# Equilibrium Melting Temperature of Syndiotactic Polypropylene

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ABSTRACT: Isothermal crystallizations from the melt of samples of syndiotactic polypropylene having different degrees of syndiotacticity have been performed. The thermal behavior and the structural features of the melt-crystallized samples have been analyzed by differential scanning calorimetry and X-ray diffraction. According to this analysis, less stereoregular samples, crystallized in disordered modifications of form I with defects implying local arrangements of the chains such as in form II, present recrystallization phenomena during heating. For most stereoregular samples relevant recrystallization phenomena are absent. Extrapolation to the equilibrium melting temperature of syndiotactic polypropylene was attempted by using the Hoffmann−Weeks method, taking into account the occurrence of recrystallization and superheating phenomena. A value of nearly 182 °C has been obtained for the equilibrium melting temperature of the fully syndiotactic polypropylene.

## Introduction

The equilibrium melting temperature ($T_m°$) of syndiotactic polypropylene (s-PP) has been reported by several authors.

A $T_m°$ value of 161 °C was estimated by Boor and Youngman[1] by extrapolation to 100% crystallinity of the melting temperatures of samples having different crystallinity fractions. The same authors determined different values for $T_m°$ in the range 140−170 °C from the extrapolation of the observed melting temperatures of samples having different lamellar thicknesses.[2] It was suggested that the higher melting temperatures observed might be attributed to the melting of isotactic polypropylene formed by isotactic blocks in the sample.[2]

Miller and Seeley[3] found a $T_m°$ of 159 °C using the Hoffman−Weeks extrapolation method,[4] in which the melting temperatures are plotted as a function of the crystallization temperatures. By assuming a dependence of $T_m°$ on the syndiotacticity and using the Flory theory for the depression of the melting temperature in copolymers,[5] they estimated a value for the equilibrium melting temperature $T_m°$ of a completely syndiotactic polypropylene of nearly 220 °C.[3]

Values for $T_m°$ of 151 and 155 °C, obtained with the Hoffman−Weeks extrapolation method for s-PP samples with relatively short syndiotactic sequences, were reported by Haftka and Konnecke.[6]

An equilibrium melting temperature of 220 °C for the fully syndiotactic s-PP was suggested by Balbontin et al.[7] based on the Hoffman−Weeks extrapolation method and on the Flory theory for the depression of the melting temperatures in copolymers.

Rodriguez-Arnold et al.[8] found a value for $T_m°$ of 160 °C using extrapolation methods based on the Hoffman−Weeks plot as well as on the relationship between the melting temperature and the reciprocal lamellar thickness.

Most of the cited literature data[1−3] were obtained from low crystallinity, regioirregular and stereoirregular s-PP samples synthesized with the vanadium-based catalyst,[9] whereas the values of $T_m°$ suggested in refs 6−8 were obtained from more stereoregular s-PP samples synthesized with the new metallocene-based catalyst.[10]

The various conflicting values of $T_m°$ reported in the literature are not reliable, and this makes the equilibrium melting temperature of s-PP still uncertain. Indeed, irregular s-PP samples obtained with vanadium-based catalysts had a stereoblock structure with syndiotactic sequences prevailing in respect to isotactic ones and head-to-tail regioirregular defects.[11,12] For this irregular s-PP, samples having low crystallinity and characterized by disorder in the packing of the chains have been generally obtained also from crystallization at high temperatures. The melting process of these metastable irregular crystals is too far from the equilibrium melting, so that the extrapolation to the equilibrium melting temperature has not much meaning. Moreover, the extrapolated melting temperature of s-PP depends on the degree of syndiotacticity;[3,7] therefore, the values of the "equilibrium" melting temperature obtained from the analysis of the samples synthesized with the vanadium-based catalyst[1−3] are too low because they are relative to a very defective s-PP, having a very low degree of syndiotacticity. On the other hand, the use of the Flory theory for the depression of the melting temperature in copolymers, to obtain the thermodynamic melting temperature of a completely syndiotactic polypropylene,[3,7] is not completely correct since this theoretical model considers the polymer as a copolymer consisting of syndiotactic units (syndiotactic diads *r*) that crystallize and isotactic *m* diads or *mm* triads that act as noncrystallizable units, excluded from the crystalline phase. Instead, these configurational defects are probably, at least in part, tolerated within the crystals.[12,13]

