NOTE

Determination of the Crystallization Enthalpy of New-TPI

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INTRODUCTION

The definition of the degree of crystallinity, obtained through measurements of the enthalpy of melting using differential scanning calorimetry (DSC), has been discussed by many authors in the scientific literature.[1-3] It is widely recognized that the first problem occurring in the analysis of chain folded polymer crystals is related to the exact definition of crystalline and amorphous phases. As highlighted by Hoffman et al.,[1] the determination of the degree of crystallinity in mass or in volume, obtained from density or enthalpy measurements, is not an accurate measure of the fraction of polymer that is not "liquid like." This intrinsic inaccuracy is essentially related with the chain folded morphology of most of the bulk crystallized polymers. In fact, lateral and chain folded surfaces exist in a polymer as a portion of a lamellar crystalline phase. The crystal surfaces are low density and energy reach regions of the lamellar crystals; they constitute a part of the crystalline phase of the polymer, although their properties are significantly different from the ones of the bulk.

The crystallinity mass fraction (X_{mc}) is usually calculated as the ratio between the melting enthalpy of the sample (ΔH_m), and the theoretical crystallization enthalpy (ΔH_0). This procedures can be rigorously applied only if a two-phase system (perfectly crystalline + perfectly amorphous) is assumed. Moreover, the measurement of the enthalpy of melting is affected by the following two main sources of error.

1. The annealing occurring during the temperature scan induces morphological changes in the lamellar structure and eventually produces additional crystallization.
2. The correct determination of the baseline for peak integration is complicated by the different specific heat characterizing the semicrystalline and molten polymer.

In order to improve the precision in the determination of the crystallinity mass, fraction isothermal DSC experiments are often applied.[4-10] The polymer is melted and then rapidly cooled to the crystallization temperature. The enthalpy is then measured as the area of the exothermic peak observed, while the sample is annealed at constant temperature. In this procedure, the above-mentioned sources of errors are avoided; but an increase of the crystallization enthalpy with isothermal crystallization temperature is typically observed. Such behavior is usually attributed to the different values of the crystallinity mass fraction developed by the polymer at different isothermal crystallization temperatures. While the effects of the crystallization temperature on the crystallization kinetics and crystal dimensions has already been assessed, the effects of temperature on the total amount of crystals is still not clear.

The analysis presented in this work intends to dem-

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onstrate that the total mass of crystals developed in a semicrystalline polymer is independent of the crystallization temperature. Then, the enthalpy differences observed in DSC experiments are only attributed to different crystal morphologies. A simple expression, based on the thermodynamic of chain folded lamellar crystals, is proposed in order to correlate the enthalpy of crystal formation measured by DSC with the isothermal crystallization temperature. The experimental data are fitted, assuming a constant value of the crystallinity mass fraction and simply accounting for the temperature dependence of the lamellar thickness. A new thermoplastic polyimide, called NEW-TPI, characterized by a crystallization process that is relatively slow with respect to the most common thermoplastics, is adopted as a model system. The experimental results analyzed in this study have been obtained by DSC measurements already reported in a previous article.[8]

CRYSTALLIZATION ENTHALPY

The crystallinity mass fraction (X_{mc}) is often calculated from DSC isothermal crystallization experiments as the ratio between the isothermal enthalpy of crystallization of a sample (ΔH_c) and the theoretical heat of crystallization (ΔH_0),[4–9] as follows:

$$X_{mc} = \frac{\Delta H_c}{\Delta H_0} \qquad (1)$$

ΔH_0 is a reference value corresponding to a perfect crystal without chain folded surfaces characterized by a melting temperature, T_m^0, significantly higher than the one observed in a DSC heating scan on the bulk crystallized polymer.

It must be noted that the density measurements are usually performed at room temperature after the crystalline phase is completely developed. In this case, the contribution of the fold surfaces to the crystallinity mass fraction depends on the degree of order of the chain segments on these surfaces. On the other hand, the isothermal crystallization enthalpy, obtained by DSC experiments, is the result of two contributions: (1) a positive one originated by the work of chain folding; and (2) a negative one given by the latent heat of formation of the bulk portion of the crystals.

