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DETERMINATION OF THE EQUILIBRIUM MELTING POINT OF THE β-FORM OF POLYPROPYLENE

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Abstract

The melting behavior of the β-form of isotactic polypropylene (β-iPP) was investigated as a function of crystallization time and temperature. Calcium suberate, a selective β-nucleating agent was used to produce samples that consist entirely of β-form i-PP. The experimental melting points were recorded at different crystallization times and were extrapolated to the start of the crystallization process in order to eliminate the effect of lamellar thickening. Using the non-linear Hoffman–Weeks approach to correlate these extrapolated experimental melting temperatures with the corresponding crystallization temperatures, an equilibrium melting point of 209°C was obtained for β-iPP. The equilibrium melting point estimated through the non-linear Hoffman–Weeks analysis is about 30°C higher than that (T_m^0=177°C) obtained on the basis of the linear extrapolation. These results are consistent with earlier claims that a linear extrapolation of T_m–T_c data leads to an underestimation of the equilibrium melting point. The results obtained for β-iPP exemplify the importance of accounting for both the isothermal lamellar thickening effects and the non-linearity in the T_m–T_c correlation, when the determination of an equilibrium melting point is carried out using a procedure based on the predictions of the Lauritzen–Hoffman secondary nucleation theory.

Keywords: β-nucleating agent, β-polypropylene, DSC, equilibrium melting point, isothermal crystallization

Introduction

The physical properties of a semicrystalline polymer depend strongly on its crystal structure and degree of crystallinity. Both are influenced by crystallization conditions. A quantitative description of the kinetics of crystallization and of its sub-processes (nucleation and growth) requires an accurate estimate of the supercooling, i.e. the difference between the equilibrium melting point, T_m^0, and the

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crystallization temperature, T_c. Indeed, the driving force for crystallization is proportional to the free energy difference between the crystal and melt phases, thus, it increases approximately linearly with supercooling. The equilibrium melting point, T_m^0, is defined as the melting temperature of a large stack of perfect, extended-chain crystals. Unfortunately, for the majority of the polymers, T_m^0 cannot be measured experimentally, since polymer crystallization generally occurs at an appreciable rate only under conditions removed from equilibrium, where the formation of chain-folded lamellar structures is kinetically favoured over that of extended-chain crystals. The thickness of these lamellar crystals increases with crystallization temperature, and is typically in the range of 10 nm. This finite, supercooling-dependent thickness accounts for the observed dependence of the measured melting point on crystallization temperature. In practice, estimates of T_m^0 are usually obtained by extrapolation using either the Gibbs–Thomson (GT) [1] or the Hoffman–Weeks (HW) [2] equations.

The GT equation Eq. (1), suggests that, as a result of finite size effects, the melting temperature of a lamellar crystal, T_m, is depressed below that of an infinite size crystal, T_m^0, to an extent which is inversely proportional to the crystal thickness, l,

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{l \Delta H_f} \right) \tag{1}$$

where σ_e is the surface free energy associated with the crystal basal plane and ΔH_f is the thermodynamic heat of fusion. This equation results from the simple thermodynamic argument that the difference in free energy per unit volume between a plate-like crystal of thickness, l, and an infinitely thick one is equal to $2\sigma_e/l$, where σ_e is the free energy per unit area associated with the surfaces normal to the thickness direction. The GT equation, thus, predicts that T_m^0 can be estimated by extrapolating T_m *vs.* $1/l$ data to infinite thickness. While this prediction is not rigorously exact (due to chain-end effects), it is a very good approximation for polymers of large chain length, as long as the surface free energy can be considered independent of lamellar thickness. The experimental procedure mandated by Eq. (1) is, however, somewhat difficult to follow rigorously, as one must ensure that the melting point and the lamellar thickness are measured for the same crystal. One should therefore be certain that, subsequent to the evaluation of the lamellar thickness, the crystal characteristics are not modified by possible melting-recrystallization, annealing or other reorganization processes during the thermal treatment necessary to record the melting temperature [1].

