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ORIGINAL CONTRIBUTION

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Crystallization of polymers in variable external conditions IV. Isothermal crystallization in the presence of variable tensile stress or hydrostatic pressure

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Abstract General equations of crystallization in variable conditions have been applied to isothermal crystallization affected by variable tensile stress or hydrostatic pressure. In a system under stress, the crystallization rate involves relaxational and athermal effects, and is controlled by the normal stress difference and the stress rate. Similarily, pressure effects include the hydrostatic pressure and its rate of change.

Key words Nucleation theory · Thermal and athermal nucleation · Crystallization · Stress-induced crystallization · Pressure-induced crystallization

Introduction

The new model of crystallization developed in Ref. [1] takes into account transient and athermal effects and a variety of time-dependent state variables. The variable temperature, T, the hydrostatic pressure, p_0, the deviatoric stress tensor, $\mathbf{p}$, and others, form a time-dependent vector of external conditions

$$\Psi(t) = \{T(t),\ p_0(t),\ \mathbf{p}(t), \ldots\} \ . \tag{1}$$

The model is based on the Kolmogoroff–Avrami–Evans treatment of phase transitions [2–5], modified to account for variable external conditions. Instead of the linear measure of the degree of transformation, $x(t)$, i.e. volume fraction of the transformed material

$$x(t) = v_{\mathrm{cr}}(t)/v_{\mathrm{tot}}; \quad x \in (0,1) \tag{2}$$

the nonlinear measure is used

$$P(t) = \{-\ln[1 - x(t)]\}^{1/m}; \quad P \in (0,\infty) \ , \tag{3}$$

where m is a model parameter which, in steady-state conditions, reduces to the Avrami exponent.

The nonlinear transformation (crystallization) rate

$$K[t, \Psi(t)] \equiv \mathrm{d}P/\mathrm{d}t \tag{4}$$

is, in general, a function of time and time-dependent external conditions, $\Psi(t)$. In the steady-state, constant external conditions, K reduces to the Avrami crystallization rate constant, K_{m}, and is inversely proportional to the crystallization half-period

$$K(t) = \mathrm{const.}\, K_{\mathrm{m}}^{1/m} \propto (t_{1/2})^{-1} \ . \tag{5}$$

In variable external conditions, $K(t)$ is the sum of thermal and athermal contributions [1]

$$\begin{aligned} K[t, \Psi(t)] &= K_{\mathrm{th}}[t, \Psi(t)] + K_{\mathrm{ath}}[t, \Psi(t)] \\ &= K_{\mathrm{th}}[1 + \dot{\Psi}\mathbf{Z}(t, \Psi)]^{\mu} \ , \end{aligned} \tag{6}$$

where $\mathbf{Z}$ is a vector in the space of external conditions Ψ. The exponent μ depends on whether the athermal mechanism affects both nucleation and growth, or only one of these processes. The thermal contribution to the crystallization rate results as an integral [1]

$$K_{\mathrm{th}}[t, \Psi(t)] = \mathrm{e}^{-\xi}\left\{K_0 + \int \mathrm{e}^{+\xi}\ K_{\mathrm{st}}[\Psi(\xi')]\mathrm{d}\xi'\right\} \ , \tag{7}$$

where

$$\xi(t) = \int_0^t \frac{\mathrm{d}t'}{\tau[\Psi(t')]} \tag{8}$$

is time reduced with the (variable) relaxation time, τ. K_{st} denotes the steady-state crystallization rate, a function of external conditions Ψ. Integration of Eq. (7) by parts yields

$$K_{\mathrm{th}}[t,\Psi(t)] = C + K_{\mathrm{st}} - \mathrm{d}K_{\mathrm{st}}/\mathrm{d}\xi \quad + \mathrm{d}^2K_{\mathrm{st}}/\mathrm{d}\xi^2 - \cdots + (-1)^n\ \mathrm{d}^nK_{\mathrm{st}}/\mathrm{d}\xi^n + \cdots \ , \tag{9}$$

where

$$C = \left[K_0 - K_{\mathrm{st}} + \mathrm{d}K_{\mathrm{st}}/\mathrm{d}\xi - \mathrm{d}^2K_{\mathrm{st}}/\mathrm{d}\xi^2 + \cdots\right]_{\xi=0} \tag{10}$$

is the integration constant. The crystallization rate, K_{th}, is controlled by the instantaneous steady-state value $K_{\mathrm{st}}[\Psi(t)]$, and by the history of the individual external conditions, components of the vector Ψ

$$\mathrm{d}K_{\mathrm{st}}/\mathrm{d}\xi = \tau\sum_i(\partial K_{\mathrm{st}}/\partial\Psi_i)(\mathrm{d}\Psi_i/\mathrm{d}t) \tag{11}$$

$$\begin{aligned}\mathrm{d}^2K_{\mathrm{st}}/\mathrm{d}\xi^2 = {} & \tau^2\sum_i\sum_j\left(\partial^2K_{\mathrm{st}}/\partial\Psi_i\partial\Psi_j\right)f(\mathrm{d}\Psi_i/\mathrm{d}t) \\ & \times\left(\mathrm{d}\Psi_j/\mathrm{d}t\right) + \tau^2\sum_i(\partial K_{\mathrm{st}}/\partial\Psi_i) \\ & \times\left[\left(\mathrm{d}^2\Psi_i/\mathrm{d}t^2\right) + (\mathrm{d}\Psi_i/\mathrm{d}t)(\mathrm{d}\ln\tau/\mathrm{d}t)\right] \ .\end{aligned} \tag{12}$$

Summation is performed over those parameters of state Ψ_i (components of the vector Ψ) which change in time, for example, $i = 1$, $\Psi_i = T$ (temperature), $i = 2$, $\Psi_i = p_0$ (pressure), $i = 3$, $\Psi_i = \Delta p$ (tensile stress), etc.

In Eqs. (9)–(12) there appear increasing orders of the relaxation time, τ, and rates of change of the individual state variables, Ψ_i. Equations (6)–(12) provide the general theoretical basis for the description of crystallization in variable external conditions.

Isothermal crystallization controlled by variable stress or pressure

Consider a diagonal, time-dependent stress tensor, $\mathbf{p}(t)$

$$\mathbf{p}(t) = \begin{bmatrix} p_{11} & 0 & 0 \\ 0 & p_{22} & 0 \\ 0 & 0 & p_{33} \end{bmatrix} \ . \tag{13}$$

We will analyze two special cases, in which the vector of external conditions, $\Psi(t)$, reduces to a single component of the tensor, $\mathbf{p}(t)$.

