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SHORT COMMUNICATION

Zero growth temperature and growth kinetics of crystallizing poly(ϵ-caprolactone)

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Abstract The lateral growth rate of polymer crystallites rises exponentially with decreasing temperature, thus indicating control by an activation step. Conventional wisdom assumes that the height of the activation barrier diverges at the equilibrium melting point together with the size of a secondary nucleus. Growth rate measurements for spherulites of poly(ϵ-caprolactone) carried out in a polarizing optical microscope at a series of stepwise increasing temperatures contradict this assumption. The barrier height is inversely proportional to the distance to the 'zero growth temperature' T_{zg}=77 °C , which is far below the equilibrium melting point T_f^∞=99 °C . The observation lends further support to our view that crystal growth is mediated by a transient mesophase. T_{zg} is to be identified with the temperature of the hidden transition between the melt and the mesophase.

Keywords Polymer crystallization · Crystal growth rate

Crystallization and melting of polymers in bulk are controlled by several laws [1]. In short form, they read as follows:

– The first law describes the melting point of the layer-like crystallites, which is depressed because of the excess free energy of the fold surface. The Gibbs–Thomson equation states that crystallites with a thickness d melt at

$$T_f = T_f^\infty - \frac{2\sigma_e T_f^\infty}{\Delta h_f}\frac{1}{d} . \quad (1)$$

T_f^∞ is the equilibrium melting point of macroscopic crystals, σ_e is the surface free energy, and Δh_f is the heat of melting. A further drop of melting points results if co-units or stereo defects are incorporated in the chains.

– A second law concerns the relationship between the crystal thickness and the crystallization temperature. It again has the form of a Gibbs–Thomson equation, but includes another controlling temperature, T_c^∞, as

$$d^{-1} = C_c(T_c^\infty - T) . \quad (2)$$

T_c^∞ is always above T_f^∞. As an important property, Eq. 2 holds commonly for the homopolymer and related statistical copolymers of a system. In plots of the inverse crystal thickness vs the crystallization temperature, all points fall on a unique common 'crystallization line'.

– Two different scenarios are observed when a sample is heated after completion of an isothermal crystallization. For crystallization temperatures above some characteristic value, the crystal thickness remains constant up to the melting point; for lower crystallization temperatures, a subsequent heating leads to recrystallization processes. This recrystallization is a continuous process following a 'recrystallization line' given by

$$d^{-1} = C_r(T_c^\infty - T) . \quad (3)$$

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Equation 3 includes again the temperature T_c^∞ but has another slope than the crystallization line ($C_r < C_c$). All recrystallized samples melt at the same temperature, independent of the initial crystallization temperature.

– Two further laws concern the temperature dependencies of the lateral size of the crystalline blocks, which are the constituent elements of the lamellae, and of the crystallinity reached at the end of isothermal crystallization processes: The lateral extension of the blocks is proportional to d, and the crystallinity is independent of the crystallization temperature.

For many decades, it was taken for granted that the growth rate of polymer crystallites is controlled by the supercooling below the equilibrium melting point of a macroscopic sample, T_f^∞. The popular Hoffman–Lauritzen theory [2] formulates for the temperature dependence of the growth rate u the equation

$$u = u_0 \exp\left(-\frac{T_A^*}{T}\right) \cdot \exp\left(-\frac{T_G}{T_f^\infty - T}\right) \quad . \tag{4}$$

It refers to crystallization experiments near the melting temperature. Growth rates in this range are controlled by an activation step, and the second exponential factor states that the height of the activation barrier diverges at T_f^∞. The first exponential factor accounts for the chain mobility using the Arrhenius form $\exp(-T_A^*/T)$. In the derivation of Eq. 4, it is assumed that

– crystal thicknesses d are near to the stability limit as given by Eq. 1, i.e., they are inversely proportional to the supercooling $\Delta T = T_f^\infty - T$
– formation of a secondary nucleus on the growth face is the activation step that controls crystal growth rates.

The nucleus extends in chain direction over the whole crystallite, i.e., it has a length d. As it is assumed that d diverges when the crystallization temperature approaches T_f^∞, the activation energy should diverge as well. As a matter of fact, the assumption $d \propto 1/\Delta T$ is contradicted by the second law cited—d is given by Eq. 2, i.e., does not diverge at T_f^∞. As a consequence, the growth rate Eq. 4 cannot be correct either.

