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On the thermodynamic driving force for nucleation at large undercoolings

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ABSTRACT

The molar free energy difference ΔG_f, between amorphous and crystalline phases, is computed using heat capacity data over a large temperature range between the melting (T_m^0) and the glass transition temperatures. These values are used to assess the validity of the approximate correction factors, $f^{H1} = T/T_m^0$ and $f^{H2} = 2T/(T+T_m^0)$, suggested by Hoffman [Thermodynamic driving force in nucleation and growth processes. J Chem Phys 1958;29(5):1192–93], and widely used in the literature for a variety of polymers to account for the change in free energy with temperature, T. Surprisingly, for polyethylene and isotactic polypropylene, which are industrially important polymers, it is found that the performance of these correction factors is worse than uncorrected estimates. For isotactic polystyrene and polyethylene oxide, it is found that the correction factor f^{H2} offers a good approximation for the free energy of fusion at moderate to large undercoolings, although Hoffman's criterion recommends the use of f^{H1}. Empirical correction factors that provide a better fit with the experimental data, and a computer program used to determine them are also provided.

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1. Introduction

The classical nucleation and growth approach to describe the crystallization of polymeric systems from a supercooled melt follows the generic derivation by Turnbull and Fischer [1] for the nucleation of molecules, metals, and other organic and inorganic low molecular mass systems. Under the assumption of a steady-state process, the nucleation rate is expressed by,

$$N = N_0 \exp\left[\frac{-E_D}{RT} - \frac{\Delta G}{RT}\right] \tag{1}$$

where E_D and ΔG are the changes in energy required for segmental transport and the formation of a stable nucleus, respectively. In formulating the free energy change ΔG, the geometry of the nucleus needs to be specified. Regardless of whether the specific geometry assumed is a three-dimensional structure or a coherent two-dimensional nucleus of the type described by Gibbs [2], the expression for ΔG comprises, in addition to the surface free energy terms, the free energy difference between the amorphous (supercooled liquid) and the crystalline (solid) phases per mole, ΔG_f. Evaluation of this term at the transformation temperature is important in the analysis of the crystallization kinetics. At any temperature T, the free energy of fusion ΔG_f is given by:

$$\Delta G_f(T) = \Delta H_f(T) - T\,\Delta S_f(T) \tag{2}$$

where the enthalpy and entropy changes accompanying phase change are, respectively:

$$\Delta H_f(T) = \Delta H_f\left(T_m^0\right) - \int_T^{T_m^0} \Delta C_p(T)\mathrm{d}T \tag{3}$$

and

$$\Delta S_f(T) = \Delta S_f\left(T_m^0\right) - \int_T^{T_m^0} \frac{\Delta C_p(T)}{T}\mathrm{d}T. \tag{4}$$

Here, $\Delta C_p = C_p^a - C_p^c$ is the difference between the specific heats of the amorphous and crystalline phases, and T_m^0 is the equilibrium melting temperature of infinitely long crystals.

At $T = T_m^0$, using the criterion for phase equilibrium, we have $\Delta G_f(T_m^0) = 0$. Thus, Eq. (2) implies $\Delta S_f(T_m^0) = \Delta H_f(T_m^0)/T_m^0$. From the phase rule, a single component, two phase system has only one degree of freedom, and hence for $T \neq T_m^0$, the criterion for phase equilibrium is not satisfied, i.e., in general, $\Delta G_f(T) \neq 0$. It is common to assume that for $T < T_m^0$, the values of the enthalpy and entropy of fusion do not deviate appreciably from their values at $T = T_m^0$. This is equivalent to the assumption that $\Delta C_p(T) = 0$ in Eqs. (3)

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and (4). Thus, using Eq. (2), we have the standard approximate form:

$$\Delta G_{\mathrm{f}}^{*}(T) \approx \Delta H_{\mathrm{f}}\left(T_{\mathrm{m}}^{0}\right)\left(1-\frac{T}{T_{\mathrm{m}}^{0}}\right) = \Delta H_{\mathrm{f}}\left(T_{\mathrm{m}}^{0}\right)\frac{\Delta T}{T_{\mathrm{m}}^{0}} \tag{5}$$

where, $\Delta T = T_{\mathrm{m}}^{0} - T$ is the degree of undercooling. Since ΔH_{f} decreases with undercooling, it has long been recognized that Eq. (5) overestimates that true driving force [3–7].