The first case is uniaxial tension

$$\begin{aligned} & p_{11} = p_{22} \neq p_{33} \\ & p_{11} + p_{22} + p_{33} = -3p_0 = \mathrm{const} \ . \end{aligned} \tag{14}$$

The variable affecting the kinetics of crystallization is the tensile stress, or normal stress difference

$$\Psi(t) = \Delta p(t) = p_{33}(t) - p_{11}(t) \ . \tag{15}$$

Temperature, pressure, and other state variables are assumed to be constants.

The second case concerns hydrostatic pressure

$$p_{11} = p_{22} = p_{33} \ , \tag{16}$$

with hydrostatic pressure, p_0, as the main variable

$$\Psi(t) = p_0(t) = -(1/3)[p_{11} + p_{22} + p_{33}] \ . \tag{17}$$

All characteristics appearing in the general model reduce to scalar functions of the stress difference, Δp, or hydrostatic pressure, p_0.

In the case of isothermal, variable-stress crystallization, one obtains

$$K_{\mathrm{th}}[t,\Delta p(t)] = \mathrm{e}^{-\xi(t)}\left[K_0 + \int_0^t \frac{\mathrm{e}^{\xi}K_{\mathrm{st}}[\Delta p(t')]\mathrm{d}t'}{\tau[\Delta p(t')]}\right] \ , \tag{18}$$

and in the expanded form

$$\begin{aligned} K_{\mathrm{th}}[t,\Delta p(t)] = {} & C + K_{\mathrm{st}} - (\tau\cdot\Delta\dot{p})(\partial K_{\mathrm{st}}/\partial\Delta p) \\ & + (\tau\cdot\Delta\dot{p})^2[\partial^2K_{\mathrm{st}}/\partial\Delta p^2 \\ & + (\partial\ln\tau/\partial\Delta p)(\partial K_{\mathrm{st}}/\partial\Delta p)] \\ & + (\tau^2\Delta\ddot{p})(\partial K_{\mathrm{st}}/\partial\Delta p) + \cdots \ . \end{aligned} \tag{19}$$

Similar equations with pressure, p_0, replacing tensile stress, Δp, apply to isothermal, pressure-controlled crystallization.

In Eq. (19) there appear rates of stress, $\Delta\dot{p}$, $\Delta\ddot{p}, \ldots$, (rates of pressure, $\dot{p}_0, \ddot{p}_0, \ldots$) multiplied by appropriate powers of the relaxation time, τ. The longer the relaxation time and/or the faster the change of stress (pressure), the more terms in Eq. (19) should be considered. At $(\tau\Delta\dot{p}) \to 0$, or $(\tau\dot{p}_0) \to 0$, the crystallization rate reduces to the steady-state value at instantaneous stress (pressure).

Like in an earlier paper on temperature-controlled crystallization [6], we assume that athermal effects are present only in primary nucleation, while growth is controlled by a pure thermal mechanism. In terms of Eq. (6) this yields $\mu = 1(n+1)$, where n denotes the dimensionality of growth, and the athermal function is a characteristic of primary nucleation. In the case considered all conditions are assumed to be constants, except for stress (or pressure). The total crystallization rate reduces to

$$K(t) = K_{\mathrm{th}}[1 + \dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}}]^{1/(n+1)} \ . \tag{20}$$

The ratio of athermal to thermal nucleation

$$\dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}} = \tau\Delta\dot{p}Q(T,\Delta p) \tag{21}$$

for tensile stress, and

$$\dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}} = \tau\dot{p}_0Y(T,p_0) \tag{22}$$

for hydrostatic pressure, is proportional to the relaxation time, τ, multiplied, respectively, by the stress rate or by the pressure rate. Q and Y are material characteristics dependent on the instantaneous external conditions.

The overall time-dependent crystallization rate controlled by tensile stress assumes the form

$$K(t) = \mathrm{e}^{-\xi(t)} \left[K_0 + \int\limits_0^t \frac{\mathrm{e}^{\xi} K_{\mathrm{st}}[\Delta p(t')]\mathrm{d}t'}{\tau[\Delta p(t')]} \right] \times [1 + \tau\Delta\dot{p}Q]^{1/(n+1)} \tag{23}$$

and a similar equation with p_0, $\dot{p}_0$, and Y, in place of Δp, $\Delta\dot{p}$, and Q holds true for the pressure-controlled case. When crystallization follows prolonged heating, K_0 and C in Eq. (19) are small and can be neglected.

The athermal correction (Eq. 21) can be expanded in a power series of stress (pressure) rates and relaxation times. For the tensile-stress case, combination of Eqs. (20) and (21) yields

$$\begin{aligned}[1 + \tau\Delta\dot{p}Q]^{1/(n+1)} = 1 &+ \tau\Delta\dot{p}Q/(n+1) \\ &+ n[\tau\Delta\dot{p}Q/(n+1)]^2 \\ &+ n(2n+1)[\tau\Delta\dot{p}Q/(n+1)]^3 \\ &+ \cdots \ .\end{aligned} \tag{24}$$

A similar formula for the hydrostatic-pressure case results from Eqs. (20) and (22).

Equations (19) and (24) can be combined to yield the total crystallization rate

$$\begin{aligned}K(t) &- C\mathrm{e}^{-\xi}[1 + \tau\Delta\dot{p}Q]^{1/(n+1)} \\ &= K_{\mathrm{st}}[1 + F_1(\tau\Delta\dot{p}) + F_{21}(\tau\Delta\dot{p})^2 \\ &\quad + F_{22}(\tau^2\Delta\ddot{p}) + \cdots]\end{aligned} \tag{25}$$

for tensile stress, and

$$\begin{aligned}K(t) &- C\mathrm{e}^{-\xi}[1 + \tau\dot{p}_0 Y]^{1/(n+1)} \\ &= K_{\mathrm{st}}[1 + G_1(\tau\dot{p}_0) + G_{21}(\tau\dot{p}_0)^2 \\ &\quad + G_{22}(\tau^2\ddot{p}_0) + \cdots]\end{aligned} \tag{26}$$

for hydrostatic pressure.

The relaxation time depends strongly on temperature, and much less so on stress or pressure. Considering isothermal, variable-stress conditions, the variation of relaxation time will be neglected

$$\partial\tau/\partial\Delta p = \partial\tau/\partial p_0 = 0; \quad \mathrm{d}\tau/\mathrm{d}t = 0 \tag{27}$$

which yields the first expansion coefficients in Eq. (25)

$$F_1 = Q/(n+1) - \partial \ln K_{\mathrm{st}}/\partial\Delta p \tag{28}$$

$$F_{21} = n[Q/(n+1)]^2 + \partial^2 \ln K_{\mathrm{st}}/\partial\Delta p^2 + (\partial \ln K_{\mathrm{st}}/\partial\Delta p)^2 \tag{29}$$

$$F_{22} = \partial \ln K_{\mathrm{st}}/\partial\Delta p \tag{30}$$

and in Eq. (26)

$$G_1 = Y/(n+1) - \partial \ln K_{\mathrm{st}}/\partial p_0 \tag{31}$$

$$G_{21} = n[Y/(n+1)]^2 + \partial^2 \ln K_{\mathrm{st}}/\partial p_0^2 + (\partial \ln K_{\mathrm{st}}/\partial p_0)^2 \tag{32}$$

$$G_{22} = \partial \ln K_{\mathrm{st}}/\partial p_0 \ . \tag{33}$$

In the general case, stress and pressure rates are functions of temperature and other thermodynamic conditions. We will concentrate below on special experimental regimes which may lead to useful procedures for determining material characteristics.

