Investigating the equilibrium melting temperature of linear polyethylene using the non-linear Hoffman-Weeks approach

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A B S T R A C T

The melting behavior of three linear polyethylene fractions with number average molecular weights of 11, 29, and 100.5 kg/mol was studied as a function of crystallization time with conventional and ultra-fast calorimetry. The initial melting temperatures of non-thickened lamellae formed under isothermal conditions over a range of crystallization temperatures were analyzed with the non-linear Hoffman-Weeks method to determine the equilibrium melting temperature. T_m^{eq} values of 138.4±0.9°C, 139.7.4±0.9°C, and 140.9±0.8°C were estimated for PE 11K, PE 29K, and PE 100K, respectively, in close agreement with those reported in the literature for the melting of extended-chain crystals or with the Gibbs-Thomson analysis. The Lauritzen-Hoffman theory and the non-linear Hoffman-Weeks treatment were modified to account for the effect of the tilt angle, θ, of the crystallized stems of linear polyethylene on the initial average lamellar thickness. Accuracy of the non-linear Hoffman-Weeks method was examined using initial lamellar thickness, ℓ_g^*, data reported for PE 29K in the literature at different crystallization temperatures. The equilibrium melting temperature obtained by the Gibbs-Thomson approach and the C_2 value extracted from the ℓ_g^* vs. $1/\Delta T$ plot were similar within the limits of experimental error to those obtained here through the non-linear Hoffman-Weeks method. Using the Huggins equation, the equilibrium melting temperature of an infinitely long linear polyethylene chain is found to be equal to 141.4±0.8°C, the same value proposed by Wunderlich.

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1. Introduction

Many research groups have studied the crystallization and melting of linear polyethylene (LPE) under quiescent conditions [1–5]. The first step in the analysis of crystallization kinetics data for any polymer consists in determining the equilibrium melting temperature, T_m^{eq}, for the relevant crystal phase, as this is the reference temperature from which the undercooling, that is, the crystallization driving force, is determined [6]. The equilibrium melting temperature is the temperature at which an infinitely large extended-chain crystal with an equilibrium concentration of defects is in equilibrium with the melt. Determination of an accurate T_m^{eq} value for LPEs has been a point of intense controversy for more than five decades [6–14]. To understand why this is so, one must recall that the morphology of semi-crystalline polymers is controlled by kinetic factors [6,15]. In the case of linear

polyethylene, its quiescent isothermal crystallization will only take place on a reasonable time scale, if it is carried out in the 120–130 °C temperature range, depending on molecular weight [16,17]. Under these conditions, crystallization yields thin, meta-stable, chain-folded, lamellar crystals, not the equilibrium, infinitely large, extended-chain crystals [1,15,18,19]. As a result, T_m^{eq} is typically estimated by one of two common extrapolative methods [6]: 1) the Gibbs-Thomson thermodynamic approach [6,14,20–22], which makes use of a correlation between the thickness and the melting temperature of lamellar crystals and 2) the Hoffman-Weeks method [23,24], which describes the correlation between crystallization and melting temperatures. Linear polyethylene is somewhat unique in the sense that the T_m^{eq} value for its ortho-rhombic crystal phase can also be estimated by two other techniques. First, theoretical approaches have been used by Broadhurst [7] and Flory-Vrij [8,9] to estimate the equilibrium melting temperature of crystals of high molecular weight linear polyethylene by extrapolation of the melting data of normal paraffin crystals. Second, Bassett et al. [15,25,26] have shown that one can make use of the exceptionally high segmental mobility in the hexagonal crystal

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phase of LPE formed under high pressure to prepare micrometer-size, extended-chain, orthorhombic crystals. Wunderlich et al. [10,13] showed that the melting temperature of such crystals provides an excellent estimate of the equilibrium melting temperature for the orthorhombic phase. From the standpoint of theory, linear polyethylene is therefore a unique material that should allow its equilibrium melting temperature to be determined unequivocally by a number of methods. The mere fact that the determination of LPE's equilibrium melting temperature has been controversial is an indication that some of the experimental methods used in its determination need to be scrutinized further.

In this publication, we first justify the use of the non-linear Hoffman-Weeks treatment [27], reminding the reader of the many reasons why its linear counterpart [23,24] is not supported by theory and observations. Then, we discuss melting data obtained, using both conventional and ultra-fast chip calorimeters, for three LPE fractions crystallized isothermally at different temperatures over a range of crystallization times. We considered the sample mass, crystallization time and heating rate dependences of the calorimetric data to minimize annealing, and melting-recrystallization-remelting phenomena, and account for superheating and thermal lag effects [13]. We extrapolated experimental melting data to zero heating rate, zero crystallinity conditions and use these extrapolated melting temperatures in the context of the non-linear Hoffman-Weeks method [27] to determine the equilibrium melting temperature for three LPE fractions. Results of the present studies show that there is perfect agreement between the equilibrium melting temperature estimates obtained using extended-chain crystals prepared under high pressure [10,13,28], the Gibbs-Thomson approach [14,21,22], the Huggins extrapolation procedure [7,29] and the non-linear Hoffman-Weeks method. Finally, the T_m^{eq} values obtained in this work will also be used to rationalize the initial lamellar thickness data obtained by Barham et al. [30] for a linear polyethylene fraction in the context of the Lauritzen-Hoffman (LH) theory and Strobl's multistage model [3,5,6].

