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# Notes

## Extrapolation to the Equilibrium Melting Temperature for Isotactic Polypropylene

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### Introduction

Extrapolations of experimental melting temperatures to the equilibrium melting temperature ($T_m°$) for isotactic polypropylene (i-PP) samples have been performed by several authors. In particular, various extrapolations according to the method suggested by Lauritzen and Hoffman,[1] in which the melting temperatures are plotted as a function of the crystallization temperatures from the melt, led to conflicting results.

Independently of the method used for the measure of the experimental melting temperatures (calorimetry, dilatometry, microscopy), these extrapolation studies can be divided into two groups: a first group led to $T_m°$ values in the range 180–187 °C[2–5] and a second group led to $T_m°$ values in the range 200–220 °C.[6–9] Moreover, the occurrence of two endothermic peaks, in the DSC scans of isothermally crystallized high molecular weight i-PP samples,[8,10] suggested the occurrence of two different equilibrium melting temperatures, 185 and 220 °C,[11] in the two cited ranges.

The literature data on the subject have been recently reviewed by Wunderlich,[12] who concluded that an equilibrium melting temperature of 187.5 °C is somewhat more probable, most on the basis of the extrapolation of Kamide and Toyoma,[13] performed by a different method based on the melting temperatures of annealed crystals. However, the various conflicting results, according to the reviewer, make the equilibrium melting temperature still somewhat uncertain.

All the cited literature data are characterized by narrow ranges of crystallization temperatures ($T_c$): in some cases $T_c < 130$ °C,[4,5] in some others $130 < T_c < 160$ °C,[6–9] and in one other $T_c > 160$ °C;[3] only in one paper[11] has a large $T_c$ range been considered ($105 < T_c < 160$ °C), but not including the highest $T_c$ values.

In our recent paper[14] it has been pointed out that the double-peak shapes of the melting endotherms of isothermally crystallized i-PP samples are due to recrystallization phenomena and the presence of two distinct melting species, segregated during the crystallization, was excluded.

In the present paper the extrapolation to the equilibrium melting temperature is attempted, considering a large crystallization temperature range ($110 < T < 165$ °C) for a high molecular weight i-PP sample, and taking into account the occurrence of the recrystallization phenomena. The aim is to contribute to the elucidation of the source of the conflicting results in the literature.

### Experimental Section

The polymeric samples were supplied by Montepolimeri S.p.A. The homopolymer is highly isotactic, being approximately 97.5% insoluble in *n*-heptane, and it has an intrinsic viscosity of 2.5 dL/g.

The isothermal crystallization from melt was effected by employing the following procedure: samples were kept for 15 min at 200 °C in a $N_2$ atmosphere; the samples were then rapidly cooled to the selected isothermal crystallization temperature.

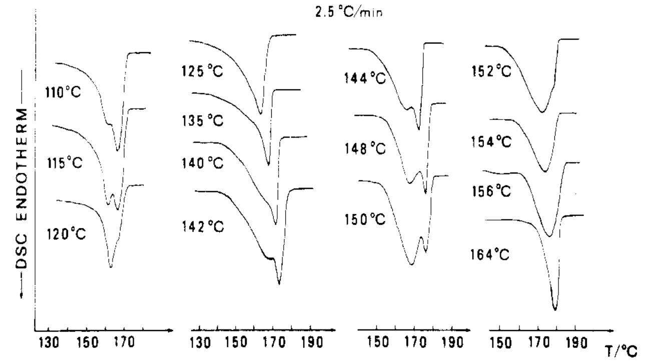

**Figure 1.** DSC scans, obtained at heating rate 2.5°C/min, for isothermally crystallized isotactic polypropylene samples. The crystallization temperatures are indicated next to the fusion curves.

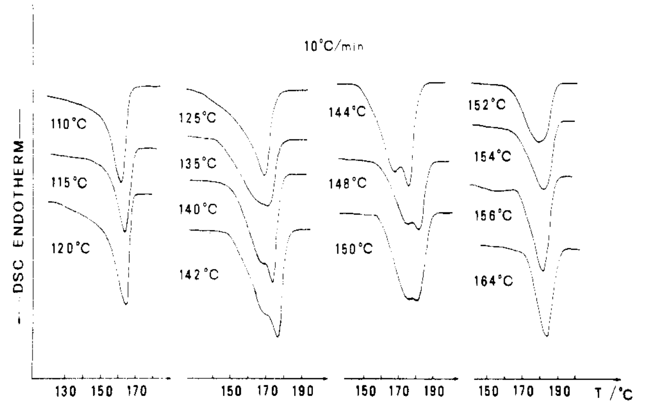

**Figure 2.** DSC scans, obtained at heating rate 10°C/min, for isothermally crystallized isotactic polypropylene samples. The crystallization temperatures are indicated next to the fusion curves.

For $T_c = 164$ °C, in order to increase the crystallization rate, the sample was heated only up to 169 °C and kept for 15 min before being cooled to the crystallization temperature. We have verified, for $T_c = 156$ °C, that this procedure does not affect the peak position of the melting endotherm of the crystallized sample.

The calorimetric measurements were carried out on a Mettler type differential scanning calorimeter (DSC 30) in a $N_2$ running atmosphere. To avoid as much as possible changes in the shape and position of the DSC peaks, the masses of the material used in the different runs performed were taken always practically identically (~5 mg).

### Results and Discussion

The DSC scans at 2.5 °C/min for isothermally crystallized isotactic polypropylene samples are reported in Figure 1. Double-peak shapes of the melting endotherms are obtained for samples crystallized in two crystallization temperature ($T_c$) regions: $T_c < 130$ °C and $140 < T_c < 150$ °C; for the other $T_c$ values single-peak endotherms are obtained.