The presence of a double melting peak behavior for these irregular s-PP samples[1,2,6] indicates the occurrence of recrystallization phenomena during the heating when determining the melting temperature; this avoids obtaining a correct extrapolated $T_m°$. Moreover, the use of a too high heating rate as in ref 3, to avoid any effects due to lamellar thickening (annealing and recrystallization), produces a superheating effect and overestimated melting temperatures.

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Highly stereoregular and regioregular s-PP has been synthesized with the new metallocene-based catalyst;[10] the properties of this new s-PP have been greatly improved, and its complex polymorphic behavior has been clarified.[13−29] Also for these highly crystalline s-PP samples the extrapolation to the equilibrium melting temperature has been attempted.[6−8] Fractions of s-PP having different molecular weights but similar values of the fully syndiotactic pentad content [*rrrr*] (85−87%) were used by Rodriguez-Arnold et al.[8] They found that $T_m°$ depends on the molecular weight and obtained a constant value of 160 °C for $T_m°$ when the molecular weight exceeds 40 000. Owing to the dependence of $T_m°$ on the degree of stereoregularity,[7] this value of $T_m°$ is too low since it has been obtained from samples with relatively low syndiotacticity ([*rrrr*] = 87%). As stated by the same authors,[8] a value of 160 °C for $T_m°$ is too low if compared with actual melting temperatures as high as 163 °C obtained for s-PP samples of higher stereoregularity.[7,17] As will be discussed below, the relatively low stereoregularity of the samples used in ref 8 is responsible for the double melting peak behavior that is due to the occurrence of recrystallization phenomena.[23]

Extrapolations to the equilibrium melting temperature for s-PP samples having very high degrees of syndiotacticity (values of [*rrrr*] up to 96%) and a successive extrapolation to [*rrrr*] = 100% were reported by Balbontin et al.[7] However, the value of 220 °C obtained for $T_m°$ of a fully syndiotactic polypropylene[7] is overestimated owing to the use of a too high heating rate (10 °C/min) when determining the actual melting temperatures of the melt-crystallized samples. This high heating rate was used in order to avoid recrystallization phenomena occurring during the heating of samples with low syndiotacticity[7] but produces a superheating effect and a consequent overestimation of the actual melting temperatures of the metastable crystals.[30]

In this paper the extrapolation to the equilibrium melting temperature of s-PP is attempted, considering s-PP samples with very high syndiotacticity and taking into account the occurrence of the recrystallization and superheating phenomena.

## Experimental Section

The polymer samples were synthesized with a syndiospecific single center catalyst composed of isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride and methylaluminoxane,[10] following the method described in ref 7. The samples are highly syndiotactic with fully syndiotactic pentad content [*rrrr*] in the range 75−96%. The molecular weights MW, the fully syndiotactic pentad content [*rrrr*], and the melting temperatures of the as-prepared specimens of the s-PP samples are reported in Table 1. The samples sPP(1)−sPP(5) of Table 1 correspond to the samples 1−5 reported in ref 7. The fully syndiotactic pentad content [*rrrr*] was evaluated from $^{13}C$ NMR spectra.

$^{13}C$ NMR spectra were recorded on a Bruker AM300 spectrometer, at 120 °C in deuterated tetrachloroethane.

Isothermal crystallizations from the melt of the s-PP samples were performed with the following procedure. The as-prepared samples were melted at ≈200 °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 cooled to room temperature and analyzed by wide-angle X-ray diffraction and differential scanning calorimetry.