2. Previous work

For polymers with a glass transition temperature in the supercooled liquid state, Hoffman [3] assumed that $\Delta C_{\mathrm{p}}(T) \approx \Delta C_{\mathrm{p}}^{*}$ was constant and is given by:

$$\Delta C_{\mathrm{p}}^{*} = \frac{\Delta H_{\mathrm{f}}\left(T_{\mathrm{m}}^{0}\right)}{T_{\mathrm{m}}^{0} - T_{\infty}} \tag{6}$$

where T_{∞} denotes the temperature at which the enthalpy of fusion vanishes, i.e., $\Delta H_{\mathrm{f}}(T_{\infty}) = 0$. Substituting Eq. (6) into Eqs. (2)–(4):

$$\Delta G_{\mathrm{f}}^{\mathrm{H}}(T) = \frac{\Delta H_{\mathrm{f}}\left(T_{\mathrm{m}}^{0}\right)}{T_{\mathrm{m}}^{0}}\left(\frac{T_{\mathrm{m}}^{0} T \ln\left(T_{\mathrm{m}}^{0}/T\right) - T_{\infty}\,\Delta T}{T_{\mathrm{m}}^{0} - T_{\infty}}\right) \tag{7}$$

where the superscript H is used to denote the approximate expression derived by Hoffman [3]. Depending on the relationship between T_{∞} and T_{m}^{0}, he obtained two simplified forms of the above equation. When $T_{\infty} \sim 0.5 T_{\mathrm{m}}^{0}$, it can be shown that Eq. (7) reduces to:

$$\Delta G_{\mathrm{f}}^{\mathrm{H1}}(T) = \left[\Delta H_{\mathrm{f}}\left(T_{\mathrm{m}}^{0}\right)\frac{\Delta T}{T_{\mathrm{m}}^{0}}\right]\left(\frac{T}{T_{\mathrm{m}}^{0}}\right) = \Delta G_{\mathrm{f}}^{*}(T) f^{\mathrm{H1}}, \tag{8}$$

where $f^{\mathrm{H1}} = T/T_{\mathrm{m}}^{0} < 1$ can be considered as a correction factor which compensates for the overprediction of $\Delta G_{\mathrm{f}}^{*}(T)$ at large undercooling.

Based on thermodynamic data and Broadhurst's analysis of *n*-alkanes [8], Hoffman and Weeks [9] suggested that for polyethylene, $T_{\infty} \approx 0$. Under these conditions, the second simplified form of Eq. (7) can be derived:

$$\Delta G_{\mathrm{f}}^{\mathrm{H2}}(T) = \left[\Delta H_{\mathrm{f}}\left(T_{\mathrm{m}}^{0}\right)\frac{\Delta T}{T_{\mathrm{m}}^{0}}\right]\left(\frac{2T}{T + T_{\mathrm{m}}^{0}}\right) = \Delta G_{\mathrm{f}}^{*}(T) f^{\mathrm{H2}}, \tag{9}$$

where $f^{\mathrm{H2}} = 2T/(T + T_{\mathrm{m}}^{0}) < 1$ is the new undercooling correction factor.

To summarize, the free energy of fusion can be estimated from experimental data on specific heats by using Eq. (2)–(4). In the absence of experimental data, assumptions about ΔC_{p} have to be made. If we assume $\Delta C_{\mathrm{p}} = 0$, we get the standard expression Eq. (5), which is expected to overestimate the actual free energy. Instead, if we assume $\mathrm{d}(\Delta C_{\mathrm{p}})/\mathrm{d}T = 0$, as Hoffman did, we can derive two correction factors f^{H1} and f^{H2} depending upon the relationship between T_{∞} and T_{m}^{0}. Further, $f^{\mathrm{H1}} < f^{\mathrm{H2}} < 1$ for temperatures below T_{m}^{0}.

Eq. (9) has been widely employed in literature as the appropriate approximation for many polymers [10–18], including polyethylene [19]. This correction is still used in the analysis of kinetics in extended temperature intervals without reviewing the appropriateness of the initial assumptions to the temperature range where experimental data are evaluated [20–22]. Furthermore, the same correction is occasionally applied to ΔH_{f} in the evaluation of crystallinity from data obtained by differential scanning calorimetry (DSC) [23]. As we will show in the next section, the correction factor f^{H2} underpredicts the thermodynamic driving force for many industrially important polymers. This feature and the possibility of analyzing kinetic data at very high undercoolings using ultrafast calorimetry [24], points to the need for a more careful evaluation of $\Delta G_{\mathrm{f}}(T)$ in an extended temperature range, especially when thermodynamic data are available for the system investigated.

