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Comparison between Polymorphic Behaviors of Ziegler-Natta and Metallocene-Made Isotactic Polypropylene: The Role of the Chain Microstructure

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Summary: An analysis of the polymorphic behavior of samples of isotactic polypropylene (iPP) prepared with heterogeneous Ziegler-Natta catalysts is presented. A comparison with the crystallization properties of iPP samples prepared with a single center homogeneous metallocene catalyst is also shown. Samples of Ziegler-Natta iPP samples, prepared with $MgCl_2$-supported catalysts, have been fractionated by extraction with boiling solvents. The irregular fraction, insoluble in diethyl ether and soluble in hexane, crystallizes from the melt almost totally in the γ form. The more stereoregular fractions crystallize instead basically in the α form. The relative amount of γ form crystallized from the melt is much lower that that observed in samples of metallocene-made iPP containing comparable amount of defects. While in the metallocene-made iPP the distribution of defects along the chains is random, in Ziegler-Natta iPP samples the majority of defects are segregated in a small fraction of poorly crystallizable macromolecules or in more irregular portions of the chain, so that much longer fully isotactic sequences can be produced, leading to the crystallization of the α form. This analysis allows concluding that some fractions of Ziegler-Natta iPP are characterized by chains with a stereo-block microstructure, consisting in regular isotactic sequences linked to more irregular sequences.

Keywords: isotactic polypropylene; polymorphic behavior; stereoblocks; Ziegler-Natta catalyst

Introduction

Isotactic polypropylene (iPP) presents a complex polymorphic behavior,[1,2] complicated by the presence of structural disorder.[3] Three different crystalline forms (α, β and γ forms),[1,2] and a mesomorphic form,[4] have been described. Commercial samples of iPP, prepared with the traditional heterogeneous Ziegler-Natta catalytic systems, generally crystallizes in the stable α form.[1,2] The β and γ forms may be obtained only under special conditions of crystallization. The

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β form, indeed, crystallizes only in the presence of nucleating agents,[2,5,6] whereas the γ form can be obtained only by crystallization from the melt at elevated pressures (about 5000 atm),[7] or by crystallization at atmospheric pressure of low molecular weight samples,[8] and of copolymers containing small amounts (in the range 5-20 mol%) of other olefins.[9]

Samples of iPP prepared with homogeneous metallocene catalysts crystallize more easily in the γ form, even at atmospheric pressure and for high molecular weight samples.[10-20] The different polymorphic behavior of iPP samples prepared with heterogeneous and homogeneous catalysts is related to the different type and distribution along the chains of insertion mistakes (that is stereodefects and regiodefects) generated by the different kinds of catalytic systems. The distribution of defects, indeed, influences the average length of the crystallizable (fully isotactic) sequences and affects the crystallization properties of iPP.

In recent papers it has been clearly shown that when the fully isotactic sequences are very short, iPP crystallizes in the γ form, whereas very long regular isotactic sequences generally crystallize only in the α form.[12,18-20] In chains of iPP samples prepared with *ansa*-metallocene catalysts the distribution of defects is random and the length of fully isotactic sequences is roughly inversely related to the content of insertion errors.[18,19] As a consequence, even a small amount of defects reduces the length of the regular isotactic sequences inducing the crystallization of the γ form.[12,18,19] In the case of iPP samples obtained with heterogeneous Ziegler-Natta catalytic systems, instead, the majority of defects may be segregated in a small fraction of poorly crystallizable macromolecules, so that much longer fully isotactic sequences can be produced, leading to the crystallization of the α form even for a relatively high overall concentration of defects.

In this paper the crystallization properties and the polymorphic behavior of fractions of Ziegler-Natta iPP are analyzed and compared with the behavior of metallocene iPP. From the amount of γ form, which develops by crystallizations from the melt, information about the microstructures of chains in the various fractions of Ziegler-Natta iPP can be obtained.

