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PERSPECTIVES

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Secondary nucleation in polymer crystallization: A kinetic view

Shujing Zhang | Zhiqi Wang | Baohua Guo | Jun Xu

Advanced Materials Laboratory of Ministry of Education, Department of Chemical Engineering, Tsinghua University, Beijing, China

Correspondence
Jun Xu, Advanced Materials Laboratory of Ministry of Education, Department of Chemical Engineering, Tsinghua University, 100084 Beijing, China.
Email: jun-xu@tsinghua.edu.cn

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Abstract

Secondary nucleation on the surfaces of growing crystals plays a vital role in polymer crystallization, which determines the lamellar thickness at growth front and the radial growth rate. Though secondary nucleation has been intensively studied in the past decades, our understanding on the molecular mechanism and kinetics is not yet complete. In this perspective, we will briefly review the major advances in the secondary nucleation of flexible polymer chains in the past decade and discuss some remained questions from a viewpoint of kinetics. The main theories, thermodynamics and kinetics of secondary nucleation are first summarized. The difference of nucleation of polymer chains from that of small molecular crystals is revealed via analysis of kinetics. Then, the interplay of various microscopic processes leading to the final crystalline structures is discussed, such as lamellar thickening versus widening, intra-chain vs inter-chain nucleation, secondary nucleation versus lateral spreading, secondary vs primary nucleation, nucleation of polymorphisms, and so forth. Finally, some remained open questions are highlighted. Combining kinetic theory considering various microscopic processes and new experimental evidences at different length and time scales would greatly help deepen our understanding on the secondary nucleation during crystallization of flexible polymer chains.

KEYWORDS
attaching and detaching, interchain nucleation, intrachain nucleation, kinetics, lamellar thickness, nucleation, polymer crystallization, secondary nucleation, the critical nucleus, the minimum stable nucleus, thermodynamics

1 | INTRODUCTION

It is generally accepted that crystallization proceeds by two consecutive events: nucleation—the generation of either a new thermodynamic phase or a new structure via self-assembly or self-organization, then followed by growth where the nuclei become larger crystals.[1] Nucleation is divided into primary, secondary and tertiary nucleation, corresponding to nucleation from amorphous state, on an existing crystal surface, and at the corner of two intersecting crystal surfaces, respectively.[2] Primary nucleation, which is associated with the local density fluctuation and amplitude amplification, plays a significant role in regions of high, local supersaturation or undercooling. However, in most cases, the prevailing levels of supersaturation or undercooling are not so high for primary nucleation to make a significant contribution.[3,4] As early as 1906, Miers[5] reported that supersaturated solutions which were stable when left undisturbed often nucleated when a seed crystal was introduced. Melia and Moffitt[6] have termed this phenomenon “secondary nucleation.” In the field of polymer crystallization, Lauritzen and Hoffman used the term “secondary nucleation” in their pioneering paper on the theory of polymer crystallization from dilute solution published in 1960.[7] Secondary is the nucleation which occurs on the sufaces of crystals of the material being crystallized.[8]

Primary nucleation is typically dominant only during the start-up phase of a non-seeded crystallization process. For polymer crystallization, the growth of lamellar crystals is suggested to be dominated by secondary nucleation on the crystal growth front in Lauritzen-Hoffman theory, based on the experimental observed dependence of lamellar thickness and spherulitic radial growth rate on undercooling. Compared to primary nucleation, secondary nucleation has a lower free energy barrier. Accordingly, the density of secondary nucleation is generally much higher than that of primary nucleation, so study on secondary nucleation is easier than that on primary nucleation. Since the morphology, the radial growth rate and thickness of polymer lamellar crystals are closely related to secondary nucleation,[9,10] understanding the mechanism of secondary nucleation is crucial for predicting and controlling the entire crystallization process.[11] In addition, in terms of the physical nature, secondary nucleation would be similar to primary nucleation except that the former occurs with the assistance of existing crystals. Due to the fact that the kinetics of secondary nucleation and molecular process is much easier to study than that of primary nucleation, there have been more facts and evidences accumulated on secondary nucleation in the field of polymer crystallization. In the past several decades, study on crystallization kinetics (radial growth rate of spherulites and total crystallization rate) and structural features (lamellar thickness, crystal lattice, chain conformation, morphology of single crystals and crystal assemblies) have substantially contributed to understanding of secondary nucleation. However, most of the previous reviews focused on structural features of polymer crystallization. Therefore, we will focus on secondary nucleation of polymer lamellar crystals from a kinetic viewpoint in this perspective. To be simple, crystallization from quiescent melt is mainly considered.

2 | THEORIES AND MODELS ON SECONDARY NUCLEATION OF POLYMER CRYSTALLIZATION

Various theories have been proposed for nucleation of polymer crystallization, from different points of view (Figure 1).[7,12–16] The readers can refer to the previous reviews for details.[17–20] Here, we will first briefly summarize the different assumptions and major conclusions of several theories.

2.1 | Lauritzen-Hoffman theory: Stem by stem surface nucleation

Lauritzen and Hoffman[7,12,21,22] proposed the most widely accepted surface nucleation theory of polymer crystallization (Figure 1(A)). In Lauritzen-Hoffman theory the elementary attaching and detaching unit is a stem with length comparable to the lamellar thickness. To allow for growth, the stem length has to be slightly longer than the minimum lamellar thickness stable at the crystallization condition. Attaching of the first stem on the flat growth front is the rate-limiting step, so the first adsorbed stem is the critical secondary nucleus. Thus, the energy barrier for secondary nucleation originates from the surface free energy of the first crystalline stem formed on a smooth growth front, corresponding to enthalpic barrier. After

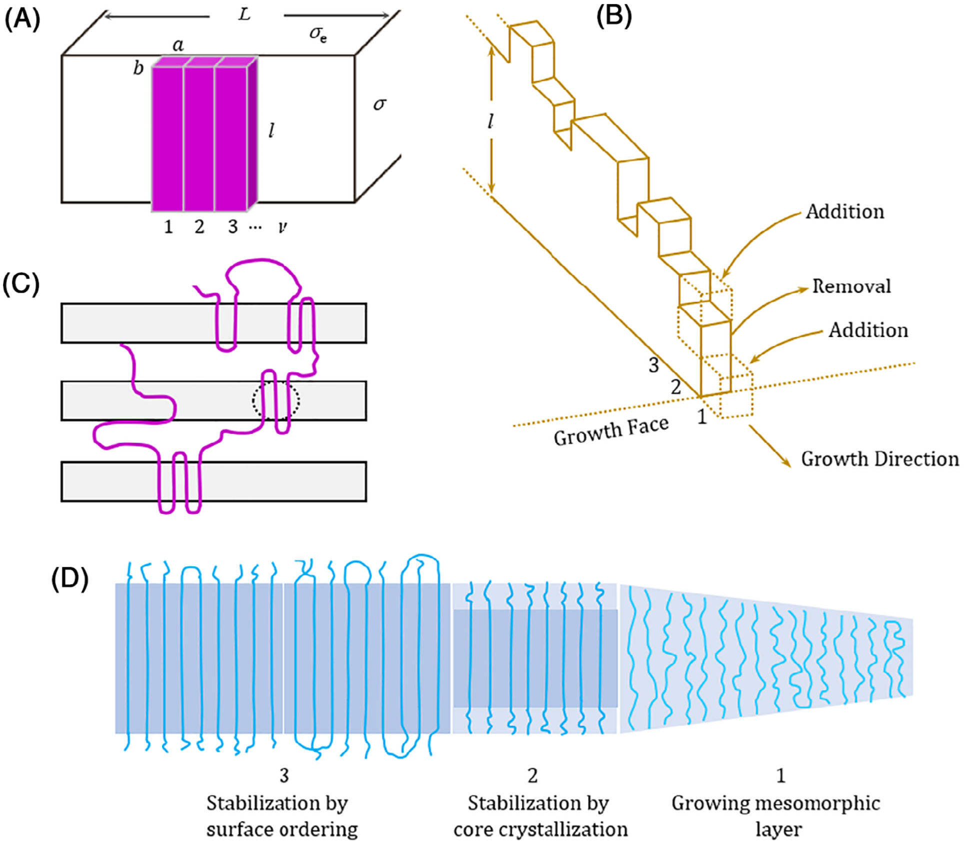


FIGURE 1 Various theories and models on polymer crystallization. (A) Lauritzen-Hoffman theory (redrawn from Reference 29). (B) Sadler-Gilmer model (redrawn from Reference 13). (C) Intramolecular nucleation model (redrawn from Reference 38). (D) Strobl model (redrawn from Reference 16)

crystallographic attachment of the first stem, new stems add in sequence on two sides of the first stem. This leads to a relatively rapid substrate completion process that produces a new layer on the growing face of a lamella. Repetition of the nucleation and substrate completion processes leads to the growth rate G. Based on the capillarity approximation, the variation of minimum lamellar thickness and radial growth rate of polymer spherulites with undercooling were deduced. The origin of chain folding was attributed to the lower interfacial free energy of fold surface compared to the fringed micelle model. The radial growing kinetics of lamellae in melt was divided into the three regimes, depending on the ratio of secondary nucleation rate to the lateral spreading rate.