As noted above, crystallization at progressively higher temperatures, usually leads to the formation of thicker crystals, which melt at higher temperatures. This observation led Hoffman and Weeks [2], to develop a direct correlation between the temperature of crystallization, T_c, and the resulting melting point, T_m. This correlation, which is expressed by an equation, known as the Hoffman–Weeks equation (Eq. (2)), suggests, in apparent agreement with experimental observations, that T_m is a linear function of T_c.

$$T_{\mathrm{m}}=T_{\mathrm{m}}^{0}\left(1-\frac{1}{\gamma}\right)+\frac{T_{\mathrm{c}}}{\gamma} \tag{2}$$

The HW equation involves a parameter γ, which accounts for the isothermal thickening of lamellae subsequent their formation. The quantity γ should therefore be understood as the ratio of the final lamellar thickness reached after thickening at T_{c}, to the initial thickness of lamellae formed at T_{c}. Examination of Eq. (2) also suggests that the value of T_{m}^{0} can be estimated by linear extrapolation of a plot of observed melting temperature, T_{m} as a function of crystallization temperature, T_{c}, to the $T_{\mathrm{m}}=T_{\mathrm{c}}$ equilibrium line. Considering the widespread availability of differential scanning calorimeters and the ease with which the necessary data can be acquired and analysed, one should not be surprised that this equation has been widely used for the determination of T_{m}^{0} for a large number of polymers. In support of this approach, one should note that experimental T_{m}–T_{c} data often show good linearity in the narrow range of accessible crystallization conditions. While it seems that this method merely requires the measurement of melting points for a sample crystallized at different temperatures, inspection of Eq. (2) indicates that a plot of T_{m} *vs*. T_{c} can only be linear, if the thickening coefficient, γ, is independent of crystallization temperature.

A number of studies have shown, however, that the extent of lamellar thickening, thus, the melting temperature, not only depend on the crystallization temperature, but also on the crystallization time [3–7]. Determination of the equilibrium melting point using the linear Hoffman–Weeks extrapolation Eq. (2) would therefore require that specific crystallization times be chosen at different crystallization temperatures, so that the extent of lamellar thickening is the same at all T_{c}'s. Meeting this condition is not practical, since evaluation of the time and temperature dependence of γ requires additional measurements, using independent techniques such as small angle X-ray scattering or Raman spectroscopy. This inconvenience may however be avoided, if the melting temperature can be recorded after crystallization for short enough times, that the extent of lamellar thickening is negligible. This approach was recently followed by Xu *et al*. [8] in a study of α-iPP's melting behavior. The melting temperature and heat of fusion were recorded as function of crystallization time for a given crystallization temperature. The melting temperature of non-thickened or original lamellae was estimated by extrapolation of the measured melting temperatures to the time where the heat of fusion vanishes.

Proper accounting of the time and temperature dependence of lamellar thickening effects is however insufficient for a rigorous determination of T_{m}^{0} from T_{m}–T_{c} data. Indeed, Marand *et al*. [3] recently showed that the HW equation provides a poor description of the correlation between T_{m} and T_{c}, expected on the basis of the LH theory [9]. The failure of the HW analysis was shown to result from the assumption that non-linear terms could be neglected in the expression relating T_{m} to T_{c}. While such an approximation may appear justified by the observed linearity of T_{m}–T_{c} plots, it should, however, be of concern, since the experimental data is generally recorded over a narrow range of temperatures and long extrapolations are often needed to determine T_m^0. To show that these non-linear effects cannot be ignored, even in the absence of lamellar thickening, these authors re-examined the specific conditions under which the HW equation was derived. In the context of the LH theory [9], the thickness, l^*, of original lamellae formed at the supercooling $\Delta T = T_m^0 - T_c$, is given by:

$$l^* = 2\sigma_e T_m^0 / (\Delta H_f \Delta T) + C_2 \tag{3}$$

where C_2 is a constant, which includes contributions from the crystallization temperature dependence of the fold surface free energy and from the δl parameter. As noted above, lamellae undergo isothermal thickening subsequent to their formation. Their thickness, l, is larger than l^* at the time of melting and is given by:

$$l = \gamma l^* \tag{4}$$

Combination of the Gibbs–Thomson equation Eq. (1) with Eqs (3) and (4), leads to the following expression for the observed melting temperature of thickened lamellae formed at T_c.