Experimental Section

The sample T1 of Ziegler-Natta iPP was prepared with a $MgCl_2$-supported catalyst modified using di(*iso*-butyl)phthalate as internal donor. The sample T1 was fractioned by exhaustive

Kumagawa extraction in boiling solvents. Fractions soluble in diethyl ether (T1(EtS)), insoluble in diethyl ether and soluble in hexane (T1(EtI-HsS)), insoluble in hexane and soluble in heptane (T1(HsI-HS)) and, finally, insoluble in heptane (T1(HI)), were separated. All fractions were characterized by ^{13}CNMR spectroscopy, differential scanning calorimetry (DSC) and X-ray diffraction (Table 1).

Three samples of metallocene-made iPP (samples R1, R2 and R3) were provided by Dr. Luigi Resconi of Basell Polyolefins (Ferrara, Italy). They were synthesized at different temperatures using the single-center catalyst *rac*-isopropylidene[bis(3-trimethylsilyl-indenyl)] zirconium dichloride, activated with methylaluminoxane (MAO), as described in ref. 21. This catalyst produces iPP samples characterized by chains containing only defects of stereoregularity (isolated *rr* triads), whose amount depends on the polymerization temperature ([*rr*] = 2.3%, 2.6% and 3.4% for the samples R1, R2 and R3, respectively,[21] with melting temperatures of 144, 141 and 137 °C, respectively).

The various fractions of the samples T1 and T2 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 X-ray diffraction. X-ray powder diffraction patterns were obtained at room temperature with an automatic Philips diffractometer using Ni-filtered CuKα radiation.

Table 1. Melting temperature and concentration of pentad stereosequences (%) in the various fractions of the sample T1.

samples	T_m (°C)	*mmmm*	*mmmr*	*rmmr*	*mmrr*	*xmrx*	*rmrm*	*rrrr*	*rrrm*	*mrrm*
T1(EtS)	-	21.08	12.51	4.45	14.61	14.60	4.28	12.45	9.75	6.28
T1(EtI-HsS)	114	47.54	11.42	1.76	12.80	6.82	-	9.22	4.85	5.60
T1(HsI-HS)	148	74.68	6.64	-	7.27	2.94	-	4.63	1.60	2.24
T1(HI)	160	91.44	3.68	-	3.07	-	-	0.63	-	1.18

Results and Discussion

The concentrations of the pentad stereosequences in the chains of the four fractions of the sample T1, evaluated from the ^{13}CNMR spectra, are shown in Table 1.

The X-ray powder diffraction profiles of samples of the three crystalline fractions T1(EtI-HsS), T1(HsI-HS) and T1(HI), isothermally crystallized from the melt are reported in Figure 1. The diffraction profiles of the as-fractionated samples are also reported in Figure 1 (profiles *a*).

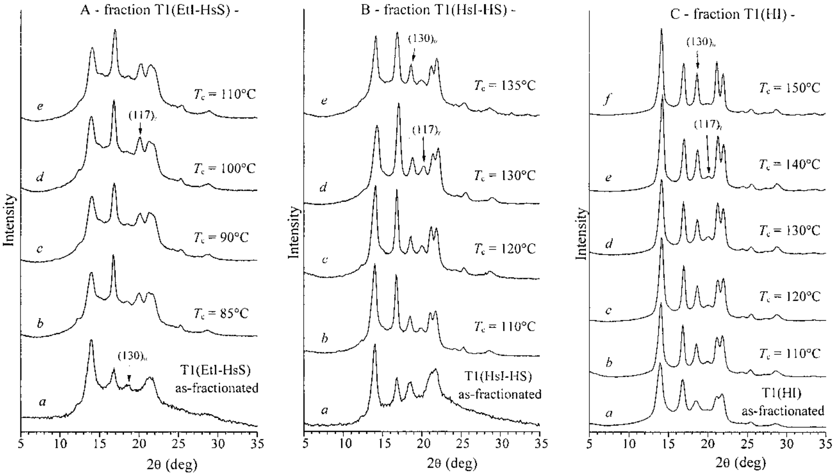

Figure 1. X-ray powder diffraction profiles of samples of the fractions T1(EtI-HsS) (A), T1(HsI-HS) (B) and T1(HI) (C) isothermally crystallized from the melt at the indicated temperatures. The $(130)_\alpha$ reflection of the α form at 2θ = 18.6° and the $(117)_\gamma$ reflections of the γ form at 2θ = 20.1° are indicated.

