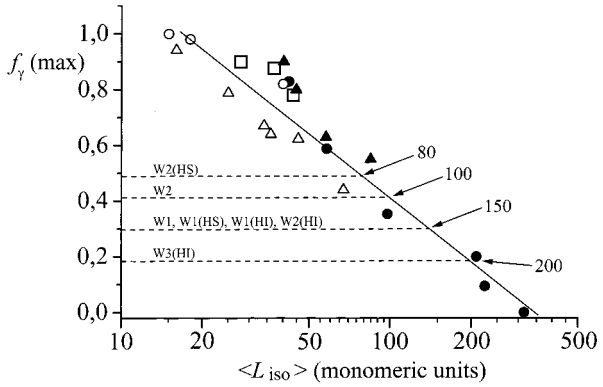

Figure 7. Maximum amount of the γ form obtained upon the melt-crystallization procedures for the various samples of iPP, f_γ(max), as a function of the average length of fully isotactic sequences, $\langle L_{iso}\rangle$, comprised between two consecutive interruptions (defects): (□) samples R*i*; (△) data from ref 4; (●) data from ref 5; (▲) data from ref 8; (○) data from ref 24. The values of f_γ(max) evaluated from the Figure 3 for the samples W*i*, W*i*(HS), and W*i*(HI) are also shown as horizontal dashed lines. The intercepts of these dashed lines on the straight line give the average lengths of fully isotactic sequences $\langle L_{iso}\rangle$ for the samples W*i* and their homogeneous fractions.

for low molecular weight iPP samples containing stereo- and regioerrors,[24] are also included in Figure 7 (open circles). As discussed above, for iPP samples prepared with metallocene catalysts having a random distribution of defects, the average length of the fully isotactic sequences has been evaluated as $\langle L_{iso}\rangle = 1/\epsilon$, with ϵ being the total concentration of errors (of stereoregularity and regioregularity) determined by the ^{13}C NMR analysis (Table 1).

It is apparent from Figure 7 that the maximum amount of γ form, which can be obtained for the various samples by the melt-crystallization procedures, is roughly linear with the logarithm of $\langle L_{iso}\rangle$, at least in the range of $\langle L_{iso}\rangle = 15-400$ monomeric units. If this relationship is kept general whichever the distribution of defects, it is possible to find the apparent length of the fully isotactic sequences also for the W*i* samples from the values of f_γ(max). The unfractioned W1 and W2 samples, for which the maximum amount of γ form achieved is nearly 30% and 40%, respectively (Figure 3), present average lengths of the fully isotactic sequences of nearly 150 and 100 monomeric units, respectively (Figure 7). The heptane-insoluble fractions of the samples W2 and W3, which show lower maximum amounts of the γ form (f_γ(max) $\approx$ 30 and 20%, respectively), are characterized by longer isotactic sequences, $\langle L_{iso}\rangle = 150$ and 200 monomeric units for the samples W2(HI) and W3(HI), respectively (Figure 7). The HS fraction of the sample W2 is instead characterized by shorter isotactic sequences, $\langle L_{iso}\rangle = 80$ monomeric units (Figure 7), since the maximum amount of γ form is nearly 50% (Figure 3). The sample W1 is probably more homogeneous since the maximum amount of the crystallized γ form is nearly the same in the unfractioned and fractioned samples ($\approx$ 30%), corresponding to a similar average length of the isotactic sequences, $\langle L_{iso}\rangle = 150$ monomeric units.

Conclusions

The polymorphic behavior of iPP samples prepared with unbridged oscillating metallocene catalysts (samples W*i*) has been analyzed and compared with the behavior of iPP samples prepared with a single center chiral

isospecific metallocene catalyst (samples R*i*), having similar amount of defects of stereoregularity. The γ form of iPP is obtained by crystallization from the melt; the amount of γ form obtained for the samples W*i*, is always lower than that obtained for the samples R*i*. Since the γ form of iPP crystallizes more easily when the length of the regular isotactic sequences in the chains is small, the samples W*i*, prepared with unbridged metallocene catalysts, behave as if the average length of the fully isotactic sequences was longer than that in the chains of the R*i* samples, even though the R*i* and W*i* samples have nearly the same overall concentration of defects. This indicates that in samples prepared with the oscillating unbridged catalysts, the distribution of defects is not random, as instead occurs in the samples R*i*, but segregated in more stereoirregular regions of the chains. These data confirms that the samples W*i*, and the corresponding homogeneous HI and HS fractions, are characterized by a stereoblock structure of the chains, with long isotactic sequences alternating to more stereoirregular sequences.

An empirical method to establish the degree of segregation of defects along iPP chains is suggested. The method is based on the construction of a calibration curve which plots the maximum amount of the γ form, f_γ(max), obtained for given iPP samples, as a function of the average length of the fully isotactic sequences $\langle L_{iso}\rangle$, using polymer samples with chains having a random distribution of defects as model systems, like for instance the samples R*i*. For these model samples $\langle L_{iso}\rangle = 1/\epsilon$, with ϵ the total concentration of defects. For iPP samples characterized by a nonrandom distribution of defects, the apparent average length of the fully isotactic sequences, $\langle L_{iso}\rangle$, can be obtained from the values of f_γ(max), obtained by X-ray diffraction, by interpolating on the calibration curve.

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