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Notes

Zero Growth Temperature of Crystallizing Polyethylene

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Even though the Hoffmann−Lauritzen theory of polymer crystallization[1] was repeatedly criticized, its foundations and main implications were generally accepted in the community. The treatment was based on the view that the layerlike crystallites grow in lateral direction by a direct attachment of chain sequences from the melt onto the growth face. It was assumed that the growth rate is controlled by an activation step over a free energy barrier whose height is proportional to the crystal thickness. Analysis of the kinetics resulted in the conclusion that the maximum growth rate is achieved by crystallites whose thickness, d, is near the stability limit as described by the Gibbs−Thomson relationship. For a crystallization temperature T it is given by

$$d = \frac{2\sigma_e T_f^\infty}{\Delta h_f (T_f^\infty - T)} + \delta \tag{1}$$

where σ_e and Δh_f denote the surface free energy and the heat of fusion. Crystal thicknesses should accordingly be inversely proportional to the supercooling below the equilibrium melting temperature T_f^∞ of macroscopic crystals, apart from a minor excess δ necessary for providing a driving force. The associated growth rate G is

$$G = G_0 \exp\left(-\frac{T_A^*}{T}\right) \exp\left(-\frac{T_G}{T_f^\infty - T}\right) \tag{2}$$

The first exponential term expresses the temperature dependence of the segmental mobility in the melt; for temperatures far above the glass transition it follows an Arrhenius law with some effective activation temperature T_A^*. The second exponential term refers to the free energy of activation associated with the chain attachment onto the growth face. It diverges together with d at T_f^∞. Hoffman and Lauritzen related the activation step to the formation of a secondary nucleus whose extension in chain direction agrees with the crystal thickness. The theory then yielded an expression for the parameter T_G of the form

$$T_G = \frac{K}{T} \tag{3}$$

with K being determined by Δh_f, σ_e, and the surface free energy σ_l of the growth face.

Proceeding on eqs 2 and 3 many workers evaluated temperature-dependent growth rate measurements by plotting $\ln(G/G_0) + (T_A^*/T)$ vs $1/[T(T_f^\infty - T)]$. These curves usually show two or three connected linear regions with different slopes. Hoffman and Lauritzen interpreted these changes as changes in the growth regime and developed detailed models for three regimes labeled I, II, and III. Numerous experiments were carried out on polyethylene, and we reproduce here in Figures 1 and 2 results from one of the last papers of Hoffman with data obtained by Armistead.[2] Figure 1 shows growth rates of spherulites as measured in a polarizing optical microscope, and Figure 2 presents the plot used in the evaluation. Three linear ranges show up. The breaks at 129 and 121 °C are interpreted as I−II and II−III regime transitions, respectively.

Different from the multitude of growth rate measurements seen as confirmations of eq 2 and the existence of different regimes, the associated relationship eq 1 was rarely checked. There is an appropriate tool, namely the determination of the crystallite thickness by small-angle X-ray scattering experiments, based upon the deduced correlation function or interface distance distribution function. Beginning about 10 years ago, we used this technique in temperature-dependent investigations of several polymer systems: s- and i-polypropylene, polyethylene, poly(ϵ-caprolactone), and poly(1-butene), if possible both for homopolymers and derived statistical copolymers.[3] The results were clear, but at first surprising because they contradict eq 1. The law for the temperature dependence of d derived from the experiments has also the form of the Gibbs−Thomson equation but includes another controlling temperature, being given by

$$d = \frac{1}{C_c (T_c^\infty - T)} \tag{4}$$

The temperature T_c^∞ which determines the crystal thickness is always located above T_f^∞. In the case of polyethylene we found $T_c^\infty = 154$ °C, which is about 10 K above the equilibrium melting point. In addition, it was observed that thicknesses of crystals, developing at a given temperature, do not change if counits or stereodefects are incorporated in the chain. d values of linear polyethylene, poly(ethylene-*co*-octene)s, and poly(ethylene-*co*-butene)s are all commonly described by eq 4 with $T_c^\infty = 154$ °C and a unique C_c. Equations 1 and 2 are related to each other. With eq 1 being incorrect, the growth rate equation becomes also questionable. So we examined its validity. The results are reported in this short note.