It is apparent that, whereas the as-fractionated samples are basically in the α form (profiles *a* of Figure 1), the diffraction profiles of samples crystallized from the melt of Figure 1 always present the $(117)_\gamma$ reflection at 2θ = 20.1° of the γ form, indicating that for all the iPP fractions, crystals of the γ form develop when the samples are crystallized from the melt (profiles *b-e* of Figure 1A, B and profiles *b-f* of Figure 1C). In particular, the fraction T1(EtI-HsS), initially in the α form with low crystallinity (profile *a* of Figure 1A), crystallize from the melt almost totally in the γ form, although with low crystallinty, as indicated by the high intensity of the $(117)_\gamma$ reflection of the γ form at 2θ = 20.1° at any crystallization temperature, and the very low intensity of the $(130)_\alpha$ reflection of the α form at $2\theta = 18.6°$ in the diffraction profiles *b-e* of Figure 1A.

The other two more stereoregular fractions T1(HsI-HS) and T1(HI) crystallize from the melt in mixtures of crystals of α and γ forms, with higher amounts of the α form at any crystallization temperature, as indicated by the high intensity of the $(130)_\alpha$ reflection of the α form at $2\theta = 18.6°$ and the low intensity of the $(117)_\gamma$ reflection at $2\theta = 20.1°$ in the diffraction profiles of Figures 1B and 1C. For these samples the crystallinity is much higher than that developed for the fraction T1(EtI-HsS).

For all the fractions of sample T1 the relative intensity of the $(117)_\gamma$ reflection of the γ form at $2\theta = 20.1°$, with respect to that of the $(130)_\alpha$ reflection of the α form at $2\theta = 18.6°$, 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, evaluated from the intensities of the $(117)_\gamma$ and $(130)_\alpha$ reflections as $f_\gamma = I(117)_\gamma/[I(130)_\alpha + I(117)_\gamma]$, is reported in Figure 2 as a function of the crystallization temperature.

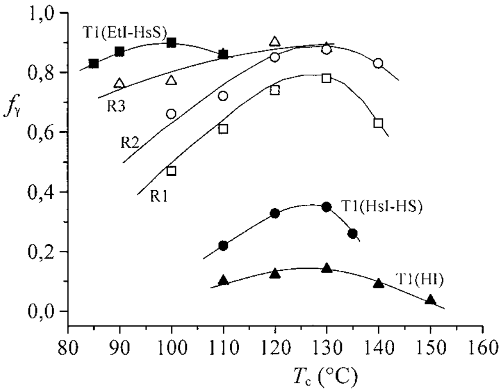

Figure 2. Comparison between the relative contents of γ form of iPP, f_γ, as a function of the crystallization temperature T_c, for metallocene-made iPP samples Ri (taken from refs. 18, 19), and fractions of the Ziegler-Natta iPP sample T1, isothermally crystallized from the melt. (■) fraction T1(EtI-HsS), [*mmmm*] = 47.5%; (●) fraction T1(HsI-HS), [*mmmm*] = 74.7%; (▲) fraction T1(HI), [*mmmm*] = 91.4%; (□) sample R1, [*mmmm*] = 89.0%; (○) sample R2, [*mmmm*] = 87.4%; (△) sample R3, [*mmmm*] = 83.4%.

The content of the γ form increases with increasing the crystallization temperatures and a maximum amount of the γ form is obtained at temperatures in the range 120-130 °C, for the more crystalline fractions T1(HsI-HS) and T1(HI), and at 100 °C for the less crystalline fraction T1(EtI-HsS).