2. Justification of the non-linear Hoffman-Weeks treatment

Pertinent theoretical aspects of the extrapolative method devised by Hoffman and Weeks [23] for the estimation of T_m^{eq} are discussed in the Appendix. In this method, the melting temperature of a polymer is correlated with its crystallization temperature for samples that are usually crystallized for long times. A linear regression of the observed melting temperature versus crystallization temperature plot is linearly extrapolated to the equilibrium line, $T_m = T_c$, to yield the equilibrium melting temperature [23].

Observation of linearity in any data set over a narrow range of variables does not enable one to claim that the same linearity should be observed outside this narrow range of variables, unless, of course, such claim is guided by sound theory. The linearity in the Hoffman-Weeks treatment can only be justified if two assumptions are met (see Appendix): first, given that the slope of a linear Hoffman-Weeks plot is associated with the reciprocal of the lamellar thickening coefficient, every data point in such a plot must be characterized by the same lamellar thickening coefficient [27,31], and second, the intercept, C_2, of a plot of ℓ_g^* versus $1/\Delta T$ for the polymer of interest must have a magnitude much smaller than that of the lamellar thickness [27]. Neither of these assumptions is met in practice, as we outline below.

In regard to the constancy of the thickening coefficient, Alamo et al. [31] have demonstrated that both the slope of the T_m vs. T_c regression line and the extrapolated equilibrium melting temperature vary systematically with the chosen range of crystallization temperatures and crystallization times. In recent reports, Toda et al.

[24,32] suggest that the linear Hoffman-Weeks treatment can be successfully applied to linear polyethylene. In this study, the crystallization times appeared to be chosen in such a way that primary crystallization was complete. From the approximate linearity of their T_m vs. T_c data, and the observation of a slope equal to ½, they conclude that the lamellar thickness doubled before the end of the primary crystallization stage and did so at all temperatures. The constancy of the slope was also suggestive that further thickening subsequent to the lamellar doubling was either slow or non-existent. This is not the first time a doubling of the lamellar thickness has been suggested to take place during the isothermal melt crystallization of linear polyethylene. Barham et al. [33] proposed that doubling, tripling and even quadrupling of the long spacing took place subsequent to lamellar formation. Studies aimed at reproducing that work were not successful [34—36]. Other evidence provided in support of the doubling in lamellar thickness is based on slow heating studies of solution crystallized ultra-high molar mass linear polyethylene single crystal mats [37]. The lamellar thickness doubling mechanism invoked by Rastogi et al. [37] for single crystal mats requires highly regular fold surfaces and adjacent reentry folding, an unlikely situation for crystallization from the melt, especially at moderate to high undercooling. Finally, the lamellar doubling mechanism was only observed during slow heating, never under isothermal conditions. Hence, the claim of an instantaneous doubling in lamellar thickness during isothermal melt crystallization without subsequent isothermal thickening does not appear to be supported by previous work in the case of linear polyethylene. The doubling in lamellar thickness at an early stage of primary crystallization followed by an invariance of the lamellar thickness at later times is also inconsistent with a number of Raman, transmission electron microscopy and small angle X-ray scattering (SAXS) studies that have unequivocally proven the existence of a continuous lamellar thickening process occurring at higher rate at higher temperature [34—36,38—43]. Hence, to ensure that all samples in a Hoffman-Weeks plot are characterized by the same thickening coefficient, γ, the crystallization times at successive crystallization temperatures must be very carefully adjusted.

In regard to the magnitude of C_2, experimental values for linear polyethylene are found to be several times larger than δ', the value predicted by the LH theory, thus contribute significantly to the lamellar thickness [30,44—48]. Similar conclusions have been reported by Jones et al. [49] for isotactic poly (styrene), by Korenaga et al. [50] for poly (oxymethylene) and by Cheng et al. [51] for poly (ethylene oxide).

A number of authors have also shown the linear Hoffman-Weeks approach to be untenable on other grounds. For instance, some have shown that the linear Hoffman-Weeks approach leads to T_m^{eq} values that are much lower than these obtained by other methods [14,45,52]. Others, have noticed upon cursory examination of the underlying theory that the linear Hoffman-Weeks equation loses its functionality for initial or non-thickened lamellae (when $\gamma(t_c, T_c) = 1$), where it simplifies to $T_m = T_c$ [31]. In other words, the linear Hoffman-Weeks equation incorrectly suggests that non-thickened lamellae are always in equilibrium with the melt. Finally, we shall see that the intrinsic non-linearity between crystallization and melting temperatures sheds light on the discrepancy [3,14,46,53,54] between the fold surface free energy obtained from a Gibbs-Thomson analysis (σ_{em}) and that determined from spherulite growth rate data (σ_{ec}) [12,17,21,27].

Large C_2 values can be rationalized in the context of the Lauritzen and Passaglia (LP) model [55], which introduced the concept of stem-length fluctuation in the framework of the LH theory. Fluctuations in stem length lead to the formation of a fold surface exhibiting a temperature-dependent roughness, hence, a temperature dependent fold-surface energy, σ_{ec}. In the LP model, the