Crystallization under tensile stress

Three stress-rate regimes will be considered:

1. Constant stress, $\Delta\dot{p} = 0$.
2. Constant stress rate, $\Delta\dot{p} = \mathrm{const.}$
3. Exponential relaxation of stress, $\Delta\dot{p}(t) = -\beta\Delta p(t) = -\Delta p/\tau_{\mathrm{rel}}$,

where τ_{rel} denotes the stress relaxation time, different from the time τ appearing in the transient nucleation and crystallization theory.

Crystallization conditions

Crystallization experiments should follow prolonged heating above the equilibrium melting temperature T_{m}. Such treatment is necessary for the destruction of ordered structures existing in the polymer prior to crystallization, and reduction to zero of the integration constant C in Eqs. (10), (19), and (25). It is highly recommended that stress-affected crystallization is studied on slightly crosslinked samples. Crosslinking prevents flow of the material and excessive change of its dimensions. It should be considered, however, that crystallization of stressed, crosslinked polymer samples may lead to bimodal crystallization. Real polymer networks consist of elastically effective and elastically ineffective network chains. Even if the uncrosslinked material (sol) is removed by extraction, the remaining (gel) part is not uniform. Only those network chains which span elastically effective crosslinks (i.e. crosslinks connected to at least three paths leading to the surface), transmit forces applied to the sample. Loops, chains attached to the gel by one end only, and some other structures are relaxed and unaffected by external stress or strain [7]. Bimodal crystallization of stressed polyethylene has been observed by Sajkiewicz and Wasiak [8].

The most desirable experimental conditions involve crystallization of stressed (elastically effective) chains in the absence of crystallization of the relaxed (elastically ineffective) portion of the network.

The critical crystallization temperature, i.e. the temperature at the onset of crystallization, depends on stress. As shown in the Appendix

$$T_\mathrm{m}(\vartheta, \Delta p) = T_{\mathrm{m},0}\frac{\Delta h_0}{\Delta h_0 - T_{\mathrm{m},0}\delta s_\mathrm{el} + (kT_{\mathrm{m},0}/v_0)\ln[4\pi w_\mathrm{s}(\vartheta, \Delta p)]} , \quad (34)$$

where $T_{\mathrm{m},0}$ and Δh_0 denote the critical crystallization temperature and the heat of crystallization in the absence of stress, respectively and ϑ is orientation of the crystal. The extra entropy of the transition, δs_el, is controlled by elastic deformation of the uncrystallized (amorphous) phase, and the orientation distribution of crystallizing chain segments, $w_\mathrm{s}(\vartheta)$. The ideal crystallization temperature, T_c, lies within the interval

$$T_{\mathrm{m},0} < T_\mathrm{c} < T_\mathrm{m}(\Delta p) \ . \quad (35)$$

Below $T_{\mathrm{m},0}$ bimodal crystallization can be expected.

Constant-stress experiments

The crystallization relaxation time, τ, can be obtained from transient isothermal, constant-stress experiments in the way described in Ref. [9]. The progress of crystallization is followed in time, and the relaxation time is obtained from the inflexion point of the crystallization rate versus time function $K(t)$

$$\mathrm{d}^2K(t)/\mathrm{d}t^2 = 0; \quad \tau = 1.107336\ t_\mathrm{infl} \ . \quad (36)$$

The steady-state crystallization rate at constant temperature and stress may be obtained directly from the asymptotic behavior of the constant-stress experiment results at $t \to \infty$

$$K_\mathrm{st}(T, \Delta p) = \lim_{t\to\infty} K(t; T, \Delta p) \quad (37)$$

or from extrapolation of the variable-stress (or variable-temperature) experiment results to zero rate of change ($\dot{T} \to 0$, or $\Delta\dot{p} \to 0$) [9]. Theoretical and empirical models for stress-dependent crystallization rates are discussed in the Appendix.

Constant stress-rate experiments

In the constant stress-rate regime, $\Delta\ddot{p}$ and higher rates of change disappear, and the total crystallization rate can be described as power expansion over the constant parameter $(\tau\Delta\dot{p})$

$$K(t) = K_\mathrm{st}[1 + F_1 \cdot (\tau \cdot \Delta\dot{p}) + F_2 \cdot (\tau \cdot \Delta\dot{p})^2 + \cdots] \ . \quad (38)$$

Equation (38) provides a convenient form for describing crystallization at slow changes of stress. At $(\tau \cdot \Delta\dot{p}) \to 0$, Eq. (38) returns the quasistatic model of crystallization dependent on instantaneous stress

$$K(t) = K_\mathrm{st}[\Delta p(t)] \quad (39)$$

and in the isothermal, steady-state conditions, reduces to the isothermal Avrami formula

$$K(t) = K_\mathrm{st}(T, \Delta p) \propto K_\mathrm{m}^{1/m} = \mathrm{const.} \quad (40)$$

The determination of the athermal function $Q(T, \Delta p)$ or the global stress-rate coefficient F_1 in Eqs. (25) and (38) requires isothermal experiments performed at several well-defined constant-stress rates, $\Delta\dot{p}$. The procedure suggested is similar to that used for the evaluation of temperature effects in Ref. [9]. Integration of the crystallization rate over time yields the time-dependent "crystallinity" $P(t)$ (cf. Eq. 3)

$$P(t) = \{-\ln[1 - x(t)]\}^{1/m} = \int_0^t K(t')\mathrm{d}t' \quad (41)$$

which, under constant temperature and constant nonzero stress rate, $\Delta\dot{p}$, can be replaced by integration over stress, Δp

$$\begin{aligned} P(t) &= \frac{1}{\Delta\dot{p}} \int_0^{\Delta p(t)} K(\Delta p')\mathrm{d}\Delta p' \\ &= \frac{1}{\Delta\dot{p}} \left\{ \int_0^{\Delta p(t)} K_\mathrm{st}(\Delta p')\mathrm{d}\Delta p' \right. \\ &\quad \left. + (\tau\Delta\dot{p}) \int_0^{\Delta p(t)} F_1(\Delta p')K_\mathrm{st}(\Delta p')\mathrm{d}\Delta p' + \cdots \right\} \ . \end{aligned} \quad (42)$$