The analysis of the microstructures of the fractions of the sample T1, performed by ^{13}CNMR (Tables 1), has shown that the iPP chains of the more stereoregular fraction T1(HI) present small concentration of defects of stereoregularity mainly represented by isolated *rr* triads. The chains of the less stereoregular fractions T1(EtI-HsS) and T1(HsI-HS) present *rr* defects, the concentrations of the *mrrm* pentad being 5.6 and 2.2%, respectively (Table 1), and also rather long syndiotactic sequences. The concentration of the fully syndiotactic *rrrr* pentad is, indeed, quite high, 9.22% and 4.63% for the chains of the fractions T1(EtI-HsS) and T1(HsI-HS), respectively (Table 1). The presence of the very weak diffraction peak at $2\theta = 12°$ in the X-ray powder diffraction profiles of the fraction T1(EtI-HsS) of Figure 1A indicates that the syndiotactic sequences are long enough to crystallize. The reflection at $2\theta = 12°$ corresponds, indeed, to the 200 reflection arising from the crystals of syndiotactic polypropylene in the stable polymorphic form with chains in two-fold helical conformation.[22] In the case of the more isotactic fraction T1(HsI-HS), with lower concentration of the *rrrr* pentad (4.6%), the intensity of the corresponding reflection at $2\theta = 12°$ in the diffraction profiles of Figure 1B is negligible, indicating the presence of a negligible amount of crystals of syndiotactic polypropylene.

The results of the structural analysis of Figure 2 indicate that for these complex microstructures of Ziegler-Natta iPP sample, the amount of γ form, which may develop by melt-crystallizations, increases with increasing the concentration of defects. The maximum amounts of γ form, f_γ(max), evaluated from the maxima of the curves of Figure 2, are nearly 10-15% for the fractions T1(HI), 35% for the fraction T1(HsI-HS) and 90% for the fraction T1(EtI-HsS). This result is in agreement with the hypothesis reported in the literature that the γ form crystallizes in samples or fractions of iPP characterized by chains having short regular isotactic sequences.[12,18-20]

The amounts of γ form obtained by melt-crystallization of iPP samples prepared with the single-center metallocene catalyst *rac*-isopropyliden[bis(3-trimethylsilyl)(indenyl)]$ZrCl_2$ (samples R1, R2 and R3), taken from refs.18,19, are also reported in Figure 2 and compared with the data obtained for the fractions of the Ziegler-Natta iPP sample T1.

Also for the metallocene iPP samples the content of γ form increases with increasing the crystallization temperature, with a maximum at temperatures of 120-130 °C, and increases with increasing the concentration of defects of stereoregularity *rr*. Since the samples Ri have a random distribution of configurational *rr* errors, the average length of the fully isotactic sequences,$<L_{iso}>$, is inversely proportional to the content of errors ($<L_{iso}> = 1/[rr]$). As a consequence the maximum amount of γ form at a given crystallization temperature, turns out to be higher for the less stereoregular sample R3 (with $<L_{iso}> = 29$ monomeric units) than for the samples R2 ($<L_{iso}> = 38$ monomeric units) and R1 ($<L_{iso}> = 43$ monomeric units).[18,19]

It is apparent from the comparison of Figure 2 that the more stereoregular fraction T1(HI) presents a content of γ form much lower than that obtained in the sample R1, having a similar isotacticity, at any crystallization temperature. The sample R1, having [*mmmm*] = 89% develops a maximum amount of γ form f_γ(max) = 78% (Figure 2), against the values of only 15% observed for the fraction T1(HI), having [*mmmm*] = 91.4%.

In the hypothesis that the γ form preferably crystallizes when the regular isotactic sequences are relatively short,[12,18,19] these data indicate that the chains in the fraction T1(HI) present regular isotactic sequences much longer than those of the chains of the sample R1, even though the overall concentration of defects is not very different. This result can be explained considering that the chains of Ziegler-Natta and metallocene iPP samples present a different distribution of defects. In the metallocene-made iPP samples Ri the distribution of defects of stereoregularity along the macromolecular chains is random so that even a small concentration of defects produces frequent interruptions of the isotactic propagation and the regular isotactic sequences turn out to be relatively short even for samples with quite high stereoregularity.[19] This explains the high concentration of γ form (78-90%) obtained in the relatively high isotactic samples R1, R2 and R3 (Figure 2).