Similar considerations made for crystal melting may explain why the degree of crystallinity determined by density is always larger than the one obtained by the enthalpy of melting.[9]

Therefore, eq. (1) should be replaced by a more complex expression capable of accounting for the different enthalpy contributions in a lamellar crystal given by the balance of the exothermic behavior of the bulk portion and of the endothermic behavior of the crystal surfaces. The enthalpy ΔH_c of a chain folded crystal may

be calculated adopting the classical expressions reported in the literature,[1–2] as follows:

$$\Delta H_c = \Delta h_0 a^2 l \rho_c - 2h_f^s a^2 - 4h_l^s l a \qquad (2)$$

where Δh_0 represents the enthalpy of crystallization per unit of mass of the bulk portion of the chain folded crystal, ρ_c is the crystal density, h_f^s is the enthalpy per unit of area of the fold surface, h_l^s is the enthalpy per unit of area of the lateral surfaces. In eq. (2), the lateral dimensions of the crystal are represented by a single parameter, a; while l is the lamellar thickness. The superscript s indicates surface properties, i.e., enthalpy per unit area. Dividing both members of eq. (2) by the crystal weight $(a^2 l \rho_c)$, the enthalpy of crystallization per unit of mass of crystals is obtained, as follows:

$$\Delta h_c = \Delta h_0 - \frac{2h_f^s}{l \rho_c} - \frac{4h_l^s}{a \rho_c} \qquad (3)$$

The last term of the second member is often neglected considering that for many polymers; h_l^s may be considered five to ten times lower than $h_f^{s\,1,2}$; and the ratio $2/a$ is about one order of magnitude lower than the ratio $1/l$.[2]

However, the values of the side and fold surface free specific energies reported by Lu et al.[7] for NEW-TPI are very similar, suggesting that the enthalpic contribution of the side surfaces cannot be *a priori* neglected.

Since the DSC-measured crystallization enthalpy (Δh_m) usually refers to the weight of the sample and not to the weight of the crystalline portion, both members of eq. (3) must be multiplied by the crystallinity mass fraction X_{mc} as follows:

$$\Delta h_m = \Delta h_c X_{mc} = X_{mc} \Delta h_0 - X_{mc} \frac{2h_f^s}{l \rho_c} - X_{mc} \frac{4h_l^s}{a \rho_c} \quad (4)$$

When a strong undercooling is used, as in most of the DSC crystallization studies,[4–9] a further correction must be introduced in eq. (4). As reported by Hoffman et al.,[1] the crystallization enthalpy Δh_0 decreases as the temperature is lowered. At high undercoolings, they proposed an empirical correction factor for Δh_0, as follows: $f = 2T/(T_m^0 + T)$. Therefore, eq. (4) may be rewritten as:

$$\Delta h_m = f X_{mc} \Delta h_0 - X_{mc} \frac{2h_f^s}{l \rho_c} - X_{mc} \frac{4h_l^s}{a \rho_c} \qquad (5)$$

The temperature dependence of a and ρ_c is negligible, while X_{mc} is here claimed to be constant, attributing the temperature dependence of Δh_m to f and to the lamellar thickness l. The main assumption on which eq. (5) is based is that the amount of crystallizable matter developed during a melt crystallization is not a function of the undercooling. In fact, no theoretical

Table I Parameters Used in Eqs. (9) and (10)

Parameter	Value	Parameter	Value
ΔH_0 (J/g)	139	ρ_c (g cm^{-3})	1.47
ρ_a (g cm^{-3})	1.33	T_m^0 (K)	672
a (nm)	56.3	X_{mc}	0.300
C_1 (nm) (eq. 9)	-3.12	C_2 (nm K) (eq. 9)	544

justification of the relationship between the amount of noncrystalline material and the crystallization temperature has been reported.

In order to obtain an experimental verification of this approach, a more suitable model can be obtained. It must be noted that in the literature values of the surface free energy σ_f of polymer crystals, rather than the surface enthalpy h_f^s, are usually available. According to the thermodynamic treatment proposed by Wu,[11] the following relationship between h_f^s and σ_f is obtained:

$$h_f^s = \sigma_f - T \frac{d\sigma_f}{dT} \qquad (6)$$

Equation (6) may be combined with eq. (5), leading to a direct relationship between the crystallization enthalpy, the specific surface free energy, and the crystallinity mass fraction, as follows:

$$\Delta h_m = f X_{mc} \Delta h_0 - \frac{2X_{mc}}{l\rho_c}\left(\sigma_f - T \frac{d\sigma_f}{dT}\right) \qquad (7)$$