$$G \propto e^{-\frac{nK_g}{T\Delta T}} \tag{1}$$

where $n = 1$ for regime II, and $n = 2$ for regime I and III. K_g is the nucleation constant. T and ΔT stands for the absolute crystallization temperature and undercooling, respectively. The Lauritzen-Hoffman theory has constructed a nice framework to understand the growth of polymer lamellar crystals, which not only describes how chain folding occurs but also provides an expression of lamellar thickness and growth rate. However, it has been constantly challenged by many experimental investigations and other theories. The controversies include δl catastrophe, the substrate length L' for lateral spreading, and the curvature of growth front.[17,23–25] Later, Hoffman modified the theory to take into account the above problems.[26–29]

2.2 | Sadler-Gilmer model: Unit by unit attaching and detaching

It is naturally to ask why the elementary unit should be a stem with length equal to lamellar thickness. Frank and Tosi,[30] Point,[31] Phillips,[32] Sadler and Gilmer[13] have all proposed that the elementary units of attaching and detaching might be a portion of stem. To interpret the observed smoothly rounded morphologies of polymer lamellar crystals, Sadler and Gilmer[13] constructed an alternative model by introducing reversible detachment and attachment of chain sequences not much larger than the molecular repeat unit but shorter than a stem as elementary steps (Figure 1(B)). From the description of these rate constants, we can see that the critical nucleus in Sadler-Gilmer model is the first adsorbed unit (only one stem in each growth layer is simulated), assumed to be smaller than the stem length. Effects of polymer chain connectivity and coiling in the fluid phase were included by the introduction of “pinning points”. An entropic barrier proportional to the lamellar thickness was proposed, which was related to the removal of unfavorable chain conformations. The results of the Sadler-Gilmer model can also explain the correlation of growth rate and lamellar thickness with undercooling[33]:

$$G \propto e^{-Kl}(l - l_m)\Delta f / k_B T \tag{2}$$

where Δf is the change in bulk free energy on crystallization. l and l_m stand for the lamellar thickness at the growth front and the minimum stable lamellar thickness, respectively. K is a constant and k_B is the Boltzmann constant.

However, neither Lauritzen-Hoffman theory nor Sadler-Gilmer model takes account of the full complexity of polymer chains. Pinning is the only connectivity feature in the Sadler-Gilmer model.[33,34] Later, Goldbeck-Wood et al.[35], Sommer and Reiter[36,37] further developed the Sadler-Gilmer model, considering the microscopic kinetics of attaching and detaching by taking into account interactions between nearest neighbor units. These treatments of molecular kinetics allowed the formation of a rough fold surface of a polymer crystal and agreed with some experimental results.

2.3 | Intramolecular nucleation model: Multiple stems in a nucleus

Lauritzen-Hoffman theory considered the first stem with length a bit larger than the minimum lamellar thickness as the critical secondary nucleus. In contrast, the intramolecular nucleation model[14,38] (the concept of molecular nucleation was first proposed by Wunderlich et al.[39,40]) assigned the secondary nucleation barrier to formation of the two-dimensional intra-chain nuclei (Figure 1(C)). During crystallization of a single chain, regular folding can effectively minimize the surface free energy and maximize the parallel stacking of backbones, both favored for crystal nucleation. This model can also interpret the regime phenomenon reproduced in molecular simulations.[41] In addition, the intramolecular nucleation model can explain the molecular segregation phenomenon, which gives long-chain fractions a priority to crystallize, as the principle of crystallization fractionation of polydisperse polymers.[42,43]

2.4 | Muthukumar's continuum model

Muthukumar et al.[15] have developed a model to unify two apparently different physical processes into a single formalism: one is observed in melt-grown crystals or solution-grown crystals of relatively high molecular weight and is dominated by nucleation control ($\Delta G \sim \exp[-1/\Delta T]$), while the other is observed in solution-grown crystals of relatively low molecular weight (as well as for small molecules) and is diffusion controlled ($G \sim \Delta T$, for small ΔT). This continuum model accounts for the accumulation of polymer chains near the growth front and invokes an entropic barrier theory to recover both limits of nucleation and diffusion control. This model explicitly takes the characteristics of long-chain polymers into account and reveals the effects of concentration and molecular weight in a quantitative manner. In addition, for a lamellar crystal formed by one chain, the folded configuration is the state with the lowest free energy. The topological structure of chain-like objects is one of the most significant features of polymers, and the incorporation of the detailed dynamics of polymer motion inevitably deepens our understanding of polymer crystallization.

2.5 | Strobl model: Block by block (from mesomorphic layer to native crystal)

In spite of the large differences in many aspects, the above approaches have one basic feature in common: They all assumed that the lamellar crystallites grew directly into the melt, representing the two-phase models. However, Strobl[16] invoked a multistage crystallization model (see Figure 1(D)) to explain the participation of a third (transient) phase in the growth process inspired by the previous findings of Keller et al. [44,45] that the hexagonal phase of polyethylene could transform to the normal orthorhombic phase and the latter would stop thickening after transformation. The Strobl model was proposed to explain the experimental observations that the random copolymers of syndiotactic polypropylene had almost the same lamellar thickness as the homopolymer and the linear extrapolation of the crystallization line to infinite large lamellar thickness reached a temperature higher than the equilibrium melting point.[46] According to the model, the lamellar thickness is determined by the minimum thickness of the mesomorphic layer that can transform into a native crystal phase.[47,48] On the other hand, the lamellar growth rate is determined by formation and incorporation of the mesomorphic layer at the growth front.[16] However, it has been argued that the introduction of the mesomorphic phase would affect the correct formation of crystals by the random incorporation of blocks.[49,50]

We should point out that some of the aforementioned models, for example, Sadler-Gilmer model and Strobl's multi-stage model, did not take nucleation into account. However, the supplementary concepts involved can be helpful to further understand secondary nucleation.

3 | THERMODYNAMICS AND KINETICS OF SECONDARY NUCLEATION

3.1 | Lamellar thickness determined by thermodynamics and kinetics

In the Lauritzen-Hoffman theory, the minimum lamellar thickness of a thermodynamically stable lamella determined by secondary nucleation is given by[7,12]:

$$l_{c,\min} = \frac{2\sigma_e}{\Delta g} \tag{3}$$

where σ_e and Δg stand for the interfacial free energy of fold surface and the change of bulk free energy per volume. It should be noted that the value is deduced for an infinitely wide lamella. Problems arise in two cases: First, when the lamellar thickness is large enough so that $2\sigma b l_c > 4\sigma_e ab$, one single stem with length equal to lamellar thickness will possess higher free energy than the folded configurations consisted of two stems. In this case, such a long stem will transform to two or multiple stems with folds. Second, for a minimum stable two-dimensional nucleus with finite width, the lamellar thickness should be larger than that determined by Equation (3).