**Table 1. Molecular Weights MW, Fully Syndiotactic Pentad Content [*rrrr*], Melting Temperatures $T_m$ of the As-Prepared Samples, Obtained from DCS Scans at 10 °C/min, and Extrapolated Melting Temperatures $T_m°$ (from Figure 5), of s-PP Samples Having Different Degrees of Stereoregularity**

| sample | MW | [*rrrr*] (%) | $T_m$ (°C) | $T_m°$ (°C) |
|---|---|---|---|---|
| sPP(1) | $2.66 \times 10^5$ | 95.8 | 153 | 172 |
| sPP(2) | $2.28 \times 10^5$ | 95.0 | 152 | 170 |
| sPP(2A) | $2.13 \times 10^5$ | 94.2 | 149 | 168 |
| sPP(3) | $1.64 \times 10^5$ | 92.5 | 146 | 164 |
| sPP(4) | $7.7 \times 10^4$ | 90.7 | 126, 140[a] | |
| sPP(5) | $1.15 \times 10^5$ | 88.6 | 122, 137[a] | |
| sPP(6) | $5.2 \times 10^4$ | 74.8 | 122 | |

[a] The two values correspond to the two peak temperatures of the melting endotherm characterized by the presence of a double peak shape owing to the occurrence of recrystallization.

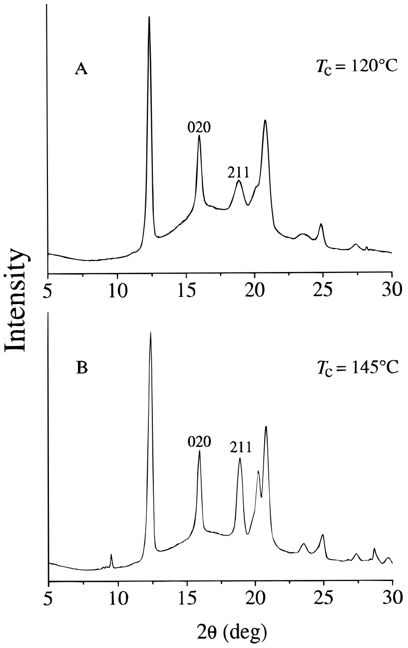

**Figure 1.** X-ray powder diffraction patterns of sPP(1) samples isothermally crystallized from the melt at the indicated crystallization temperatures. The indices of 020 and 211 reflections are given for the unit cell of form I with $b = 11.2$ Å.

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

The melting temperatures of the melt-crystallized samples were obtained with a differential scanning calorimeter Perkin-Elmer DSC-7 performing scans in a flowing $N_2$ atmosphere and at heating rates of 10 and 2.5 °C/min. The maximum of the endothermic peak, as well as the end of the melting interval, were taken as the melting temperature.

## Results and Discussion

The X-ray powder diffraction patterns of the melt-crystallized samples indicate that, for all samples of Table 1, crystallization in the most stable form I always occurs at every crystallization temperature.[25] The X-ray diffraction patterns of as-prepared and melt-crystallized sPP(1) and sPP(4) samples have been reported in Figures 4 and 6 of ref 25. The patterns of two sPP(1) samples, crystallized at low (120 °C) and high (145 °C) temperature, are redrawn in Figure 1. As shown in ref 25, form I of s-PP crystallizes from the melt in different modifications characterized by variable amounts of disorder depending on the crystallization temperature.

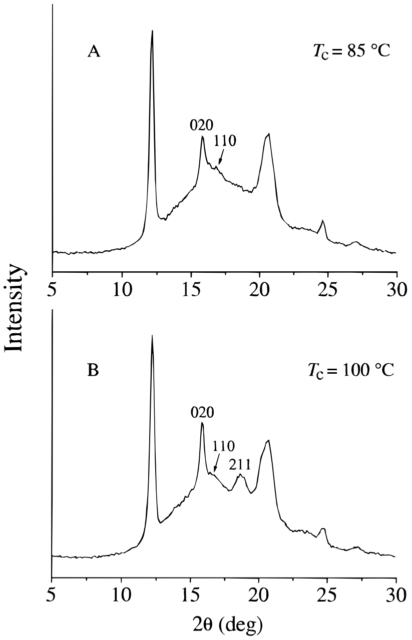

**Figure 2.** X-ray powder diffraction patterns of sPP(6) samples isothermally crystallized from the melt at the indicated crystallization temperatures. The indices of 020 and 211 reflections are given for the unit cell of form I with $b = 11.2$ Å, whereas those of the 110 reflection are given for the unit cell of form II with 5.6 Å.