Performing isothermal crystallization runs at different (constant) stress rates one obtains the information required for the material function F_1. The evaluation of the experimental data is based on the comparison of crystallinities, P, found at the same final stress, Δp, and different (constant) stress rates, $\Delta\dot{p}$. What is analyzed, is the product $(P \cdot \Delta\dot{p})$ plotted versus stress rate, $\Delta\dot{p}$, at different (constant) final stress levels, Δp. Like in the former paper [9], the intercept

$$\lim_{\Delta\dot{p}\to 0}(P \cdot \Delta\dot{p}) = \int_0^{\Delta p} K_\mathrm{st}(\Delta p')\mathrm{d}\Delta p' \quad (43)$$

subsequently differentiated with respect to final stress, Δp, yields the steady-state crystallization rate

$$K_{\mathrm{st}}(\Delta p) = \frac{\mathrm{d}}{\mathrm{d}\Delta p} \lim_{\Delta\dot{p}\to 0} (P \cdot \Delta\dot{p}) \tag{44}$$

and the initial slope

$$\lim_{\Delta p\to 0} \frac{\mathrm{d}(P \cdot \Delta\dot{p})}{\mathrm{d}\Delta\dot{p}} = \int_0^{\Delta p} \tau F_1(\Delta p')K_{\mathrm{st}}(\Delta p')\mathrm{d}\Delta p' \tag{45}$$

yields the sum of the relaxational and athermal effects

$$F_1(\Delta p) = \frac{1}{\tau K_{\mathrm{st}}} \frac{\mathrm{d}}{\mathrm{d}\Delta p} \lim_{\Delta\dot{p}\to 0} \frac{\mathrm{d}(P \cdot \Delta\dot{p})}{\mathrm{d}\Delta\dot{p}} \quad . \tag{46}$$

The basis for the theoretical prediction of athermal effects is provided by nucleation theory (Appendix). The characteristic Q in Eqs. (23)–(25) can be expressed through free energy, Δf, or undercooling, ΔT, both of which are dependent on stress. Assuming a quadratic dependence of the elastic entropy of deformation, and a linear dependence of the orientation term (first terms in Eqs. A9 and A10) one obtains

$$\begin{aligned} Q(T, \Delta p) &= \text{const.} \left(\frac{1}{\Delta f}\right)^5 \frac{\mathrm{d}\Delta f}{\mathrm{d}\Delta p} \\ &= \text{const.} \left(\frac{T_{\mathrm{m}}}{\Delta T}\right)^5 \left(\frac{N^2 v_0 \Delta p}{3kT} + \frac{3}{2}\cos^2\vartheta\right) \quad . \end{aligned} \tag{47}$$

Stress-relaxation experiment

In the exponential regime, the stress rate is proportional to stress

$$\Delta\dot{p} = -\beta\Delta p;\ \Delta\ddot{p} = -\beta\Delta\dot{p} = \beta^2\Delta p, \text{ etc.} \tag{48}$$

and the result is expanded over the variable including stress and the ratio of relaxation times, $\beta\tau\Delta p = \Delta p(\tau/\tau_{\mathrm{rel}})$

$$K = K_{\mathrm{st}}\{1 - F_1(\beta\tau\Delta p) + [F_{21} + F_{22}/\Delta p](\beta\tau\Delta p)^2 + \cdots\} \quad . \tag{49}$$

A sample stressed to the level Δp_0 is crystallized isothermally in the conditions of freely relaxing stress. The initial conditions ($t = 0,\ \Delta p = \Delta p_0,\ T = T_{\mathrm{c}}$) can be realized in two different ways:

1. A crosslinked sample is heated under stress above the melting temperature, and is then rapidly cooled to the crystallization temperature, T_{c}.
2. The sample is thermostated in the relaxed state at $T = T_{\mathrm{c}}$, rapidly loaded to the predetermined initial stress level, Δp_0, and then allowed to relax.

The temperature is adjusted in the range

$$T_{\mathrm{m},0} < T_{\mathrm{c}} < T_{\mathrm{m}}(\Delta p_0) \quad . \tag{50}$$

Crystallization starts at the initial stress, Δp_0, and is switched off when the stress falls to the level Δp^*, such that

$$T_{\mathrm{c}} = T_{\mathrm{m}}(\Delta p^*); \quad 0 < \Delta p^* < \Delta p_0 \quad . \tag{51}$$

The stress-relaxation parameter, β (or relaxation time, τ_{rel}), is a material characteristic controlled, first of all, by temperature. In isothermal conditions it can hardly be controlled, and its actual value has to be determined from separate stress-relaxation measurements. What can be evaluated in relaxation experiments is the global crystallinity, P_∞, produced in the relaxation run starting with Δp_0 and ending with Δp^*

$$P_\infty(\Delta p_0) = \int_{t(\Delta p)}^{t(\Delta p^*)} K(t')\mathrm{d}t' = -\frac{1}{\beta} \int_{\Delta p_0}^{\Delta p^*} \frac{K(\Delta p')\mathrm{d}\Delta p'}{\Delta p'} \quad . \tag{52}$$

Final crystallinities are obtained in crystallization runs involving the same temperature, T, but different initial stresses, Δp_0. Differentiation of the function obtained with respect to initial stress yields the total crystallization rate reduced by a relaxation parameter

$$\frac{\mathrm{d}P_\infty}{\mathrm{d}\Delta p_0} = \frac{1}{\beta} \frac{K(\Delta p_0)}{\Delta p_0} = \tau_{\mathrm{rel}} K(\Delta p_0)/\Delta p_0 \quad . \tag{53}$$

The total crystallization rates obtained can be compared with separately determined steady-state values to find deviations from quasistatic behavior caused by relaxational and athermal effects

$$K(\Delta p_0) - K_{\mathrm{st}}(\Delta p_0) = f(\tau, \dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}}) \quad . \tag{54}$$

The fact that in isothermal conditions the relaxation rate, β, cannot be easily controlled eliminates the possibility of finding individual components of the crystallization rate.

Crystallization under hydrostatic pressure

Crystallization experiments under pressure do not require precautions related to flow. In addition to constant-pressure experiments, we will discuss the constant-pressure-rate regime, in which the hydrostatic pressure changes linearly with time. When pressure is applied via compressed gas, controlled influx (or outflux) of gas to the pressurizing chamber is needed. Alternatively, in driven piston devices, controlled piston motion or steady motion of a dead load along a lever can be used.

Constant-pressure experiment

Transient and steady-state crystallization experiments performed at constant temperature and pressure are required for determination of the characteristic crystallization relaxation time, τ, and the steady-state crystallization rate, K_{st}, in the same way as suggested for tensile stress (see the preceding section) or temperature effects [9]. Theoretical and empirical models of crystallization rate under hydrostatic pressure are discussed in the Appendix.