$$T_m = T_m^0 \left[1 - \frac{1}{\gamma} \left(\frac{T_m^0 - T_c}{T_m^0} \right) \frac{1}{1 + \dfrac{C_2 \Delta H_f}{2\sigma_e} \left(\dfrac{T_m^0 - T_c}{T_m^0} \right)} \right] \tag{5}$$

Examination of Eq. (5) indicates that even in the absence of isothermal lamellar thickening effects ($\gamma=1$), the observed melting temperature is a non-linear function of the supercooling. The extent to which non-linear effects can be observed in T_m–T_c data, depends on both the supercooling and the magnitude of the term ($C_2\Delta H_f/2\sigma_e$), hereafter denoted by the dimensionless constant, a. Assuming $a=0$ in Eq. (5) is therefore equivalent to ignoring the intrinsic non-linearity in the T_m–T_c correlations and leads in a straightforward fashion to Eq. (2) (the linear HW equation). Estimations of the constant a show, that while this quantity is not large ($a\sim2$–5 in the case of PE [3], α-iPP [8], I-iPB [10], PEO [11]), it cannot be neglected when the goal is an accurate determination of T_m^0. It can therefore be concluded, that while non-linearity effects may be small enough that a distinct curvature may not be experimentally observable in a T_m–T_c plot over the usually narrow range of accessible crystallization temperatures, they are large enough to make a linear extrapolation of T_m–T_c data to the equilibrium $T_m=T_c$ line very inaccurate.

From a practical point of view, the determination of T_m^0 from T_m–T_c data therefore requires, that 1) observed melting points associated with different crystallization temperatures correspond to crystals that have thickened by the same amount (constant γ), and 2) the non-linearity effects resulting from the non-zero value of a be considered. As indicated above, issues related to the time and temperature dependence of γ, can be handled by extrapolating observed melting points to the 'zero' time of crystallization, where γ should be equal to unity. Proper consideration of the theoretical non-linearity between T_m and T_c is achieved by using Eq. (5), rather than Eq. (2), for the determination of T_m^0. To avoid the use of a dubious non-linear extrapolation or data fitting procedure for the estimation of T_m^0, Marand *et al.* [3, 8] suggested an approach based on the linearization of Eq. (5). If one defines scaled crystallization and melting temperatures by $X=T_m^0/(T_m^0-T_c)$ and $M=T_m^0/(T_m^0-T_m)$, respectively, Eq. (5) can be rewritten as:

$$M=\gamma(X+a) \tag{6}$$

$M(X)$ is only a linear function of X, if γ is constant. If each melting and scaled melting temperatures, T_m and M, refer to the melting of original or non-thickened lamellae, then a plot of M *vs.* X should be linear with slope equal to one. Since M and X are defined in terms of the a priori unknown T_m^0, the determination of the equilibrium melting point, T_m^0 can be simply achieved by calculating the slope of M *vs.* X plots obtained with different choices of T_m^0, the true T_m^0 being the temperature for which the slope is actually equal to one.

As a polymorphic material, isotactic polypropylene (iPP) has three main crystal forms [12]. The most common is the monoclinic α-form. The trigonal β-form [13–15] is usually formed using selective β-nucleating agents, while the orthorhombic γ-form is favored under high pressure or when some microstructural heterogeneity is present along the polymer chain (stereo- or regio-defects, comonomers). There is considerable scatter in the values reported for the equilibrium melting point of each crystal form [12, 16]. T_m^0 values for the α-form have been reported in the range between 184°C and 220°C [16–22]. Using their non-linear Hoffman–Weeks approach, Xu *et al.* [8] reported T_m^0 ≈212°C. The equilibrium melting points reported for the β-form also cover a wide temperature range between 170 and 200°C [16–18, 23–27]. The origin of this scatter may be associated with the use in different studies of samples containing multiple crystal forms, or exhibiting dissimilarities in stereo- and regio-defect content in the different studies. The β-nucleated samples of Ullmann and Wendorff [18], as well as these of Lovinger *et al.*, prepared using the temperature gradient method [23], contained crystals of both the α and the β-form, resulting in overlapping melting peaks in a DSC heating trace. An additional experimental difficulty encountered during the measurement of melting points arises from the phenomenon of β-α recrystallization. Cooling a partially crystallised sample below a temperature, T_R^*≈100°C, leads, during subsequent heating, to the observation of an exothermic recrystallization peak, superposed on the melting endotherm [25, 28]. Varga and Garzó [26] showed that these problems are readily eliminated by preparing samples consisting exclusively of β-iPP and by starting the heating run at the crystallization temperature. Using the linear Hoffman–Weeks approach, they obtained an equilibrium melting point of 184±4°C for β-iPP.