Applying eq 2 means to assume from the beginning as a fact that the activation energy diverges at the equilibrium melting point, thus bringing the growth rate down to zero. Actually, whether or not this is true can be checked in a straightforward manner by the growth rate measurements. We replace in the equation the set parameter T_f^∞ by a variable temperature T_{zg}, write

$$\ln\frac{G}{G_0} + \frac{T_A^*}{T} = -\frac{T_G}{T_{zg} - T} \tag{5}$$

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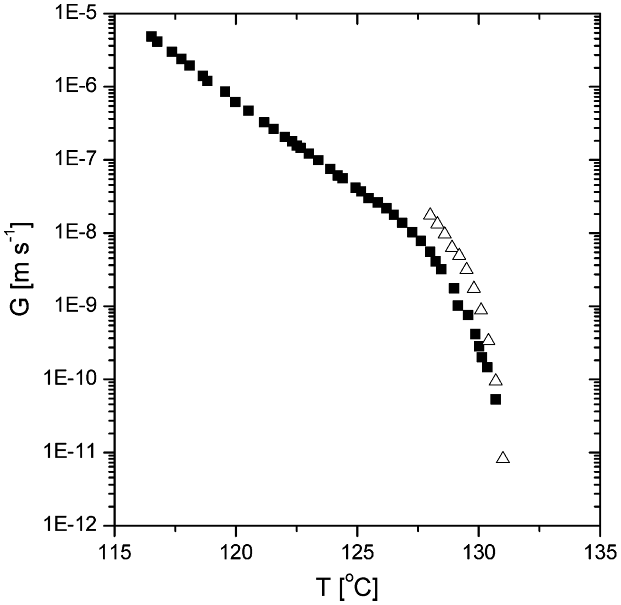

Figure 1. Temperature dependence of the radial growth rate G of linear polyethylene: data of Armistead and Hoffman[2] (filled squares) and our data (open triangles).

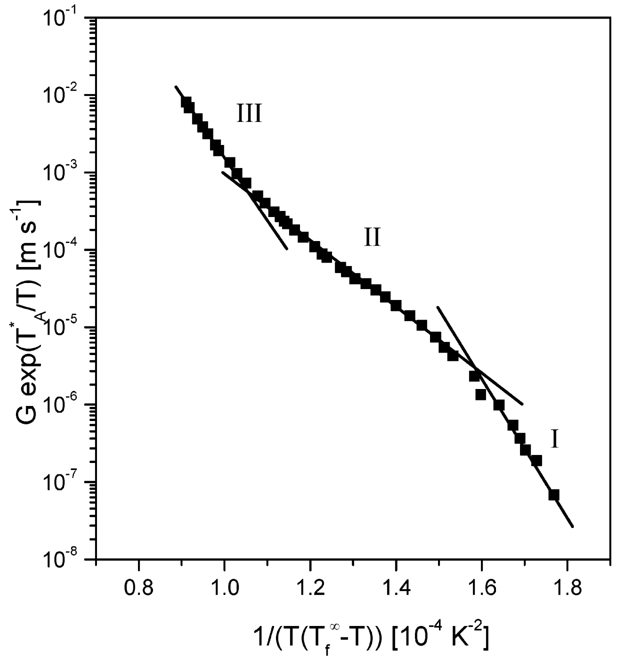

Figure 2. Data of Armistead and Hoffman:[2] representation suggested by eq 2 ($T_A^* = 2890$ K, $T_f^\infty = 144.7$ °C).

and differentiate. A reordering leads to

$$\left(-\frac{\mathrm{d}\ln(G/G_0)}{\mathrm{d}T}+\frac{T_A^*}{T^2}\right)^{-1/2}=T_G^{-1/2}(T_{zg}-T) \qquad (6)$$

Application of this equation enables T_{zg} to be determined. The prerequisite is an accurate determination of the derivative d ln(G/G_0)/dT. We first applied the procedure to the data of Armistead and Hoffman of Figure 1, and the result is shown in Figure 3. According to eq 6, a linear continuation of the data down to zero yields the "zero growth temperature" T_{zg}. As is obvious, such an extrapolation does not lead to $T_f^\infty = 144.7$ °C. However, the accuracy of the data is insufficient for a reliable determination of T_{zg}.