Constant-pressure-rate experiment

In full analogy to the tensile stress case, $\ddot{p}_0$ and higher rates of pressure change disappear, and the total crystallization rate can be described as a power expansion over the constant parameter $(\tau\dot{p}_0)$

$$K(t) = K_{\mathrm{st}}[1 + G_1 \cdot (\tau\dot{p}_0) + G_2 \cdot (\tau\dot{p}_0)^2 + \cdots] \ . \tag{55}$$

Isothermal, constant-pressure-rate experiments are interpreted in the same way as in the tensile-stress case. By replacing Δp and $\Delta\dot{p}$ in Eq. (42) with p_0 and $\dot{p}_0$, respectively, the development of crystallinity assumes the form

$$\begin{aligned} P(t) = P[(p_0(t)] &= \frac{1}{\dot{p}_0}\int_0^{p_0} K(p_0')\mathrm{d}p_0' \\ &= \frac{1}{\dot{p}_0}\left[\int_0^{p_0} K_{\mathrm{st}}(p_0')\mathrm{d}p_0' \right. \\ &\quad \left. + (\tau p_0)\int_0^{p_0} G_1(p_0')K_{\mathrm{st}}(p_0')\mathrm{d}p_0' + \cdots\right] \ . \end{aligned} \tag{56}$$

Isothermal crystallization runs at constant pressure rates, $\dot{p}_0$, yield information about the steady-state crystallization rate and the first expansion function, G_1 in Eq. (26). Like in the tensile-stress case, the differentiated intercept of the experimental plot $(P \cdot \dot{p}_0)$ versus $\dot{p}_0$ yields the steady-state crystallization rate

$$K_{\mathrm{st}}(p_0) = \frac{\mathrm{d}}{\mathrm{d}p_0}\lim_{p_0 \to 0}(P \cdot \dot{p}_0) \tag{57}$$

and the initial slope determines the first expansion function, G_1, controlled by relaxational and athermal effects

$$G_1(p_0) = \frac{1}{\tau K_{\mathrm{st}}}\frac{\mathrm{d}}{\mathrm{d}p_0}\lim_{\dot{p}_0 \to 0}\frac{\mathrm{d}(P \cdot \dot{p}_0)}{\mathrm{d}\dot{p}_0} \ . \tag{58}$$

The theoretical prediction of athermal effects from nucleation theory is described in the Appendix. The ratio of athermal to thermal nucleation in isothermal, variable-pressure conditions is

$$\dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}} = \tau p_0 \cdot Y(T, p_0) \ . \tag{59}$$

In analogy to the tensile-stress case, the athermal characteristic Y in Eq. (22) can be expressed through the pressure-dependent free energy, or supercooling, ΔT. Assuming a linear dependence of Δf on p_0 (Appendix) one obtains

$$Y(T, p_0) \cong [\Delta f(T, p_0)]^{-5}\frac{\partial \Delta f}{\partial p_0} = \mathrm{const.}\left(\frac{T_{\mathrm{m}}}{\Delta T}\right)^5 \tag{60}$$

The pressure-dependent melting temperature is a well-defined characteristic, widely studied theoretically and experimentally. Some data for various polymers are collected in the Appendix (Table A1).

Appendix

Effect of tensile stress on crystal nucleation and crystallization rates of flexible-chain polymers

In the presence of tensile stress, Δp, the bulk free-energy density of crystallization assumes the form (cf. Ref. [6] Appendix, and Ref. [10])

$$\begin{aligned} \Delta f(\vartheta, \Delta p) &= \Delta f_0 + \delta f(\vartheta, \Delta p) \\ &= \Delta h - T\Delta s_0 \\ &\quad + T\delta s_{\mathrm{el}}(\Delta p) - (kT/v_0)\ln[4\pi w_{\mathrm{s}}(\vartheta; \Delta p)] \ . \end{aligned} \tag{A1}$$

Δf_0, Δh_0, and Δs_0 denote densities of bulk free energy, heat, and entropy of crystallization in the absence of stress. v_0 is the molecular volume of the crystallizing unit (chain segment). The extra free energy of crystallization due to stress is controlled by the entropy of the crystallizing amorphous phase, including the average elastic entropy of the polymer chains, δs_{el}, and the entropy of mixing differently oriented molecular units. The latter term appears as a result of the requirement that particles participating in an effective act of nucleation (clusters and single kinetic units) have to be consistently oriented with respect to each other [10]. All functions except w_{s} represent averages in the system of many chains. The orientation-dependent term is controlled by the distribution

Table A1 Effect of hydrostatic pressure on melting temperatures of various polymers (1 atm = 0.0981 MPa)

Polymer	$T_{\mathrm{m},0}$, K	$(\mathrm{d}T_{\mathrm{m}}/\mathrm{d}p_0)_0$, $K/10^3$ atm	Source
Polyethylene	415.7	26.1	[21]
		21	[22]
iso-Polypropylene	460.7	38.5	[23]
		24	[24]
	452.4	28.4	[25]
PET		50	[26]
	537.2	49.6	[25]
PVDF	480	38	[27]
Nylon 66	540	22.4	[25]
Polyoxymethylene	458	15.8	[28]

of crystallizing units, $w_s(\vartheta;\Delta p)$ and gives rise to selective crystallization: differently oriented crystals are nucleated at different temperatures and different speeds [10]. The orientation of the growing cluster and that of the oncoming kinetic unit, ϑ, is represented by a set of Euler angles which, for uniaxial, tensile stress, reduces to the single angle, ϑ.

With the intramolecular statistics of a polymer chain characterized by the inverse Langevin function, $L^*(x)$

$$W_0(\mathbf{h}) = \text{const.}\exp\left(-N\int_0^{h/N1} L^*(x)\mathrm{d}x\right) \tag{A2}$$

the elastic entropy density reduces to

$$\begin{aligned}\delta s_{\text{el}} &= (k/Nv_0)\langle \ln W(\mathbf{h})\rangle \\ &= -(k/v_0)\iiint\left(\int_0^{h/N1} L^*(x)\mathrm{d}x\right)W(h)\mathrm{d}^3\mathbf{h} \ .\end{aligned} \tag{A3}$$

The orientation distribution of segments

$$\begin{aligned}w_s(\mathbf{T}) = \iiint &\frac{L^*(h/N1)}{2sh[L^*(h/N1)]} \\ &\times \exp[L^*(h/N1)(\mathbf{h}\cdot\mathbf{T})/h1]W(\mathbf{h})\mathrm{d}^3\mathbf{h} \ .\end{aligned} \tag{A4}$$

T is a unit vector directed along the symmetry axis of a chain segment. Averaging in Eqs. (A3) and (A4) is performed with the actual, stress-controlled end-to-end distribution function, $W(\mathbf{h})$.