In this paper, we present the results of a new study aimed at the determination of the equilibrium melting point of β-iPP. Using calcium suberate, a very efficient and highly selective nucleating agent for isotactic polypropylene [29, 30], we prepared samples with nearly hundred per cent β-iPP in the temperature range of 100–140°C. The melting behavior of these β-nucleated samples was investigated by differential scanning calorimetry as a function of crystallization time and temperature. The heating of these samples in the calorimeter was initiated at the temperature of crystallisation. The equilibrium melting point is determined using the non-linear approach [3, 8] and its value is compared to that obtained by the linear extrapolation.

Experimental

In a high-speed mixer (n=560 min^{-1}, t=3 min), 1000 ppm Irganox 1010 stabiliser and 2000 ppm calcium suberate were added to neat iPP powder (made by TVK Rt., MFI=2 g/10 min at 230°C/2.16 kg). The polypropylene powder did not contain any additives that could influence its crystallization. The polymer was extruded on a Haake Rheocord EU-10V Rheomex S 3/4” single screw extruder and granulated. Crystallization and melting studies were carried out with 5±0.5 mg samples, using a Perkin Elmer DSC-7 calorimeter operated under constant nitrogen flow and in fast data collection mode (20 data points/s). The instrument was calibrated on a daily basis at 10°C min^{-1} heating rate with an indium standard. Crystallization temperatures were calibrated by extrapolation of the melting temperature of indium to zero heating rate.

The dependence of melting temperature on crystallization temperature and time was studied in order to determine T_m^0. Samples were kept for 5 min at 200°C to erase any previous thermal history, then cooled at a rate of 80°C min^{-1} to the crystallization temperature, T_c, where they were held for a desired time, t_c. The heating trace for each sample was subsequently recorded up to 200°C at a rate of 10°C min^{-1}. The peak temperature of the melting endotherm, T_{mp}, was taken as the melting point.

At each crystallization temperature, the described thermal cycle was performed with 7 or 8 different crystallization times. The shortest t_c was always longer than the time needed for the completion of primary crystallization.

Crystallization temperatures were changed between T_c=131.0 and 140.0°C, in one degree steps. Below 130°C the crystallization proved to be too fast and began during the cooling process. The upper temperature limit for the formation of β-iPP is approximately 140°C. Above this temperature, the βα–transition takes place at the β crystal growth front, resulting in a significant decrease in the β-phase content, since α-form crystals exhibit, in this temperature range, a larger growth rate than β-form crystals [16].

The same sample was used for all measurements carried out at a given crystallization temperature, in order to eliminate the effect of sample preparation (sample mass, contact area on the DSC pan, mass of the sample pan, etc.). Since samples used for crystallization studies at one temperature were repeatedly taken to the melt state to erase previous thermal history, it was important to ensure that thermal degradation did not take place to a significant extent. We therefore followed the evolution of the polymer melting point after repeated heating-cooling cycles. A sample was heated to 200°C, held there for 5 min, cooled down to 132°C at a rate of 80°C min^{-1}, held there for 10 min and heated back to 200°C at a rate of 10°C min^{-1}. This cycle was repeated 30 times. After an initial decrease of 0.1°C during the first six cycles, the observed melting peak temperatures did not change. This procedure was also followed with an upper melt temperature of 220°C. After 12–15 cycles, the melting peak temperatures showed a small, but monotonous decrease, which is likely to be the consequence of thermal degradation.