The limit-ordered modification of form I, characterized by a regular alternation of right- and left-handed 2-fold helical chains along both axes of the unit cell,[14,17] is obtained at high values of the crystallization temperature (Figure 1B).[25] At lower crystallization temperatures, modifications characterized by a disorder in this regular alternation are formed,[17,25] as indicated by the low intensity of the 211 reflection at $2\theta = 18.8°$ (Figure 1A, see also Figure 4 of ref 25). At very low crystallization temperatures disorder can also arise from defects in the stacking of *bc* layers of chains along the *a* axis, implying *b*/4 shifts among consecutive layers.[16,17] This is indicated by the broadening of the 020 reflection at $2\theta = 16°$,[25] as also occurs in single crystals of s-PP grown at low temperatures.[16,17] It is worth noting that in the melt-crystallized sPP(1) samples (Figure 4 of ref 25) modications of form I much more ordered (very close to the limit fully antichiral modification) than those obtained in ref 8, have been reported (Figure 1B), owing to the higher degree of syndiotacticity. Similar X-ray diffraction patterns have been obtained for sPP(2), sPP(2A), and sPP(3) samples.

For lower stereoregular samples (sPP(5) and sPP(6) with [*rrrr*] = 88.6 and 74.8%, respectively) disordered modifications of form I are always obtained by melt crystallization;[29] the ordered form I, characterized by a fully antichiral packing, is never obtained even at high crystallization temperatures.[29] The X-ray powder diffraction patterns of two sPP(6) samples crystallized at low and high temperature are reported in Figure 2. They are very similar to those reported in Figure 2 of ref 29 and are characterized by a broad 020 reflection with a shoulder at $2\theta = 17°$ and a 211 reflection with a very low intensity. This indicates that in the less stereoregular melt-crystallized samples small amounts of crystals of form II are present and/or a mode of packing of form II occurs as a defect in a prevailing mode of packing of form I. This kind of defect corresponds to a disorder in the stacking of *bc* layers of chains, implying *b*/4 shifts among consecutive *bc* layers piled along *a*; it is observed also in single crystals of s-PP grown at low temperatures.[16,17] Less stereoregular samples are therefore not able to crystallize from the melt in the ordered form I owing to the tendency to form local arrangements of the chains such as in form II. These samples are very similar to those analyzed by Rodriguez-Arnold et al.,[8] which have [*rrrr*] in the range 85−87%, and X-ray diffraction patterns characterized by a broad 020 reflection and very low intensities of the 211 reflection. Also in the samples of ref 8, besides the disorder in the alternation of right and left-handed helical chains along the axes of the unit cell, the *b*/4 shift disorder is present, which avoids the developments of ordered crystals of form I.

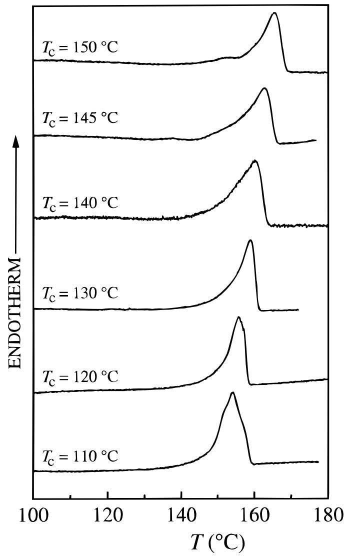

**Figure 3.** DSC scans obtained at the heating rate of 2.5 °C/min of sPP(1) samples isothermally crystallized from the melt at the indicated crystallization temperatures $T_c$.