For a two-dimensional secondary nucleus, the most probable stem length corresponds to that with the minimum free energy. Considering the capillarity approximation proposed by Gibbs,[51] which assumes that the change of bulk free energy per volume and the interfacial free energy per area do not vary with nuclei size, the preferred shape of a secondary nucleus can be deduced as follows:

$$\frac{l_c}{w} = \frac{\sigma_e}{\sigma} \tag{4}$$

Thus, during the stage of secondary nucleation, both thickening and widening occurs simultaneously for a secondary two-dimensional nucleus so as to keep a constant thickness/width ratio until it reaches the minimum size of a stable one.

This theoretical prediction has been confirmed by simulations[14,52,53] and experimental observations.[54,55] Considering long-range correlation in the attaching and detaching rate constants, Xu et al.[53] simulated the secondary nucleation on the existing lamellar crystal surface via a microscopic kinetics model. The results showed that both thickening and widening happened simultaneously during secondary nucleation (see Figure 2). The size of the minimum stable two-dimensional secondary nucleus with both finite thickness and lateral width can be deduced[56]:

$$l_{c,\min} = \frac{4\sigma_e}{\Delta g_{\text{nuclei}}} \text{ and } w_{\min} = \frac{4\sigma}{\Delta g_{\text{nuclei}}} \tag{5}$$

As a result, the minimum lamellar thickness should be around two folds of the thickness of the just stable lamella with infinite width. According to previous theories, during lateral spreading by attaching stems at the two sides of the secondary nucleus, the minimum stem thickness will decrease with increasing width. Consequently, the minimum stem length will lie between the value determined by Equations (3) and (5).

To assure a steady growth rate, the lamellar thickness should be a bit larger than the minimum thickness. Lauritzen and Hoffman considered the fluctuation of stem length and obtained the average lamellar thickness via growth kinetics, which led to an approximate increase about $RT/\sigma b$ (R is the gas constant, σ is the free energy of lateral surface, b is the thickness of a layer on the growth front) in average lamellar thickness, corresponding to an increase in energy barrier of secondary nucleation around $2RT$. The increment is usually small compared to the energy barrier of secondary nucleation reported with the scale of tens of RT.

As stated above, the minimum thickness of a stable nucleus is determined by thermodynamics. However, in the post-nucleation stage (or lateral spreading growth of the secondary nuclei on growth front), whether widening and thickening prevails is mainly determined

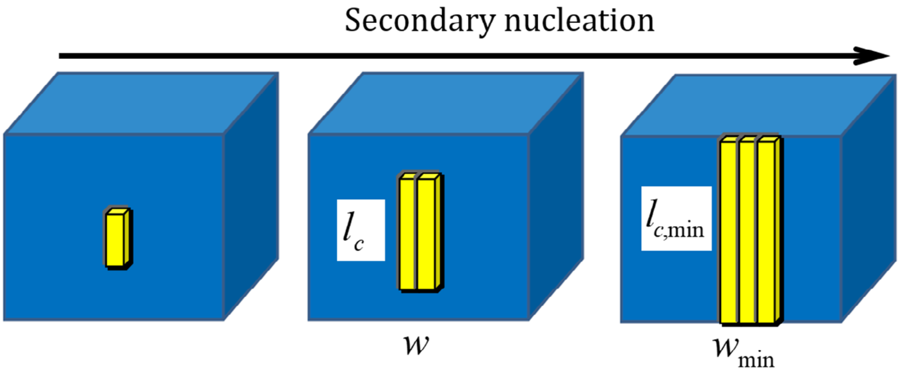


FIGURE 2 Scheme showing the simultaneous thickening and widening of the secondary nucleation at the growth front of polymer lamellar crystals.[56] Copyright 2016. Reproduced with permission from American Chemical Society

by kinetics. Further lamellar thickening will be accompanied by increased energy barrier with arising lamellar thickness, thus the increase of lamellar thickness is proportional to the logarithm of time.[57] In contrast, the growth in width direction via coalescence of neighboring nuclei or lateral spread needs only to overcome a constant energy barrier, so the width increases linearly with time. Consequently, in the lateral growth stage after secondary nucleation, widening will be kinetically more preferred than thickening. In addition, in the post-nucleation stage, whether the lamellae thicken or not depends on the chain mobility in the crystal lattice. If the chains in crystals are mobile, for example, the polymers with α_c relaxation, the lamellae may further thicken with time, even at the isothermal crystallization temperature. However, the thickening behind the growth front will not affect the radial growth rate of the lamellae, which is determined by the lamellar thickness at the growth front. On the contrary, for the lamellae without α_c relaxation, lamellae can only thicken via melting-recrystallization.

As aforementioned, it is theoretically predicted that the minimum lamellar thickness should vary with the lateral width. If the growth of a layer of stems on the growing front occurs mainly by coalescence of the two-dimensional minimum stable nuclei, for example, in Regime III where the lateral spreading can be omitted, the minimum thickness of lamellae might be determined by the minimum size of stable secondary nuclei.

On the other hand, in Regime II and Regime I, lamellae grow by secondary nucleation and lateral spreading. In these cases, the fraction of polymer chains involved in lateral spreading is usually much higher than that in secondary nucleation, so the minimum lamellar thickness is predominantly determined by the minimum stable thickness during lateral spreading. Since the lateral width is sufficiently large compared to the thickness, the minimum thickness during lateral spreading at positions far from the site of secondary nucleation is comparable to the average lamellar thickness and can be determined by Equation (3).

Because the minimum lamellar thickness at different undercoolings should be deduced from different equations (Equations (3) and (5)), it is expected that there should be a change of the slope of the crystallization line and the Hoffman-Weeks (H-W) plot. This phenomenon has been observed in poly(butylene succinate) (PBS).[56] With increasing crystallization temperature, the slope of H-W plot of PBS increased from 0.63 to 1.0, namely, the H-W plot at low undercooling was parallel to $T_m = T_c$ line. The parallel H-W plot to $T_m = T_c$ line has also been observed in polyethylene (PE),[58] polycaprolactone,[59] poly(butylene terephthalate) and poly(ethylene terephthalate),[60] which indicates that extrapolation of H-W plot to obtain the equilibrium melting point is not viable. Marand et al.[61] have developed a nonlinear extrapolation method to fit the nonlinear H-W plot. However, for the H-W plot parallel to $T_m = T_c$ line, all the extrapolation methods fail to obtain T_m^0. In addition, if the minimum lamellar thickness is determined by different equations at different undercoolings, for example, Equations (3) and (5), the lnG $\sim 1/T\Delta T$ plot may show more than three regimes after considering the competition of secondary nucleation and lateral spreading. We note that this is the ca

se for *cis*-polyisoprene, which shows four regimes.[62] From high to low undercooling, the ratio of the slopes is around 2:1:2:1.

Are there really different thicknesses at the site of secondary nucleation and at the lateral spreading region? If the answer is YES, it will lead to the result that the secondary nucleation in the following layers should occur at the same position as that in the previous layers rather than the random position previously considered for the uniform lamellar thickness. The above proposition of different local lamellar thickness along the width direction normal to the fastest growing direction still needs validation from direct measurement of lamellar thickness.

All the above theories except that of Strobl have assumed that the nuclei have the same interfacial free energy per area and the same change of bulk free energy per volume as the large crystal. Nonetheless, Mandelkern and Alamo[63] have pointed out that the fold surface free energy will vary with lamellar thickness and the enthalpy and entropy fusion per repeating unit change with the chain length. In addition, the variation of interfacial free energy with temperature has been considered, for example, by Toda[60], Marand[61], et al. If this effect is considered, nonlinear Gibbs–Thomson equation[60] and nonlinear H-W plot[61] should be expected.