Results and discussion

The peak melting temperatures of samples isothermally crystallised at different temperatures are shown in Fig. 1 as a function of crystallization time. Each melting curve exhibited a single endothermic peak, suggesting that the samples consisted entirely of β-form crystals. As the crystallization time increases, the melting peak shifts towards higher temperatures, indicating the development of thicker, thus, more stable crystals. The time dependence of the peak melting temperature, T_{mp}, is well described by a linear function of the logarithm of time over the investigated temperature range.

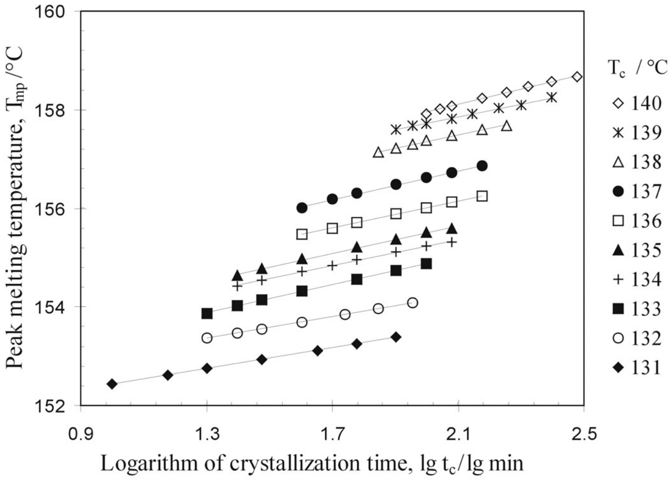

Fig 1 Peak melting temperatures, T_{mp}, as a function of crystallization time, t_c, at various crystallization temperatures

The observed crystallization time dependence of measured melting points confirms that it is indeed very important to account for lamellar thickening, in the determination of equilibrium melting point for β-iPP. In order to avoid complications in the analysis due to thickening, the melting point, T_m, of initial (non-thickened) lamellae is obtained by extrapolation of the measured peak melting temperatures to zero crystallinity. While Xu *et al.* [8] used an extrapolation of melting enthalpies to zero for the determination of the initial melting temperature, we find it more reliable to use the apparent induction time for crystallization as a basis for the extrapolation. The apparent induction time can be obtained by considering the shape of the heat flow curve recorded during isothermal crystallization (Fig. 2). The apparent induction time for crystallization, t_0, can be defined as the time associated with the inflection point, observed after magnification of the initial section of the crystallization

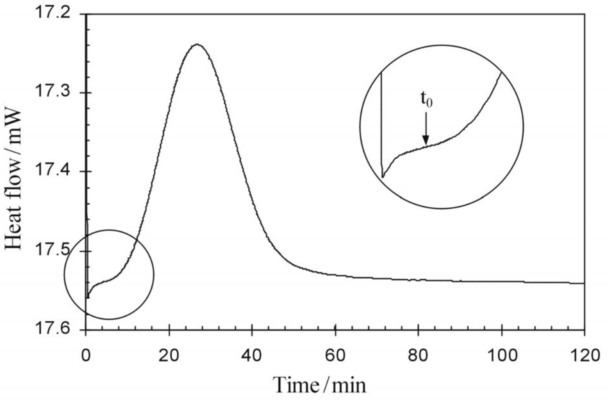

Fig. 2 Apparent induction time of an isothermal crystallization exotherm, t_0

exotherm (inset on Fig. 2). No heat of crystallization can be detected until this time, consequently the measured crystallinity is zero at this point.

The method used in this work for the determination of induction times was published previously [31, 32] and considers that t_0 is most reliably determined as the time where the first sign of a deviation of the heat flow curve from the baseline is observed. In other studies, the induction time was calculated though diverse iterative procedures, where a kinetic model is fitted to the crystallization curve [32–34]. Since our study is not concerned with theoretical aspects of the kinetics of crystallization, we find it sufficient to use the practical method outlined above, as a systematic and objective criterion for the start of the crystallization process.