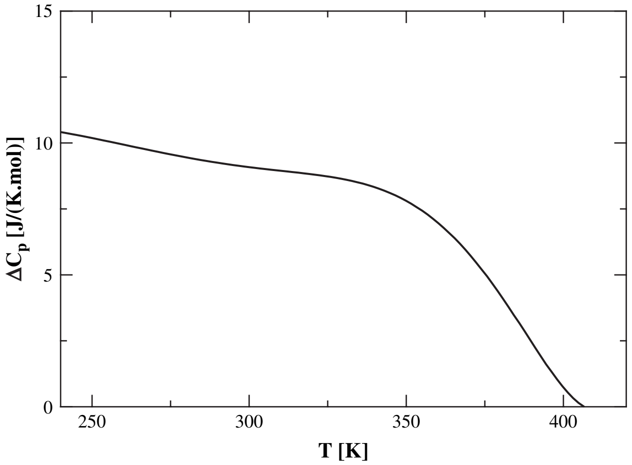

Fig. 1. The temperature dependence of $\Delta C_{\mathrm{p}} = C_{\mathrm{p}}^{\mathrm{a}} - C_{\mathrm{p}}^{\mathrm{c}}$ for polyethylene from the ATHAS database [25].

3. Results

We obtained specific heat data on PE from the advanced thermal analysis system (ATHAS) database [25] (currently hosted at http://athas.prz.rzeszow.pl). Fig. 1 shows the temperature dependence of ΔC_{p}. Recall that Eq. (7) was derived by assuming that ΔC_{p} was independent of temperature. Since $\Delta H_{\mathrm{f}}(T_{\mathrm{m}}^{0}) = 4.142$ kJ/mol and $T_{\mathrm{m}}^{0} = 418.7$ K, we have, from Eq. (6), $\Delta C_{\mathrm{p}}^{*} = 9.89$ J/(mol K), assuming $T_{\infty} = 0$ [8,9,4,5]. While this is a reasonable approximation for temperatures between the glass transition temperature T_{g} (237 K) and about 350 K, it fails at higher temperatures. Thus, the experimental data on specific heats undermine the basic Eq. (7), and hence both its approximations.

The temperature dependence of the free energy of fusion for $T_{\mathrm{g}} < T < T_{\mathrm{m}}^{0}$ is depicted in Fig. 2. We used Eq. (2)–(4), in conjunction with the experimental specific heat data shown in Fig. 1, to obtain an accurate "experimental" estimate of ΔG_{f}. We compared the experimental data with the crude approximation $\Delta G_{\mathrm{f}}^{*}$ given by Eq. (5), and the supposedly more accurate expression $\Delta G_{\mathrm{f}}^{\mathrm{H2}} = \Delta G_{\mathrm{f}}^{*} f^{\mathrm{H2}}$, given by Eq. (9). For temperatures close to the equilibrium melting temperature, the approximate expressions, with or without the correction factor, appear to be in good agreement with the experimentally determined ΔG_{f}. However, as the crystallization temperature is

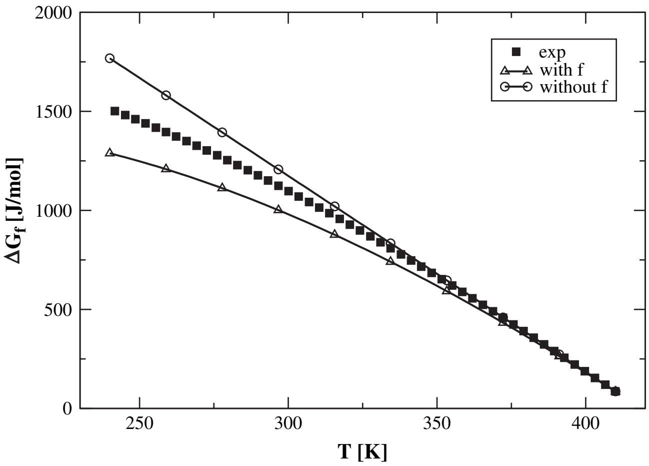

Fig. 2. Comparison of the free energy of fusion for polyethylene computed using (i) experimental specific heat data (solid squares), (ii) $\Delta G_{\mathrm{f}}^{*}$ from Eq. (5) without compensating for undercooling (open circles), and (iii) $\Delta G_{\mathrm{f}}^{*} f^{\mathrm{H2}}$ with the correction factor (open triangles).

lowered, ΔG_f^* overpredicts the experimental curve, which when corrected with f^{H2} underpredicts it.