3.2 | Nucleation kinetics derived from microscopic kinetics of attaching and detaching

To compare the aforementioned different theories, we should put them into the same frame of consideration. Since most of the

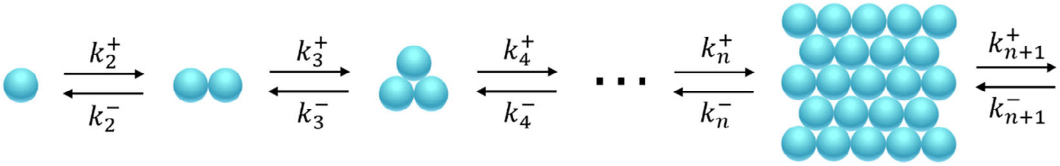


FIGURE 3 Microscopic kinetic process of crystal nucleation. k_i^+ and k_i^- indicate the rate constant of a motif attaching to form the cluster with *i* motifs and detaching from the cluster with *i* motifs, respectively

nucleation kinetics of these theories is derived from the microscopic kinetic process consisted of attaching and detaching elementary units (originally proposed by Becker and Döring[64] for gas–liquid phase transition and later further developed by Turnbull and Fisher[65] to obtain the rate of primary nucleation) to obtain the size of critical nuclei and the steady nucleation rate (Figure 3), we will compare these theories from the aspect of elementary attaching/detaching unit and the corresponding kinetics.

First, we should point out that the microscopic kinetics model could describe both nucleation and spinodal like process of crystallization. If $k_i^+ > k_i^-$ stands for all *i*, crystallization would proceed without energy barrier, which is a spinodal decomposition process. Otherwise, crystallization is initiated by nucleation. For the nucleation process, assuming that the system is in a transiently steady state during the nucleation stage, namely, the flux is a constant so that the concentrations of the clusters with different sizes remain invariant with time, the flux of nucleation can be deduced:[65]

$$J = k_{n*}^+ C_0 \left(\frac{\Delta G^*}{3\pi k_B T n^{*2}}\right)^{0.5} \exp\left(-\frac{\Delta G^*}{k_B T}\right) \tag{6}$$

where n^* is the number of units in a critical nucleus and C_0 is the concentration of amorphous units. Equation (6) reveals that ΔG^*, the work to form a critical nucleus, plays a very important role in determining the nucleation rate.

Will the chosen unit in attaching and detaching affect the nucleation kinetics? Thermodynamically, if nucleation happens via the same pathway, the change of total free energy and the maximum energy barrier during nucleation will not vary with the size of the chosen elementary unit. In addition, the formation of critical nuclei is near equilibrium, so the kinetics is also independent of the choice of unit size provided that the chosen unit is smaller than the critical nuclei size. For a critical nucleus consisted of n^* units, if *m* consecutive units are considered as a motif, now the number of motifs in such a critical nucleus becomes n^*/m. The rate constant $k_i^{+\prime}$ and $k_i^{-\prime}$ of the new motifs should change accordingly:

$$k_{n*/m}^{+}{}' = k_{n*}^{+}/m \tag{7}$$

Thus the nucleation rate will not change with the motif size considered in the microscopic kinetic model. While for $i < n^*/m$, we should have:

$$\frac{k_i^{+\prime}}{k_i^{-\prime}} = \frac{\prod_{im-m+1}^{im} k_i^+}{\prod_{im-m+1}^{im} k_i^-} \tag{8}$$

so that the free energy of the pre-nuclei clusters will not be changed.

3.3 | Size of critical secondary nucleus of folded chain lamellae: One stem or multiple stems?

The classical nucleation theory considers a free energy barrier for nucleation of a small domain of the new phase resulting from a surface free energy penalty higher than the gain in volume free energy.[51,66,67] The change of the total free energy exhibits a maximum at the critical nucleus size. It means that the critical nucleus refers to a cluster of crystalline units that has the highest Gibbs free energy in the system. If a cluster reaches a size larger than this critical size, it grows spontaneously, accompanied by a decrease of free energy.[68]

Different theories predict different sizes of critical secondary nucleus. In Lauritzen-Hoffman theory, the first stem with length equal to the minimum lamellar thickness adsorbed on the flat growth front is the critical secondary nucleus.[7,12] In contrast, the intrachain nucleation model considers folded multiple stems from a part of one chain as a secondary nucleus.[14] Whether the multiple stems from the same chain adopt the adjacent reentry folding or not depends on the relative value of the interfacial free energy.

Based on the capillarity approximation, the size of a critical secondary nucleus (two dimensional) and the corresponding energy barrier are calculated as follows:

$$l_c^* = \frac{2\sigma_e}{\Delta g} \text{ and } w^* = \frac{2\sigma}{\Delta g} \tag{9}$$

$$\Delta G^* = \frac{4b\sigma\sigma_e}{\Delta g} \tag{10}$$

where l_c^* and w^* indicate the thickness and width of a critical secondary nucleus on the growth front, respectively. Equation (9) shows that the critical thickness equals the minimum lamellar thickness of an infinitely wide lamella determined by Equation (3). As a result, Lauritzen-Hoffman theory and the intramolecular nucleation model give the same critical stem length and the same energy barrier for the secondary nucleation. This coincidence is the reason why Lauritzen-Hoffman theory can be applied to interpret the minimum lamellar thickness and the kinetics of radial growth though it gives an over-simplified view of the microscopic process of secondary nucleation.

However, the possibility that a nucleus may have different thermodynamic parameters from the mature lamellar crystals makes theoretical calculation of critical nuclei size difficult.[16] Rastogi did observe that the orthorhombic phase of PE was transformed from the metastable hexagonal phase when growing from melt.[69] Thus, molecular simulation has been utilized to observe the nucleation process in molecular level to reveal the size of critical nuclei. Using Langevin dynamics simulations, Muthukumar et al.[52] reveals that a single polymer chain can participate in several nuclei, each of which consists of several stems during primordial stages of polymer crystallization from solutions. By molecular dynamics simulations, Rutledge et al.[70] simulated homogeneous nucleation from a PE melt at deep undercooling. There, the critical nucleus contained about 150 carbons on average and is significantly smaller than the radius of gyration of the chains.

To validate the nucleation theories, delicate experimental designs have been applied to obtain the size of critical nuclei. Wang et al.[71] established an elegant method to determine the size of critical primary nuclei of ice using nanofillers with various sizes. Floudas et al.[72] used nanoporous alumina to study the crystallization of polypropylene under confinement, and the absence of nucleation below 20 nm pores indicated the size of the critical primary nucleus should be larger than the pore size. Kumaki et al.[55] suggested a multistep mechanism of primary nucleation based on the real-time observations of the crystallization process of folded-chains at the molecular level by atomic force microscopy (AFM). However, it is still difficult to determine the size of critical nuclei via real time observation. Only when the number distribution of the clusters of different sizes formed during the nucleation process can be precisely obtained, could the size of critical nuclei be determined. However, it is still a great challenge to observe the mobile pre-critical nuclei.

Recently, we have proposed a method to determine the size of critical nucleus based on the probability to select a number of crystallizable repeating units in melt of random copolymers (Figure 4).[73,74] We assume that the nucleation process is a stochastic process and the mobility of the random copolymers are the same as that of the homopolymer provided that they have similar molecular weights. For a random copolymer with the volume percentage of the crystallizable units as p_{A}, the probability to select a crystallizable unit during nucleation is exactly p_{A}, thus the probability of consecutively choosing n^* crystallizable units is $p_{\mathrm{A}}^{n^*}$. As a result, the rate of nucleation of random copolymer is that of homopolymer multiplied by $p_{\mathrm{A}}^{n^*}$. When crystallized in Regime III, the radial growth rate of spherulites is proportional to the rate of secondary nucleation, so the double logarithmic plot of the spherulitic growth rate of random copolymers versus the volume percentage of the crystallizable repeating units gives the number of units in a critical nucleus. In fact, a very similar method was proposed long ago by Andrews et al.[75] in 1971, though they made a mistake to state that the number of units in the critical nucleus was the slope minus 1. Similarly, the double logarithmic plot of the spherulitic radial growth rate of crystallizable polymer/amorphous polymer blends versus the volume fraction of the crystallizable polymer gives the number of chains involved in a critical secondary nucleus. The method only lies on the assumption of stochastic nature of crystal nucleation, which is independent of the detailed mechanism of nucleation. In fact, this simple deduction can also be obtained from the nucleation theorem proposed by Kashchiev[76] and later further discussed by Schmelzer[77]. Xu et al.[78] utilized the nucleation theorem to determine the number of urea molecules in a critical secondary nucleus of poly(ethylene oxide) (PEO)-urea inclusion compound by diluting the crystallizable components.