The critical transition temperature, T_m, like other thermodynamic and kinetic characteristics, depends on stress and orientation. From the condition

$$\Delta f(\vartheta,\Delta p) = 0. \tag{A5}$$

combined with Eq. (A1) one obtains

$$T_m(\vartheta;\Delta p) = \frac{\Delta h_0}{\Delta s_0 - \delta s_{\text{el}} + (k/v_0)\ln[4\pi w_s(\vartheta,\Delta p)]} \ . \tag{A6}$$

In an unstressed and unoriented system we have, independent of orientation,

$$T_{m,0} = \Delta h_0/\Delta s_0 \tag{A7}$$

and Eq. (A6) can be presented in the reduced form, as

$$\begin{aligned}&T_m(\vartheta;\Delta p) \\ &\quad = T_{m,0}\frac{\Delta h_0}{\Delta h_0 - T_{m,0}\delta s_{\text{el}} + (kT_{m,0}/v_0)\ln[4\pi w_s(\vartheta,\Delta p)]} \ .\end{aligned} \tag{A8}$$

The critical transition temperatures under stress are elevated in the range of preferred orientations (high values of the distribution density, $w_s > 1/4\pi$), and are suppressed for infrequent orientations ($w_s \le 1/4\pi$). Changes in crystallization (and melting) temperatures are commonly observed in stress-induced crystallization.

It can be shown that the average elastic entropy of flexible chains, which contributes to the crystallization temperature, can be expanded in a series of the average tensile stress, starting with the quadratic term

$$\begin{aligned}\delta s_{\text{el}}(\Delta p) = -(k/6v_0)\big[&(\Delta pNv_0/kT)^2 \\ &- (2/9)(\Delta pNv_0/kT)^3 + \cdots\big] \ .\end{aligned} \tag{A9}$$

N is the number of statistical segments in the chain, and v_0 is the molecular volume of a single segment. On the other hand, expansion of the logarithm of the orientation distribution function starts with a linear stress term

$$\begin{aligned}&(k/v_0)\ln[4\pi w_s(\vartheta,\Delta p)] \\ &\quad = \left(3k\cos^2\vartheta/2Nv_0\right) \\ &\qquad \times [\Delta pNv_0/kT + (\cdots)(\Delta pNv_0/kT)^2 + \cdots] \ .\end{aligned} \tag{A10}$$

The critical cluster size, g^*, and the corresponding maximum free energy, ΔF^*, can be presented in the reduced form (cf. Ref. [6], Appendix) as

$$\begin{aligned}\frac{g^*(\vartheta,\Delta p)}{g_0^*} &= \left(\frac{\Delta f_0}{\Delta f(\vartheta,\Delta p)}\right)^3 \\ &= \left(\frac{T_{m,0}-T}{T_m(\vartheta,\Delta p)-T}\right)^3\left(\frac{T_m}{T_{m,0}}\right)^3 .\end{aligned} \tag{A11}$$

$$\begin{aligned}\frac{\Delta F^*(\vartheta,\Delta p)}{\Delta F_0^*} &= \left(\frac{\Delta f_0}{\Delta f(\vartheta,\Delta p)}\right)^2 \\ &= \left(\frac{T_{m,0}-T}{T_m(\vartheta,\Delta p)-T}\right)^2\left(\frac{T_m}{T_{m,0}}\right)^2 \ .\end{aligned} \tag{A12}$$

The ratio of the athermal to the thermal nucleation rate is determined by the cluster density function, ρ, and its gradient near $g = g^*$ [cf. Ref. [6], Appendix]

$$\dot{N}_{\text{ath}}/\dot{N}_{\text{th}} = \frac{1}{D_{\text{gr}}(g^*)}\frac{\mathrm{d}g^*}{\mathrm{d}t}\frac{\rho(g^*)}{(\partial\rho/\partial g)_{g^*}} \ . \tag{A13}$$

The "growth diffusion coefficient", D_{gr}, is inversely proportional to the crystallization relaxation time, τ, related to molecular mobility. Using the approximate cluster distribution described in the Appendix of Ref. [6] the ratio of athermal and thermal nucleation rates reduces to a function of the critical cluster size, g^*

$$\begin{aligned}\dot{N}_{\text{ath}}/\dot{N}_{\text{th}} &\cong -\text{const.}\,\tau\cdot(g^*)^{1/3}\frac{\mathrm{d}g^*}{\mathrm{d}t} \\ &= -\text{const.}\tau\cdot(g^*)^{1/3}\frac{\partial g^*}{\partial\Delta p}\frac{\mathrm{d}\Delta p}{\mathrm{d}t} \ .\end{aligned} \tag{A14}$$

Alternatively (cf. Eq. A11)

$$\dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}} \cong \mathrm{const.}\,\tau\left(\frac{1}{\Delta f}\right)^{5}\frac{\partial\Delta f}{\partial\Delta p}\frac{\mathrm{d}\Delta p}{\mathrm{d}t}$$
$$= \mathrm{const}'\tau\left(\frac{T_{\mathrm{m}}}{\Delta T}\right)^{5} T\left[\frac{\partial\delta s_{\mathrm{el}}}{\partial\Delta p} - \frac{k}{v_0}\frac{\partial\ln w_{\mathrm{s}}}{\partial\Delta p}\right]\frac{\mathrm{d}\Delta p}{\mathrm{d}t}\ . \tag{A15}$$

Considering the first terms of Eqs. (A9) and (A10) we obtain

$$\dot{N}_{\mathrm{ath}}/\dot{N}_{\mathrm{th}} \cong \mathrm{const.}\,\tau\left(\frac{T_{\mathrm{m}}}{\Delta T}\right)^{5}\left[\frac{N^2 v_0}{3kT}\Delta p + \frac{3}{2}\cos^2\vartheta\right]\frac{\mathrm{d}\Delta p}{\mathrm{d}t}\ . \tag{A16}$$

It should be noted that the observed crystallization (or melting) temperature, T_{m}, which is sensitive to local orientation, does not provide a good variable for experimental correlations.