Table 1 Crystallization temperatures, T_c, apparent induction times, t_0, and melting points of original lamellae, T_m

T_c /°C	t_0 /min	T_m/°C
131.00	0.42	150.98
132.00	0.56	151.66
133.00	0.74	151.83
134.00	0.97	152.60
135.00	1.19	152.86
136.00	1.78	153.57
137.00	2.37	154.21
138.00	2.92	155.17
139.00	4.24	155.57
140.00	4.64	155.94
141.00	6.92	–

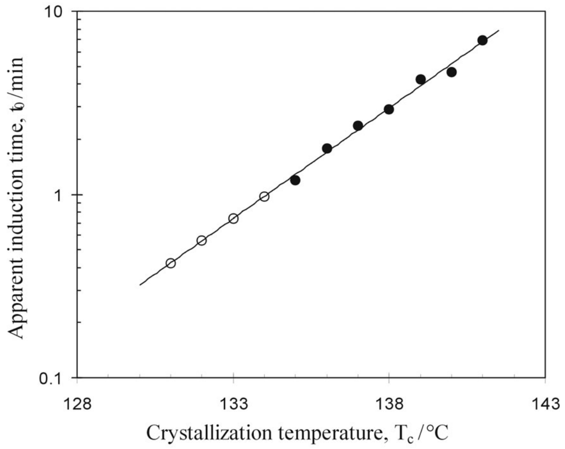

Fig. 3 Apparent induction time as a function of crystallization temperature (● – measured, o – calculated

We find that the measured apparent induction time is well described by an exponential function of the temperature of crystallization (Fig. 3). The empirical relationship between t_0 and T_c is given by the following equation:

$$\ln t_0 = A + BT_c \tag{7}$$

The main advantage of this method is that t_0 can be determined by extrapolation in a relatively wide temperature range. At lower crystallization temperatures, where the determination of t_0 is made difficult by rapid crystallization and is limited by the response time of the calorimeter, the t_0 values can be estimated by extrapolation. The determination of the melting point of initial lamellae formed at different crystalliza-

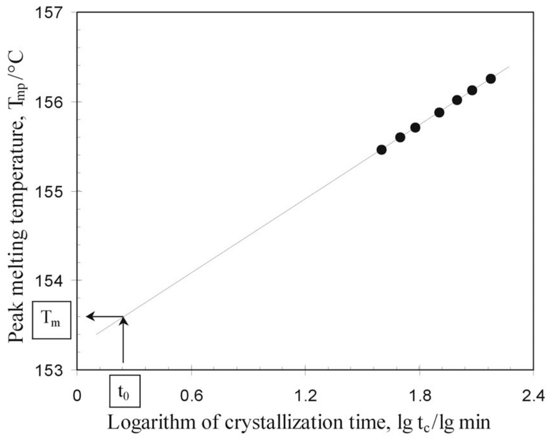

Fig. 4 Determination of the melting point of the initial lamellae, T_m, using the apparent induction time, t_o

tion temperatures is illustrated in Fig. 4. The plot of measured peak melting points, T_{mp}, as a function of the logarithm of crystallization time is well described by a linear function. This linear function is then extrapolated to the apparent induction time of crystallization, t_0, from which we obtain T_m, the melting point of the original lamellae. The T_m values determined in this fashion for each crystallization temperature are summarized in Table 1.

Comparison of the conventionally determined melting points (samples crystallized up to 20% crystallinity [35]) with melting points obtained by extrapolation to t_0 shows that the melting point increases during crystallization (Fig. 5). The slope of the

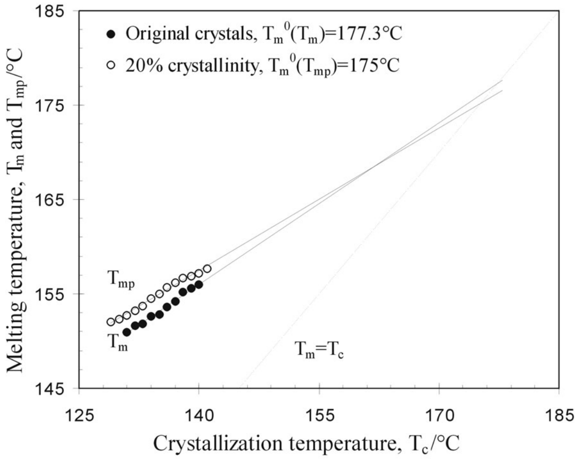

Fig. 5 Determination of the thermodynamic melting point by the linear Hoffman–Weeks approach, using extrapolated melting points for the original lamellae, T_m, and melting points of partially crystallized samples, T_{mp}