Applying the method shown in Figure 4, Xu et al.[73] revealed that a critical secondary nucleus of PBS consisted of 5 to 8 stems and these stems were contributed by one or two polymer chains when the polymers were isothermally crystallized at temperatures ranging from 70 to 95°C. For α-form poly(L-lactide) (PLLA) crystal, at the

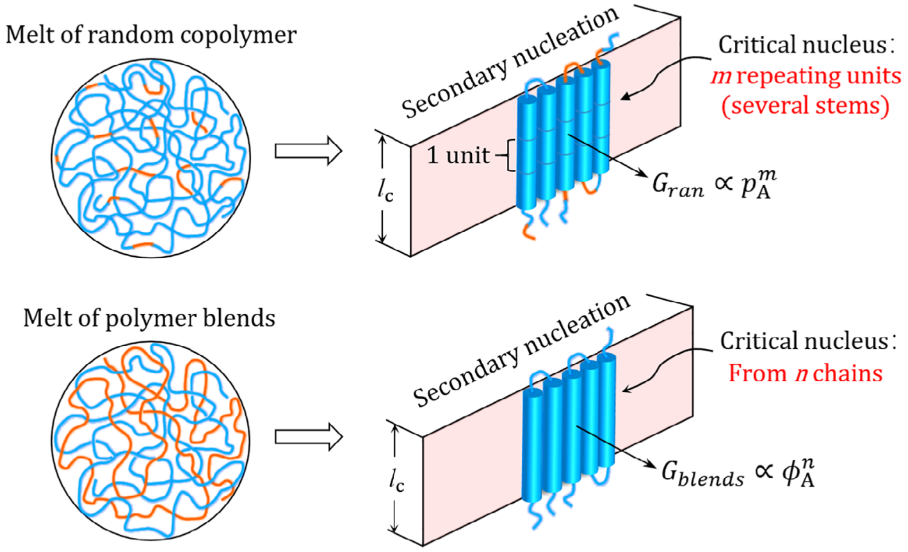


FIGURE 4 Scheme for determining the size of a critical secondary nucleus based on the stochastic nucleation kinetics of random copolymers and miscible crystallizable/amorphous polymer blends.[73] Copyright 2019. Reproduced with permission from American Chemical Society

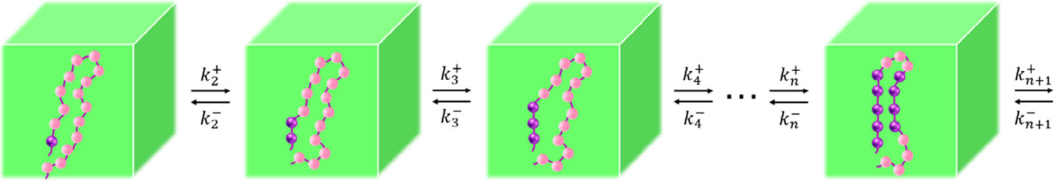


FIGURE 5 Microscopic kinetic process of secondary nucleation of flexible polymer chains. k_i^+ and k_i^- indicate the rate constant of attaching and detaching, respectively

crystallization temperature from 120 to 140°C, the lower limit of the number of stems in a critical secondary nucleus is between 1.6 and 2.1, and the upper limit of the number of stems is around 4.1 to 5.4, considering lamellar thickening during isothermal crystallization of PLLA.[74] Moreover, these stems within a critical secondary nucleus were contributed, depending on crystallization temperature, by 1.5–1.9 different polymer chains on average. From the two polymers, comparable trends are obtained that the number of stems in a critical secondary nucleus increases and the number of polymer chains decreases with increasing isothermal crystallization temperature. The results reveal that a critical secondary nucleus of polymer lamellar crystals includes multiple stems, which is derived from one or two polymer chains. These results contest the Lauritzen-Hoffman theory in which the first stem is taken as a critical secondary nucleus.

3.4 | Kinetics of secondary nucleation: Difference of flexible polymer chains from small molecules

The previous Equation (6) on nucleation kinetics is derived from the microscopic attaching and detaching process of small molecules. However, there is an essential difference between crystal nucleation of small molecules and flexible polymer chains. In the case of small molecules, the attaching units are different molecules, and the attachment rate constants (per area) are usually considered constant for the clusters of various sizes. But for flexible polymer chains, the consecutive units from the same chain are covalently linked so that the adsorption events of these units are not independent any more (Figure 5). Consequently, the Markovian process of attaching and detaching a unit for small molecular crystals could not be applied to crystal nucleation of flexible polymer chains. If the units in a nucleus is from one chain and these units are not statistically far away from each other, the attachment rate constant of forming such a nucleus should be proportional to the exponential of the number of all units in a nucleus, which leads to an entropic barrier:

$$k_i^+ = A\exp(-bi), \tag{11}$$

where A and b are constants.

Another remarkable consequence of the above difference is that the formation of the critical nuclei is the rate-limiting step of crystal nucleation of small molecules, while the formation of thermodynamically minimum stable nuclei becomes the rate-limiting step for the intramolecular nucleation of flexible polymer chains.

3.5 | Intramolecular vs intermolecular nucleation of flexible polymer chains

Our previous results revealed that a secondary nucleus formed at low temperatures chose the stems from two chains rather than those from one chain, namely both intra and intermolecular nucleation occurred.[73,74] Why not only intramolecular nucleation? The reason may be attributed to the competition between intra and intermolecular nucleation from the viewpoint of thermodynamics and kinetics.[79–82] Thermodynamics determines the equilibrium concentration while kinetics gives the formation rate. Adjacent re-entry chain folding in intramolecular nucleation causes lower surface free energy but the entropy penalty to choose the stems from the same chain slows the kinetic rate. In contrast, the intermolecular nucleation randomly choosing the stems needs no such entropy penalty and is thus kinetically favored, though causing higher surface free energy than adjacent re-entrant folding. As a compromise of the two effects, both intramolecular and intermolecular nucleation happen at the studied low temperatures. But at high temperatures, the thermodynamic effect prevails, resulting in intra-molecular nucleation.

Adjacent re-entry chain folding could be achieved in the nucleation stage (whatever primary, secondary and tertiary nucleation) until the nuclei become thermodynamically stable and are constrained in the crystal lattice. However, in the post-nucleation stage after a nucleus reaches the minimum size to survive (the size of thermodynamically stable nucleus rather than that of a critical one), lateral spreading growth might very probably choose stems from other chain or from the same chain but randomly select the stem statistically far away from the already adsorbed ones to avoid the high entropy barrier caused by consecutive reentry folding of the same chain.

What is the number of adjacent reentry chain folding? Several methods have been proposed to determine the number of adjacent reentry folding in polymer lamellar crystals. Direct information about the chain conformation can be evaluated from neutron scattering studies of mixtures of deuterated and protonated samples of the same polymers. Applied this technique to PEO, Fischer[83] reported that the average number of crystalline stems contained in a cluster of folded chain is between 4 and 9, varying with the molecular weight and crystallization temperature. Fitting the number of successive folds of polymer chains via solid-state nuclear magnetic resonance (ssNMR) data, Miyoshi et al.[84–86] revealed that the adjacent re-entry folding included multiple stems. For example, in solution-grown PLLA crystals, the average number of chain-folds is 7 under the assumption of full adjacent re-entry structure,[84,85] whereas the number is only 1.5–2 when crystallized from the melt[86]. Zhang et al.[87] established a method to quantify the chain folding in polymer single crystals by using AFM-based single-molecule force spectroscopy. The fingerprint spectrum of force-induced chain motion allows to decipher the adjacent and nonadjacent re-entry folding with spatial resolution of sub-nanometers. The average fraction of adjacent re-entry folds was determined as 91–95% for PLLA, supporting the adjacent re-entry model for solution-grown single crystals.[87]

During secondary nucleation of flexible polymer chains, the minimum lamellar thickness and the nucleation rate is determined by the minimum stable nuclei, which determines the number of adjacent reentry chain folding as well. Whether secondary nucleation or lateral spreading determines the average number of consecutive adjacent re-entry folding is not clear yet. The number is probably determined by lateral spreading in solution or in melt crystallization in regime I and II, since lateral spreading occurs in most area of the lamellar crystals. While in regime III, the number is most likely determined by the secondary nucleation.

