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A distribution kinetics approach for polymer crystallization and phase separation

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A DISTRIBUTION KINETICS APPROACH FOR POLYMER CRYSTALLIZATION AND PHASE SEPARATION

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemical Engineering

By
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B.S. East China University of Science and Technology, Shanghai, China, 1999
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December 2006
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Abstract

The mechanism of polymer crystallization is extensively studied and still far away from consensus. This research adopted cluster size distribution kinetics approach to explore the kinetics of polymer crystallization and phase separation within spinodal region.

The kinetics of polymer crystallization is studied by integrating nucleation, crystal growth and ripening. Population balance equations based on crystal size distribution and concentration of amorphous polymer segments are solved numerically and the related differential moment equations are also solved. The model accounts for nucleation and crystal growth. Different mass dependences of growth and dissociation rate coefficients are proposed to investigate the fundamental features of crystal growth.

The effect of temperature is also investigated for isothermal and nonisothermal polymer crystallization. Incorporating temperature effects of nucleation and crystal growth rate, the model presents time dependencies of polymer concentration, number and size of crystals, and crystallinity for different temperatures and cooling rates. The effect of denucleation is investigated by comparing moment and numerical solutions of the population balance equations. Incubation periods introduced in nonisothermal crystallization are studied under different cooling rates and different initial temperatures.

The distribution kinetics approach is also extended to the investigation of crystallization of polymer blends. Blending effects from polymer-polymer interactions are incorporated into the diffusion coefficient. The melting temperature, activation energy of diffusion, and phase transition enthalpy also depend on polymer blends composition, and lead to characteristic kinetic behavior of crystallization. The influence of different
composition is presented through the time dependence of polymer concentration, number and size of crystals, and crystallinity.

Another extended application of distribution kinetics approach is the study of the kinetics of spinodal decomposition. Spinodal decomposition occurs under conditions of large supersaturation and/or small ratio of interfacial to thermal energy when the energy barrier for nucleation is negligible. A cluster distribution kinetics model without nucleation is established to describe the unique kinetics of new phase domain growth. Population balance equations show how clusters aggregate and rapidly lead to phase separation.
Chapter 1 Introduction

1.1 Overview

Many macromolecular species are structured as linear, long-chain molecules, for example, protein, DNA, cellulose and numerous synthetic polymers. These macromolecules consist of thousands of repeating units and show characteristic behaviors different from simple molecules during aggregation, degradation, crystallization, and macromolecule chain folding. One of the unique characteristic behaviors is the formation of finely ordered structure from the entangled polymer chains during processes such as protein folding and polymer crystallization. These processes have attracted much interest since the idea of chain folding was first reported by Keller [1957]. Though the formation of a macromolecular folded structure was widely studied in detail by many scientists in the past five decades, no consensus has been reached about the mechanism for how the entangled structure finally yields a finely ordered structure, thus the investigation of the polymer chain folding mechanism is a great scientific challenge.

Understanding the mechanism of self-assembly during polymer crystallization also has practical applications in industry. Synthetic polymers show unique features in their nucleation and crystallization. Understanding the mechanism of nucleation and crystal growth is critical for manufacturing process and determination of the final product properties, such as crystal size distribution, thermal stability and mechanical properties. In practice, polymers such as biomedicine and plastic have wide applications in manufacturing industry, pharmaceutical industry, agriculture and transportation in our daily life. For instance, aramid fibers and superoriented polyethylene fibers, high-modulus and high-strength engineering
plastics comparable to metals have replaced metallic material in some fields, for example, engineering plastics are used to make a whole car body. There are also medical applications in artificial organs and diagnostic equipment materials. It is interesting to note that many macromolecules can crystallize into ordered structure, a process that also involves chain folding. For these reasons, the mechanism of macromolecule chain folding needs to be studied in more detail.

The science of polymer crystallization has a long history, but there is no unified theory that satisfactorily describes polymer crystallization; it remains a great academic challenge. Polymer crystallization arouses scientific interest in several fields, ranging from basic polymer science to polymer processing and application. Because crystallization occurs during the manufacture of polymeric materials, the understanding of its mechanism is necessary for macroscopic structure design and final product properties control. Besides macroscopic structure design, future nanometer-size composites and blends also open new possible application fields with improved thermal stability and mechanic properties.

1.2 Structure Models of Polymer Crystal

In the early days of polymer physics, it was suggested that polymer does not form well-defined structure. The first model of polymer crystal structure is the fringed micelle model, as shown in Figure 1.1.a, based on the fact that many polymers are partly crystalline and partly amorphous, the fringed micelle model is termed semi-crystalline model [Herman et al., 1930; Flory, 1962]. Because of the specific long chain characteristics of polymer molecules, the polymer chains inevitably entangle with each other randomly so that free volume exists between these chains. During cooling and solidification, the chains become aligned and pack into ordered arrays. These ordered arrays are termed as crystallite and are separated from each other by the amorphous regions. Because the polymer chain length is
much longer than the dimension size of crystal, a polymer molecule may meander from one crystal to another crystal through the intervening amorphous region.

Inspired by the fringed micelle model, Keller [1957] proposed a folded chain lamellar model. The folded chain lamellar model gained overwhelming acceptance over the fringed micelle model in the field of polymer science. The folded chain lamellar model suggested the crystalline region takes the form of thin platelets or thin lamellae (crystallites) in which the polymer chains are aligned perpendicular to the flat face of platelets and fold repeatedly, as shown in Figure 1.1.b [Mandelkern, 2001]. The thickness of the lamellae is typically around 10nm, while the lateral size of the lamellae is up to 0.01mm for most polymers. It was found, during crystal growth, the crystallites grow up from a thin lamella nucleus into large structures termed spherulites. Between each thin lamella is a flat amorphous region. Each spherulite comprises many small lamellae bridged by flat amorphous regions as suggested by the fringed micelle model, as shown in Figure 1.1.a. Although the folded chain model is accepted by most of polymer scientists, there is still much controversy about the

![Figure 1.1 (a) Fringed micelle model [Herman et al., 1930; Flory, 1962] and (b) Folded chain model [Mandelkern, 2001]](image-url)
detail surface configuration of lamellae crystals. The adjacent re-entry model suggested that the polymer chain adjacent to an aligned polymer chain would bend over and find another unoccupied region to reenter into the same crystallites rather than go through an amorphous region to enter into another, as shown in Figure 1.1.b. The adjacent model is also termed the perfectly folded chain model. On the contrary, the switchboard model proposed that the polymer chain never reenters the crystallites where its adjacent chain crystallizes but goes through an amorphous region to deposit on another lamella surface, as shown in Figure 1.2 [Flory, 1962; 1981]. Both of these two models are perfect cases and can represent only limiting cases; the actual crystal structure is more complex than all of these models.

1.3 Theory of Polymer Crystallization Kinetics

Formation of ordered solid phase, such as crystals, typically starts with nucleation, in which a seed, or a tiny embryo of the new phase, is formed. Nucleation occurs during a first order phase transition, in which a new phase is generated from an old phase that has higher free energy. Crystal growth, the overlapping process accompanying nucleation, is the successive deposition of polymer chains on the nucleus, the aligned polymer chains. However, not all nuclei are able to lead to stable crystal structure. Only the nuclei with size
greater than the critical size are stable and keep growing. Otherwise, the nuclei will dissolve because of the instability, which is termed denucleation. According to classical nucleation

![Density fluctuation of liquid phase](image)

**Figure 1.3** Density fluctuation of liquid phase [Vekilov, 2004]

theory, the formation of a new phase is caused by density fluctuation that happens everywhere in the liquid system. When fluctuation density is higher than the new phase, the free energy of fluctuation, $\Delta G$, will be greater than the free energy of nucleation $\Delta G^*$, hence nuclei of the new phase appear, as shown in Figure 1.3 [Vekilov, 2004]. The theoretically postulated mechanism as a superposition of fluctuations along the order parameters density and structure was proposed recently. According to this theory, a density fluctuation may never lead to the formation of a dense liquid droplet when the system is above the liquid-liquid coexistence line, as shown in Figure 1.4 [Asherie and Lomakin, 1996]. On the contrary, a density fluctuation may selectively lead to the formation of a new phase as the system is below the liquid-liquid coexistence line. According to the Gibbs capillarity approximation [McClurg and Flagan, 1998], the free energy for homogenous nucleation is the sum of surface energy and free energy of formation for a spherical particle of radius $r$,
\[ W(r) = 4\pi r^2\sigma - \left(\frac{4}{3}\right)\pi r^3\left(\rho_c/x_m\right)k_BT\ln S \] (1.1)

where \( \sigma \) is the particle interfacial energy and \( k_BT\ln S \) is the chemical potential difference between two phases in terms of supersaturation, \( S \). For a supersaturated system, the particle energy \( W(r) \) reaches its maximum, \( W^* \), at the critical particle radius, \( r^* \),

\[ r^* = \frac{2\sigma x_m}{(\rho_ck_BT\ln S)} \] (1.2)

The nucleation rate can be presented as the flux over the nucleation energy barrier, \( W^* \). A well known explanation of polymer crystallization kinetics is Avrami's phase transition theory. Avrami first related the extent of crystallinity \( X(t) \) to crystallization time \( t \), by the general Avrami equation \([Avrami, 1939; 1940; 1941] \),

\[ 1 - X(t) = e^{-K_t^m} \] (1.3)

where \( X(t) \) is the crystallinity, \( t \) represents crystallization time, \( m \) is termed as the Avrami exponent, and \( K_t^m \) is the volume of crystallization material, which should be determined by considering the following two cases: (a) the nuclei are predetermined, that is, they all develop at once on cooling the polymer to the preset temperature, which is termed heterogeneous

Figure 1. 4 The phase diagram of polymer solution \([Asherie and Lomakin, 1996] \).
nucleation, and (b) there is sporadic nucleation of spherical crystals, which is named homogeneous nucleation. Based on the work of Avrami, Evans [1945] and Hay [1971]

Table 1.1 The Avrami parameters for different crystal structures

<table>
<thead>
<tr>
<th>Crystallization mechanism</th>
<th>Avrami constants</th>
<th>Restrictions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>m</td>
</tr>
<tr>
<td>Spheres</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sporadic</td>
<td>$2/3 \pi g^3l$</td>
<td>4.0</td>
</tr>
<tr>
<td>Predetermined</td>
<td>$4/3 \pi g^3L$</td>
<td>3.0</td>
</tr>
<tr>
<td>Discs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sporadic</td>
<td>$1/3 \pi g^2ld$</td>
<td>3.0</td>
</tr>
<tr>
<td>Predetermined</td>
<td>$\pi g^2Ld$</td>
<td>2.0</td>
</tr>
<tr>
<td>Rods</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sporadic</td>
<td>$1/4\pi gld^2$</td>
<td>2.0</td>
</tr>
<tr>
<td>Predetermined</td>
<td>$1/2\pi gld^2$</td>
<td>1.0</td>
</tr>
</tbody>
</table>

simplified the derivation of the original Avrami equation and reported the Avrami parameters for polymer crystallization shown in Table 1.1 and Table 1.2. Depending on whether preexisting nuclei are presented or not, nucleation can be classified into primary (homogeneous nucleation) and secondary nucleation (heterogeneous nucleation). In homogeneous nucleation, formation of a stable nucleus is brought about by the ordering of polymer chains in a parallel array stimulated by intermolecular force. The preexisting seeds, such as extraneous dust, initiate heterogeneous nucleation. As a polymer melt or solution is cooled there is a tendency for the molecule to move toward their lowest energy conformation, and this will lead to the formation of ordered chains. However, two factors impede the ordering required for nucleation: cooling, which reduces diffusion coefficients, and chain entanglements. The second step, the growth of a crystalline region, is impeded by low
diffusion coefficient at low temperature and thermal redispersion of the chains at the crystal/melt surface at higher temperature. Therefore the crystallization process is limited to a range of temperature between the glass transition temperature $T_g$ and the melting point $T_m$. Strong intermolecular force favors the alignment of polymer chains at specific distances from one another to form crystalline nuclei.

