Size distribution of folded chain crystal nuclei of polyethylene on active centers

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Kinetic equations describing temporal evolution of the size distribution of crystalline nuclei of folded chain polyethylene on active centers are solved numerically. Basic characteristics of nucleation processes (the total number of supercritical nuclei and the size distribution of nuclei) are determined and compared with the experimental data. It is shown that even though the total number of supercritical nuclei coincides with the experimental data, the size distribution prediction fails. This is caused by the fact that the total number of nuclei (usually used in analysis of the experimental data), in contrast to the size distribution of nuclei, represents an integral quantity. Using the experimental data of the steady state size distribution of nuclei enables us to determine thermodynamic parameters (especially interfacial energies) of the studied system more precisely and consequently to correct kinetic parameters to get coincidence of kinetic model with the experimental data in both, the total number of supercritical nuclei and also the size distribution of nuclei. © *2011 American Institute of Physics*. [doi:10.1063/1.3571457]

I. INTRODUCTION

Nucleation is a process leading to the formation of a new phase. During formation of nuclei some energetic barrier (called nucleation barrier) must be overcome. The work of formation of nuclei has a maximum at the critical size. The subcritical nuclei have a tendency to shrink and the supercritical nuclei grow to macroscopic sizes.

Up to this time, nucleation is not fully comprehensible, especially in polymer systems, where building units (monomers) of a new phase consist of several molecules. For polyethylene, crystallization building unit corresponds to CH_2 group, which is bounded with other building units even within the melt. Thus, it is difficult to model kinetics of crystallization of such a complex system. Nevertheless, it is important to have the crystallization of polymers under control in order to influence the structure and the morphological stability and, consequently, the physical properties of polymeric materials.[1–3]

Various theoretical models studied nucleation and crystallization of polymers. Molecular dynamics studies[4–6] enable detailed studies on the structures under isothermal and nonisothermal conditions. The effect of temperature on homogeneous nucleation and crystal growth for isothermal polymer crystallization was modeled by the size distribution model.[7] Monte Carlo simulations[8] provide a useful tool to understand the conformational and statistical properties of polymers. The continuum theory of polymer crystallization[9] accounts for the accumulation of polymer chains near the growth front and shows consequences for nucleation and diffusion processes. The phase behavior of athermal polymer/nanoparticle blends near a substrate was investigated using the density functional theory.[10] Despite by these theoretical efforts, nucleation and crystallization of polymers are not fully understood up to this time.

We studied kinetics of crystal nucleation of folded chain polyethylene on active centers. Adding of nucleation agent to the melt increased the number of nuclei of crystalline polyethylene formed within a unit volume.[11–13] Kinetic model of nucleation on active centers[14,15] was modified for the case of polymer crystallization.[16,17] In this model we took into account the depletion effect, when the active center serves as a nucleation site (where nucleation process starts) only if there was no new nucleus formed. As a consequence, the number of active centers decreases with time as nuclei are formed. We used[16] available thermodynamic parameters for polyethylene crystallization, supposing the three-dimensional shape of critical nucleus (3D model). For such parameters, analysis of the experimental data shows that the height of nucleus was lower than the mean distance between building units and this is a reason why we consider the two dimensional-model (2D model). In this case the total number of supercritical nuclei was in very good coincidence with the experimental measurement.[11] Recently, Okada *et al.*,[18,19] experimentally determined, using small angle x-ray scattering, the relative size distribution of nuclei. These recent experimental data (the time dependence of the size distribution for the near-critical nucleus size) give us the possibility to test the standard analysis of nucleation process, when the total number of nuclei is computed and compared with the experimental data.[20,21] The aim of this work is to show if the standard analysis (based on the total number of nuclei, which is an integral quantity in difference to the direct comparison with the size

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distribution) gives the reasonable predictions also for the size distribution.

II. MODEL

We use the same model of polymer crystallization on active centers as in our previous work (for details see Kožíšek *et al.*[16] and the references therein). Kinetic model of nucleation on active centers was originally used for nucleation of crystallites on heterogeneous surface from a vapor phase.[14] Let us briefly summarize the basic equations.