This equation still requires one expression to describe the temperature dependence of the lamellar thickness. The following simple model is assumed:[1,2]

$$1 = C_1 + \frac{C_2}{T_m^0 - T} \qquad (8)$$

where C_1 and C_2 are two fitting parameters. The values $\Delta h_0 = 139$ J/g; $\rho_c = 1.47$ g/cm^3; $\rho_a = 1.33$ g/cm^3; and constant free energies for the fold surface, $\sigma_f = 0.041$ J/cm^2, and for the side surface, $\sigma_l = 0.029$ J/cm^2, are taken from Lu et al.[7] A value of $T_m^0 = 672$ K was previously calculated for this material.[8]

Therefore, combining eqs. (7) and (8), the following expression is obtained:

$$\Delta h_m = f X_{mc} \Delta h_0 - \frac{2X_{mc}\sigma_f}{\rho_c\left(C_1 + \dfrac{C_2}{(T_m^0 - T)}\right)} - \frac{4X_{mc}\sigma_l}{\rho_c a} \qquad (9)$$

The crystallinity mass fraction is assumed constant and equal to the maximum measured value, $X_{mc} = 0.3$. The parameters used in eq. (9) are given in Table I, and the correlation observed between the ex-
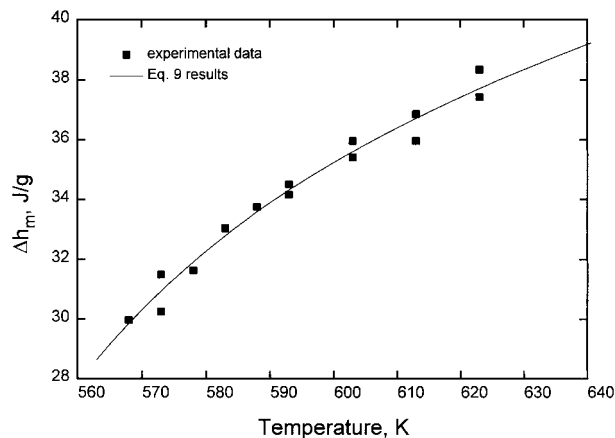
Figure 1 Correlation between the experimental crystallization enthalpy (symbols) and the results of eq. (9).

perimental data and the model results are shown in Figure 1. A very good agreement between the experimental data and the predictions of eq. (9) is observed in this case. The constants C_1, C_2, and a, obtained by nonlinear regression, are reported in Table I. Computed lamellar thickness, reported in Figure 2, range between 2.33 nm at 573 K and 7.98 nm at 623 K, which is comparable with the data reported by Lu et al.[7] The value of $a = 56.3$ nm computed indicates that, indeed, the last term on the right-hand side of eq. (9) could be neglected. A rapid analysis of both terms indicated that its contribution to the total enthalpies is lower than 2%.

CONCLUSIONS

The assumption of a constant value of the crystallinity mass fraction as a function of the isothermal crystalli-
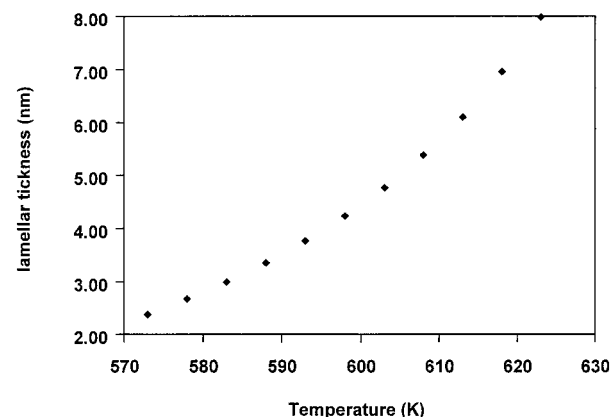
Figure 2 Computed lamellar thickness as a function of crystallization temperature.

zation temperature has been proposed and experimentally verified for NEW-TPI. The simple assumption of a chain folded lamellar structure, the most common in polymer systems, leads to the attribution of the temperature dependence of the isothermal crystallization to different crystal morphologies rather than to a change of the total mass fraction of crystals with the crystallization temperature.

The presented results demonstrate that the contribution of the side free energy can be neglected, although its value is comparable with the fold surface free energy as a consequence of an unfavorable aspect ratio of the lamellar crystal. The proposed simple expression could be used to estimate the lamellar thickness by simply measuring the isothermal heat of crystallization by DSC. An extensive analysis on DSC crystallization data obtained on different polymers and in different growth regimes is in progress.

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