Table 1.2 Avrami exponent, m, for specific polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Range of Avrami Exponent $m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-3, 3-bischloromethylloxacyclobutane</td>
<td>$1.7 \sim 3.3$</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>$2.6 \sim 4.0$</td>
</tr>
<tr>
<td>Polymethylene</td>
<td>$1.8 \sim 2.6$</td>
</tr>
<tr>
<td>Polyethylene oxide</td>
<td>$2.0 \sim 4.0$</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>$2.8 \sim 4.1$</td>
</tr>
<tr>
<td>Polydecamethylene terephthalate</td>
<td>$2.7 \sim 4.0$</td>
</tr>
<tr>
<td>Isotactic Polystyrene</td>
<td>$2.0 \sim 4.0$</td>
</tr>
</tbody>
</table>

Soon after the discovery of the unique chain-folded structure in polymer crystals, Hoffman and Lauritzen [1960], based on the surface nucleation theory, established the foundation of the kinetic theory of polymer crystallization from solution and melt (LH model) by paying particular attention to the formation energy of chain-folded nuclei. Surface nucleation of a new layer on the thin side of the lamellae was regarded as the key process of polymer crystallization. It was assumed that there is an ensemble of crystals of different thickness, each of which grows with constant rate. The crystals with most rapid growth rate will dominate this ensemble; hence the average thickness of the ensemble, which is the
observed thickness in experiments, is close to the thickness of the crystals with fast growth rate. The growth rate is derived by assuming that a new crystalline layer grows by the deposition of a succession of stems (straight portions of the polymer chain that go through the crystal once) along the growth front. Two major factors, thermodynamic driving force and the free energy barrier of deposition of the first stem in a layer, determine the growth rate. Thermodynamic driving force favors crystallization when the thickness of the lamellae is greater than $\delta_{\text{min}}$, the minimum thickness of stable nuclei. The free energetic cost of forming the two lateral surfaces on either growth front of the lamellae increases as the crystal thickness increases. The crystallization of thick crystals is increasingly slow. The free energy

$$A(N_{\text{stem}}) = 2b\delta\sigma + 2(N_{\text{stem}} - 1)ab\sigma_f - N_{\text{stem}}ab\delta\Delta F$$  \hspace{1cm} (1.4)$$

where $a$ and $b$ are the width and depth of a stem, $\delta$ is the thickness of the lamellae, $\sigma$ is the lateral surface free energy, $\sigma_f$ represents the fold surface free energy, and $\Delta F$ denotes the free

Figure 1.5 Energy profile of polymer chain folding in crystallization [Lauritzen and Hoffman, 1960]
energy of crystallization. Thus the growth rate passes through a maximum at an intermediate value of thickness, which is slightly greater than $\delta_{\text{min}}$. Another relative newly developed approach, established by Sadler and Gilmer [1986], is termed as the entropic barrier model. It is a simplified model of polymer growth based on the interpretation of Monte Carlo simulations and rate-theory calculations. As in the surface nucleation theory, it was also suggested that the average thickness results from the competition between the thermodynamic driving force and free energy barrier contribution to the growth rate. However, a different cause of the free energy barrier was suggested. As the polymer crystal surface in the model can be very coarse, it was concluded that the details of the surface nucleation of new layer could be very unpredictable. Furthermore, the outer layer of crystal was found experimentally to be thinner than in the bulk; this rounded geometry profile prevents further deposition of polymer stems. Therefore, growth of a new layer can only start once a fluctuation occurs to an entropically unlikely configuration in which the crystal rounded profile is ‘squared-off’. The free energy barrier to crystallization increases with thickness because this fluctuation becomes more unlikely with increasing crystal thickness.

Looking into the free energy profile of crystallization pathway in detail, Doye and Frenkel [1998] proposed that the initial nucleus is not a single stem but two incomplete stems connected by a single fold, hence there is no energy barrier in the ‘saw tooth’ energy profile, shown in Figure 1.5, corresponding to the formation of the first fold. It was also proposed, after basic thermodynamics study, that the two-dimensional polymer gradually adopts a three-dimensional configuration termed as desorption transition and that crystallization is always preceded by adsorption. By removing some of the constraints in the LH model, the unconstrained Lauritzen-Hoffman model (ULH) was recently proposed by Doye and Frenkel [1998, 1999] to critically examine the LH and SG theories, in which the polymer stem does
not have to be the same length of the thickness of lamellae, but can be of any length since it will grow by the deposition of the individual polymer unit. The simulation results of the ULH model confirmed that the initial nucleus was not a single stem, and also suggested that the average stem length in a layer was not determined by the properties of the initial nucleus. So the thickness of the lamella layer is not the same as that of the previous layer. Furthermore, a different thickness selection mechanism was proposed: the lamellar crystals select the value of the thickness for which growth with constant thickness can occur, and not the thickness for which the crystal lamellae grow most. Except for these two constraints, there is also a kinetics factor that affects the stem length. The growth of the stem can be terminated by the successful initiation of a new stem whenever a stem is longer than $\delta_{\text{min}}$.

The process of crystallization reported in Yamamoto’s work [1997; 2004] was classified into three stages: the initial stage for the local chain ordering into small clusters, the intermediate stage for the coalescing of the cluster into small lamellae, and the last stage for the completion of a single lamella. With the molecule dynamics model, the molecular process of lamellar thickening was reproduced and a new mechanism of lamellar thickness was proposed. The lamellar thickness increases continuously except for a slight slow down when the chain ends come close to the growth surface and stop at the limiting thickness, where both ends of the chain are located at the fold surface. In order to investigate the microscopic process of polymer crystal growth, two systems were considered, one is made of 640 chains of C100 and the other is made of 64 chains of C1000, both of them being placed between two parallel substrates which represent the growth surfaces of the polymer lamellae. In both systems, the growth of chain folded lamellae with marked tapered edges was observed. The crystallization rate was found to be very sensitive to the crystallization temperature and would stop growing at a certain temperature. In addition, the fold surfaces
are covered with relatively short chain folds, at least about 60-70% of the length of the nearest inner layer, which also results in rounded surface profile.

Polymer crystal seldom fully represents the structure suggested by any structure model. For example, chain ends can be observed as cilia emerging from a crystal surface as a type of crystal defect; a significant number of polymer chains adsorbed on the crystal surface fold parallel to the growth direction while most of polymer chains fold perpendicular to the growth direction. A three-dimensional bond fluctuation model was presented by Chen and Higg [1998] in their crystallization study of monodisperse polymers and extremely long chain polymers in solution. Stiff parameter (or kink energy) and global chain flexibility were introduced in their model. It was proposed that polymer chain with small stiffness would lead to a folded chain crystal with sharp boundary and few defects while large stiffness would result in an irregularly folded crystal with more defects.

United-atom Langevin dynamics simulations were performed to reproduce early stage polymer crystallization, which include the regime of single nucleation and secondary nucleation and growth, at the microscopic level by Liu and Muthukumar [1998]. It was found that polymer crystallization is characterized by the competition between configuration entropy in the available torsional states and the enthalpy of the Lennard-Jones attraction. Meanwhile, slow kinetics caused by chain entanglement also has a strong effect on it. For a short chain polymer molecule, it was found that the local orientational order parameter displays a sharp initial increase followed by a constant growth rate since chain entanglement for a short chain is not an important factor. The time evolution indicated that straight segments form rapidly and assemble in small domains while the chain readjusts itself into a more perfect, more stable conformation in a long time range. It was also found that chains
with lengths of integer multiples of the growth front thickness crystallize more efficiently than other chains.

Besides the investigation of kinetics and thermodynamics of neat polymer crystallization, our research interest is also extended to the crystallization of polymer blends. Blending is a useful and economical way to produce new materials with a variety of properties. Many high-performance thermoplastics are prepared by the crystallization of polymer blends. The polymer-polymer interactions during crystallization complicate nucleation and chain folding crystal growth, and consequently alter crystal structure, thermal stability, and mechanical properties such as rigidity and toughness. Understanding how adding a polymer component affects the morphology, crystallization, and mechanical and thermal properties of the polymer blend is very important not only in scientific investigation but also in industrial materials manufacturing. The existence of polymer-polymer interactions influences the deposition mechanism, causing either an increase or decrease of the crystal growth rate. For example, the spherulite radial growth rate of PEM [poly(ethyl methacrylate)] was found to decrease as PEO [poly(ethylene oxide)] is added as the binary component [Cimmino, 1999]. By contrast, the presence of poly(vinyl methyl ether) was found to enhance the spherulite growth rate of isotactic polystyrene [Bartczak et al., 1984]. Crystallization of PHBV [poly (3-hydroxybutyrate-co-hydroxyvalerate)] and PCL [poly(ε-caprolactone)] was analyzed by the Avrami equation by using two-step crystallization in the PHBV/PCL blends [Qiu et al., 2005], the crystallization rate of PHBV at 70°C decreased with the increase of PCL in the PHBV/PCL blends, while the crystallization mechanism did not change. On the contrary, the crystallization rate of PCL at 42°C was found to increase with the addition of PHBV, indicating the addition of PHBV change the crystallization mechanism of PCL. Increases in the spherulitic growth rate and crystallinity were also found
for poly(vinyl methyl ether) added as a second ingredient in isotactic polystyrene [Martuscelli et al., 1985]. The miscibility and crystallization of PES [poly(ethylene succinate)] and PVPh [poly(vinyl phenol)] blends were investigated and it was found that the growth rate of neat PES was higher than that of blended PES crystallized at the same temperature, which indicates that the addition of PVPh reduces the spherulite growth of PES in blends [Qiu et al., 2004]. A theoretical model was developed by Rostami [1990] to explain the slower rate of spherulite growth in thermodynamically miscible blends of semicrystalline and amorphous polymer. The effects of blending on crystal growth and nucleation were investigated in detail by considering the loss of supersaturation caused by blending for miscible polymer blends. Harris and Robeson [1987] also proposed a hypothesis to explain the enhancement of the crystallinity of a crystallizable component diluted with a miscible polymer. The interlamellar region, which contains the amorphous fraction, increased as the amorphous component is added to semicrystalline polymer. The increased amorphous fraction reduces the glass transition temperature and lends additional mobility to the crystallizable ingredient, thus allowing a higher fraction of this ingredient in the crystalline phase.