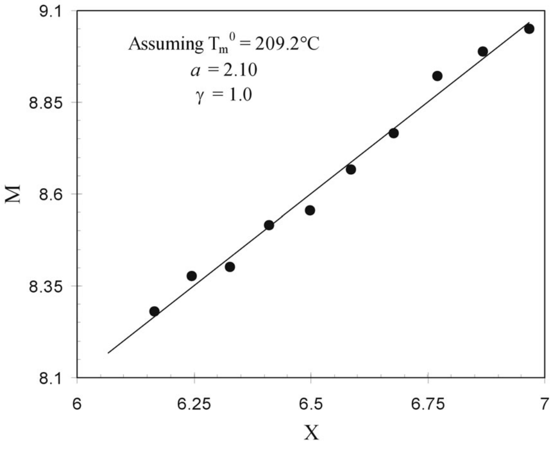

Fig. 6 Plot of M *vs*. X assuming that T_m^0=209.2°C

straight-line fitted to the T_{mp} *vs.* T_c data is smaller than the one obtained after correction for thickening effects (T_m *vs.* T_c). Examination of the linear Hoffman–Weeks equation Eq. (2) suggests that the reciprocal value of the slope should correspond to the lamellar thickening coefficient. If this was indeed true, the results shown on Fig. 5 would lead us to conclude that the lamellar thickening coefficient, γ, is larger for samples, which were crystallized for extremely short times (T_m calculated at t_0), than for samples crystallized for much longer times (20% crystallinity). This conclusion is obviously not physically realistic. Furthermore, we note that the slope of the T_m *vs.* T_c line differs from unity, which is inconsistent with the fact that these melting temperatures correspond to non-thickened lamellar crystals. These two observations confirm the existence of an intrinsic flaw in the linear Hoffman–Weeks equation. For future reference, we report here the value of the apparent 'equilibrium melting point' calculated by extrapolation using the linear Hoffman–Weeks equation (T_m^0=175°C using the 20% crystallinity data and T_m^0=177.3°C, using the extrapolated melting points of initial lamellae). The present values are similar to those reported in the literature, which were also derived using the linear extrapolation.

We now proceed to the determination of the equilibrium melting point, using the non-linear approach. We choose a hypothetical value for T_m^0 and plot *M vs. X* for that value of T_m^0 (Fig. 6 for illustration). We then calculate the slope, γ, for this *M–X* plot and estimate the value for *a* from the intercept. The process is repeated over a range of values of T_m^0, so we can prepare plots of γ and *a* as a function of T_m^0 (Fig. 7). Examination of Fig. 7 indicates that the true value of the equilibrium melting point should be T_m^0=209.2°C, since this choice leads to γ=1. Under these conditions, the constant, *a*, has a value *a*=2.10. These values of *a* and T_m^0 can then be used to generate a theoretical plot of T_m *vs.* T_c shown in Fig. 8. It is apparent that this theoretical plot fits the experimental data very well. The non-linear approach leads to an equilibrium melting