We compared the absolute percentage error between the experimental and approximate curves, and found that the crude approximation ΔG_f^* is better off without the correction factor, except at temperatures close to T_g. A closer examination in Fig. 1 offers a partial explanation for this unexpected result. Near T_m^0, it can be observed that $\Delta C_p(T)$ is quite small, which justifies the assumption $\Delta C_p(T) = 0$ used to derive Eq. (5). Thus, the range of its validity is extended.

Since $f^{H1} < f^{H2}$ at all temperatures below the melting temperature, f^{H1} is never a better approximation than f^{H2}, and is hence not considered here as an alternative. An empirical best fit correction factor f_{exp} obtained by minimizing the least-square error is:

$$f_{exp} = 0.847 + 0.156\left[1 - \left(\frac{T_m^0 - T}{T_m^0 - T_g}\right)^2\right] \qquad (10)$$

with $T_m^0 = 418.7$ K, and $T_g = 237$ K. The estimate of the free energy thus calculated, viz., $\Delta G_f^* f_{exp}$, is within 0.3% of the experimental data over the entire temperature range $T_g < T < T_m^0$. There is a suggestion in the literature that the true T_g of PE is not 237 K [25]. Note that this does not affect Figs. 1–3 in the temperature window depicted, since T_g does not explicitly enter in the calculation of ΔG_f. The ATHAS database suggests $T_m^0 = 414.6$ K and $\Delta H_f = 4.11$ kJ/mol. While these values affect the results slightly, they do not negate the primary conclusions drawn.

The isothermal crystallization temperature range to follow crystallization kinetics of linear PE using classical DSC, dilatometry, X-ray diffraction and other spectroscopic techniques is between 388 and 405 K [26–28]. In this temperature range, examination of Fig. 2 clearly indicates that ΔG_f of PE is unaffected by the correction. This invariance was acknowledged by Hoffman [29], yet the f^{H2} correction was used by Phillips et al. in subsequent related kinetic studies [30]. Using a recently developed ultrafast nanocalorimetric technique [31], PE melts were supercooled at rates up to 10^6 K/s. At these superfast cooling rates, PE crystallites developed in a temperature range between 293 and 373 K. We notice from Fig. 2 a steep deviation of ΔG_f from linearity at these temperatures; hence any analysis of structural data or nucleation and growth at such large undercoolings would require a correction factor for ΔG_f. In this case, the empirical expression given by Eq. (9), rather than f^{H1} or f^{H2}, provides a more accurate representation.

4. Discussion

In this section, we extend and qualify the arguments presented above for PE to other polymers, viz., isotactic polypropylene (iPP), isotactic polystyrene (iPS) and polyethylene oxide (PEO).

4.1. Isotactic polypropylene

The free energy term with Hoffman's f^{H2} correction has been invariably used in the analysis of crystallization kinetics of iPP and iPP copolymers. Not only is the T_g relatively high for this polymer, but iPP also requires much higher undercoolings for crystallization. It was, thus, tacitly assumed that for the interval of isothermal crystallization temperatures where kinetics can be experimentally followed, i.e., 400–420 K for classical Ziegler–Natta iPP, the ΔG_f^{H2} correction offered by Hoffman was the appropriate correction factor. We repeated the analysis reported earlier for PE to iPP, as shown in Fig. 4. As before, specific heat data on iPP were obtained from the ATHAS database. For iPP, $\Delta H_f(T_m^0) = 8.7$ kJ/mol, $T_m^0 = 460.7$ K, and $T_g = 270$ K. It is obvious that compared to ΔG_f^{H2}, ΔG_f^* offers a significantly better representation of the experimental driving force, over the entire temperature range between the glass transition and equilibrium melting points. Hoffman's correction is also not justified for this industrially relevant polymer. It has been suggested in the literature that for iPP $T_g = 258$ K and $T_m^0 = 485$ K, instead of the values reported in the ATHAS database. As mentioned previously, a different value of T_g has no effect whatsoever on Fig. 4. Although a different value of T_m^0 influences Fig. 4 quantitatively, there is no qualitative change, and does not affect any of the conclusions drawn.