The DSC scans performed with a heating rate of 2.5 °C/min of isothermally melt-crystallized sPP(1) samples are reported in Figure 3. The corresponding X-ray powder diffraction patterns are reported in Figure 4 of ref 25. The presence of a single endothermic peak indicates that for these samples, for every crystallization temperature, relevant recrystallization phenomena during the heating are absent. On the other hand, the DSC scans registered at higher heating rate (10 °C/min, as in ref 7) always present a single endothermic peak but shifted at temperatures higher than those obtained in the scans at 2.5 °C/min. This confirms the absence of recrystallization phenomena and indicates the occurrence of the superheating effect in the scans performed at higher heating rate.[30] It is worth noting that in the melt-crystallized samples of Rodriguez-Arnold et al.[8] the melting temperatures obtained by DSC scans performed at low heating rate (2.5 and 5 °C/min) are higher that those obtained by scans performed at 10 °C/min (see Figure 5 of ref 8), indicating the occurrence of recrystallization phenomena during the heating.

Isothermal melt-crystallized samples obtained from sPP(2), sPP(2A), and sPP(3) samples present DSC scans similar to those of Figure 3. Also for these samples a single endothermic peak is observed for every crystallization temperature; melting temperatures slightly lower than those of sPP(1) samples are obtained for the less stereoregular sPP(3) samples.

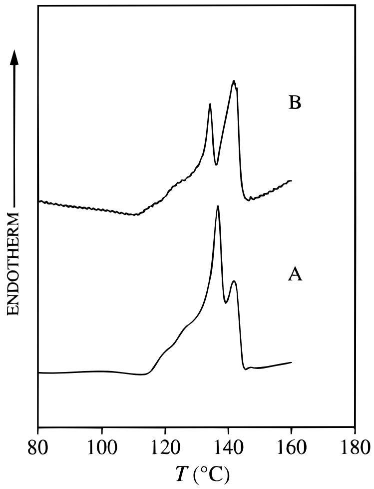

**Figure 4.** DSC scans performed at heating rates of 10 (A) and 2.5 °C/min (B) of the sPP(4) sample isothermally crystallized from the melt at 110 °C.

For sPP(4), sPP(5), and sPP(6) samples, having lower degrees of syndiotacticity, recrystallization phenomena during the heating are observed for the as-prepared samples, as already shown for the sPP(5) sample in ref 23. The DSC scans performed at 2.5 °C/min, as well as at 10 °C/min, of the as-prepared samples present endotherms with a double peak shape;[23] the enthalpy of the high-melting peak increases with the decrease of the heating rate,[23] as expected for a recrystallization phenomena.[30]

Also for the melt-crystallized sPP(4), sPP(5), and sPP(6) samples, recrystallization phenomena are observed during the heating. The DSC scans performed at 2.5 and 10 °C/min of the sPP(4) sample, crystallized from the melt at 110 °C, are shown in Figure 4 as an example. The presence of two melting peaks is apparent; the enthalpy of the high-melting peak increases with the decrease of the heating rate, indicating the occurrence of recrystallization.

As expected, less stereoregular sPP(4), sPP(5), and sPP(6) samples, which are crystallized from the melt in very disordered modifications of form I with defects corresponding to local arrangements of the chains such as in form II,[29] show a thermal behavior similar to that of the melt-crystallized samples of ref 8 (which have similar degrees of syndiotacticity). The recrystallization process corresponds to the partial melting of the irregular low-melting crystals in the disordered form I containing most of the *b*/4 shift defects; successive recrystallization in the most ordered form I, characterized by higher degrees of order in the alternation of right- and left-handed helical chains along the axes of the unit cell; and finally, melting at higher temperature of these more ordered crystals of form I.[8,23]

Owing to the occurrence of the recrystallization process during the melting of samples 4, 5, and 6, also at high heating rate (10 °C/min), the melting temperatures of the metastable crystals obtained at different crystallization temperatures cannot be obtained. On the other hand the use of very high heating rates in determining the melting temperature, to avoid the recrystallization process, produces strong superheating effects that give overestimated melting temperatures.[30] Therefore, these samples cannot be used in the Hoffman–Weeks method[4] for the extrapolation to the equilibrium melting temperature.