In the fraction T1(HI) the same amount of stereodefects is not randomly distributed along the chains, the defects are segregated in more irregular, noncrystallizable, portions of chains so that the more regular isotactic sequences are always very long and crystallize preferably in the α form. A rough evaluation of the average length of the isotactic sequences in polypropylene chains may be obtained with the empirical method proposed by us in the ref. 18 for stereoblock polypropylene. The method is based on the use of a calibration plot of the maximum amount of the γ form, f_γ(max), as a function of the average length of the fully isotactic sequences $\langle L_{iso} \rangle$, obtained for iPP samples prepared with metallocene catalysts having a random distribution of defects. The average length of the fully isotactic sequences may be evaluated as $\langle L_{iso} \rangle = 1/\varepsilon$, with ε the total concentration of errors determined by the ^{13}C NMR analysis. For these samples the maximum amount of γ form, which can be obtained by the melt-crystallization procedures, is roughly linear with the logarithm of $\langle L_{iso} \rangle$ (see figure 7 of ref. 18). If this linear relationship is kept general whichever the distribution of defects, it is possible to find the length of the fully isotactic sequences also for polypropylene samples characterized by nonrandom distribution of defects from the values of f_γ(max). The calibration plot of f_γ(max) as a function of $\langle L_{iso} \rangle$ is reported in Figure 3 and the indirect method is applied to the various fractions of the Ziegler-Natta iPP. From the value of f_γ(max) = 15%, evaluated from Figure 2 for the fraction T1(HI), a value of the average length of the isotactic sequences $\langle L_{iso} \rangle$ of 220 monomeric units for the chains of the fraction T1(HI) has been found (Figure 3).

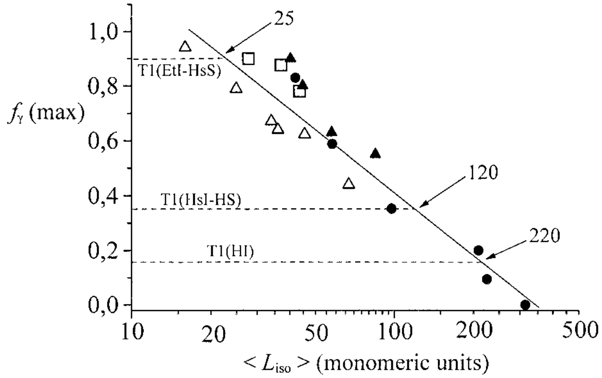

Figure 3. Maximum amount of γ form of iPP obtained upon melt-crystallization procedures for various samples of iPP, f_γ(max), as a function of the average length of fully isotactic sequences, $\langle L_{iso} \rangle$. □) samples Ri from refs. 18-19; △) data from ref. 15; ●) data from ref. 12; ▲) data from ref. 16. The values of f_γ(max) evaluated from the Figure 2 for the fractions of the Ziegler-Natta iPP sample 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 chains of the fractions T1(EtI-HsS), T1(HsI-HS), T1(HI) of the sample T1.

The content of γ form is higher in the case of the more irregular fractions of the Ziegler-Natta iPP sample, T1(HsI-HS) and T1(EtI-HsS) (Figure 2). It is apparent, however, that even though the fraction T1(HsI-HS) is less stereoregular ([*mmmm*] = 75%, Table 1) than the metallocene samples Ri, it shows a maximum amount of γ form of 35%, much lower than those observed for the samples Ri. As discussed above the fraction T1(HsI-HS) is characterized by a appreciable concentration of *rr* defects (2.2%, Table 1), and a high concentration of syndiotactic sequences ([*rrrr*] = 4.6%, Table 1). Despite this high concentration of defects, the sample T1(HsI-HS) still crystallizes preferably in the α form, f_γ(max) being only 35% (Figure 2). This indicates that also for this fraction the regular isotactic sequences are still quite long, even in the presence of so many defects, in any case longer than those in the chains of Ri samples, which instead are characterized by a lower concentration of defects. This suggests that also for the fraction T1(HsI-HS) the defects (*rr* stereodefects and longer syndiotactic sequences *rrrr*) are segregated in more irregular noncrystallizable (or hardly crystallizable) portions of the chains. The more regular isotactic sequences would be, therefore, rather long and able to crystallize preferably 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}CNMR spectrum, is very low.