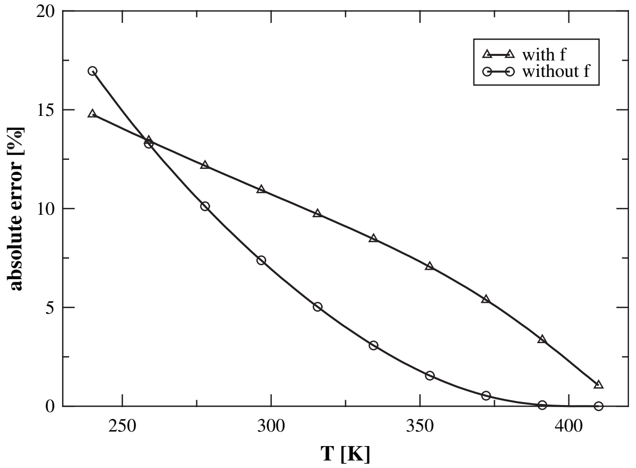

Fig. 3. Comparison of the absolute percentage error for polyethylene when the free energy of fusion is computed with (open triangles) and without (open circles) the correction factor for undercooling. When the crystallization temperature is not too close to T_g, the expression without the correction factor offers a better approximation to experimental data.

With the advent of the metallocene catalyst technology, poly(propylenes) with a very wide range of isotacticities are now feasible, allowing production of iPP materials with tunable properties that can be controlled from the thermoplastic to elastomeric behavior [32–34]. While the glass transition temperature of these homo-poly(propylenes) is weakly affected in reference to the highly isotactic iPP, the range of crystallization temperatures is shifted to much lower values, due to a decrease in T_m^0, as the level of isotacticity decreases. The decrease in T_m^0 is mainly caused by a preferential rejection of stereo- and regio-irregularities from the crystalline regions [35,36]. Copolymerization of iPP with 1-alkene comonomers has a similar effect: a large decrease in crystallization temperatures, and a relatively small decrease in T_g with increasing

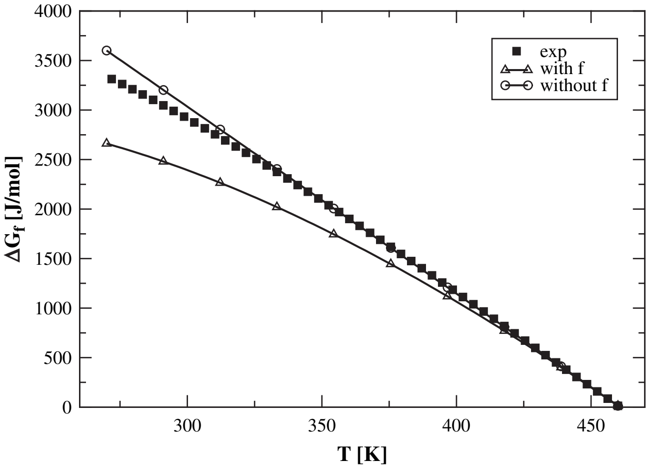

Fig. 4. Comparison of the free energy of fusion for iPP computed using (i) experimental specific heat data (solid squares), (ii) ΔG_f^* from Eq. (5) without compensating for undercooling (open circles), and (iii) $\Delta G_f^* f^{H2}$ with the correction factor (open triangles).

comonomer content. It has been recently shown that iPP copolymers with 15–25 mol% of ethylene crystallize in the 300–350 K range [35]. Ultrafast nanocalorimetric data have also shown crystallization of iPP at temperatures close to T_g [31]. Thus, following previous assertions, one expects that the non-linearity of ΔG_f^* with temperature will be especially marked in the low temperature range and that the correction will be most effective for these data. However, as shown in Fig. 4, even for iPPs that crystallize at temperatures very close to T_g, the f^{H2} correction to the free energy of fusion is not justified. The corrected ΔG_f data deviate more strongly from the calculated experimental ΔG_f than the uncorrected ΔG_f^*. The empirical relation that best follows the variation of ΔG_f with temperature, also obtained by minimization of the least-square error, is given by:

$$f_{\rm exp} = 0.0765 + 0.939\left[1 - \left(\frac{T_m^0 - T}{T_m^0 - T_g}\right)^2\right] \qquad (11)$$

The maximum percentage error between this regressed fit and the experimental data is 1.5.

