

# KINETIC MODEL OF POLYMER CRYSTALLIZATION UNDER HIGH TENSILE STRESS OR MOLECULAR ORIENTATION

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## 1. General

Molecular deformation and orientation in the amorphous phase subjected to tensile stresses strongly accelerates crystallization of polymers by orders of the magnitude. Closed-form analytical formula is derived for the crystallization rate under high tensile stresses in the entire range of crystallization temperature and the temperature rates. Such formula, lacking in the literature, is needed for modelling of the dynamics of crystallizing polymers processing and predicting structure development in obtaining highly oriented materials of enhanced tensile modulus and tenacity. Rapid online crystallization strongly influences the rheological behaviour during the processing and introduces coupling of crystallization with the processing dynamics. Tensile stress affects the crystallization rate mainly by influencing the configurational entropy of the chain macromolecules in amorphous phase. In our earlier publication [1], a series expansion approach of the crystallization rate over the amorphous orientation factor has been considered basing on the Gaussian statistics of configurations of linear flexible chains, limited to low tensile stresses and orientation. None of the actually available models are capable to account for the effects of high molecular orientation in the crystallization kinetics.

In the present approach, non-Gaussian chain statistics is considered to account for finite extensibility of real macromolecules in the amorphous phase under high tensile stresses which results in non-linear effects in the model. The Hoffman-Lauritzen model of crystallization kinetics is extended to account for free energy of deformation of the amorphous component under uniaxial molecular orientation produced by the tensile stresses. The crystallization rate is considered as controlled by predetermined and sporadic nucleation present in real systems. The involvement of both nucleation mechanisms in the crystallization kinetics varies strongly with the level of tensile stress and amorphous orientation, with domination of sporadic nucleation at high orientations. The closed-form analytical formulas are validated by computations. Example numerical calculations illustrate influence of amorphous orientation on the crystallization free energy and the crystallization rate function involving both nucleation mechanisms.

## 2. The model formulations

The progress of crystallization  $X(t)$  is controlled by nucleation followed by crystal growth, both driven by the crystallization free energy affected by the tensile stress and orientation in the entire crystallization temperature range. We use the crystallization rate formula in the quasi-static approximation extended for the transformations under variable amorphous orientation factor  $f_a(t)$  and temperature  $T(t)$

$$\frac{dX}{dt} = nK[T(t), f_a(t)](1-X)[\ln(1-X)]^{-(n-1)/n}$$

where temperature- and orientation-dependent function  $K(T, f_a)$  represents the rate of crystallization and is inversely proportional to the crystallization half-time.  $f_a$  characterizes orientation of the chain segments in the amorphous phase and varies from zero at no orientation and unity at full uniaxial chain alignment,  $n$  is the Avrami exponent. For the transformation controlled by predetermined nucleation, the  $K(T, f_a)$  function expresses by the linear growth rate of crystals, while for the processes controlled by sporadic, homogeneous nucleation – by the product of the nucleation and the crystal growth rates. The orientation-dependent free energy of crystallization  $\Delta g(T, f_a)$  increases with increasing  $f_a$ , and the thermodynamic barriers of nucleation

and crystal growth are reduced the more, the higher is the orientation. The largest contribution of the orientation, or the orienting stress, to the thermodynamic driving force of crystallization comes from the decrease of the configurational entropy,  $\delta s_a(f_a) < 0$ , of  $\nu$  amorphous macromolecules per unit volume

$$\Delta g(T, f_a) \cong \Delta g^0(T) + T\delta s_a(f_a)$$

where  $\delta s_a = \nu Nk \left[ \left\langle \int_0^{h/Na} L^{-1}(x) dx \right\rangle_{w(\mathbf{h}, t)} - \left\langle \int_0^{h/Na} L^{-1}(x) dx \right\rangle_0 \right]$  is the difference of the molecular entropies

averaged over the distributions of the chain end-to-end vectors  $\mathbf{h}$  under the stress at the instant of time  $t$  and at the isotropic relaxed state, respectively,  $N$  is the number of statistical segments of length  $a$  in the macromolecule,  $L^{-1}(x)$  - the inverse Langevin function,  $k$  - the Boltzmann constant.