A new examination was necessary. We carried out growth rate measurements and chose poly(ϵ-caprolactone) as a first system. Its crystallization and melting properties were well characterized in previous experiments. The equilibrium melting point is T_f^∞=99 °C , and the temperature controlling the crystal thickness according to Eq. 2 is T_c^∞=125 °C . The difference between these two temperatures is especially large. Furthermore, in poly(ϵ-caprolactone), a low number of spherulites is slowly growing to large sizes, which is a favorable situation for accurate growth rate measurements. The study was carried out in a polarizing optical microscope with a heating stage. The experiment started at 47.6 °C after a rapid cooling from the melt. Growth of one selected isolated spherulite was observed and registered with a digital camera. Growth rates were measured for this spherulite at a series of temperatures separated by steps of 1 K. Image processing yielded the spherulite area as a function of time, and from the area, the radius was derived. The accuracy in the determination of growth rates thus achieved was quite satisfactory. This is demonstrated by the results shown in Fig. 1, giving growth rates as measured up to a temperature of 57.6 °C .

Using Eq. 4 means to include as a basic assumption that the activation energy diverges at T_f^∞. Actually, whether or not this is correct, this can be checked by the experiment. We replace the set parameter T_f^∞ by a variable temperature T_{zg}. A differentiation of $\ln u$ with regard to T and some reordering leads directly to

$$\left(-\frac{\mathrm{d}\ln(u/u_0)}{\mathrm{d}T} + \frac{T_A^*}{T^2}\right)^{-1/2} = {T_G}^{-1/2}(T_{zg} - T) \tag{5}$$

Application of this equation allows T_{zg} to be determined. The experimental prerequisite is an accurate determination of the derivative $\mathrm{d}\ln(u/u_0)/\mathrm{d}T$ as a function of temperature. Values for T_A^* are available in the literature from melt viscosity measurements

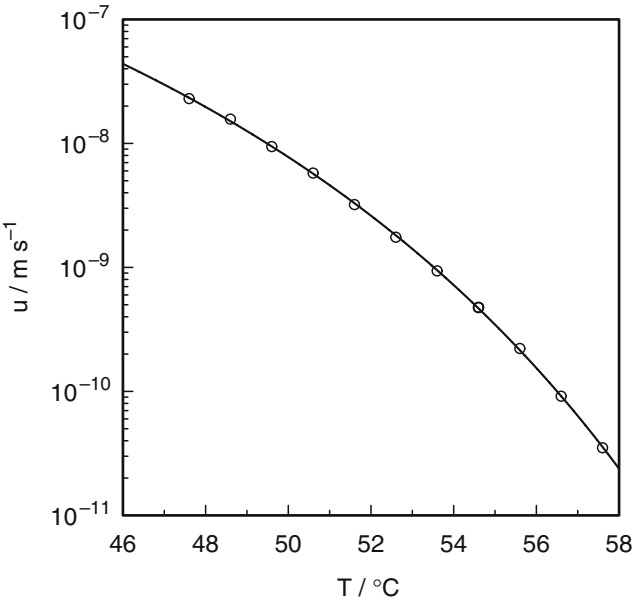

Fig. 1 PϵCL: temperature dependence of the radial growth rate. Representation by Eq. 6 with $T_A^* = 4,650$ K, T_G=397 K, and $T_{zg} = 77$ °C

(T_A^*=4,650 K [3]). Figure 2 presents a plot as suggested by Eq. 5. As it is obvious, the equation can indeed be used for a determination of the 'zero growth temperature'. Data points are all on a straight line, and the extrapolation down to zero yields T_{zg} with a value of 77 °C . This temperature is far below the equilibrium melting point of 99 °C . Hence, as we suspected, Eq. 4 is incorrect. The activation energy does not diverge at T_f^∞ but much earlier. We conclude that Eq. 4 has to be replaced by

$$u = u_0 \exp\left(-\frac{T_A^*}{T}\right) \cdot \exp\left(-\frac{T_G}{T_{zg} - T}\right) \quad . \tag{6}$$

T_{zg} is the third temperature characteristic for a system, different from both T_f^∞ and T_c^∞. The curve in Fig. 1, which perfectly passes through all points, was calculated using Eq. 6 with T_{zg} and T_G taken from Fig. 2.

What does this result mean? How can it be understood? Actually, for us, it came as anticipated. In our view, crystal growth does not proceed by direct attachment of chain sequences onto a crystal growth face, but is mediated by a transient mesomorphic phase [4]. A thin layer with mesomorphic structure forms between the lateral crystal face and the melt, stabilized by epitaxial forces. All the stereo defects and co-units are already rejected on its front. A high inner mobility allows a spontaneous thickening of the layer from an initial value right of the stability limit up to a critical value where the core region crystallizes under the formation of a block. In the last step, the surface region of this block, at first still disordered, perfects, which leads to a further stabilization.