In nucleation theory formation of clusters plays an important role (subcritical or supercritical nuclei), which can be expressed for the (3D) polyhedral form by

$$\Delta G = -nlm\Delta\mu + 2lm\sigma^1 + 2nm\sigma_e^1 + nl\Delta\sigma^1, \quad (1)$$

where $\Delta\sigma = \sigma_{CL} + \sigma_{AC} - \sigma_{AL}$ and σ_{CL}, σ_{AC}, and σ_{AL} designate the interfacial energies between nucleus and liquid, nucleus and nucleation agent, and nucleus agent and liquid, and n, m, l designate the numbers of monomers on corresponding walls of the nucleus. The dimensions of the elementary unit of polyethylene $a_0 = 4.55 \times 10^{-10}$ m, $b_0 = 1.27 \times 10^{-10}$ m, and $c_0 = 4.15 \times 10^{-10}$ m (for details see Kožíšek *et al.*[16]). Superscript 1 in Eq. (1) expresses that the interfacial energies are taken per one monomer (growth unit), i.e., $\sigma^1 = b_0 c_0 \sigma$ and similarly for σ_e^1 and $\Delta\sigma^1$. The difference in chemical potentials is given by

$$\Delta\mu = \frac{\Delta h_E}{N_A T_m^0}\Delta T, \quad (2)$$

where $\Delta h_E = 4.11$ kJ/mol, $T_m^0 = 412.65$ K (for polyethylene), N_A is the Avogadro constant, $\Delta T = T_m^0 - T$ is supercooling, and T denotes the absolute temperature. Condition of ΔG extreme implies the critical numbers of monomers on the sidewalls

$$n^* = \frac{4\sigma^1}{\Delta\mu}, \quad l^* = \frac{4\sigma_e^1}{\Delta\mu}, \quad \text{and} \quad m^* = \frac{2\Delta\sigma^1}{\Delta\mu}. \quad (3)$$

The critical number of monomers forming the nucleus is thus

$$i^* = n^* l^* m^* = \frac{32\sigma^1\sigma_e^1\Delta\sigma^1}{(\Delta\mu)^3}. \quad (4)$$

We suppose that the nucleus shape remains unchanged during phase transition and exhibits the same form as the critical nucleus (we are interested in the behavior of the system near the critical size), thus

$$\frac{n}{l} = \frac{n^*}{l^*} = \frac{\sigma^1}{\sigma_e^1}; \quad \frac{n}{m} = \frac{n^*}{m^*} = \frac{2\sigma^1}{\Delta\sigma^1}. \quad (5)$$

The work of formation of nuclei can be simplified (for numerical computation) to be

$$\Delta G = -i\Delta\mu + \beta i^{2/3}, \quad (6)$$

where $i = nlm$ denotes the number of monomers forming the nucleus and

$$\beta = 3\sqrt[3]{4\sigma^1\sigma_e^1\Delta\sigma^1}. \quad (7)$$

At critical size, ΔG reaches its maximum value. Subcritical nucleus has a tendency to shrink and supercritical one grows.

In our previous analysis,[16] we determined critical sizes on the sidewalls to be $n^* = 9.8$, $l^* = 118$, and $m^* = 0.57$ at the supercooling $\Delta T = 10.4$ K. We are interested in nucleation near the critical size and that is why we fixed $m = 1$ for physical reasons. Thickness of nucleus was fixed to "monolayer" and we denote this model as 2D model. Recently, Okada *et al.*[18] showed that the interfacial energies of nucleus near nanometer cluster size (i.e., near the critical size) are lower than macroscopic values, and for these new values of the interfacial energies we determined the critical sizes to be: $n^* = 8.9$, $l^* = 24.9$, $m^* = 2.2$, and $i^* = 487.5$—for details see Sec. III. The height of the critical nucleus $m^* > 1$ and there is no reason to fix $m = 1$. We denote this model as 3D model (m is not fixed in the difference of 2D model).