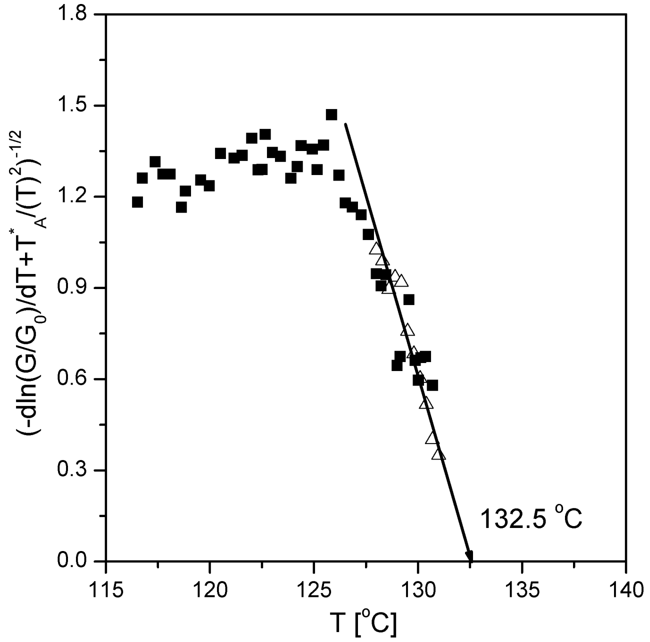

Figure 3. The two sets of data in Figure 1: representation applying eq 6 to determine T_{zg} ($T_A^* = 2890$ K). Linear extrapolation yields $T_{zg} = 132.5$ °C.

We therefore carried out an experiment on linear polyethylene ourselves. Our sample, purchased from Sigma-Aldrich Co., had a molar mass of 6×10^4 g mol^{-1}. We purified it by a dissolution in hot toluene in order to keep the number of heterogeneous nuclei as low as possible. Since we were only interested in the range of high crystallization temperatures, the experiment in a polarizing optical microscope with a heating stage was started at 128 °C, after cooling a melt from 160 °C. We observed and registered with a digital camera the growth of spherulites in a layer with a thickness of about 1 μm. One isolated spherulite was selected and then its growth followed at a series of temperatures which were passed through upon a stepwise heating ($\Delta T = 0.3$ K). Five values of the spherulite size were determined as a function of time at each temperature to derive the growth rate. Because the spherulites did not show up as perfect circles, we determined the smallest ellipse which enclosed the selected spherulite. From the area A of the enclosing ellipse we derived the length R entering into the growth rate determination setting $A = \pi R^2$. At each temperature we determined as a function of time the changes ΔR with regard to the respective initial value. Figure 4 collects the results thus obtained. The slope of unity in the log−log representation for all temperatures demonstrates the linearity of the growth process. Growth rates can be directly derived, and they are included in Figure 1 in a comparison with the Armistead−Hoffman data. As to be noted, the growth rates of our sample are enhanced against the Armistead sample by a constant factor—with the only exception of the two points at the highest temperatures in the Armistead experiment. The enhancement might be due to the somewhat lower molar mass (the Armistead sample had $M_w = 7.4 \times 10^4$ g mol^{-1}). The constant factor vanishes if we consider the derivatives in the manner of eq 6. Our data are also included in Figure 3, and as comparison shows, both sets of data agree with each other within the error limits of the experiments. As also to be noted, our data have indeed the higher accuracy we were striving for. They allow to carry out a linear extrapolation down to zero, with an unambiguous result: The zero growth temperature of linear polyethylene is 132.5 ± 0.5 °C. This is far away from the equilibrium melting point. Hence,