From Figure 3, by using the structural datum of the maximum amount of γ form of 35%, an average length of the isotactic sequences $<L_{iso}>$ of 120 monomeric unit has been evaluated for the chains of the fraction T1(HsI-HS). In this fraction the iPP chains are characterized by a microstructure consisting in long, rather regular, isotactic sequences linked to more irregular sequences. The hypothesis of a stereo-block microstructure is in agreement with the experimental observation that the fraction T1(HsI-HS) presents a melting temperature of 148 °C (Table 1), higher than that of the more stereoregular sample R1 (144 °C).

Figure 2 shows that the more irregular fraction T1(EtI-HsS) of the Ziegler-Natta iPP sample crystallize almost totally in the γ form, the maximum amount of γ form, f_γ(max) being nearly 90%, similar to that obtained for the samples R2 and R3. It is worth noting, however, that the metallocene iPP samples R2 and R3, having [*mmmm*] = 87.4% and 83.4%, respectively, are much more stereregular than the fraction T1(EtI-HsS) of the Ziegler-Natta iPP sample, which is characterized by [*mmmm*] = 48% (Table 1). This clearly indicates that samples or fractions of Ziegler-Natta iPP may crystallize from the melt at atmospheric pressure almost totally in the γ form only when the concentration of defects is much higher than that needed for the metallocene-made iPP samples. From the value of f_γ(max) = 90% and from Figure 3, an average length of the isotactic sequences $<L_{iso}>$ of 25 monomeric units has been evaluated for the chains of the fraction T1(EtI-HsS), similar to that of the sample R3.

This result suggests that also for the fraction T1(EtI-HsS) most of the defects are segregated in more irregular noncrystallizable portions of the chains, producing slightly more regular isotactic sequences able to crystallize. These sequences are, however, poorly isotactic, contain appreciable amount of defects and tend to crystallize in the γ form (Figure 1A). This microstructure is in agreement with the experimental observation that the fraction T1(EtI-HsS) crystallizes either from solution or from the melt (Figure 1A) with a relatively high crystallinity (nearly 17%) and melting temperature (114 °C), despite the high content of defects.

The presence in the fraction T1(EtI-HsS) of syndiotactic sequences ([*rrrr*] = 9.2%, Table 1), indicates that the more irregular sequences contain relatively long syndiotactic sequences along with atactic sequences. The syndiotactic sequences are long enough to crystallize and this explains the presence of the weak reflection at $2\theta = 12°$ in the diffraction profiles of Figure 1A, which indicates the presence of crystals of sPP.[22] However, the possibility that the syndiotactic sequences are more concentrated in different macromolecules, difficult to separate with the methods of the extraction with boiling solvent, cannot be excluded.[23]

Conclusions

The different polymorphic behavior of metallocene and Ziegler-Natta iPP samples is related to the different distribution of defects in the chains generated by the different kinds of catalytic systems. The distribution of defects, indeed, influences the average length of the crystallizable (fully isotactic) sequences. While in the metallocene iPP the defects are randomly distributed along the chains, in Ziegler-Natta iPP samples the majority of defects are segregated in a small fraction of poorly crystallizable macromolecules or in more irregular portions of the chain, so that much longer fully isotactic sequences can be produced, leading to the crystallization of the α form even for a relatively high overall concentration of defects. A method for the evaluation of the average length of regular isotactic sequences in chains of Ziegler-Natta iPP fractions, characterized by a non-random distribution of defects, is proposed. The method is based on the analysis of the polymorphic behavior of iPP fractions and gives interesting information about the microstructure of chains in the different fractions. For instance, the study of the crystallization properties, and in particular the analysis of the maximum amount of γ form crystallized from the melt, allows revealing the presence of stereo-blocks in some fractions of Ziegler-Natta iPP samples.

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