Temporal evolution of the number density of nuclei formed by i monomers, F_i, is governed by

$$\frac{dF_i}{dt} = k_{i-1}^+ F_{i-1} - [k_i^+ + k_i^-]F_i + k_{i+1}^- F_{i+1} = J_{i-1} - J_i, \quad (8)$$

where

$$J_i = k_i^+ F_i - k_{i+1}^- F_{i+1} \quad (9)$$

denotes the number of nuclei of size i formed in unit volume per unit time. Attachment frequency, k_i^+, can be expressed as (for details see Kožíšek *et al.*[16])

$$k_i^+ = 2l\left(\frac{k_B T}{h}\right)\exp\left(-\frac{E}{k_B T}\right)\exp\left(-\frac{q\Delta g_i}{k_B T}\right), \quad (10)$$

where $\Delta g_i = \Delta G_{i+1} - \Delta G_i$, $q = 0.5[1 + \text{sign}(\Delta g_i)]$, k_B is the Boltzmann constant, h denotes the Planck's constant. In contrast to simple atomic systems, each monomer belongs to the polymer chain. E gives the mean value of the activation energy of diffusion of monomers across the phase interface. Detachment frequency, k_i^-, is determined from the principle of local thermodynamical equilibrium:

$$k_i^+ F_i^0 = k_{i+1}^- F_{i+1}^0, \quad (11)$$

where the self-consistent equilibrium distribution function of nuclei is given by

$$F_i^0 = N_0 \exp\left(-\frac{\Delta\mu + \beta}{k_B T}\right)\exp\left(-\frac{\Delta G_i}{k_B T}\right). \quad (12)$$

Above, N_0 denotes the number of active centers at time $t = 0$.

The total number of nuclei, Z_v, greater than certain size v, can be computed from the number density of nuclei as follows:

$$Z_v(t) = \sum_{i>v} F_i(t) = \int_0^t J_v(t')dt'. \quad (13)$$

Finally, the initial and boundary conditions read

$$F_{i>1}(t = 0) = 0, \quad (14)$$

$$F_M(t) = 0, \quad (15)$$

$$F_1(t) = N_0 - \sum_{i>1} F_i(t), \quad (16)$$

where M denotes the maximum size of nucleus in our computations and N_0 is the number of active centers. Due to condition (16) the number of active centers decreases as new nuclei are formed, i.e., the number of active centers is depleted during the phase transition process. We suppose that on one active center only one nucleus can be formed.

III. RESULTS AND DISCUSSION

In our previous work[16] we analyzed the experimentally determined[11] total number of nuclei Z_ν^{exp} [see Eq. (13)] greater than 567 monomers ($\approx$ critical size), i.e., we supposed that $\nu = 567$. Nucleation agent NA11-SF was mixed with polyethylene by 3 wt. % and the phase transition process occurred isothermally at $\Delta T = 10.4\,$K. Nucleation centers have various sizes and thus it is difficult to determine the number of active centers, N_0. That is why N_0 has to be considered as a parameter. Role of nucleation agent in nucleation of polymers was studied by Okada *et al.*[12] We chose the following parameters typical for a system under consideration: $\sigma = 8 \times 10^{-3}\,$Jm^{-2}, $\sigma_e = 87.8 \times 10^{-3}\,$Jm^{-2}, $\Delta\sigma = 0.25 \times 10^{-3}\,$Jm^{-2}, $N_0 = 4.99 \times 10^{17}\,$m^{-3}, and $E = 29.29$ (in $k_B T$ units) to get the best coincidence with the experimental data for Z—for details see Kožíšek *et al.*[16,17] Let us denote these parameters as "macroparameters." Recently, temporal dependencies of the number densities of nuclei for polyethylene crystallization were measured.[18] It is shown that 2D model with macroparameters is unable to predict the size distribution of nuclei—for details see Okada *et al.*[18] It was supposed that at the near nanometer cluster size (subcritical or supercritical nuclei) the interfacial energies differ from macroscopic ones. The "nanoparameters" of the interfacial energies were determined from the experimental values of the steady state size distribution of nuclei[19] to get $\sigma^{nano} = 7.3 \times 10^{-3}\,$Jm^{-2}, $\sigma_e^{nano} = 18.5 \times 10^{-3}\,$Jm^{-2}, and $\Delta\sigma^{nano} = 1.0 \times 10^{-3}\,$Jm^{-2}. Using nanoparameters of the interfacial energies lowers the energy barrier of nucleation and increases the number density of nuclei in comparison with macroparameters. Application of 3D model with nanoparameters well predicts the stationary size distribution of nuclei—for details see Okada *et al.*[18]