4.2. Isotactic polystyrene

For iPS, Suzuki and Kovacs [6] reported that $T_m^0 = 515.2$ K and $T_\infty = 213$ K [6], and hence $T_\infty/T_m^0 = 0.41$. According to Hoffman's criterion, based on the value of T_∞, the correction factor $f^{H1} = T/T_m^0$ is applicable. When Suzuki and Kovacs compared the thermodynamic driving force using experimental specific heat data [37] with ΔG_f^* and ΔG_f^{H1}, their results (Fig. 5 in Ref. [6]) were qualitatively similar to those obtained here for polyethylene. Quite surprisingly, although T_∞ is not close to 0, and hence Hoffman's criterion is not satisfied for f^{H2}, ΔG_f^{H2} fits the data almost quantitatively.

4.3. Polyethylene oxide

PEO is another system for which crystallization kinetics following secondary nucleation theory have been amply studied over a wide range of molecular masses [16,17,38]. Because most of these works included the f^{H2} correction term, we have also evaluated the appropriateness of this correction using the available heat capacity data, and the parameters $\Delta H_f(T_m^0) = 8.66$ kJ/mol, $T_m^0 = 342$ K, and $T_g = 206$ K. However, it is important to point out that for this system $T_\infty/T_m^0 \approx 0.3$, and hence f^{H1} is the appropriate correction factor according to Hoffman's criterion. The results, depicted in Fig. 5, show that for PEO, f^{H2} presents an excellent approximation for the variation of the free energy with temperature, even at large undercoolings.

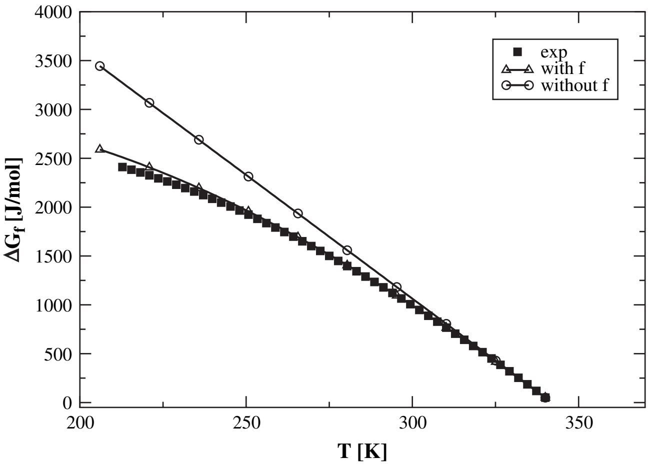

Fig. 5. Comparison of the free energy of fusion for PEO computed using (i) experimental specific heat data (solid squares), (ii) ΔG_f^* from Eq. (5) without compensating for undercooling (open circles), and (iii) $\Delta G_f^* f^{H2}$ with the correction factor (open triangles).

The empirical relation that best follows the variation of ΔG_f with temperature, also obtained by minimization of the least-square error, is given by:

$$f_{\rm exp} = 0.277 + 0.691\left[1 - \left(\frac{T_m^0 - T}{T_m^0 - T_g}\right)^2\right] \qquad (12)$$

The maximum percentage error between this regressed fit and the experimental data in the temperature window examined is 3.3.

5. Conclusion

The temperature coefficient of the free energy of fusion, an important parameter in formulating the free energy change required for the formation of a critical stable nucleus, is revisited in this work for PE, iPP, iPS and PEO. Corrections suggested by Hoffman to account for the change in ΔG_f with temperature are not found to be justified for PE and iPP, which are often crystallized at large undercoolings. Instead, empirical correction factors that provide a better fit with the experimental data are presented. A computer program that can be used to determine these empirical correction factors for any crystalline polymer is provided (see Supplementary data). It requires specific heat capacity data at different temperatures for the liquid and crystalline phases and knowledge of thermodynamic parameters such as $\Delta H_f(T_m^0)$, T_m^0, and T_g. For iPS and PEO, it is found that f^{H2}, and not f^{H1}, offers a reasonable estimate of the free energy of fusion at moderate to large undercoolings, although Hoffman's criterion based on the relative magnitudes of T_∞ and T_m^0 suggests the opposite.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2008.03.024.

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