Obviously, chain folding is a fundamental phenomenon in polymer crystallization. Our study aims to look into the underlying fundamental mechanism for these phenomena and establish valid mathematic models to provide a better approximation for the kinetics and thermodynamics of polymer crystallization. Assuming a unified free energy of monomer addition and dissociation, the rate coefficient is represented in terms of cluster mass and activation energy for deposition. A cluster size distribution model is developed to investigate the kinetics of polymer crystallization initiated by homogeneous and heterogeneous nucleation in Chapter 2. In Chapter 3 and 4, we investigated the crystallization kinetics under
isothermal and nonisothermal conditions respectively by considering the temperature
dependence of nucleation and growth rate coefficient. Incorporated the blending effects on
nucleation and crystal growth, the distribution kinetics approach is extended to investigate
the characteristic behaviors for polymer blends crystallization in Chapter 5. The validity of
the application of cluster distribution theory in polymer crystallization is examined by the
comparison with Avrami phase transition theory and experimental measurements. The
kinetics distribution approach is also redeveloped to investigate the kinetics of spinodal
decomposition in Chapter 6. The basic processes in condensation phase transition are
nucleation, dispersed cluster growth by reversible monomer deposition, cluster aggregation
(coalescence), and Ostwald ripening (coarsening). However, the nucleation barrier is
vanishingly small as supersaturation is large or interfacial energy is small in spinodal region,
thus unhindered cluster coalescence dominates the phase transition. Thus population balance
equations without nucleation are established to investigate phase separation kinetics.
Chapter 2  Distribution Kinetics of Polymer Crystallization and the Avrami Equation*

2.1. Introduction

Since the discovery of crystallization of thin lamellar polymer crystals in solution [Keller, 1957], the study of polymer crystallization has received considerable attention. Polymer crystallization controls the macroscopic structure of the material, and thereby determines the properties of final polymer products [Sperling, 1992; Chen and Higg, 1998]. The morphology of polymer crystals is different from that of crystals consisting of simple molecules, due mainly to the difference between the chain connectivity in polymers and the assemblies of simple molecules [Doye and Frenkel, 1999]. This not only affects the equilibrium crystal structures but also the kinetics of crystal growth. When the system is cooled from the equilibrium melting temperature (T_m) to a lower crystallization temperature, the polymer crystals can form two-dimensional lamellar structures in both melt and solution via the stages: nucleation, lamellae growth, and spherulite aggregative growth [Mandelken, 2001; Shanks and Yu, 1996]. The formation of three-dimensional crystal structure from a disordered state begins with nucleation and involves the creation of a stable nucleus from the disordered polymer melt or solution [Ryan and Fairclough, 1999]. Depending on whether any second phase, such as a foreign particle or surface from another polymer, is present in the system, the nucleation is classified as homogenous nucleation (primary nucleation) or heterogeneous nucleation (secondary nucleation) [Frank and Tosi, 1961]. In primary nucleation, creation of the stable nucleus by intermolecular forces orders the chains in a parallel array. As the temperature goes below the melting

* Portion of this chapter is from J. Yang, B.J. McCoy and G. Madras, J. Chem. Phys., 122, 064901(2005)
temperature $T_m$, the molecules tend to move toward their lowest energy conformation, a stiffer chain segment, favoring the formation of ordered chains and thus nuclei. Facilitating the formation of stable nuclei, secondary nucleation is also involved at the beginning of crystallization through heterogeneous nucleation agents, such as dust particles. Following nucleation, crystals grow by the deposition of chain segments on the nucleus surface. This growth is controlled by a small diffusion coefficient at low temperature and by thermal redispersion of chains at the crystal/melt interface at high temperature [Doye and Frenkel, 1998]. Thus crystallization can occur only in a range of temperatures between the glass transition temperature $T_g$ and the melting point $T_m$, which is always higher than $T_g$.

As a consequence of their long-chain nature, subsequent entanglements, and particular crystal structure, polymers crystallized in the bulk state are never totally crystalline and a fraction of the polymer is amorphous. Polymers fail to achieve complete crystallinity because polymer chains cannot completely disentangle and align properly during a finite period of cooling. Lamellar structures can be formed, but a single polymer chain may pass through several lamellae with the result that some segments of the polymer chain are crystallized into the lamellae and some parts of the polymer chain are in the amorphous state between adjacent lamellae.

A well-known description of crystallization kinetics is the heuristic Avrami phase transition theory. Based on work of Avrami [1939], who adapted the formulations intended for metallurgy to the needs of polymer crystallization, the original derivations were simplified by Evans [1945] and rearranged for polymer crystallization by Meares [1965] and Hay [1971]. For the bulk crystallization of polymers, the crystallization kinetics can be represented as,

$$1 - X = e^{-Vt}$$

(2.1)
where $X$ is the degree of crystallization, and $V_t$ is the volume of crystallization material, which should be determined by considering the following two cases: (a) the nuclei are predetermined, that is, they all develop at once on cooling the polymer, and (b) the crystals nucleate sporadically. For a spherical crystal in case (a),

$$dV_t = 4\pi r^2 L dr$$

(2.2)

where $r$ represents the radius of the spherical crystal at time $t$ and $L$ is the number of nuclei. Assuming the radius grows linearly with time, $r = \kappa t$, upon integration of Eq. (2.2) and substitution into Eq. (2.1), one obtains

$$1 - X = e^{-K t^3}$$

(2.3)

where $K = (4/3)\pi\kappa^3 L$ is the growth rate. For sporadic nucleation, case (b), the above argument is followed, but the number of spherical nuclei is allowed to increase linearly with time at rate, $u$. Then nucleation from time $t_i$ to time $t$ will create a volume increase of

$$dV_t = (4/3)\pi\kappa^3(t_t - t_i)^3 u dt_i$$

(2.4)

Upon integration of Eq. (2.4) between $t_i = 0$ and $t$, and substitution into Eq. (2.1), one obtains

$$1 - X = e^{-K t^4}$$

(2.5)

where $K = (1/3)\pi\kappa^3 u$. The equations can be generalized by replacing the power of $t$ with the Avrami exponent $m$,

$$1 - X = e^{-K t^m}$$

(2.6)

Thus, according to these arguments, the Avrami exponent $m$ depends not only on the structure of the crystal but also on the nature of nucleation [Avrami, 1940].

 Though numerous models of crystal growth kinetics have been developed [Long et al., 1995], the Avrami equation with its basis in rather empirical ideas is still applied to polymer crystallization. Our aim is to investigate if the Avrami equation can be established by a more
fundamental approach to crystallization that incorporates homogeneous and heterogeneous nucleation, uneven growth of crystals into a particle size distribution, and final Ostwald ripening of the crystal size distribution. The distribution kinetics model [McCoy, 2001; Madras and McCoy, 2004] of nucleation, growth and aggregation results in an S-shape curve of crystallinity versus time. Considering the deposition of polymer chain on a crystal surface is similar to monomer attachment on a cluster, we adapt this kinetics model to explore polymer crystallization. An advantage of this model is the representation by rate coefficients of the microscopic polymer crystallization kinetics, making the model straightforward to understand, yet based on modern molecular concepts. To examine the validity of this model, we will compare the results with the Avrami equation [Avrami, 1941] and also relate the parameters of the two models.

2.2. Distribution Kinetics Theory of Polymer Crystallization

Homogenous nucleation can occur when the solution is supersaturated and thus metastable. Because of the great increase of the colliding probability among solute molecules in supersaturated solution, density fluctuations increase in intensity and frequency allowing nuclei to form sporadically. Classical homogeneous nucleation in the capillarity approximation [McClurg and Flagan, 1998] is based on the sum of surface energy and formation free energy for a spherical cluster of radius $r$,

$$W(r) = 4\pi r^2 \sigma - \frac{4}{3} \pi r^3 \left( \rho / x_m \right) k_B T \ln S$$

Here, $\sigma$ is the crystal interfacial energy and $\Delta G = -k_B T \ln S$ is the chemical potential difference between the two phases (the polymer solution or melt and crystal phase) in terms of supersaturation $S$. The typical structure of polymer crystal is thin lamellae and because of the equal probability of deposition in the $x$ and $y$ directions, an equilateral lamellar structure is proposed. The total energy of such a 2-D lamellar crystal is presented as
\[ W(a) = 4a \delta \left( \frac{\sigma}{x_m} \right) k_B T \ln S \tag{2.8} \]

where \( a \) is the lateral length and \( \delta \) is the thickness of the lamellae. Obviously, the energy \( W(a) \) of a crystal increases with \( a \) and then decreases from the maximum value \( W^* \) at the critical lamellar length,

\[ a^* = \frac{2\sigma x_m}{(\rho k_B T \ln S)} \tag{2.9} \]

Thus the maximum energy of the crystal, by replacing \( S \) with \( m(0)/m_\infty(0) \) according to the definition of supersaturation, is represented as,

\[ W^* = 4x_m \delta \sigma^2 / [\rho k_B T \ln (m(0)/m_\infty(0))] \tag{2.10} \]

Here the local-equilibrium concentration is \( m_{eq}(0) \) and the solubility of a flat surface is \( m_\infty(0) \). The expression for the nucleation rate [McCoy, 2001] is derived from the flux over the energy barrier at the critical nucleus size,

\[ I = k_n \exp \left( -\frac{W^*}{k_B T} \right) \tag{2.11} \]

with prefactor

\[ k_n = (m(0))^2 (2\sigma x_m/\pi)^{1/2} \rho^{-1} \tag{2.12} \]

written in terms of monomer concentration \( m(0) \) and crystal density \( \rho \).