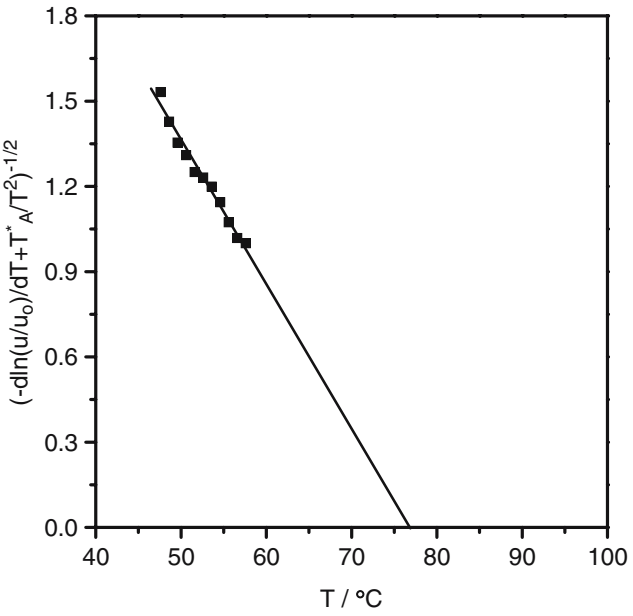

Fig. 2 PϵCL: temperature dependence of the radial growth rate. Plot based on Eq. 5 giving T_{zg} = 77 °C and T_G = 397 °C

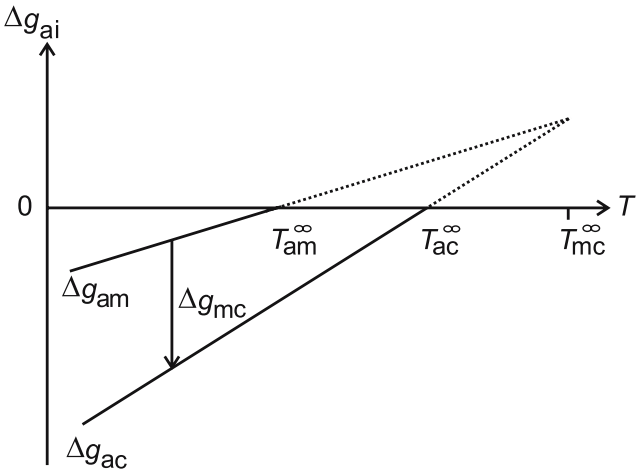

Fig. 3 Thermodynamic conditions assumed for crystallizing polymers: temperature dependencies of the chemical potentials of a mesomorphic and the crystalline phase. The potentials are referred to the chemical potential of the melt and denoted Δg_{am} and Δg_{ac}

The thermodynamic conditions under which such a mesomorphic phase can interfere and affect the crystallization process are described in the drawing of Fig. 3. The schematic plot shows for both the crystalline phase (label 'c') and the mesomorphic phase ('m') the difference of the chemical potential to that of the melt ('a'):

$$\Delta g_{ac} = g_c - g_a \quad ,$$
$$\Delta g_{am} = g_m - g_a \tag{7}$$

Coming from high temperatures, the chemical potential of the crystalline phase drops below the value of the melt when crossing the equilibrium melting point, now denoted T_{ac}^∞. The mesomorphic phase requires a lower temperature, T_{am}^∞, to fall with its chemical potential below that of the melt. The plot includes also the temperature T_{mc}^∞. It represents the temperature of a virtual transition, namely, that between the mesomorphic and the crystalline phase. The transition temperatures have the order $T_{mc}^\infty > T_{ac}^\infty > T_{am}^\infty$. Because the chemical potential of the crystal is always below that of the mesomorphic phase, the mesomorphic phase is only metastable for macroscopic systems. However, for small objects with sizes in the nanometer range, stabilities can be inverted. Because of the usually lower surface free energy, thin mesomorphic layers can have a lower Gibbs free energy than a crystallite with the same thickness.

Which could be the rate controlling step in this multistage process? We think that the first step—attachment of a chain sequence on the growth front of the

mesomorphic layer—is dominant, and the observations support that. Before a sequence, which lies coiled in the melt, is incorporated into the growing mesomorphic layer, it has to be activated by a transfer into an overall straightened form as required for an attachment—different from the crystal, the mesomorphic layer, thereby, allows for a variety of conformations. The straightening has to reach at least the length given by the initial thickness of the mesomorphic layer. This thickness is again determined by the Gibbs–Thomson equation, now applied to mesomorphic layers in the melt:

$$d = \frac{2\sigma_{\mathrm{am}} T^{\infty}_{\mathrm{am}}}{\Delta h_{\mathrm{ma}}} \frac{1}{T^{\infty}_{\mathrm{am}} - T} \,. \tag{8}$$