Empirical expressions for crystallization rates in stressed (oriented) polymers have been proposed by several authors. The most popular approach, dating back to Kobayashi and Nagasawa [11] and later used by other authors [12, 13], refers to nucleation and growth rates with the free energy modified by the elastic energy of the crystallizing chains. n-dimensional crystal growth combined with sporadic (thermal) nucleation yields the Avrami crystallization rate constant

$$K_{\mathrm{m}} = \mathrm{const.}\ \dot{N}_{\mathrm{th}}G^{n}\ , \tag{A17}$$

where $\dot{N}_{\mathrm{th}}$ denotes the primary nucleation rate and G is the secondary nucleation-controlled, linear growth rate. The kinetic characteristics scale with free energy and supercooling as

$$\dot{N}_{\mathrm{th}}(\Delta p) = \mathrm{const.}\,\tau^{-1}\exp\left(-C_1/T\Delta f^2\right)$$
$$= \mathrm{const}'\,\tau^{-1}\exp\left(-C_1' T_{\mathrm{m}}^2/T\Delta T^2\right) \tag{A18}$$

$$G(\Delta p) = \mathrm{const.}\,\tau^{-1}\exp(-C_2/T\Delta f)$$
$$= \mathrm{const}'\,\tau^{-1}\exp\left(-C_2' T_{\mathrm{m}}^2/T\Delta T\right)\ . \tag{A19}$$

The stress-affected crystallization rate in the reduced form assumes the form [11]

$$K_{\mathrm{m}}(\Delta p)/K_{\mathrm{m},0} \cong \exp\left[\frac{C_1}{T}\left(\frac{T_{\mathrm{m},0}^2}{\Delta T_0^2} - \frac{T_{\mathrm{m}}^2}{\Delta T^2}\right) + \frac{nC_2}{T}\left(\frac{T_{\mathrm{m},0}}{\Delta T_0} - \frac{T_m}{\Delta T}\right)\right]\ . \tag{A20}$$

The "relaxation time", τ, in Eqs. (A18) and (A19) accounts for the molecular mobility which can be approximated with an Arrhenius or Williams–Landel–Ferry (WLF) model (cf. Eq. A32). The relaxation time, τ, the heat of melting, Δh_0, and the interface tensions, σ_{s} and σ_{e}, implicitly included in Eqs. (A15)–(A20), are assumed to be independent of stress, and do not appear in the reduced formula. For n-dimensional growth of predetermined nuclei, the first term in the exponent of Eq. (A20) drops out, and the crystallization rate reduces to

$$K_{\mathrm{m}}(\Delta p)/K_{\mathrm{m},0} \cong \exp\left[\frac{nC_2}{T}\left(\frac{T_{\mathrm{m},0}}{\Delta T_0} - \frac{T_{\mathrm{m}}}{\Delta T}\right)\right]\ . \tag{A21}$$

Application of Eq. (A20) requires knowledge of at least five material characteristics: C_1, C_2, $K_{\mathrm{m},0}$, n, and the stress-dependent free energy, Δf, or undercooling, ΔT. At least four characteristics are required for evaluation of Eq. (A21).

An alternative, empirical approach has been proposed by Ziabicki [14, 15] and subsequently applied by Alfonso et al. [16]. The steady-state crystallization rate in an oriented system, $K_{\mathrm{st}}(T, f_{\mathrm{or}})$ is presented in the form of an empirical expression

$$K_{\mathrm{st}}(f_{\mathrm{or}}) = K_{\mathrm{st},0}(T)\exp\left[A(T)f_{\mathrm{or}}^2\right]\ , \tag{A22}$$

where f_{or} is an axial orientation factor. The square term accounts for the deformation entropy, δs_{el}, [14], similar to Eq. (A9). Based on the "stress-optical relation", f_{or} can be converted to the stress difference Δp, to yield

$$K_{\mathrm{st}}(\Delta p) = K_{\mathrm{st},0}(T)\exp\left[A(T)\Delta p^2\right]\ . \tag{A23}$$

The steady-state crystallization rate in the absence of stress is approximated using a truncated Gaussian function [15, 17]

$$K_{\mathrm{st},0}(T) = \begin{cases} K_{\max}\exp[-4\ln 2(T - T_{\max})^2/D_{1/2}^2] & \text{for Tm>T>T}g \\ 0 & \text{for Tm}\geq\text{T} \\ & \text{or T}\leq\text{T}g\ . \end{cases} \tag{A24}$$

Evaluation of Eqs. (A23) and (A24) requires three material constants, $K_{\max}$, $T_{\max}$, and $D_{1/2}$, for unoriented (unstressed) conditions, plus the stress (orientation) function, $A(T)$. All these characteristics can be obtained empirically. Available data for unstressed crystallization have been compiled in Ref. [15] and other sources. Values of the temperature-dependent orientation characteristic, $A(T)$, for preoriented polyethylene terephthalate have been discussed in Ref. [16].

The mathematical simulation of crystallization in fiber spinning processes (which involves simultaneous changes of temperature and tensile stress) was based on variations of the Kobayashi–Nagasawa model, [12, 13, 18] or empirical relations using Eqs. (A23) and (A24). No systematic studies of stress-dependent crystallization rates or selective, orientation-differentiated crystallization have been published.

Effects of hydrostatic pressure on nucleation and crystallization rates of flexible-chain polymers

The lack of orientation makes average thermodynamic characteristics universally applicable, and experimentally observed melting temperatures can be used for the description of thermodynamic and kinetic behavior.

The relation between melting temperature, T_{m}, and hydrostatic pressure, p_0, is given by the Clausius–Clapeyron equation

$$\frac{\mathrm{d}p_0}{\mathrm{d}T_{\mathrm{m}}} = \frac{\Delta h}{T_{\mathrm{m}}\Delta v} \ , \tag{A25}$$

where Δh is the heat of crystallization, and Δv is the volume change. The equilibrium melting temperature can be expanded over pressure to yield

$$T_{\mathrm{m}}(p_0) = T_{\mathrm{m},0}\left[1 + a_1 p_0 + a_2 p_0^2 + \cdots\right] \ . \tag{A26}$$

$T_{\mathrm{m},0}$ refers to selected standard conditions (most often atmospheric pressure, $p_0 = 0$). The excess pressure, p_0, affects, above all, the density of the crystallizing system. Consequently, in the bulk free energy of crystallization there appears an additional (usually negative) term expandable in powers of pressure

$$\begin{aligned}\Delta f(p_0) &= \Delta f_0 + \delta f(p_0)\\ &= \Delta h_0 - T\Delta s_0 - \left(\alpha_1 p_0 + \alpha_2 p_0^2 + \cdots\right) \ .\end{aligned} \tag{A27}$$

In contrast to tensile stress, hydrostatic pressure does not induce orientation. The pressure-dependent critical transition temperature, T_{m}, results in the form

$$T_{\mathrm{m}}(p_0) = \frac{\Delta h_0 + \delta f(p_0)}{\Delta s_0} = T_{\mathrm{m},0}\left[1 + \delta f(p_0)/\Delta h_0\right] \ . \tag{A28}$$

Δh_0, Δs_0, and $T_{\mathrm{m},0}$ denote thermodynamic characteristics in the reference state (standard pressure). As a rule, crystallization (melting) temperatures for polymers lie above the atmospheric level.

Pressure-dependent crystallization (or melting) temperatures have been studied for several polymers. Some results are shown in Table A1.