For a crystal with curved surface, the local equilibrium interfacial concentration at the crystal surface \( m_{eq}(0) \) is related to the solubility of a flat surface \( m_\infty(0) \) by the Gibbs-Thomson equation,

\[ m_{eq}(0) = m_\infty(0) \exp(\Omega) \tag{2.13} \]

where \( \Omega = 2\sigma x_m / r \rho k_B T \) in terms of monomer molecular weight \( x_m \), surface energy \( \sigma \), radius of curvature \( r \), Boltzmann constant \( k_B \), and absolute temperature \( T \). For a 2-D crystal lamella, however, the growth front is a flat surface and the radius of curvature \( r \) is infinite. Thus, consistent with Eq. (2.13), the difference between local-equilibrium concentration, \( m_{eq}(0) \), and the
The solubility of a flat surface, \( m^{(0)} \), is negligible because \( \Omega \) vanishes as \( r \) approaches infinity. Therefore \( \Omega \) presents the effects of microscopic structure.

The crystal mass distribution is defined so that \( c(x, t)dx \) represents the molar concentration of crystals having values of mass in the range of \( x \) to \( x + dx \) at time \( t \). Integral forms of the rate expressions in the population balance equation lead to moment calculations of the crystals and monomers. The general moments are defined as integrals of the crystal distribution over \( x \),

\[
c^{(n)}(t) = \int_0^\infty c(x, t) x^n \, dx
\]  

(2.14)

The zeroth moment \((n = 0)\) is the total number (or concentration) of crystals; the first moment stands for the mass concentration of the crystals. The average crystal mass is the ratio of first moment over zeroth moment, \( c^{\text{avg}}(t) = c^{(1)}(t) / c^{(0)}(t) \). The monomers are assumed monodisperse with moments \( m^{(n)}(t) = x_m^n \, m^{(0)}(t) \).

Similar to cluster growth in the distribution kinetics model [McCoy, 2001], crystallization is the gradual building up of monomer on the nucleus surface in a melt or solution. A general representation of chain deposition on the crystal surface is

\[
k_g \quad C(x) + M(x_m) \xrightarrow{k_d} C(x + x_m)
\]  

(2.15)

The rate coefficients \( k_g \) and \( k_d \) are for growth and dissociation, respectively. Different from general cluster distribution theory, crystal breakage and aggregation are usually not considered in polymer crystallization.

The population balance equations [Madras and McCoy, 2004] that govern the distributions of crystals and monomer are

\[
\frac{\partial c(x, t)}{\partial t} = -k_d c(x, t) + k_d \int_x^\infty c(x', t) \delta(x - (x' - x_m)) \, dx' - k_g c(x, t) \int_0^\infty m^{(0)}(t) \delta(x' - x_m) \, dx'
\]
\[ + k_g m^{(0)} \int_{0}^{x} c(x', t) \delta(x - x_m) dx' + I \delta(x - x^*) \]  

(2.16)

and,

\[
\frac{dm(x, t)}{dt} = -k_d c(x, t) + k_d c(x+x_m) - k_g c(x) m^{(0)} + k_g c(x-x_m) m^{(0)} + I \delta(x-x^*) \]  

(2.17)

where the homogeneous nucleation rate for crystals of critical nucleus \(x^*\) is \(I \delta(x - x^*)\). The distribution of the crystals changes according to Eq. (2.16), which becomes, when the integrations over the Dirac distributions are performed, the finite-difference differential equation,

\[
\frac{dc(x, t)}{dt} = -kd c(x, t) + kd c(x+x_m) - k_d c(x) m^{(0)} + k_g c(x-x_m) m^{(0)} + I \delta(x-x^*) \]  

(2.18)

### 2.2.1 Moment Methods

The general moment equations are determined by applying the operation \(\int_{0}^{\infty} \) \(x^n dx\) to Eqs. (2.16) and (2.17), which yields

\[
\frac{dc^{(n)}}{dt} = -(kd + kgm^{(0)}) c^{(n)} + \sum_{j=0}^{n} (-1)^{n-j} k_d c^{(j)} x_m^{n-j} + I x^* \]  

(2.19)

and,

\[
\frac{dm^{(0)}}{dt} = (kd - kgm^{(0)}) c^{(0)} - I x^*/x_m \]  

(2.20)

For \(n = 0\) and 1 the first two moment equations for crystals are

\[
\frac{dc^{(0)}}{dt} = I \]  

(2.21)

\[
\frac{dc^{(1)}}{dt} = -x_m(k_d - kgm^{(0)}) c^{(0)} + I x^* \]  

(2.22)

Multiplying \(\frac{dm^{(0)}}{dt}\) by \(x_m\) gives monomer mass, and then Eqs. (2.20) and (2.22) satisfy the mass balance, \(x_m \frac{dm^{(0)}}{dt} = - \frac{dc^{(1)}}{dt}\). As time approaches infinity, the nucleation rate will vanish as the supersaturation approaches unity, and a thermodynamic equilibrium condition will finally be achieved. At equilibrium or steady state the derivative with respect to time equals zero, and by Eq. (2.20) or (2.22), the total concentration of polymer chains in solution becomes

\[
m^{(0)}_{eq} = \frac{kd}{kg} \]  

(2.23)
We define the dimensionless quantities,

\[ S = \frac{m^{(0)}}{m_{eq}^{(0)}}, \quad C^{(n)} = \frac{c^{(n)}}{m_{eq}^{(0)}x_m^n}, \quad \theta = \tau k_g m_{eq}^{(0)}, \quad J = \frac{I}{(m_{eq}^{(0)})^2 k_g} \]  

(2.24)

The moment equations can be written in dimensionless form,

\[
\frac{dS}{d\theta} = (1 - S)C^{(0)} - \left(\frac{x^*}{x_m}\right)J \\
\frac{dC^{(0)}}{d\theta} = J \\
\frac{dC^{(1)}}{d\theta} = - (1 - S)C^{(0)} + \left(\frac{x^*}{x_m}\right)J
\]  

(2.25, 2.26, 2.27)

Microscopic reversibility provides the thermodynamic equilibrium, \( S_{eq} = 1 \), in Eq. (2.25), as \( dS/d\theta = 0 \) and \( J = 0 \) at the end of crystallization. For homogeneous nucleation, the initial conditions are \( S(\theta = 0) = S_0, C^{(0)}(\theta = 0) = 0, C^{(1)}(\theta = 0) = 0 \), meaning that no preexisting nuclei are involved. The source term, \( J \), represents the nucleation rate of crystals of mass \( x^* \).

The mass of a critical nucleus relative to the monomer mass depends solely on the interfacial energy and the supersaturation [McCoy, 2001],

\[ \frac{x^*}{x_m} = \left(\frac{\omega}{\ln S}\right)^d \]  

(2.28)

where \( d \) represents the dimension of the crystal structure and \( \omega \) presents the ratio of interfacial energy to thermal energy, written as

\[ \omega = \frac{(4\pi \rho / 3x_m)^{1/3} 2\sigma x_m / \rho k_BT}{\rho k_BT} \]  

(2.29)

for 3-D spherical structures and,

\[ \omega = \frac{2\sigma (x_m \delta / \rho)^{1/2}}{k_BT} \]  

(2.30)

for 2-D lamellar systems. The critical nucleus mass increases with time as supersaturation \( S \) decreases. The scaled mass balance equation in a closed system follows from Eqs. (2.25) and (2.27),

\[ C^{(1)}(\theta) + S(\theta) = C^{(1)}_0 + S_0 \]  

(2.31)

where \( C^{(1)}_0 \) is the initial mass of crystals in polymer solution or melt, representing heterogeneous nucleation nuclei or seeds, \( S_0 \) represents the initial number of amorphous monomers.
homogeneous nucleation, $C_0^{(1)} = 0$. Based on Eq. (2.5), the homogeneous nucleation rate is written in dimensionless form as,

$$J = \alpha S^2 \exp \left[-(d-1)^{-1} \omega^d / (\ln S)^{d-1}\right]$$  \hspace{1cm} (2.32)

with $\alpha = (2\sigma_{xm}/\pi)^{1/2}/\rho_{kg}$. By Eq. (2.28), the number of monomers included in the critical nucleus, $x^*/x_m$, is written in terms of supersaturation $S$, for the specific lamellar structure,

$$x^*/x_m = \frac{\omega^2}{(\ln S)^2}$$  \hspace{1cm} (2.33)

The substitution of the scaled nucleation rate yields the fully dimensionless equations for 2-D lamellae system,

$$\frac{dS}{d\theta} = (1-S)C^{(0)} - \alpha \omega^2 S^2 \exp(-\omega^2 / \ln S) / (\ln S)^2$$  \hspace{1cm} (2.34)

$$\frac{dC^{(0)}}{d\theta} = \alpha S^2 \exp(-\omega^2 / \ln S)$$  \hspace{1cm} (2.35)

and,

$$\frac{dC^{(1)}}{d\theta} = -(1-S)C^{(0)} + \alpha \omega^2 S^2 \exp(-\omega^2 / \ln S) / (\ln S)^2$$  \hspace{1cm} (2.36)

For 3-D spherical crystal growth, however, the difference between the local equilibrium interfacial concentration at the curved crystal surface, $m_{eq}^{(0)}$, and the solubility of a flat surface, $m_{\infty}^{(0)}$, cannot be neglected. The Gibbs-Thomson factor $\Omega$ in Eq. (2.13) is written in term of crystal size $x/x_m$,

$$\Omega = \frac{\omega}{(x/x_m)^{1/d}}$$  \hspace{1cm} (2.37)

where $d$ is the dimension of the crystal structure and $\omega$ is the interfacial energy. Instead of being scaled by $m_{eq}^{(0)}$ as in 2-D systems, the dimensionless quantities are redefined as,

$$S = m^{(0)}/m_{\infty}^{(0)}, \quad C^{(n)} = c^{(n)}/(m_{\infty}^{(0)}x_m^n), \quad \theta = t k_g m_{\infty}^{(0)}, \quad J = I / (m_{\infty}^{\theta^2} k_g)$$  \hspace{1cm} (2.38)

Eqs. (2.20) - (2.22) are moment equations, so the single crystal size $x/x_m$ is approximated by average size of crystal $C^{avg}$. Thus Eqs. (2.20) - (2.22) are scaled in the form,

$$\frac{dS}{d\theta} = (-S + c^{(2n)})C^{(0)} - \alpha \omega^3 S^2 \exp(-\omega^3 / 2 (\ln S)^2) / (\ln S)^3$$  \hspace{1cm} (2.39)
\[ \frac{dC^{(0)}}{d\theta} = \alpha S^2 \exp\left( -\omega^3 / 2 \left( \ln S \right)^2 \right) \]  

(2.40)

and,

\[ \frac{dC^{(1)}}{d\theta} = -\left( -S + e^{\epsilon_{\text{as}}} \right) C^{(0)} + \alpha \omega^3 S^2 \exp\left( -\omega^3 / 2 \left( \ln S \right)^2 \right) / \left( \ln S \right)^3 \]  

(2.41)

where \( \Omega_s = \omega / (C^{\text{avg}})^{1/3} \) represents the average Gibbs-Thomson effect.