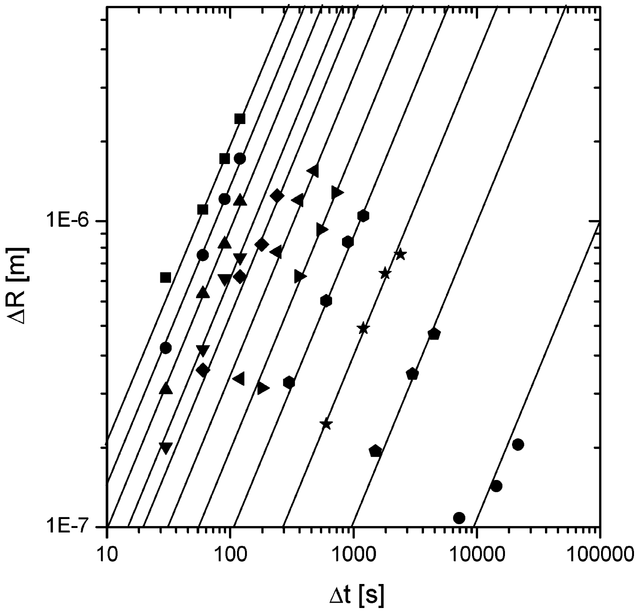

Figure 4. Sample of polyethylene ($M_w = 6 \times 10^4$ g mol^{-1}): increase of the radius of a spherulite ΔR as a function of Δt observed at a series of steplike increasing temperatures beginning at 128 °C and ending at 131 °C (steps $\Delta T = 0.3$ K).

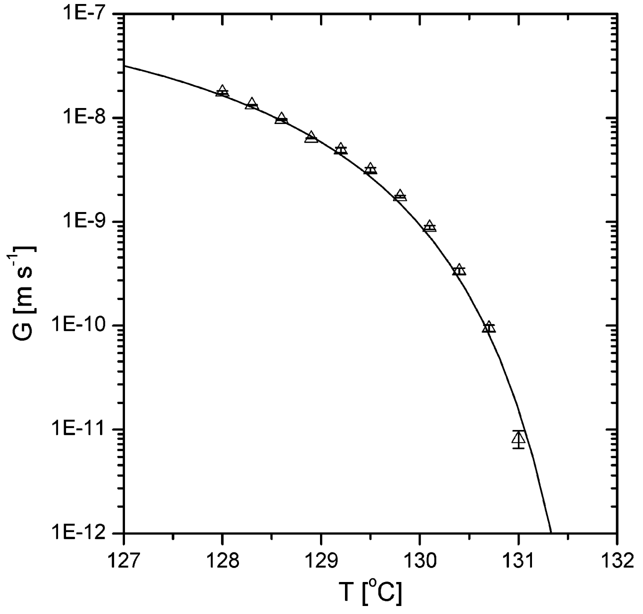

Figure 5. Sample of polyethylene ($M_w = 6 \times 10^4$ g mol^{-1}): data fit based on eq 2 ($T_A^* = 2890$ K). The fitting procedure yields again $T_{zg} = 132.5$ °C.

the growth rate of polyethylene is determined by the distance to $T_{zg} = 132.5$ °C rather than the supercooling below T_f^∞ as is conventionally assumed.

In the differentiation which transforms eq 2 into eq 6, we neglected the weak temperature dependence of T_G expressed by eq 3. To be sure whether or not this weak temperature dependence is really negligible, we determined T_{zg} additionally by a least-squares fit of our data to eq 2 with eq 3, replacing T_f^∞ by the variable T_{zg}. The procedure yielded exactly the same value for T_{zg}, and Figure 5 presents the data points together with the adjusted theoretical curve. Also, the prefactor G_0 might show some weak temperature dependence, but the effect is surely just as small as for T_G.

If one accepts 132.5 °C as the correct zero growth temperature, one can ask again about the occurrence of different growth regimes. Figure 6 shows the corresponding plot, with a clear result: The break in Figure 2 which was interpreted as indicating a transition from regime I to II has disappeared in both sets of data. We cannot comment on the relevance of the apparent growth regime transition at 121 °C in Figure 2 but notice that it does not show up in the plot of the temperature derivatives in Figure 3. On the other hand, in this figure there appears a break at 125 °C in-between the two breaks in Figure 2. We cannot comment on this feature either. In our experiment we did not reach this range of lower temperatures. Both a too high spherulite density and the much enhanced growth rate hindered us to obtain reliable results.