σ_{am} is the excess free energy of the mesomorphic layer surface, Δh_{ma} is the enthalpy change between the mesomorphic and the amorphous phase. Because the straightening leads to a decrease in entropy, which is proportional to the sequence length, it introduces an entropic activation barrier

$$-\frac{\Delta S}{k} \propto d \,. \tag{9}$$

Transition of the barrier takes place with a probability

$$\exp\left(\frac{\Delta S}{k}\right) = \exp\left(-\frac{\mathrm{const}}{T^{\infty}_{\mathrm{am}} - T}\right) \,. \tag{10}$$

If T_{zg} is identified with T^{∞}_{am}, this agrees with the experimental result as given by Eq. 6. Hence, we think that it is the distance to T^{∞}_{am}—rather than to T^{∞}_{f}—which controls the growth rate of polymer crystallites.

Crystallization, recrystallization, and melting of bulk polymers can always be discussed in the framework of a generally applicable scheme [5]. The scheme, described with the aid of a (T, d^{-1}) diagram valid for polymer layers with thicknesses in the nanometer range, is composed of three lines:

- the crystallization line representing the relationship between the crystallization temperature, as being given by Eq. 2,
- the recrystallization line that controls the course of recrystallization processes, being given by Eq. 3,
- the crystallite melting line on which all final melting points T_{f} are located, being given by Eq. 1, i.e., by

$$d^{-1} = C_{\mathrm{f}}(T^{\infty}_{\mathrm{f}} - T_{\mathrm{f}}) \tag{11}$$

- an analogous melting line for the mesomorphic layers, being given by Eq. 8 or

$$d^{-1} = C_{\mathrm{am}}(T^{\infty}_{\mathrm{am}} - T_{\mathrm{f}}) \tag{12}$$

Fig. 4 shows the four lines of poly(ϵ-caprolactone) in the nanophase diagram. Crystallization line, recrystallization line, and the crystallite melting line were previously determined by temperature-dependent small-angle X-ray scattering experiments. With the determination of the zero growth temperature $T_{\mathrm{zg}} = T^{\infty}_{\mathrm{am}}$, the $a \Rightarrow m$ transition line can also be fixed. It starts off from T^{∞}_{am} and has to pass through X_s, the point where recrystallization line and melting line intersect each other [5]. The temperature at X_s can additionally be determined by differential scanning calorimetry measurements: At this temperature, all recrystallized samples melt. For poly(ϵ-caprolactone), this occurs at 55 °C [6]. Knowing all four lines, the nanophase diagram is completed. As explained in [5], an evaluation provides the enthalpy differences between the three phases and the excess free energies associated with the interfaces.

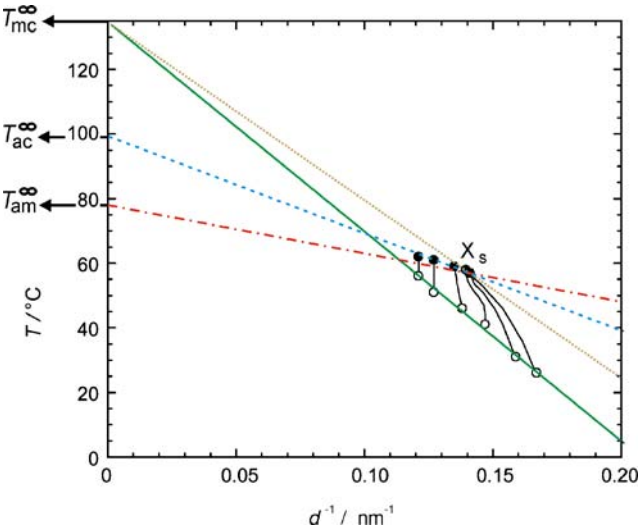

Fig. 4 Nanophase diagram of PϵCL: crystallization line, recrystallization line (*dots*), and melting line (*dashes*) determined by small-angle X-ray scattering [5], zero growth temperature T^{∞}_{am} and $a \Rightarrow m$ transition line (*dash–dots*)

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References

1. Strobl G (2006) Prog Polym Sci 31:398
2. Hoffman JD, Davis GT, Lauritzen JI (1976) In: Hannay NB (ed) Treatise on solid state chemistry, vol 3. Plenum, New York, p 497
3. Acierno S, Di Maio E, Iannace S, Grizzuti N (2006) Rheol Acta 45:387
4. Strobl G (2000) Eur Phys J E 3:165
5. Strobl G (2005) Eur Phys J E 18:295
6. Heck B, Hugel T, Iijima M, Sadiku E, Strobl G (1999) New J Phys 1:17