The DSC scans at 10 °C/min for the same samples are reported in Figure 2. Double-peak shapes for the melting endotherms are obtained only for the samples crystallized in the $T_c$ range 140–150 °C.

The peak positions of the melting endotherms ($T_m$) of Figures 1 and 2 are reported vs. $T_c$ in Figures 3 and 4, respectively; for the $T_c$ values, for which double-peak-shape

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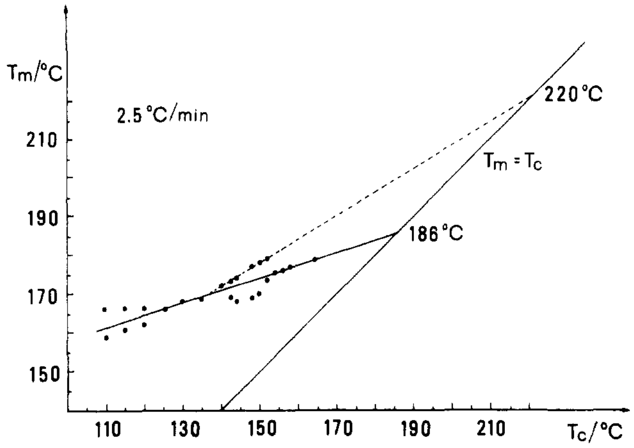

**Figure 3.** Plot of the peak positions of the melting endotherms ($T_m$), taken from the DSC scans at 2.5°C/min (Figure 1), vs. the crystallization temperatures ($T_c$). Two extrapolations to the line representing the relation $T_m = T_c$ are also drawn (see text).

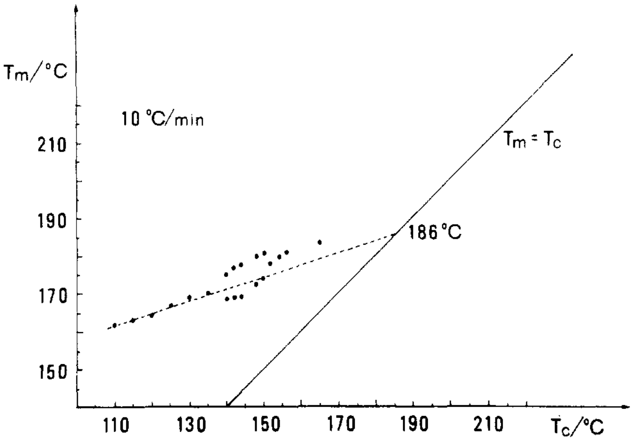

**Figure 4.** Plot of the peak positions of the melting endotherms ($T_m$), taken from the DSC scans at 10°C/min (Figure 2), vs. the crystallization temperature ($T_c$). The dashed line corresponds to the lower extrapolation line of Figure 3.

endotherms are obtained, both the lower and higher peak temperatures, hereafter referred to as $T_m'$ and $T_m''$, are indicated.

As previously discussed,[14] all these double-peak-shape endotherms are due to the occurrence of recrystallization phenomena: the melting peak on the lower temperature side may be indeed attributed to the fusion of original crystals, its position being determined by the competition of melting and recrystallization processes; the melting peak on the higher temperature side may be attributed to the fusion of crystals generated by the recrystallization processes occurring during the scan. At least for the $T_c$ range 135–150 °C, we have shown[14] that neither $T_m'$ nor $T_m''$ are melting peak positions of species obtained at the corresponding crystallization temperature but are located below and above, respectively, the ideal melting peak which should characterize the species crystallized at $T_c$, in the absence of subsequent reorganization phenomena. Hence, $T_m'$ and $T_m''$ values are not useful for the extrapolation procedure.

The single-peak temperature data of the DSC scans at 2.5 °C/min (Figure 3) are well fitted by a single straight line; the extrapolation of this line, to the line representing the relation $T_m = T_c$, indicates an equilibrium melting temperature equal to $\simeq$186 °C. The same extrapolation line fits well the $T_m$ data for $T_c$ less than 130 °C, when the heating rate is 10 °C/min (Figure 4). The single-peak melting data for the highest $T_c$ values ($T_c > 150$ °C) are not fitted by this line owing to superheating phenomena which would characterize especially more perfect crystals.[12]

Since the $T_m''$ peaks are due to the melting of crystals generated by recrystallization phenomena, no theoretical argument may justify a linear extrapolation of such data to the equilibrium melting value. However, for the sake of comparison with the literature data also the linear extrapolation of the $T_m''$ values corresponding to the $T_c$ range 140–150 °C, to the line representing $T_m = T_c$, have been reported in Figure 3; an extrapolation value of nearly 220 °C has been evaluated.

In our opinion, these results allow an easy interpretation of the conflicting literature results on the $T_m°$ value for i-PP: investigations in the $T_c$ ranges below 130 °C (carried out at high heating rates (above 10 °C/min))[4,5] or above 160 °C[3] have produced $T_m° \cong 185$ °C; investigations in the $T_c$ range 130–160 °C have produced $T_m° = 210$–220 °C, if only the end of the melting phenomenon was taken into account,[6,9] or both $T_m°$ values, when the two endothermic peaks were considered.[11]

As a final remark, we wish to point out the unusual positive slope of the line which fits the $T_m''$ values, reported vs. $T_c$, for the range 140–150 °C; generally the melting peak positions of species generated by recrystallization during the measurement scans are largely independent of the original crystallization temperature,[12] as happens also for i-PP crystallized at low $T_c$ values (Figure 3). Further investigations on this subject are in progress.

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## Site Isolation in Macroreticular Divinylbenzene Polymers

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The question of site isolation is of concern in the interpretation of chemical phenomena involving functionality immobilized on insoluble polymer supports. It is now

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