The crystallinity is defined as the ratio of the mass crystallized at time \( t \) divided by the total mass crystallized,

\[ X = \frac{C^{(1)} - C^{0(1)}}{C^{\text{eq}(1)} - C^{0(1)}} \]  

(2.42)

The ordinary differential moment equations are readily solved by standard software.

### 2.2.2 Numerical Methods

The growth and dissociation rate coefficients are assumed constant in the above moment method, but more generally, the rate coefficients are power law expressions for the mass dependence [Madras and McCoy, 2002]. For crystal growth, the rate coefficient may be written

\[ k_g(x) = \kappa_g x^\lambda \]  

(2.43)

where \( \kappa_g \) is a prefactor whose units are determined by the power \( \lambda \). The dissociation rate is determined by applying microscopic reversibility for the growth process,

\[ k_d(x) = m_{\text{eq}^{(0)}} k_g(x) \]  

(2.44)

The exponent \( \lambda \) equal to 0, 1/3, and 2/3 represents surface-independent, diffusion-controlled, and surface-controlled deposition rates, respectively [Madras and McCoy, 2002].

We define dimensionless quantities [McCoy, 2001] consistent with Eq. (2.24),

\[ \xi = x / x_m, \quad \theta = t \kappa_g m_{\infty}^{(0)} x_m^\lambda, \quad S = m^{(0)}/m_{\infty}^{(0)}, \]

\[ C = c x_m / m_{\infty}^{(0)}, \quad C^{(n)} = c^{(n)} / m_{\infty}^{(0)} x_m^{-n}, \quad J = I / \kappa_g m_{\infty}^{(0)} x_m^\lambda \]  

(2.45)

and note that \( \xi \) is the number of monomers in a crystal. The time \( \theta \), crystal size distribution \( C(\xi, \theta) \), and monomer concentration \( S(\theta) \) are scaled by the equilibrium monomer concentration.
Substitution of Eq. (2.45) into Eqs. (2.16) and (2.17) yields population balance equations in dimensionless form,

$$\frac{dS(\theta)}{d\theta} = (-S(\theta) + e^{\Omega_a})C(\lambda) - J \xi^*$$  \hspace{1cm} (2.46)

and,

$$\frac{\partial C(\xi, \theta)}{\partial \theta} = S(\theta)[-\xi^k C(\xi, \theta) + (\xi-1)^k C(\xi-1, \theta)] - \exp(\Omega(\xi)) \xi^k C(\xi, \theta) + \exp(\Omega(\xi+1)) (\xi+1)^k C(\xi+1, \theta) + J \delta(\xi-\xi^*)$$  \hspace{1cm} (2.47)

where $\Omega(\xi)$ is related to the crystal dimension $d$ [Madras and McCoy, 2003],

$$\Omega(\xi) = \omega / \xi^{1/d}$$  \hspace{1cm} (2.48)

Since Eq. (2.46) is a moment equation, $\Omega_a$ is related to the average number of monomers in the crystal, $C_{\text{avg}}$,

$$\Omega_a = \omega / (C_{\text{avg}})^{1/d}$$  \hspace{1cm} (2.49)

We note that moment equations cannot be derived because of $\xi$ in the exponential term. Thus, moment methods are not applicable for $\lambda > 0$ and numerical schemes have to be employed to solve the equations.

### 2.2.3 Heterogeneous Nucleation

To promote nucleation in supersaturated liquid or glass, small impurity (second phase) particles are often introduced deliberately. These impurity particles, acting as nucleation seeds, grow by depositing monomer on their surface. The activation energy for homogeneous nucleation presents a significant barrier for stable nuclei to be formed, whereas heterogeneous nucleation is limited only by monomer diffusion to the solid surfaces. For these ideal conditions, homogeneous nucleation would be negligible and heterogeneous nucleation dominant, the case we now consider. For heterogeneous nucleation, we set $I = 0$, thus the growth rate of the number of crystals, $dC^{(0)}/d\theta$, equals zero, and the population balance equations reduce to a single
ordinary differential equation. For the case of lamellar crystal growth, Gibbs Thompson effect $\Omega = 0$,

$$\frac{dS}{d\theta} = (1 - S)C_0^{(0)}$$

(2.50)

where $C_0^{(0)}$ is the number of nucleation agents. The exact solution, given the initial condition $S(\theta = 0) = S_0$, is written as

$$S = 1 + (S_0 - 1) \exp (-C_0^{(0)} \theta)$$

(2.51)

Consistent with the crystallinity definition, Eq. (2.42), and mass conservation, Eq. (2.31), the crystallinity for heterogeneous nucleation is expressed in terms of supersaturation $S$ and scaled time $\theta$,

$$X = (S_0 - S(\theta)) / (S_0 - S_{eq})$$

(2.52)

Substitution of Eq. (2.51) into Eq. (2.52) results directly in the crystallinity versus time evolution equation,

$$X = 1 - \exp (-C_0^{(0)} \theta)$$

(2.53)

which is the Avrami equation with growth rate $K = C_0^{(0)}$ and Avrami exponent $m = 1$.

2.3. Results and Discussion

The flat growth surface of lamellar crystal simplifies polymer nucleation and growth into readily solved moment equations by reducing the Gibbs-Thomson effects. These moment differential equations, Eqs. (2.34) ~ (2.36), are solved by NDSolve in Mathematica for various values of the parameters. The parameter $\omega$ represents the ratio of interfacial energy to thermal energy (Eq. (2.29)) and, based on published values for the interfacial energy [Singh and Glicksman, 1989], is chosen to span two orders of magnitude, 0.1~10. The nucleation rate prefactor $\alpha$, chosen to span widely from 0.0001 to 100, depends on the combination of the liquid-solid interfacial energy $\sigma$, monomer molecular weight $x_m$, solid phase density $\rho$, and growth rate
coefficient $k_g$. For homogeneous nucleation, the initial source term, $C_0^{(0)}$, is set to zero. An initial condition of $S_0 = 50$ is chosen to minimize the effects of denucleation in the computation.

Figure 2.1 presents the time dependence of the key variables in polymer crystallization, as computed via distribution kinetics. The time evolutions of supersaturation $S$ (Fig. 2.1.a), number of crystals $C^{(0)}$ (Fig. 2.1.b), the average number of crystallized monomers $C_{\text{avg}}$ (Fig. 2.1.c), and the degree of crystallinity $X$ (Fig. 2.1.d) are shown at various values of $\alpha$ for the 2-D system. A typical S-shape curve of polymer crystallization is confirmed in Figure 2.1.a. As the prefactor $\alpha$ increases, the overall crystallization rate increases, which is shown by the time needed to reach the steady state. A large $\alpha$ also leads to a large number of crystals at equilibrium.

Figure 2.1 Time evolution of $S$, $C^{(0)}$, $C_{\text{avg}}$, and $X$ as $\alpha$ varies among $10^{-1}$, $10^{-2}$, $10^{-3}$ and $10^{-4}$ with $\omega = 5$ and $\lambda = 0$. 
(Fig. 2.1.b). The average number of monomers in the crystal at equilibrium, $C_{\text{avg}}$, decreases as $\alpha$ rises (Fig. 2.1.c), since large $\alpha$ means a greater nucleation rate and results in a larger number of crystals at equilibrium. The prefactor $\alpha$ also has a negative influence on the induction time of crystallization because a large initial nucleation rate will shorten the induction time. The crystallinity time dependence (Fig. 2.1.d) is a mirror image of the supersaturation time evolution (Fig. 2.1.a). Following an S-shape curve, as observed in experiments, the crystallinity evolves to unity as supersaturation decreases to the equilibrium state.

Table 2.1 Effect of $\alpha$ on Avrami exponent $m$ for $\lambda = 0$, $\omega = 5$, $S_0 = 50$, and $C_0^{(0)} = 0$.

<table>
<thead>
<tr>
<th>$\alpha$</th>
<th>$10^{-4}$</th>
<th>$10^{-2}$</th>
<th>$10^{-1}$</th>
<th>$10^{0}$</th>
<th>$10^{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (2-D)</td>
<td>2.20</td>
<td>2.17</td>
<td>2.10</td>
<td>1.44</td>
<td>1.00</td>
</tr>
<tr>
<td>m (3-D)</td>
<td>1.00</td>
<td>1.23</td>
<td>1.46</td>
<td>1.00</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Table 2.2 Effect of $\omega$ on Avrami exponent $m$ for $\alpha = 0.1$, $\lambda = 0$, $S_0 = 50$, and $C_0^{(0)} = 0$.

<table>
<thead>
<tr>
<th>$\omega$</th>
<th>0.1</th>
<th>4.0</th>
<th>5.0</th>
<th>6.0</th>
<th>7.0</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (2-D)</td>
<td>1.97</td>
<td>1.80</td>
<td>1.77</td>
<td>1.76</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td>m (3-D)</td>
<td>1.9</td>
<td>1.48</td>
<td>1.46</td>
<td>1.35</td>
<td>1.12</td>
<td>----</td>
</tr>
</tbody>
</table>

Table 2.3 Effect of $\lambda$ on Avrami exponent $m$ for $\alpha = 0.1$, $\omega = 5$, $S_0 = 50$, $C_0^{(0)} = 0.0001$, and $C_0^{(1)} = 0$.

<table>
<thead>
<tr>
<th>$\lambda$</th>
<th>0</th>
<th>1/3</th>
<th>2/3</th>
<th>0.93</th>
<th>0.98</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (2-D)</td>
<td>1.70</td>
<td>2.00</td>
<td>3.09</td>
<td>5.27</td>
<td>5.32</td>
</tr>
<tr>
<td>m (3-D)</td>
<td>1.44</td>
<td>1.64</td>
<td>2.57</td>
<td>4.29</td>
<td>4.50</td>
</tr>
</tbody>
</table>
Because the plotted experimental data and simulations are not strictly straight lines, a defined method is needed to determine the slopes. The straight part of most plots begins at \( X = 0.1 \) and ends at \( X = 0.9 \), and includes the most significant range of data. We therefore used points corresponding to this interval in the measurement of slopes reported in Tables 2.1∼2.3.