3.6 | Entropic versus enthalpic barrier for secondary nucleation

The origin of the energy barrier of crystal nucleation of polymer chains has been studied extensively in the past decades. The major achievements have been summarized in the review by Lotz and Cheng[88,89] and the book written by Cheng.[81] It is generally accepted that both entropic and enthalpic effect contributes to the energy barrier of nucleation. Thus, for a deeper understanding of polymer crystallization, both enthalpy and entropy contributions should be comprehensively considered. We will briefly mention it here.

The entropic effect arises from the selection of the right chain conformation (including the chiral sense of helical conformations in isotactic polymers), the crystallizable sequences in random copolymers, the crystallizable components in blends and solutions, etc. Crystallization process of a polymer chain begins with the adsorption of a part of the chain and ends with the incorporation of that chain into the crystal lattice. Whether or not this process can go forward and how fast this process can occur depends on several selection processes on different length- and time-scales.[49,50] In the small scale of a tenth to a few nanometers, the chain molecule must fit into a crystallographic lattice with a specific repetition scheme, and the selection of all-trans, or chiral but racemic helical conformations of stems with right or left handedness should be considered. The molecular selection processes at the crystal growth front, such as the choice of stems with the right helical conformations and the extent of lateral spreading, have been elegantly revealed by Lotz et al.[88,90,91] based on structural determination via crystallography. This approach will continue to play important role in the future study on nucleation of polymer crystals. In an even larger scale of several to tens of nanometers, the selection of a special sequence length occurs, and chain folding sets in. If these sequence lengths are selected continuously within a single polymer chain, it corresponds to intramolecular nucleation. For random copolymers composed of two types of chain units, the minor chain units are usually excluded from the crystalline lamellar cores of the major units.[24,92–94] Only the trials choosing sufficient sequence lengths of the major chain units are effective to form the thermodynamically stable nuclei. However, there exist exceptions. Isomorphism represents two types of units co-crystallize in the same crystal lattice when the two types of units have the very similar size and configuration.[95–99] The above selection processes must be sequential and cooperative.

One type of enthalpic effect is contributed by removing the wrong adsorbed configurations (e. g. folded chains with shorter stem length), which needs to overcome an energy barrier. Self-poisoning, a minimum on the curve of radial growth rate versus crystallization temperature has been attributed to removal of the adsorbed folded chains with shorter stem length (which could not survive to support further crystal growth) on the growth front of extended chain crystals in long chain alkanes and PEO oligomers.[100,101] Recently, Alamo et al.[102,103] revealed that at the transition temperature range, occasional attaching secondary nuclei of the metastable phase would lead to self-poisoning of the crystal growth of the stable phase. Another type of enthalpic effect might result from the seemingly repulsive force between two adsorbed units. As a result, ordering of the segments in the nuclei smaller than the critical size increases the free energy. Only when the nuclei are larger than the critical size, can the free energy depress after growing. One specific example is the mixture of crystallizable/un-crystallizable components with only attractive force between the crystallizable units, in which there is only entropic barrier during nucleation. The process of crystal nucleation in such system should be very similar to that of nucleation of phase separation of an amorphous component from its solution, thus the geometric shape of the separated phase should be spheres with isotropic intermolecular interaction or ellipsoids with anisotropic intermolecular interaction. The facets of the separated phase could not be observed in the case of only entropic barrier.

The molecular interaction in the nucleus and the crystals should be of long range, which is distinctly different from that in melt. If only the molecular interaction among the nearest neighbors were considered, the critical nucleus should be one stem, which contradicts with the multiple stems in a critical nucleus. In addition, the large but finite enthalpic barrier of nucleation implies a local maximum between the two minimum points in the curve of molecular interaction energy versus molecular distance. The two minimum points correspond to the liquid with long distance and the crystal phase with shorter distance between molecules, respectively. In fact, there is only one minimum on the generally adopted Lennard-Jones (L-J) potential in simulation of crystal nucleation. As a result, the simulated nucleation results with L-J potential might only consider the entropic barrier, which should be different from both the entropic and enthalpic barrier in the actual nucleation of polymer chains. The details of molecular interaction in crystal nuclei needs further investigation, which is crucial for simulation of crystal nucleation.

4 | INTERPLAY OF DIFFERENT KINETIC PROCESSES

The real crystallization process of polymer chains involves competition and interplaying of various kinetic processes, such as primary nucleation, secondary nucleation, lateral spreading, diffusion of segments and chain disentanglements in high molecular weight polymers, competitive nucleation of polymorphism, and so forth. All these processes play a certain role in determining the final crystalline structures of polymer materials. In this section, we will briefly discuss some interplays.

4.1 | Competition between secondary nucleation and lateral spreading

In regime II, the substrate width for lateral spreading is a result of competition between secondary nucleation and lateral spreading (Figure 6(A)):

$$i_s L_1 t = 1 \text{ and } L_1 = 2gt \tag{12}$$

where i_s and g represent the rate of secondary nucleation and that of lateral spreading, respectively. The symbol t indicates the time to form a secondary nucleus. The substrate width for lateral spreading of one secondary nucleus, L_1 can be obtained:

$$L_1 = \left(\frac{2g}{i_s}\right)^{1/2} \tag{13}$$

It is still a big challenge to experimentally determine the substrate length for lateral spreading. Lotz et al.[91] have established a delicate method to estimate the value in solution grown, twinned single crystals of isotactic poly(vinylcyclohexane). The substrate length for lateral spreading ranges from roughly 60 stems at 220°C to about 35 stems at 120°C. Up to our knowledge, this is the only example to determine the substrate length for lateral spreading. It is a pity that such method only works for the special polymer and is difficult to apply to other polymers. At present, it is still not clear whether the lateral spreading occurs via attaching a stem or multiple folded stems once a time, which deserves further investigation.

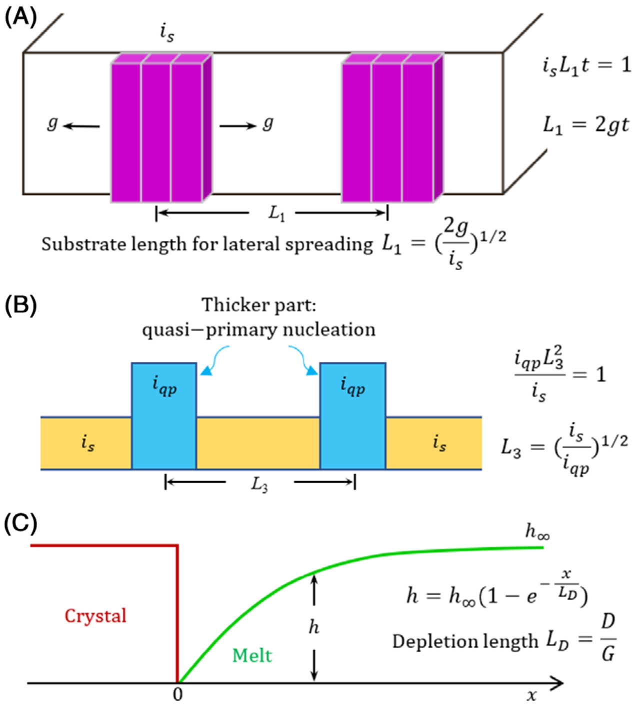


FIGURE 6 Interplay of various kinetic processes in polymer crystallization. (A) Interplay of secondary nucleation with lateral spreading. (B) Interplay of secondary nucleation with quasi-primary nucleation or screw dislocation. (C) Interplay of crystal growth with diffusion

4.2 | Competition between primary and secondary nucleation

The density of the primary nucleation in polymer crystallization is determined by its competition with secondary nucleation. Considering the general two-dimensional growth in thin film, we have:

$$L_2 = 2Gt \text{ and } i_p L_2{}^2 t = 1 \tag{14}$$

where G and i_p are the rate of radial growth of spherulites and the rate of primary nucleation, respectively. The symbol t in Equation (14) indicates the time to form a primary nucleus. The average spherulite diameter, L_2 can be calculated:

$$L_2 = \left(\frac{2G}{i_p}\right)^{1/3} \tag{15}$$

where G and i_p represents the radial growth rate of polymer spherulite via secondary nucleation and the rate of primary nucleation, respectively.