The critical cluster size, g^*, reduced by a similar quantity for a standard-pressure system ($p_0 = 0$), reads

$$\begin{aligned}\frac{g^*(p_0)}{g_0^*} &= \left(\frac{\Delta f_0}{\Delta f(p_0)}\right)^3\\ &= \left(\frac{T_{\mathrm{m},0} - T}{T_{\mathrm{m}}(p_0) - T}\right)^3 \left(\frac{T_{\mathrm{m}}(p_0)}{T_{\mathrm{m},0}}\right)^3 \ .\end{aligned} \tag{A29}$$

Similarly, the reduced maximum free energy of nucleation, ΔF^*, reads

$$\begin{aligned}\frac{\Delta F^*(p_0)}{\Delta F_0^*} &= \left(\frac{\Delta f_0}{\Delta f(p_0)}\right)^2\\ &= \left(\frac{T_{\mathrm{m},0} - T}{T_{\mathrm{m}}(p_0) - T}\right)^2 \left(\frac{T_{\mathrm{m}}(p_0)}{T_{\mathrm{m},0}}\right)^2 \ .\end{aligned} \tag{A30}$$

The way in which nucleation characteristics are used for calculation of the overall crystallization rates is the same as in the case of tensile stress. In analogy to Eq. (A20), one can write the pressure-dependent Avrami crystallization rate constant in the form

$$\begin{aligned}&K_{\mathrm{m}}(p_0)/K_{\mathrm{m},0}\\ &= \left[\tau_0/\tau(p_0)\right]\exp\left[\frac{C_1}{T}\left(\frac{1}{\Delta f_0^2} - \frac{1}{\Delta f^2}\right) + \frac{nC_2}{T}\left(\frac{1}{\Delta f_0} - \frac{1}{\Delta f}\right)\right]\\ &= \left[\tau_0/\tau\right]\exp\left[\frac{C_1}{T}\left(\frac{T_{\mathrm{m},0}^2}{\Delta T_0^2} - \frac{T_{\mathrm{m}}^2}{\Delta T^2}\right) + \frac{nC_2}{T}\left(\frac{T_{\mathrm{m},0}}{\Delta T_0} - \frac{T_{\mathrm{m}}}{\Delta T}\right)\right] \ .\end{aligned} \tag{A31}$$

There are reasons to expect that molecular mobility (and relaxation time, τ) would change with pressure. If τ is approximated by the WLF model [29], the ratio of relaxation times can be related to the pressure-affected glass-transition temperature, T_{g}

$$\begin{aligned}\tau(T,p_0)/\tau_0(T) \cong{}& \left[\tau(T_g,p_0)/\tau_0(T_{g,0})\right]\\ &\times \exp\left[-17.44\left(\frac{T - T_g(p_0)}{T - T_g(p_0) + 51.6}\right.\right.\\ &\left.\left.- \frac{T - T_{\mathrm{g},0}}{T - T_{g,0} + 51.6}\right)\right] \ .\end{aligned} \tag{A32}$$

Alternatively, one can approximate the overall steady-state crystallization rate $K_{\mathrm{st}}(p_0)$ with an empirical expression, similar to Eq. (A23)

$$K_{\mathrm{st}}(T,p_0) = K_{\mathrm{st},0}(T)\exp[B(T)\cdot p_0] \ . \tag{A33}$$

The function $K_{\mathrm{st},0}(T)$ is given by Eq. (A24) and the additional material function, $B(T)$, should be found from experiments.

Using the approximate cluster distribution described in Ref. [6] the ratio of athermal and thermal nucleation rates can be expressed through the critical cluster size, g^*

$$\frac{\dot{N}_{\mathrm{ath}}}{\dot{N}_{\mathrm{th}}} \cong -\text{const.}\ (g^*)^{1/3}\tau\frac{\partial g^*}{\partial p_0}\frac{\mathrm{d}p_0}{\mathrm{d}t} \ . \tag{A34}$$

Expressed in terms of the free energy or undercooling

$$\begin{aligned}\frac{\dot{N}_{\mathrm{ath}}}{\dot{N}_{\mathrm{th}}} &\cong -\text{const.}\ \tau\left(\frac{1}{\Delta f}\right)^5\frac{\partial\Delta f}{\partial p_0}\frac{\mathrm{d}p_0}{\mathrm{d}t}\\ &= \text{const.}\ \tau\left(\frac{T_{\mathrm{m}}}{\Delta T}\right)^5\frac{\partial\delta f}{\partial p_0}\frac{\mathrm{d}p_0}{\mathrm{d}t} \ .\end{aligned} \tag{A35}$$

Assuming a linear change of free energy with pressure (first term of Eq. A27) Eq. (A35) reduces to

$$\frac{\dot{N}_{\mathrm{ath}}}{\dot{N}_{\mathrm{th}}} = \tau\dot{p}_0\cdot Y(T,p_0) = \text{const.}\ \tau\left(\frac{T_{\mathrm{m}}}{\Delta T}\right)^5\dot{p}_0 \ . \tag{A36}$$

According to the nucleation model considered, the main pressure-sensitive characteristic is the melting temperature, T_m. The available experimental data show an increase of T_m with pressure (Table A1) and a considerable effect of T_m on crystallization rates. The experimental study of the crystallization kinetics of isotactic polypropylene and Nylon 66 [25] indicates a linear dependence of the logarithm of the Avrami constant with temperature and a considerable increase to the crystallization rates with pressure. Although crystallization of polyethylene terephthalate (PET) could not be described with a linear Avrami plot, the effect of pressure was quite evident [25]. A crystallization study of PET by Phillips and Tseng [30] and crystallization of isotactic polypropylene [24] indicated a considerable increase in nucleation and spherulite growth rates with pressure.

Accumulation of empirical data makes simulation of crystallization in industrial processes possible. For this purpose, Ito et al. [31] used nucleation-based equations somewhat similar to Eq. (A31). Hieber [32] analyzed the experimental data of Karl et al. [28], He and Zoller [33], and Leute et al. [34] on crystallization kinetics of polypropylene under pressure and found a useful correlation for the temperature- and pressure-controlled crystallization rate in the form

$$\ln K(T, p_0) = B_1 + B_2(T - T_{\text{shift}}) + B_3(T - T_{\text{shift}})^2 \ , \tag{A37}$$

where

$$T_{\text{shift}}(p_0) = B_4 p_0 + B_5 (p_0)^2 \ . \tag{A38}$$

More recently, Fasano et al. have studied the isobaric, nonisothermal crystallization of polypropylene and arrived at another empirical formula for the crystallization rate:

$$\begin{aligned} K(T, p_0) = K_0 \exp\left(\frac{E_a}{R[T - T_g(p_0)]}\right) \\ \times \exp\left(\frac{-K_g[T_m(p_0) + T]}{2T^2[T_m(p_0) + T]}\right) \ , \end{aligned} \tag{A39}$$

where K_0 and K_g are constants, and the melting (T_m) and glass-transition (T_g) temperatures are linear functions of pressure, p_0.

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