The effects of \( \alpha \) on the Avrami exponent are compared for 2-D and 3-D systems in Figure 2.2. The interfacial energy \( \omega \) is set to 5, a surface independent growth and dissociation rates is proposed (\( \lambda = 0 \)), and the prefactor \( \alpha \) is chosen to span widely from \( 10^{-4} \) to \( 10^{2} \). According to Eq. (2.6), the Avrami exponent \( m \) is the slope of the double logarithm plot of \( -\ln (1-X) \) versus scaled time \( \theta \). Figure 2.2 presents the Avrami plots for 2-D and 3-D systems as \( \alpha \) varies from 0.0001 to 100. In contrast to the Avrami equation, these plots are not strictly straight lines, but curve slightly up at the beginning of crystallization and down at the final stage of crystallization. Curving up at the beginning is caused by the induction time, and the final curving down shows the approach to saturation. Hay [1971] reported that the Avrami equation provided a poor approximation at the final stage of crystallization because experimental data deviated from the straight line by curving down. We conclude that the distribution kinetics model, by accurately

![Figure 2.2](image_url)

Figure 2.2 The effects of \( \alpha \) on (a) 2-D and (b) 3-D crystallinity plots with \( \omega = 5 \), \( \lambda = 0 \), \( S_0 = 50 \), and \( C_0^{(0)} = 0 \).
predicting this behavior, more realistically represents the curve. In the 2-D system, an apparent slope difference of the Avrami plots is observed. The slope value for each plot is measured and tabulated in Table 2.1. We note the slope increases from 1.00 at $\alpha = 10^2$ to 2.20 at $\alpha = 10^{-4}$. However, when $\alpha$ is less than $10^{-4}$, the lines move horizontally right and the slope variation is too small to be measured, and all plots collapse into one straight line when $\alpha$ is greater than $10^2$.

In 3-D a smaller slope difference is observed (Fig. 2.2.b). The slope increases as $\alpha$ varies from $10^{-4}$ to 0.1, and drops down to 1.00 as $\alpha$ increases to 1. When $\alpha$ is greater than unity or less than $10^{-4}$, no measurable slope change is confirmed. All the plots with $\alpha$ greater than 1.0 collapse into one straight line and all the plots with $\alpha$ less than $10^{-4}$ are only transposed horizontally.

As the ratio of interfacial to thermal energy, $\omega$ influences nucleation and growth. By moment computations, the effects of $\omega$ are investigated for the 2-D and 3-D systems (Fig. 2.3). Figure 2.4 shows results of numerical computations for $\omega$ equal to 4, 5, and 6. The dotted lines represent 3-D while the solid lines represent the 2-D solution. The slopes for Figs 2.3 and 2.4 are reported in Table 2.2. The slope variation as $\omega$ changes is quite small in both 2-D and 3-D, and a larger slope is observed in the 2-D case. According to Eq. (2.33), a small value of $\omega$ leads to a

![Figure 2.3](image)

Figure 2.3 The effects of $\omega$ on (a) 2-D and (b) 3-D crystallinity plots by a moment solution with $\alpha = 0.1$, $\lambda = 0$, $S_0 = 50$, and $C_0^{(0)} = 0$. 
small critical size of crystal at constant supersaturation, and finally leads to a large nucleation rate. Increasing $\omega$ delays nucleation and the decrease of supersaturation. Figure 2.3.a presents the double logarithm plots as $\omega$ varies among 0.1, 4, 5, and 7 for the 2-D system. Different slopes, ranging from 1.75 at $\omega = 7$ to 1.97 at $\omega = 0.1$, are observed (Table 2.2). Similar to the effect of the nucleation prefactor $\alpha$, the influence of interfacial energy is notable only if $\omega$ is small. The slope difference disappears when $\omega$ is large, e.g., the slope at $\omega = 7$ is almost same as at $\omega = 10$. A reasonable explanation is that the crystal growth becomes the dominant term if $\omega$ is large, since the nucleation term exponentially decreases with $\omega^2$ as shown in Eq. (2.32). In the 3-D system, a more noticeable slope variation is observed at different $\omega$. The slope varies from 1.90 to 1.12 as $\omega$ changes from 0.1 to 7. The explanation for the greater influence of $\omega$ in the 3-D system, according to Eq. (2.25), is that the nucleation rate is a function of $\omega^3$ in 3-D and of $\omega^2$ in 2-D. Comparing the numerical and the moment results (Figs. 2.3 and 2.4, respectively) reveals that the numerical result of crystallinity reaches an asymptotic value at large time while the moment result continues to increase. This is the influence of denucleation, which is ignored in the moment computations. Different values of $\alpha$ and $\omega$ have the expected effects as shown in Fig. 2.4.
2.5, larger values of $\alpha$ shift the curves to smaller times, whereas larger values of $\omega$ give larger times. These findings for 2-D are similar to 3-D results. Figure 2.6 shows that the effect of increasing the initial supersaturation is to shift the Avrami curves to smaller times. Changing $S_0$ has little influence on the slope, which increases from 1.69 to 1.78 when $S_0$ is increased from 5 to 100.

The exponent of growth and dissociation rates, $\lambda$, is 0, 1/3, and 2/3, for surface-
independent, diffusion-controlled, and surface-controlled deposition rate, respectively (Fig. 2.7).

To explore more thoroughly the effect of $\lambda$, we included $\lambda = 0.93$ and 0.98 in Table 2.3. A possible explanation for the larger $\lambda (>2/3)$ is the increasing mass dependence of deposition rate caused by shear force during fluid movement or by microscopic structural changes [Yoshioka and Tashiro, 2003]. Eqs. (2.40) and (2.46) were solved by Runge-Kutta technique with an adaptive time step and $C(\xi,0)$ is evaluated at each time step sequentially. The mass variable, $\xi$, is divided into 5000 intervals and the adaptive time step varied from $10^{-5}$ to $10^{-2}$ ensuring stability and accuracy at all values of the parameters. At every time step the mass conservation was verified. According to Eqs. (2.46) and (2.49), a nonzero initial condition of $C_0^{(0)}$ should be chosen to avoid singularities near $t = 0$ in the numerical computation. In our simulation, $S_0 = 50$, $C_0^{(0)} = 0.0001$ and $C_0^{(1)} = 0$ are the initial conditions. Figures 2.7.a and 2.7.b present the effects of $\lambda$ on 2-D and 3-D systems, respectively. Different slopes are confirmed as $\lambda$ varies in both 2-D and 3-D cases, as shown in Table 2.3. The range of slope values is consistent with reported experimental measurements [Nagarajan et al., 2000] for the Avrami exponent $m$ in Eq. (2.6), $1 \leq m \leq 4$. Avrami exponents greater than 4 are occasionally reported; for example, slopes

![Figure 2.7](image_url)

Figure 2.7 The effects of $\lambda$ with $\alpha = 0.1$, $\omega = 5$, $S_0 = 50$, $C_0^{(0)} = 0.01$ and $C_0^{(1)} = 1$ for (a) 2-D and (b) 3-D.
of up to 5.0 for syndiotactic polystyrene crystallization were found by Yoshioka and Tashiro [2003], who suggested cone-like spherulite growth as a potential explanation for the large value of \( m \).

The influence of geometry dimension is also confirmed by comparing the slopes for 2-D and 3-D systems. Smaller slopes are found in the 3-D system, as shown by Tables 2.1~2.3. The parametric effects are also different for 2-D and 3-D systems. We note that \( \omega \) has less effect on the Avrami exponent in the 2-D system, whereas \( \alpha \) has a larger effect. Compared with the effects of the other parameters, \( \lambda \) has a substantial influence on the Avrami exponent.

A comparison of moment methods and numerical methods is made for the 2-D system to investigate the effects of denucleation (Fig. 2.8). Figure 2.8.a presents the comparison of moment and numerical solutions as \( \alpha \) varies. Figure 2.8.b shows the comparison of these two solutions, both for flat growth surfaces, at different \( \omega \). The dotted line presents the moment simulation and the solid line is the numerical solution. Although the two solutions are consistent at the beginning of crystallization, an increasing discrepancy is observed near the end of crystallization, where crystallinity \( X \) is about 0.99. This discrepancy caused by the increasing effect of denucleation that can only be computed numerically. Denucleation, the reverse process of nucleation, results from the stability shift of formed crystals from stable to unstable. The reduction of supersaturation during crystallization, according to Eq. (2.33), increases the nucleus critical size. As the supersaturation decreases, nuclei smaller than the critical size become unstable and dissolve instantaneously [McClurg and Flagan, 1998], while nuclei larger than the critical size keep growing. At the beginning of crystallization when the supersaturation is large, the denucleation rate, compared with nucleation rate, is too small to have a noticeable effect on the time evolution of degree of crystallinity [McCoy, 2001]. As the crystal keeps growing, however, more and more nuclei become unstable and tend to dissolve because of the increasing
critical size of nucleus. At the end of crystallization, the effect of denucleation, compared with the nucleation rate, can become substantial, and is manifested as Ostwald ripening.

The validity of the distribution kinetics model is also examined by comparison with experimental data (Fig. 2.9). The points are experimental data [Weng et al., 2003] for nylon-6 based on real time t (min) at T = 188°C, 190°C, and 192°C. The initial supersaturation, S₀, has not been reported for the experiments and is assumed to be 50 in the computations. To compare
with the model based on dimensionless time $\theta = t \, k_g m_{eq}^{(0)}$, a transposition of the simulation results is applied. According to the definition of dimensionless time, Eq. (2.24), a distance of $\log(k_g m_{eq}^{(0)})$ units is transposed horizontally to the left to convert the simulation results into plots based on real time $t$ (min). A zero horizontal distance is transposed to fit the experimental data at $T = 188^\circ C$; thus $k_g m_{eq}^{(0)} = 1.00 \, \text{min}^{-1}$. Similarly, the values of $k_g m_{eq}^{(0)}$ at $T = 190^\circ C$ and $192^\circ C$ are readily determined by the measurements of the horizontal transposition distance to be $0.80 \, \text{min}^{-1}$ and $0.68 \, \text{min}^{-1}$, respectively. The experimental measurements at $T = 190^\circ C$ and $192^\circ C$ are horizontal transpositions of the simulation results at $T = 188^\circ C$, and there is no slope variation. This is consistent with the understanding that $k_g m_{eq}^{(0)}$ depends on temperature.