4.3 | When secondary nucleation meets quasi-primary nucleation

In previous theories, on a flat growth surface, the secondary nucleation happens via adsorption and ordering of chain stems with the same thickness as the substrate lamella. Only one layer of polymer chains is involved in the secondary nucleation, since more layers will lead to higher activation barrier. However, there is possibility that the surface nucleation may form stems thicker than the substrate lamella, involving several layers of polymer chains. The latter case may happen via melt-recrystallization during heating or via forming a primary-like nucleus at the growth front during the isothermal crystallization process. Such quasi-primary nucleation needs higher activation barrier and will occur with a lower probability than the normal secondary nucleation with the same thickness. As a result, the quasi-primary nucleation at the lamellar growth front is a rare event and will not substantially affect the macroscopic radial growth rate. Nonetheless, it may lead to formation of new layers of lamellae, thus may affect the lamellar morphology.

Figure 6(B) shows a scheme of forming a quasi-primary nucleus at the growth front of a growing lamella. The thickness of the quasi-primary nucleus in the Figure 6(B) is twice of that of a lamella. This mechanism is primary-like since the nuclei is of three dimensional. However, the energy barrier for such quasi-primary nucleation is only a half of that to form a normal primary nucleus from the melt.

The quasi-primary nucleation could only occur at the growth front of a lamella, which is different from the primary nucleation possible at any sites in the melt. The ratio of the probability of a quasi-primary nucleation to that of a secondary nucleation, p is:

$$p = \frac{i_{qp}}{i_s} \tag{16}$$

where i_s and i_{qp} represent the rate of secondary nucleation and the rate of quasi-primary nucleation, respectively. For two-dimensional crystallization in thin film, the average distance between two neighboring quasi-primary nucleation sites, L_3 can be deduced:

$$pL_3^2 = 1 \tag{17}$$

$$\text{So } L_3 = \left(\frac{i_s}{i_{qp}}\right)^{1/2} \tag{18}$$

We can see that the above three cases are similar in that in each case the interplay of two processes with different kinetics leads to a characteristic length.

4.4 | Competitive nucleation of polymorphisms

A polymer can exhibit two or more crystalline forms, called polymorphism.[104] Among the different crystal forms, which form will finally present is a result of competition between nucleation and growth of the various crystalline forms. Cross nucleation is a special experimental phenomenon in which one crystal form nucleates on the surface of another crystal type, which has been observed in crystals of small molecules[105,106] and polymers[107–110]. During the isothermal crystallization process of poly(butylene adipate) at a certain temperature range, non-banded α form crystals are formed first, and then the banded β form crystals appear at the periphery of the α form crystals after a certain period of time.[107] Since the β form crystal has a larger radial growth rate than the α form, the late appearing β form crystal eventually surrounds the α form in the center of the spherulite. The competitive growth of the two crystalline forms can be explained by the nucleation kinetics, as schemed in Figure 7.[111] In the low-temperature range, the nucleation barriers (both primary and secondary) of the β form are smaller than those of the α form, resulting in only the β form. In the high temperature range, the situation is completely reversed, leading to the α form. In the intermediate temperature range, primary nucleation of α form and secondary nucleation of β form are preferred, with the former appearing in the center of the spherulites and the latter nucleating on the surface of the former. From this perspective, cross-nucleation reflects the competition between nucleation of different crystal phases. In addition, cross nucleation indicates that both secondary nuclei of α form and β form have certain probabilities (though different, depending on temperature) to be formed at the crystal growth front, which could not be explained by a defined mesophase. At the transition temperature range, the radial growth rate of poly(butylene adipate) shows a local minimum with varying temperature, which is similar to the self-poisoning effect observed by Alamo et al.[102,103] in other polymers.

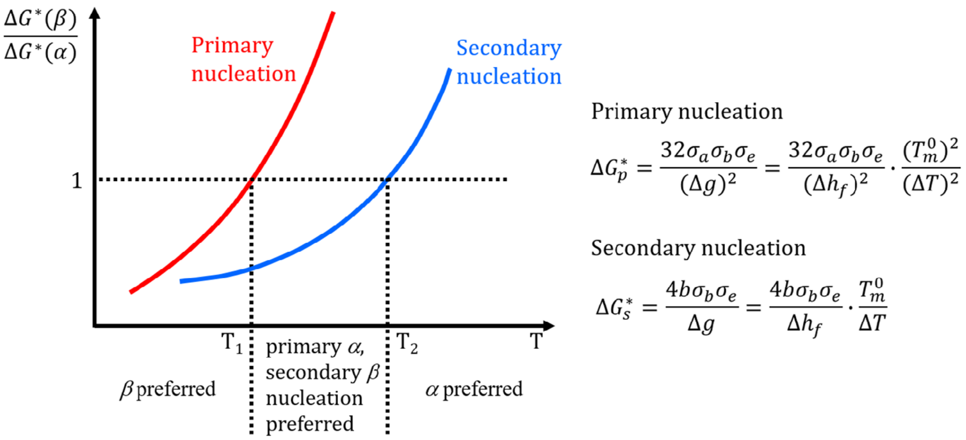
The metastable crystal phases might be easier to appear in random copolymers than in homopolymers.[112,113] One of the reasons may be due to the different numbers of repeating units in the critical nuclei of the metastable and stable crystal phase. Compared to homopolymer, the nucleation rates of the two crystal phases in the random copolymers both decrease with introduction of more non-crystallizable units. At the same isothermal crystallization temperature, if the metastable crystal has smaller critical nuclei, the decrease of nucleation rate in a random copolymer compared to homopolymer would be smaller in the metastable crystal than that in stable crystal. As a result, the previously faster nucleated phase in homopolymer may turn into a slower nucleated phase in random copolymers. Consequently, the rarely observed crystal phase in homopolymer may be easier to form in random copolymers. Surely, there might be other reasons for selection of polymorphism, which calls further study.

4.5 | Interplay among crystal growth, self-induced nucleation and chain diffusion

In the classical microscopic kinetics of nucleation developed by Becker and Döring[64] and Turnbull and Fisher,[65] the diffusion coefficient for each step is assumed to be the same, which is valid for small molecules above glass transition temperature and polymer chains crystallized from dilute solution. However, for growth of lamellar crystals from melt of polymer chains, the interplay between secondary nucleation, lateral spreading, chain diffusion and chain disentangling will lead to a complicated sequence,[20] including the effect of molecular weight on nucleation kinetics, the density and length of tie chains between two neighboring lamellae, and the final morphology (lamellar branching, with facets or not).

Depletion length is just a result from interplay of crystal growth and melt diffusion in thin film. Figure 6(C) illustrates the depletion length L_D as determined by the growth rate G and diffusion coefficient D at the crystal growth front.