Influence of macroscopic and nanoscopic parameters using 2D and 3D models on the stationary distribution is shown in Fig. 1. Experimental data were obtained up to $i = 10^5$, but hereafter we restricted to the smaller values of nucleus size (central processing unit time increases with the increasing nucleus size as the number of solved kinetic equations increases). Use of macroparameters for the interfacial energies predicts a faster decrease in the number of nuclei with their size in comparison with the experimental data (squares). Temporal evolution of the number of nuclei as a function of their size is measured for an arbitrary volume,[18] i.e., the number of nuclei are determined relatively for various sizes of nuclei. That is why it is necessary to normalize computed number densities of nuclei by some numerical factor c_N. We chose c_N to get coincidence with the experimental data of F_{20} (the number of nuclei formed by 20 monomers).

Similarly, as in our previous analysis of the experimental data,[16] we also used the experimental data for the time
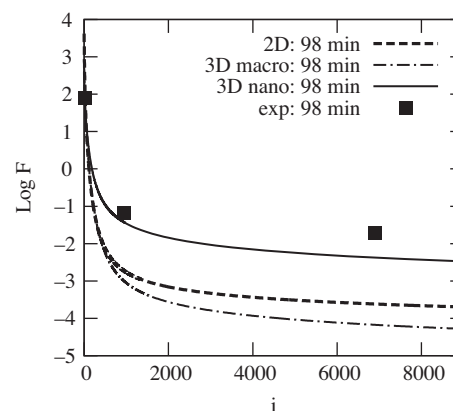

FIG. 1. Decimal logarithm of the size distribution, F, as a function of nucleus size, i. Solid, dashed, and dotted-and-dashed lines corresponds to 3D model using nanoparameters, 2D model using macroparameters, and 3D model using macroparameters at time $t = 98$ min. Squares correspond to the experimental data.

dependence of the total number of nuclei Z_ν^{exp}. Three-dimensional model with nanoparameters for the interfacial energies was used and parameters N_0 and E were selected to have coincidence with the Z_ν model computation [Eq. (13) and Fig. 2] with the experimental data to get: $N_0 = 2.5 \times 10^{16}\,$m^{-3} and $E = 28.75$ (in $k_B T$ units). It was supposed that $\nu = 567$ (similarly as in Kožíšek *et al.*[16]) in the experimental dependency of the total number of nuclei.

Using these parameters, we computed time dependent number density, F, for sizes $i = 20$, 940, and 6900 ($c_N = 24 \times 10^{-14}$ was chosen to get coincidence with the experimental value of F_{20} at sufficiently long time)—see Fig. 3. Selection of c_N sets the absolute values of the size distribution but it does not change the relative ratios between the number of nuclei of different sizes. The number of nuclei at sufficiently long time corresponds to the experimental data quite well, but the time delay of nucleation is lower in our computations for selected values of parameters. One can consider that the experimental data of the total number of nuclei Z_ν^{exp} does not exactly correspond to the size $\nu = 567$, but the nucleus size can be lower or higher. If we consider that the
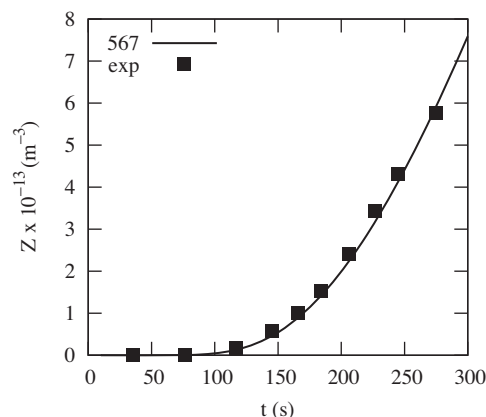

FIG. 2. The total number of nuclei, Z, greater than nucleus size $\nu = 567$ as a function of time for 3D model using nanoparameters. Squares correspond to the experimental data.
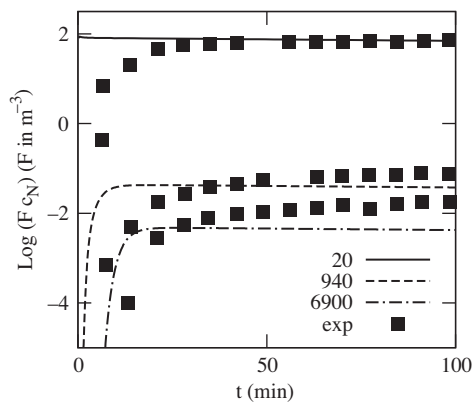
FIG. 3. Decimal logarithm of the number density of nuclei, F, as a function of time, t. Squares correspond to the experimental data for size $i = 20$, 940, and 6900 (from higher to lower values). Solid, dashed, and dotted-and-dashed lines correspond to the sizes $i = 20$, 940, and 6900 for 3D model using nanoparameters for the interfacial energies and the normalized factor $c_N = 24 \times 10^{-14}$.