Figure 2.10 presents an Avrami plot for experimental polypropylene (PP) data at $110^\circ C$ [Ryan and Fairclough, 1999]. The scattered points are experimental measurements, the solid line is a fit of the distribution kinetics model, and the dashed line is the Avrami equation with $m = 3.0$. Figure 2.10.a shows the evolution of crystallinity $X$ versus real time. The Avrami equation with $m = 3.0$ fits the data fairly well except where the data curve down and deviate from the Avrami equation at the end of crystallization (Fig. 2.10.b). The solid line is our model prediction for $\lambda = 2/3$, $\alpha = 0.1$, and $\omega = 5$. The predicted slope is 3.09, as reported in Table 2.3, and is close to the value 3.0 reported by Ryan and Fairclough [1999]. The scaling factor for time is $\kappa_g m_{\infty}^{(0)} x_m^\lambda = 6.76 \times 10^{-3} \, \text{min}^{-1}$. It is interesting that the curving down at the end of crystallization is predicted in the crystal size distribution model and fits the experimental data quite well. The Avrami equation, by contrast, provides a constant slope, and thus fits only the intermediate data.

We also compared the Avrami exponent determined in our theory with published experimental measurements. According to Tables 2.1 ~ 2.3, for $\lambda < 2/3$, the model shows a range
of $1 \sim 5$ for the Avrami exponent, consistent with most published values [Kuo et al., 2003; Kajaks and Flores, 2000; Qiu et al., 2004].

For heterogeneous nucleation, the distribution kinetics directly results in an Avrami equation with growth rate $K = C_0^{(0)}$ and Avrami exponent $m = 1$, as suggested in Eq. (2.52). The double logarithm plots are made to investigate the effect of $C_0^{(0)}$. It is confirmed that the crystallization rate increases with the number of nucleation agents, as shown in Figure 2.11. The Avrami exponent, which is the slope of the double logarithm plot, always equals unity for $\lambda = 0$. It is possible, however, that homogeneous and heterogeneous nucleation occur simultaneously, yielding $m > 1$.

The effect of $\lambda$ on the Avrami exponent is also investigated for heterogeneous nucleation, as shown in Figure 2.12. It is observed that the overall crystallization rate increases as $\lambda$. The final crystallinity arrives at $\theta = 10$, 100 and 1000 at $\lambda = 2/3$, 1/3, and 0 respectively. The Avrami exponent $m$ also increases with $\lambda$, predicting values 1.76 at $\lambda = 2/3$, 1.31 at $\lambda = 1/3$ and 1.00 at $\lambda$.

![Figure 2.10](image)

Figure 2.10 The fit of crystal size distribution model to the experimental data of polypropylene [Ryan and Fairclough, 1999]; the solid line is a fit of the distribution kinetics model and the dashed line is the Avrami equation with $m = 3.0$. 
Figure 2. 11 The Avrami plot as $C_0(0)$ varies from 0.01 to 0.03 in steps of 0.01 for heterogeneous nucleation with $\lambda = 0$ and $S_0 = 50$.

= 0. Compared with $m$ for homogeneous nucleation in Table 2.3, the $m$ values for heterogeneous nucleation are small. This is explained by the additional kinetics contribution caused the increase of the number of nuclei in homogeneous nucleation, which does not arise in heterogeneous nucleation because the number of nuclei is constant. We also note that the slope variation is

Figure 2. 12 The effect of $\lambda$ for heterogeneous nucleation at $C_0(0) = 0.01$, $C_0^{avg} = 75$, $S_0 = 50$ and $\omega = 5$.

smaller than homogeneous nucleation because the additional kinetics contribution in homogeneous nucleation increases as $\lambda$. 
2.4. Conclusion

Nucleation and crystal growth are essential phenomena in quantitatively describing the evolution of a crystallizing polymer solution or melt. A kinetics model based on cluster distribution dynamics incorporates these processes and realistically represents the time evolution of crystallinity. The model includes rate coefficients for crystal growth, $k_g$, and crystal dissociation, $k_d$. Based on widely accepted notions, a 2-D lamellar structure for the polymer crystal nucleus is proposed, and thus the Gibbs-Thomson effect is excluded for the 2-D lamellar structure system. A 3-D spherical structure is also investigated to demonstrate the influence of Gibbs-Thomson effects. Population balance equations based on crystal and amorphous polymer segments lead to the dynamic moment equations for the molar concentrations for mass independent monomer deposition rate coefficients. Numerical solution is required if the deposition rate is diffusion- or surface-controlled and the rate coefficients are consequently size-dependent power expressions.

Although it is widely agreed that the Gibbs-Thomson effect is critical for understanding nucleation and crystal growth, less acknowledged is that the Gibbs-Thomson effects can be neglected for the flat growth surface of a specific lamellar structure. Our proposal is that the combined processes of nucleation and crystal growth can be described by moment equations developed from distribution kinetics, i.e., population dynamics theory. The validity of moment methods is examined by comparison with the numerical methods. Consistency is confirmed between these two methods except for the discrepancy at the end of crystallization caused by denucleation.

Another goal of our current work has been to reconcile distribution kinetics and the empirical Avrami equation by examining the detailed, fundamental features of nucleation mechanism and crystal growth. The comparison with general experimental observations suggests
that distribution kinetics is a more realistic approximation at the end of crystallization than the
Avrami transition theory. The investigation of model parameters offers a quantitative way to
determine Avrami parameters, which can only be determined empirically by Avrami transition
theory.
Chapter 3 Temperature Effects for Isothermal Polymer Crystallization Kinetics

3.1 Introduction

Polymer crystallization is a complex phenomenon in materials and pharmaceutical processing that profoundly affects microscopic structure and properties of polymer products. Understanding the kinetics of polymer crystallization is a significant scientific challenge. The nucleation and growth of polymer crystals involve the dynamics of polymer chains, including the formation of folded chain structures. To explore the kinetics of polymer crystallization, we adopted a cluster size-distribution kinetics model in Chapter 2 for nucleation accompanied by crystal growth and Ostwald ripening [Yang et al., 2005a]. Population balance equations based on crystal size distribution and concentration of amorphous polymer segments were established and the related dynamic moment equations were also developed. The model accounted for heterogeneous or homogeneous nucleation and crystal growth. The results were graphed as Avrami plots, thus providing a fundamental basis for this common method of crystallization analysis. In this chapter, we will focus on temperature effects for isothermal polymer crystallization.

Frequently overlapping with crystal growth [Madras and McCoy, 2004; Robson, 2004], nucleation initiates the phase transition from fluid (liquid) phase to solid (crystal) phase. Among other features, this overlap complicates the kinetics and dynamics of such systems. The effect of temperature on interfacial energy, growth rate coefficients, and equilibrium solubility can potentially be used to design manufacturing methods and to control product properties, e.g., average size of polymer crystal, microscopic structure, and polydispersity of crystal size.

* Portion of this chapter is from J. Yang, B. J. McCoy and G. Madras, J. Chem. Phys., 122, 244905(2005)
Much research effort has been directed toward polymer crystallization, but a detailed understanding of temperature effects is still lacking. Recent experimental studies [Supaphol and Spruiell, 2000; Kim and Chung, 2000; Guo et al., 2001; Xu et al., 2002; Hama and Tashiro, 2004; He et al., 2004] for isothermal crystallization of different polymers reported that small changes in temperature caused substantial changes in the crystallization rate. The characteristic Avrami exponents (slopes of Avrami plots) varied from 1 to 4 and were independent of temperature. Most of the data also show a deviation from straight-line Avrami plots at long times (large crystallinity) by curving toward a constant asymptote. Classical nucleation theory based on estimates of the interfacial free energy was applied for nucleation between $T_g$ (glass transition temperature) and $T_m$ (melting temperature) and showed that the crystallization kinetics were sensitive to small temperature changes [Ciora and Magill, 1990]. A study of the molecular weight effect for isothermal crystallization indicated that the crystallization rate is essentially not affected by the polymer molecular weight [Acierno and Grizzuti, 2002]. A challenge in modeling temperature effects for polymer crystallization is to represent quantitatively these effects, and in particular the strong influence of temperature on crystallinity.

Crystal growth temperature dependence is controlled by the competition among kinetic and thermodynamic phenomena [Doye and Frenkel, 1999]. High temperature favors a large crystal growth rate but also enhanced crystal solubility. The nucleation rate temperature dependence complicates the temperature effect even more. For the polymer melt, nucleation occurs when the temperature drops below the melting temperature $T_m$. By enhancing the equilibrium solubility, increasing temperature decreases supersaturation. Furthermore, interfacial energy and thus nucleation vanish at $T_m$. Decreasing temperature to the glass temperature $T_g$, however, also causes nucleation to vanish or become infinitesimal because of
the drastic increase of fluid viscosity. Therefore nucleation for polymer melt is limited to the temperature range between $T_g$ and $T_m$, and a maximum nucleation rate is expected between these two temperatures [McCoy, 2004].

Crystallites in polymers exert a major influence on their bulk properties. Modification of crystallinity can significantly alter mechanical and optical properties. Thus the thermal history of a polymer, in particular between $T_g$ and $T_m$, greatly influences its end-use value [Leisen and Beckham, 2004]. Understanding the temperature effect, the key parameter influencing industrial crystallization, is essential for rational manufacturing design and operation. Potentially one can exploit the competition between kinetics and thermodynamic driving forces to manipulate the crystallization rate, crystal size, and particle polydispersity. Here the distribution kinetics approach is to represent the dynamics and kinetics of nucleation and growth processes by a cluster size-distribution model. The temperature effect is incorporated into the model by considering the temperature dependence of interfacial energy, equilibrium solubility, and growth rate coefficient. We begin in the next section by reviewing the theory of nucleation, growth, and coarsening for polymer crystallization. In a following section, quantitative results of the theory are presented and discussed, along with comparison with published experimental data. Conclusions are presented last.

3.2 Modified Distribution Kinetics Model for Isothermal Crystallization

Temperature influences nucleation and crystal growth in polymer processing through kinetics and thermodynamics. As polymer melt or solution is cooled, the molecule tends to move toward the lowest energy conformation, leading to the formation of ordered chains [Doye and Frenkel, 1998]. Chain entanglement, however, impedes the ordering required for nucleation. As the polymer solution or melt is cooled, diffusion coefficients decrease. When cooled to the glass transition temperature $T_g$, the polymer solution or melt becomes glassy and nucleation is totally
quenched because no molecules are able to overcome the diffusion resistance to aggregate and align into a nucleus. The growth of the crystalline region is also impeded by reduced diffusion at low temperature and thermal redispersion of the chains at the crystal/melt surface at higher temperature.