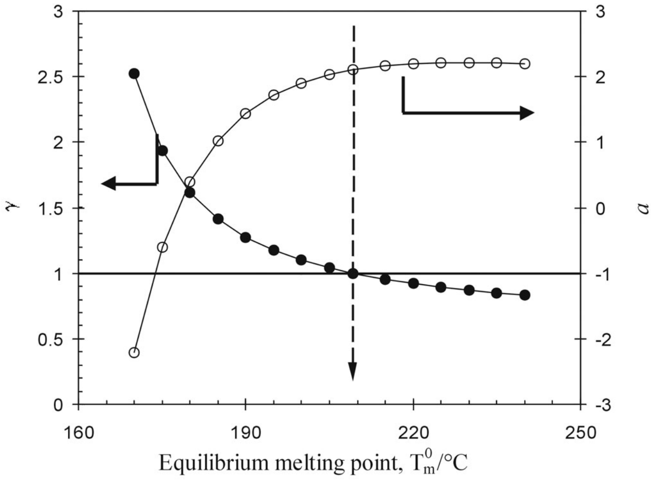

Fig. 7 Dependence of γ and *a* on the choice of T_m^0

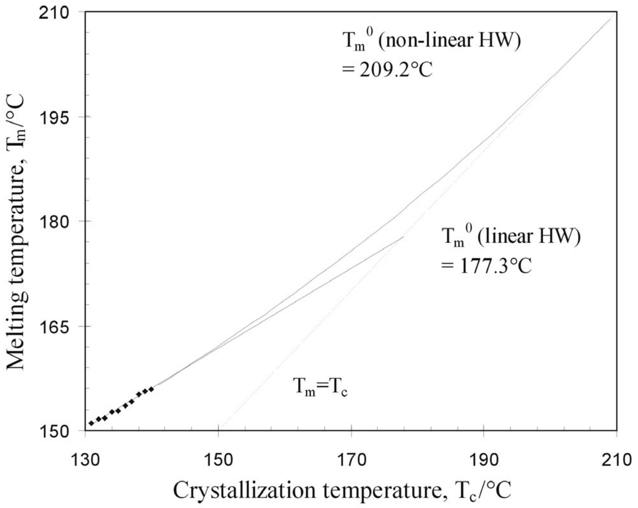

Fig. 8 Melting *vs.* crystallization temperatures, analyzed with the linear and non-linear approaches for the initial lamellae

point that exceeds by more than 30°C the value predicted by the linear extrapolation. Examination of Fig. 8 confirms that the curvature in the T_m–T_c data is indeed fairly small in the case of β-iPP (low value of *a*) and cannot be readily recognized when experimental data is collected in a fairly narrow temperature range. The analysis carried out here for β-iPP shows that, as was reported for β-iPP [8], an accurate estimation of the equilibrium melting point cannot be achieved in the context of the LH theory unless the small but intrinsic non-linearity of T_m–T_c data is accounted for.

The value of *a* for β-iPP (*a*=2.10) is somewhat lower than the one reported earlier for α-iPP (*a*=3.45) [8]. Without additional information as to the extent to which the latent heat of fusion and the fold surface free energies differ for α- and β-iPP, it is impossible to shed more light on the origin of this large difference in the value of *a* for these two crystal forms. It is however important to note that such a difference, if real, should also be reflected in the temperature dependence of their spherulitic growth rates. We also note that the T_m^0 values determined in the present work is very close to that reported for the α form by Xu *et al.* [8].

Conclusions

Isotactic polypropylene samples consisting entirely of β-phase crystals were prepared using calcium suberate, a nucleating agent that is highly selective for that crystal form. The observation that, the melting point of β-iPP increases linearly with the logarithm of crystallization time, indicates that, β-form crystals, like α-form crystals are susceptible to thickening processes. The equilibrium melting point of β-iPP was estimated using the non-linear Hoffman–Weeks approach after proper consideration of the effect of isothermal lamellar thickening on the measured melting point. Specifically, to avoid the complications associated with the time and temperature dependence of the lamellar thickening process, we estimated by extrapolation the melting points of original (non-thickened) crystals formed at different crystallization temperatures. The extrapolation procedure is based on the use of induction times to define a melting point in the limit of zero crystallinity (i.e. melting point of original crystals). Using the non-linear Hoffman–Weeks approach, the equilibrium melting point of β-iPP was found to be T_m^0=209.2°C, some 32°C above the value obtained using the linear Hoffman–Weeks extrapolation (T_m^0=177.3°C). The large difference in these values is similar to that reported for the α form [8] and suggests that, for both α and β forms, intrinsic non-linearity in the evolution of T_m with T_c cannot be neglected when evaluating the equilibrium melting point in the context of the Lauritzen–Hoffman theory.

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