FIG. 5. Decimal logarithm of the number density of nuclei, F, as a function of nucleus size, i, at time $t = 98$ min using 3D model with nanoparameters for the interfacial energies (normalized by factor $c_N = 9.8 \times 10^{-14}$). Solid, dashed, and dotted-and-dashed lines correspond to $\Delta\sigma = 1.0$, 1.2, and 0.9 $\times 10^{-3}$ Jm^{-2}. Dotted line corresponds to the equilibrium number density of nuclei.

experimental data of the total number of nuclei correspond to slightly different value of ν [see Eq. (13)], we get the different values of parameters E and N_0. These parameters influence the time dependence of nucleation process. That is why we analyzed Z_ν^{exp} data supposing $\nu = 500$ and 630 (Fig. 4), i.e., the parameters N_0 and E were chosen in numerical solution of kinetic equation (8) in order to cover the experimental data for $\nu = 500$ and 630. Assumption $\nu = 500$ leads to better coincidence in the time delay of nucleation process (Fig. 4).

We tried to improve agreement of our computation with the stationary values of the number of nuclei as a function of their sizes. That is why we changed the interfacial energy $\Delta\sigma^{\text{nano}} = 1$ to 1.2, respectively 0.9 $\times 10^{-3}$ Jm^{-2}. Using various values for $\Delta\sigma^{\text{nano}}$ leads to the different values of the work of formation of clusters [see Eq. (1)] and also the stationary size distribution changes (Fig. 5). It seems that using $\Delta\sigma^{\text{nano}} = 0.9$ Jm^{-2} fits the experimental data better. From the viewpoint of nucleation kinetics it is not important which interfacial energy is changed ($\sigma, \sigma_e, \Delta\sigma$), but how the parameter
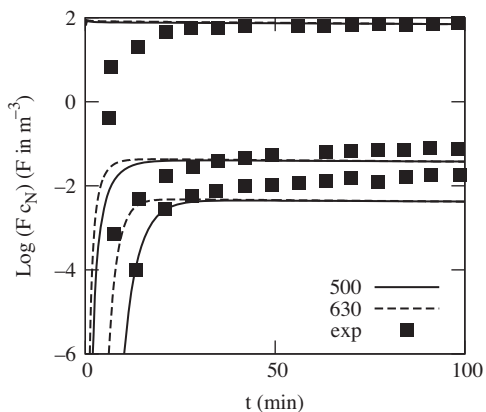
β [see Eq. (7)] is influenced. The equilibrium number density of nuclei (dotted line in Fig. 5) is determined by Eq. (12). At equilibrium the number of nuclei formed per unit time is equal to zero for any size i, i.e., $J_i = 0$. It is important to note that the equilibrium size distribution of nuclei, F^0, does not correspond to real equilibrium of the system under consideration due to the evolution of nuclei. Minimum in the equilibrium size distribution corresponds to the critical size. The equilibrium number density of nuclei is a reasonable approximation for subcritical nuclei within the standard model, when depletion of the active centers is not taken into account. In our case, the depletion of the active centers is incorporated to our computation and that is why the equilibrium number density of nuclei in the subcritical region is slightly higher.