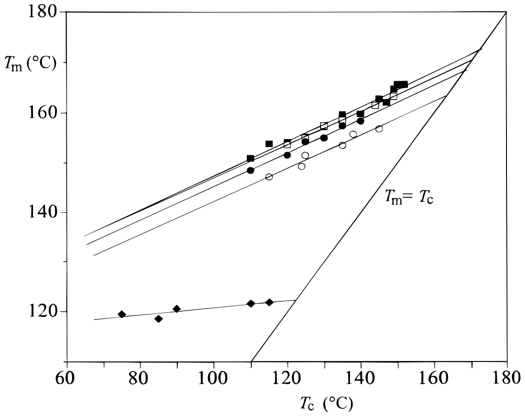

**Figure 5.** Melting temperatures $T_m$ of the melt-crystallized s-PP samples, taken from DSC scans performed at 2.5 °C/min, as a function of the crystallization temperature $T_c$. Extrapolations to the line $T_m = T_c$ are also drawn. Key: (■) sPP(1); (□) sPP(2); (●) sPP(2A); (○) sPP(3); (◆) sPP(6).

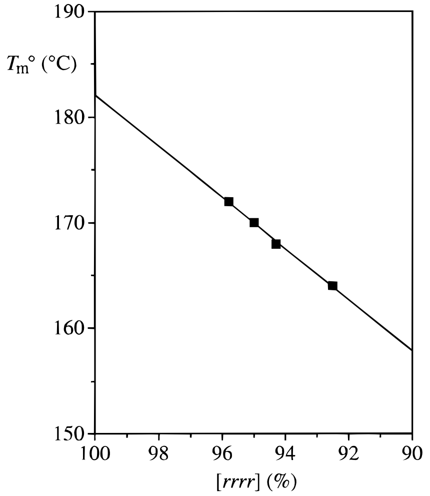

**Figure 6.** Extrapolated melting temperatures $T_m$° (from Figure 5, reported in Table 1) of the s-PP samples as a function of the fully syndiotactic pentad content [*rrrr*].

The melting temperatures $T_m$ of the melt-crystallized sPP(1), sPP(2), sPP(2A), and sPP(3) samples, obtained from the maxima of the endothermic peaks in the DSC scans performed at 2.5 °C/min, are reported in Figure 5 as a function of the crystallization temperature $T_c$. The data are well fitted by straight lines; the intersections of these straight lines with the line $T_m = T_c$ give the values of equilibrium melting temperatures $T_m$° of s-PP samples having different degrees of stereoregularity. The melting temperatures have been also evaluated from the DSC scans by taking the end of the melting interval, where the curves return to the baseline, but no significant changes of the extrapolated melting temperatures $T_m$° have been observed. The melting temperatures of the melt-crystallized sPP(6) samples are also reported in Figure 5 in order to show, as an example, the occurrence of the recrystallization process. The line fitting the data corresponding to the high melting peak temperatures is nearly parallel to the $T_c$ axis, indicating that the temperature of the high melting peak does not depend on $T_c$, as expected for a recrystallization process.[30]

As demonstrated in refs 7 and 8 for samples with high molecular weights, the value of $T_m$° depends only on the stereoregularity whereas the influence of the molecular weight can be neglected. The values of $T_m$°, obtained from the extrapolations of Figure 5, are reported in Table 1 and plotted in Figure 6 as a function of the degree of syndiotacticity, expressed as pentad content [*rrrr*]. The extrapolation of the straight line to [*rrrr*] = 100% provides a value of 182 °C for the equilibrium melting temperature of the fully syndiotactic polypropylene.

The value of 182 °C for the $T_m°$ of the fully syndiotactic polypropylene seems reasonable if compared with the value of 186 °C found for isotactic polypropylene.[31,32]

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