Another typical example of interplay of nucleation, growth and diffusion is the crystal morphology of isotactic polystyrene grown from thin melt film.[114,115] For very thin film, one-layer single crystals are usually observed. At large undercooling, each single crystal shows



$$\Delta G_p^* = \frac{32\sigma_a\sigma_b\sigma_e}{(\Delta g)^2} = \frac{32\sigma_a\sigma_b\sigma_e}{(\Delta h_f)^2}\cdot\frac{(T_m^0)^2}{(\Delta T)^2}$$

$$\Delta G_s^* = \frac{4b\sigma_b\sigma_e}{\Delta g} = \frac{4b\sigma_b\sigma_e}{\Delta h_f}\cdot\frac{T_m^0}{\Delta T}$$

FIGURE 7 Scheme showing the competitive nucleation of different crystal forms.[111] Copyright 2017. Reproduced with permission from Elsevier B.V

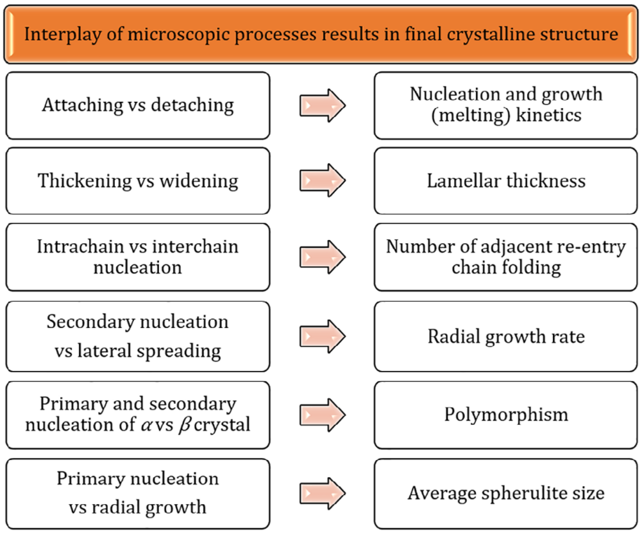


FIGURE 8 Main physical processes included in this perspective

a spherical shape, indicating no preference of the sites of secondary nucleation.[116] In contrast, at low undercooling, the single crystal is hexagonal, with the six corners preferred for secondary nucleation. With increase of film thickness, multi-layer single crystals appear due to the effect of self-induced nucleation to produce new layers of crystals. The probability of self-induced nucleation is much lower than that of the secondary nucleation. The competition of lamellar growth, self-induced nucleation (or in other cases macro screw dislocations) and chain diffusion leads to formation of non-birefringent banded spherulites caused by the periodical variation of the number of layers of the single crystals.[114,116–119] The formation of such non-birefringent banded spherulites has been summarized in a review.[120] With increase of film thickness, the band spacing increases while the depletion length decreases, which implies that the band spacing may be affected mainly by the density of self-induced nucleation or screw dislocations. The corresponding mechanism deserves further study, which should take the interplay of the involved various kinetic processes into account.

In very thin film, the competition of secondary nucleation, lateral spreading and chain diffusion can lead to regular lamellar branching. In fast growing crystals of small molecules, branching has been attributed to Mullins-Sekerka instability resulting from interplay of crystal growth, diffusion of impurities and dissipation of heat.[121–125] For many cases of branching polymer single crystals, the growth of crystals is very slow and diffusion may not be limited, so we speculate that the density of secondary nucleation may play an important role in determining the spacing of branches, which deserves further investigation.

In fact, even the secondary nucleation itself is an interplay of microscopic attaching and detaching processes, as mentioned above. We summarize in Figure 8 the main interplays of microscopic processes discussed in this perspective. Interplay of these kinetic processes results in the final crystalline structures.

5 | SUMMARY AND PERSPECTIVE

Nucleation and growth control the assembly of ordered crystalline structures from polymer chains. Due to the multiple length and time scales, the final crystalline structures of polymers are mainly determined by kinetics rather than thermodynamics. To date, controversial arguments on the mechanism of secondary nucleation for polymers still remain, which demand further experimental investigations and theoretical developments. The present theories and models have large differences in many aspects, such as atomically smooth or rough growth faces, intermediate phase involved or not, short-chain sequences or whole stems as elements for attaching and detaching. Briefly, crystallization process is a consequence of the various sets of counterparts (see Figure 8), such as thermodynamic and kinetics, intramolecular versus intermolecular nucleation, entropic versus enthalpic barrier, and so forth. The interplay of these factors finally endows polymers various levels of hierarchical order, for example, chain conformation, lamellar crystals, crystalline textures, and so forth.

There are more and more evidences that secondary nucleation occurs at the crystal growth front. Due to thermal fluctuation, the ordered (or semi-ordered) chain stems or clusters with different sizes

(e. g. different stem lengths, different number of foldings) and various chain conformations will be randomly born at the growth front. However, only those that recognize the topology of growing surface and are thus difficult to detach are finally chosen to be incorporated into the crystals. Namely, there are selecting or screening processes at the crystal growth front. Finally, the ordered structures that are faster produced (kinetically preferred) and with stronger molecular interaction with crystal surfaces (thermodynamically favored) survive and remain to be observed.

The biggest difference between crystal nucleation of small molecules and that of flexible polymer chains is that the units are covalently linked in each polymer chain. Analysis of the microscopic kinetics reveals that the nucleation rate and the minimum thickness of the nuclei are determined by the minimum stable nuclei (in which the change of total free energy is zero) rather than the critical nuclei (in which the differential of free energy change with size equals zero). This is the most important key point of this perspective and has seldom been considered in the previous theories. Can we modify the Lauritzen-Hoffman theory with the entropic barrier to obtain the kinetics considering intrachain nucleation? Should we consider each intrachain folded cluster as a motif for attaching and detaching? Answers to these questions are not clear yet.

So far, polymer crystallization has been studied for over 60 years. There are still some fundamental open questions to answer: For example, what is the nature of crystallization? What is the basic difference between the molecular interactions in crystals and melts? Is interfacial free energy contributed by only interfaces or both interfaces and bulk? What is the optimal order parameter to describe the detailed pathway of secondary crystallization? These are basic key questions to answer.

The starting state of melt surely affects polymer crystallization. There have been numerous reports that self-nucleation and stresses affect both the crystallization kinetics and final morphology. Are there some local ordered structures in the quiescent melt before crystallization happens? For instance, will local fluctuation in density, chain orientation and chain conformation affect the rate of secondary nucleation? Is epitaxial crystallization similar to secondary nucleation? These questions still deserve further examination.

Melting point represents the degree of stabilization of polymer crystals. How can we obtain information of secondary nucleation from melting? Recently, the force-induced melting in polymer single crystals was studied by single-molecule force spectroscopy.[126] A direct observation of desorption of a melt of long polymer chains was given by employing fast scanning calorimetry.[127] We may expect that these new methods will provide a technological breakthrough to establish links between crystallization mechanism and melting.

Chemical structures of the polymer chains considerably affect the thermodynamics and kinetics of crystallization. Previously, studies on crystallization of homopolymers with different molecular weights and random copolymers with various compositions have gained deep insight into secondary nucleation. Recently, the random copolymers and polymers with equally spaced substituent groups have been utilized to study the melt memory effect.[94,128] It is expected that further studies on the polymers with defined sequence length of crystallizable units, different chain topologies (e. g., cyclic polymers, multi-arm polymers and crosslinked polymers with the same strand length) and tuned intra- and inter-molecular interaction would provide deeper information on secondary nucleation.

Real-time observation of adsorption and crystallization process of polymer chains on a substrate surface would reveal more molecular information during nucleation. Langmuir–Blodgett films prepared via different compressive pressures provide various amorphous states with different initial densities. In addition, application of different forces on a single chain to induce crystallization or melting of single crystals via single molecular force spectroscopy would help reveal the molecular interaction during secondary nucleation. These novel characterization techniques are expected to reveal more molecular information.

Observation of nucleation in colloid crystals have been intensively studied, which deepens our understanding on crystallization of small molecules.[129,130] Can we use chains consisted of connected colloids to simulate polymer crystallization? The nucleation of colloidal crystals has to overcome an entropic barrier, however, it is not clear yet whether nucleation of colloidal chains could simulate the enthalpic barrier during nucleation of polymer crystallization or not.

Combining new theories, simulation tools, delicate design of molecular structures and intra/intermolecular interactions, new characterization methods and novel observations will be greatly beneficial to further understanding of the remaining open questions in nucleation of polymer crystallization, whatever primary and secondary nucleation. Provided we could draw a detailed picture of nucleation one day, we can then effectively control the crystalline structures of polymer materials at any stage through appropriate processing steps. After establishing a quantitative relationship between structure and properties, we may tune the functions for various applications at will. Thus, a profound understanding of secondary nucleation will optimize the molecular design, ordered functional assemblies of polymer chains and industrial manufacturing process of crystalline polymeric materials.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

ORCID

Jun Xu https://orcid.org/0000-0003-2345-0541

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