Finally, we reanalyze the experimental data for the total number of nuclei, Z_ν^{exp}, for $\nu = 500$ and $\Delta\sigma = 0.9$ Jm^{-2} (other parameters of the interfacial energies were chosen as nanoparameters) to determine the parameters of our model: $N_0 = 5.8 \times 10^{16}$ m^{-3} and kinetic parameter E

FIG. 4. Decimal logarithm of the number density of nuclei, F, for $\nu = 500$ (normalized by $c_N = 9.8 \times 10^{-14}$) and for $\nu = 630$ ($c_N = 22.4 \times 10^{-14}$). Squares correspond to the experimental data for $i = 20$, 940, and 6900 (from higher to lower values). Solid and dashed lines correspond to $\nu = 500$ and 630.
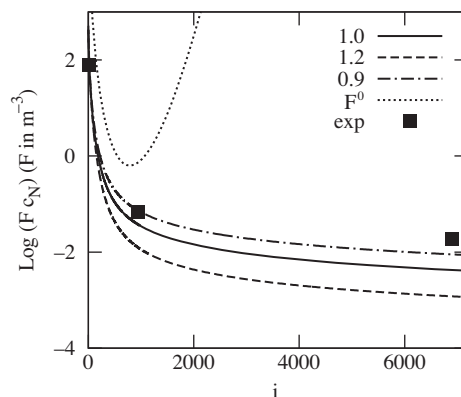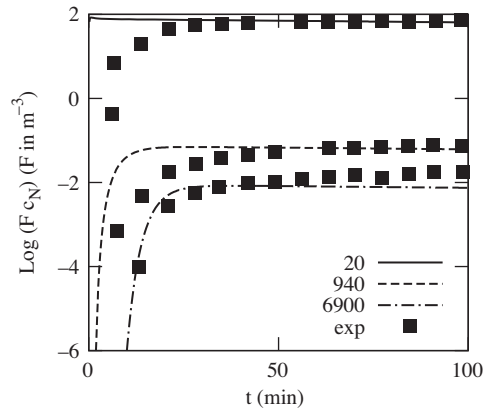

FIG. 6. Decimal logarithm of the number density of nuclei, F, using 3D model, nanoparameters (for σ and σ_e) and $\Delta\sigma = 0.9 \times 10^{-3}$ Jm^{-2} normalized by $c_N = 9.8 \times 10^{-14}$. Squares correspond to the experimental data for $i = 20$, 940, and 6900 (from higher to lower values). Solid, dashed, and dotted-and-dashed lines correspond to $i = 20$, 940, and 6900.

$= 29.2$ (in k_BT units). For these parameters we determined the number of nuclei for $i = 20$, 940, and 6900 (Fig. 6). The normalized factor c_N was chosen to be 9.8×10^{-14} to get coincidence for the number of nuclei of size $i = 20$. These parameters fits the experimental data better.

Time delay of nucleation for $i = 6900$ coincides with the experimental data. For smaller sizes of nuclei ($i = 940$ and 20) the time delay is longer in experiments. It can be caused by various factors. We suppose in our model that all active centers have the same size and physical properties. In reality, the size distribution of the active centers plays also an important role[13,22] and taking into account this effect could improve coincidence of the model with the experimental data. Time delay of nucleation is influenced predominantly by the kinetic parameter E, which determines the probability of transition of the monomer from the liquid phase near the phase interface to a new crystalline phase. The kinetic parameter E is taken as the mean value over various sizes of nuclei. Probability of incorporation of the monomer to a newly formed crystalline structure [it is equal to $\exp(-E/k_BT)$] is closely connected with the nucleus surface. In general, the surface roughness of smaller clusters (nuclei of new phase) is higher and the probability of incorporation of the monomer to crystalline nucleus is higher too (lower E). Structure of very small nuclei probably differs from the larger one and as a consequence E will also depend on the nucleus size. Dependence of kinetic parameter for nucleus size i could improve the coincidence of our model with the experimental data in time delay of nucleation, but it is out of scope of this article. Moreover using the standard model predictions, based on the classical approach and the mean values of physical parameters, is problematic for very small sizes of nuclei (several monomers).

IV. CONCLUSION

Kinetic model is presented to determine kinetics of the folded chain polyethylene crystal nucleation by numerical solution of kinetic equations. Kinetic parameters of our model are determined from the experimental data of the total number of nuclei and also from the size distribution of nuclei. It is shown that good agreement between the model computations and the experimental data of the total number of nuclei does not generally imply the correct prediction in the size distribution of nuclei. It is necessary to compare both dependencies, the total number of nuclei and the size distribution of nuclei, to get all parameters correctly. Relatively simple model explains kinetics of polyethylene nucleation quite well.

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