The orientation factor  $f_a$  and deformation entropy  $\delta s_a$  are calculated for distribution of chain macromolecules in the fluid subjected to uniaxial elongational flow. Effectivity of the tensile stress on the orientation and the deformation entropy in the flow is determined by the product  $\dot{q}\tau$  of the elongation rate and a molecular stretch relaxation time. Time-evolution of the molecular deformation is described by the coupled equations for the chain extension coefficients  $\lambda$  and  $\lambda_{\perp}$  along and perpendicular to the flow axis, respectively [2]

$$\frac{d\lambda^2}{d(t/\tau)} + [E(\lambda, \lambda_{\perp}) - 2\dot{q}\tau]\lambda^2 - 1 = 0, \quad \frac{d\lambda_{\perp}^2}{d(t/\tau)} + [E(\lambda, \lambda_{\perp}) + \dot{q}\tau]\lambda_{\perp}^2 - 1 = 0$$

where  $E$  is the Peterlin modulus of non-linear elasticity of the system dependent on the average chain extension coefficients which varies between unity at zero tensile stress and infinity at full extension of the macromolecules. Analytical formulas are derived for the dependence of the orientation factor  $f_a$  and the deformation entropy  $\delta s_a$  on the coefficients  $\lambda$  and  $\lambda_{\perp}$  during the deformation time,  $t/\tau$ . The inverse Langevin function is approximated by a series expansion with the first non-Gaussian term,  $L^{-1}(x) = 3x + 9x^3/5$ , and by a Padé approximation,  $L^{-1}(x) = x(3-x^2)/(1-x^2)$ , valid in the entire range of the chain extensions. The values of the deformation entropy  $\delta s_a$  vs. orientation factor  $f_a$  coincide in a single master plot formula  $\delta s_a(f_a)$ , independently on the elongation rate  $\dot{q}\tau$  and the time  $t/\tau$ , but affected by the inverse Langevin function approximations.

### 3. The main results

For the Padé approximation, the master plot  $\delta s_a(f_a)$  is predicted for the entire range of the orientation factor  $f_a$  between zero and unity. In the range of low  $f_a$  values, the master relation based on the first non-Gaussian term approximation shows slightly better formula than that obtained basing on the Padé approximation, and approaches the Gaussian limit at zero orientation. The closed-form analytical formulas approximate the  $\delta s_a(f_a)$  master relation, one in the range of small and intermediate orientations (basing on the first non-Gaussian term approximation) and second one for high orientations (basing on the Padé approximation). The analytical formulas are very well validated by the exact computations of  $f_a$  and  $\delta s_a$  at various elongation rates and the deformation times. The master relation can be expressed also in terms of the tensile stress,  $\Delta p$ , with the use of the stress-orientation formula presented in ref. [3] for both molecular statistics. With the  $\delta s_a(f_a)$  or  $\delta s_a(\Delta p)$  relations the rate functions  $K(T, f_a)$  based on the Hoffman-Lauritzen model of crystallization kinetics express in terms of  $f_a$ , or  $\Delta p$ , for predetermined, as well as for sporadic nucleation. Conditions for equal contribution of both nucleation mechanisms in terms of  $f_a$  or  $\Delta p$  are defined.

### References

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- [2] A. Schoene, A. Ziabicki and L. Jarecki. Transient uniaxial orientation of flexible polymer chains in a wide range of elongation rates. *Polymer*, 46:3927, 2005.
- [3] L. Jarecki and B. Misztal-Faraj. Non-linear stress-orientation behavior of flexible-chain polymers under fast elongational flow. *Eur. Polymer J.*, 95:36, 2017.