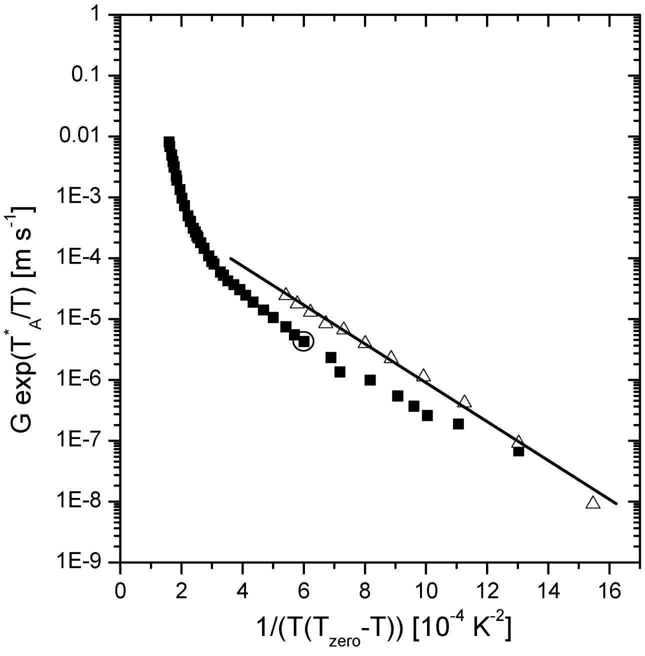

Figure 6. Data representation suggested by eq 7 with $T_{zg} = 132.5$ °C ($T_A^* = 2890$ K). The position of the break at 129 °C in Figure 2 is indicated by a circle.

Hence, in conclusion, the experiments show that crystallization of polyethylene is controlled by two characteristic temperatures which both are different from T_f^∞: (i) The crystal thickness is given by eq 4 with $T_c^\infty = 154$ °C. (ii) The growth rate is given by

$$G = G_0 \exp\left(-\frac{T_A^*}{T}\right) \exp\left(-\frac{T_G}{T_{zg} - T}\right) \qquad (7)$$

with $T_{zg} = 132.5 \pm 0.5$ °C ($T_G = 18$ K; the first exponential factor has to be changed at low temperatures when the full Vogel−Fulcher expression $\exp(-(T_A/(T - T_V))$ must be used). The findings for polyethylene are not exceptional. We obtained similar results for poly(ϵ-caprolactone), with different temperatures for T_f^∞ (=99 °C), T_c^∞ (=135 °C), and T_{zg} (=77 °C),[4] and for i-polystyrene, with $T_f^\infty = 289$ °C , $T_c^\infty = 310$ °C, and $T_{zg} = 275$ °C.

For us, these results come as expected. They agree with the view proposed and advocated by us since several years.[5] We are convinced that the pathway followed in the growth of polymer crystallites includes an intermediate phase of mesomorphic character. We think that a thin layer with mesomorphic inner structure forms between the lateral crystal face and the melt, stabilized by epitaxial forces. The first step in the growth process is an attachment of chain sequences from the melt onto the growth face of the mesomorphic layer. The high mobility of the chains in the layer allows a spontaneous thickening up to a critical value where the layer solidifies under formation of blocklike crystallites. A perfectioning of the crystallites then leads to their final state. We constructed a thermodynamic scheme dealing with the transitions between melt, mesomorphic layers, and crystallites which follow one after the other during the growth process.[6] T_c^∞ and T_{zg} are identified in this scheme with the temperatures of the (hidden) transitions from the mesomorphic to the crystalline and from the amorphous to the mesomorphic phase. The mesomorphic phase of polyethylene seems to be identical with the well-known hexagonal phase stable under high pressure–high temperature conditions. Figure 14 in ref 6 shows a p/T diagram of the three phases of polyethylene as conjectured from various observations. It predicts for normal pressure conditions a value of 134 °C for the temperature of the hidden transition between the amorphous and the mesomorphic phase, in nearly perfect agreement with this experiment. In our view, the activation step controlling crystal growth in polyethylene is to be related to a straightening of chain sequences prior to the attachment onto the surface of a mesomorphic layer. Different from a direct transition into the all-trans conformation, attachment onto the mesomorphic layer is possible for a variety of overall straightened conformations, which reduces the entropic energy barrier. The height of the mesomorphic growth front increases when the crystallization temperature is raised and would diverge at 132.5 °C. A crystallization mediated by a transient mesomorphic phase cannot continue up to this temperature but ends before, probably already very near to the highest temperature (131 °C) reached in this experiment. From thereon, crystallites must grow by direct attachment of chain sequences on crystalline growth faces. The growth rate equation then turns into a dependence as described by eq 2. As a matter of fact, so far this range was never reached in experiments. They all ended at 131–132 °C.

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References and Notes

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