Temperature effects on nucleation rate, according to the classic nucleation theory [McClurg and Flagan, 1998], originate from the interfacial energy difference and equilibrium solubility change at various temperatures. Temperature influences incorporated in crystal growth rate include the prefactor of growth rate coefficient, the Gibbs-Thomson effect of particle curvature [Oxtoby, 1992], and the phase transition energy (heat of solidification). The dissociation rate coefficient is related to the growth rate coefficient by microscopic reversibility, thereby determining its temperature dependence.

For a 2-D equilateral lamellar crystal, according to classical homogeneous nucleation theory, the sum of surface energy and formation free energy can be represented as Eq. (2.8) [Yang et al., 2005a; Madras and McCoy, 2003]. The total energy $W(a)$ of a cluster increases with crystal lamella length, $a$, and then decreases from the maximum value $W^*$ at the critical lamellar length, $a^*$, Eq. (2.9). According to the similarity of thermodynamic driving force expressions for nucleation from polymer solution and polymer melt [Yang and Qiu, 1986; Oxtoby, 1992; Vekilov, 2004], the supersaturation $S$ can be written in terms of number of free macromolecules $m^{(0)}$ and $m_\infty^{(0)}$, $S = m^{(0)}/m_\infty^{(0)}$, instead of melting enthalpy and temperature driving force, thus the maximum energy of the cluster can be represented in terms of $m^{(0)}$ and $m_\infty^{(0)}$, as in Eq. (2.10). The nucleation rate, according to classical homogeneous nucleation theory, is the flux over the maximum energy barrier (at $a = a^*$), as shown in Eqs. (2.11) and (2.12). Thermodynamics provides the temperature dependence of solubility for the corresponding flat surface,

$$m_\infty^{(0)} = \mu_\infty \exp(-\Delta H/RT)$$  (3.1)
where $\Delta H$ represents the molar energy of phase transition between solid (crystal) phase and liquid phase, and $\mu_\infty$ stands for the flat-surface polymer solubility at high temperature.

The temperature dependence of interfacial energy $\sigma$ is approximated by [Rowlinson and Widom, 1982],

$$\sigma = \sigma_0 (1 - T/T_m)^n$$

causing interfacial energy $\sigma$ to vanish at reference temperature $T_m$. For $n = 0$ or 1, $\sigma$ is constant or linearly decreasing, respectively [Rowlinson and Widom, 1982]. But for $n \approx 20$, $\sigma$ falls sharply for $T << T_m$, and then decreases gradually to zero as $T$ approaches $T_m$. For the present model, this dependence of interfacial energy on $T$ is critical for explaining the temperature dependence of polymer crystallinity.

Similar to cluster growth in the kinetics model of McCoy [2001], crystal growth can be considered as the gradual building up of polymer molecules on the surface of the nucleus in a melt or solution. A general representation of the reversible deposition of chain segments on the crystal surface is expressed in Eq. (2.15), where $C(x)$ represents the cluster of mass $x$ and $M(x_m)$ is the polymer of uniform molecular weight $x_m$ with a distribution written as $m(x, t) = m^{(0)} \delta(x - x_m)$. The mass-dependent rate coefficients $k_g(x)$ and $k_d(x)$ are for cluster growth and dissociation, respectively. Developed from Eq. (2.43), an activation energy for the growth coefficient accounts for its temperature dependence,

$$k_g(x) = \gamma x^\lambda \exp (-E/RT)$$

The exponent $\lambda$ can be set equal to 0, 1/3, and 2/3, representing surface independent, diffusion controlled, and surface dependent growth rate [Madras and McCoy, 2003]. Numbers larger than 2/3 are also occasionally suggested [Nagarajan et al., 2000; Yang et al., 2005], for the increasing mass dependence of deposition rate caused by microstructure changes or shear force during fluid
movement. The rate coefficient for dissociation is simply related to \( k_g(x) \) by microscopic reversibility, 
\[ k_d(x) = m_{eq}^{(0)} k_g(x), \]
where \( m_{eq}^{(0)} \) represents equilibrium concentration at local cluster surface.

For a lamellar crystal with flat growth front, the Gibbs-Thomson effect vanishes, so that the difference between local equilibrium interfacial concentration \( m_{eq}^{(0)} \) and solubility \( m_\infty^{(0)} \) for a flat surface vanishes, thus \( m_{eq}^{(0)} = m_\infty^{(0)} \). The population balance equations that govern the distributions of crystals and macromolecules are represented in Eqs. (2.16) and (2.17) [Yang et al., 2005a; Madras and McCoy, 2003]. In consistent with the definition of growth rate coefficient in Eq. (3.3), the population balance equations are based on unit of mole/volume. We define dimensionless quantities as follows,

\[
C = \frac{c}{x_m/\mu_x}, \quad C^{(n)} = \frac{c^{(n)}}{x_m^n}, \quad \xi = \frac{x}{x_m}, \quad \theta = \frac{\gamma \mu_x x_m^\lambda}{\mu_x}, \quad S_T = \frac{m^{(0)}}{m_\infty^{(0)}}, \quad \Theta = \frac{T}{T_m}, \quad w = \frac{2\sigma_0 (x_m^\delta/\rho)^{1/2}}{RT_m}, \quad J = \frac{1}{\gamma \mu_x x_m^\lambda}, \quad \epsilon = \frac{E}{RT_m}, \quad h = \frac{\Delta H}{RT_m}
\]

where numbers of polymer molecules and polymer crystals, \( S_T \) and \( C^{(0)} \), are scaled by solubility at high temperature \( \mu_x \). The supersaturation, \( S = m^{(0)}/m_\infty^{(0)} = S_T \exp(h/\Theta) \), evolves to unity at thermodynamic equilibrium. The temperature is scaled by a reference temperature \( T_m \), the melting temperature of polymer crystal. The interfacial energy, \( \omega = w (1 - \Theta)^n/\Theta \), is expressed in terms of scaled temperature \( \Theta \) and the temperature-independent parameter \( w \). With the definition of the nth moment, 
\[
C^{(n)} = \int_0^\infty \xi^n C(\xi, \theta)d\xi,
\]
for the special case \( \lambda = 0 \) the dimensionless population balance equations for crystal growth and nucleation can be represented as moment equations,

\[
dS_T(\theta)/d\theta = \exp(-\epsilon/\Theta) \left[ -S_T(\theta) + \exp(-h/\Theta) \right] C^{(0)} - J \xi^* \quad (3.5)
\]

and

\[
dC^{(0)}(\theta)/d\theta = J \quad (3.6)
\]

\[
dC^{(1)}(\theta)/d\theta = -\exp(-\epsilon/\Theta) \left[ -S_T(\theta) + \exp(-h/\Theta) \right] C^{(0)} + J \xi^* \quad (3.7)
\]
Here J represents the scaled homogeneous nucleation rate of crystal of critical mass size $\xi^*$ and is a source term in Eqs. (3.5), (3.6), and (3.7). The number of macromolecules in the critical crystal nucleus is also related to temperature and $S_T$,

$$
\xi^* = [w (1 - \Theta) n / \Theta (\ln S_T + h/ \Theta)]^2
$$

(3.8)

$\xi^*$ varies with time, because of the time dependence of the scaled number of crystallizing polymers $S_T$, and is strongly dependent on temperature. The initial conditions are $S_T(\theta = 0) = S_{T0}$ and $C^{(0)}(\theta = 0) = 0$ for homogeneous nucleation. For a batch system without agitation, crystallizing temperature is the only operating condition. In terms of the initial number of polymer molecules $S_{T0}$, the scaled mass conservation for a closed system follows from the population balance equations, Eqs. (3.5) and (3.7),

$$
C^{(1)}(\theta) + S_T(\theta) = C_0^{(1)} + S_{T0}
$$

(3.9)

where $C_0^{(1)}$ is the initial cluster mass, representing heterogeneous nuclei and seeds, and is zero for homogeneous nucleation, and $S_{T0}$ is the initial number of polymer molecules. At thermodynamic equilibrium, supersaturation $S$ equals unity, so that the thermodynamic driving forces for crystal growth and nucleation rate vanish. Thus the time evolution rates of moments are zero, $dS_T(\theta)/d\theta = 0$ and $dC^{(0)}(\theta)/d\theta = 0$. The degree of crystallinity, $X$, is defined as the ratio of the mass crystallized at time $t$ divided by the total mass crystallized,

$$
X = (C^{(1)} - C_0^{(1)})/(C_{eq}^{(1)} - C_0^{(1)})
$$

(3.10)

Substitution of the mass conservation equation, Eq. (3.9), simplifies Eq. (3.10) to,

$$
X = (S_{T0} - S_T(\theta))/(S_{T0} - e^{-h/\Theta}) \approx 1 - S_T/S_{T0}
$$

(3.11)

where at equilibrium, consistent with Eq (3.5), $S = 1$ and $S_T = e^{-h/\Theta} \approx 0$, for $h >> \Theta$. By defining the temperature-independent prefactor,

$$
J_0 = (2\sigma_0/\pi)^{1/2} / \rho \gamma X_m^{\lambda-1/2}
$$

(3.12)
The nucleation rate can be written as,

\[ J = J_0 (1 - \Theta)^{n/2} S_T^2 \exp \left[ -w(1 - \Theta)^n / (\Theta \ln S_T + h/\Theta) \right] \quad (3.13) \]

The growth and dissociation rate coefficients are assumed to be mass independent \((\lambda = 0)\) in the above moment method. However, these rate coefficients are not always mass independent, especially for polymer solutions with high viscosity. A more general expression for the mass dependence is the power law dependence in Eq. (3.3) [Madras and McCoy, 2003]. With the dimensionless quantities of Eq. (3.4), Eqs. (2.16) and (2.17) can be rewritten as

\[
\frac{dS_T}{d\Theta} = \exp(-\varepsilon/\Theta) \left[ -S_T(\Theta) + \exp(-h/\Theta) \right] C^{(\lambda)} - J \xi^* \quad (3.14)
\]

and

\[
\frac{\partial C(\xi, \Theta)}{\partial \Theta} = S_T(\Theta) \exp(-\varepsilon/\Theta) \left( -\xi^* C(\xi, \Theta) + (\xi-1)\xi C(\xi-1, \Theta) \right) - \xi^* \exp(- (\varepsilon+h)/\Theta) C(\xi, \Theta)
\]

\[ + (\xi+1)\xi \exp(- (\varepsilon+h)/\Theta) C(\xi+1, \Theta) + J \delta(\xi-\xi^*) \quad (3.15) \]

Here, \(\partial C(\xi, \Theta)/\partial \Theta\) represents the generation rate of clusters with \(\xi\) polymers. Numerical schemes are employed to solve the equations.

### 3.3 Results and Discussion

To grasp the temperature dependence of the whole process of crystallization, it is important to understand the temperature dependence of the two overlapping processes [Madras and McCoy, 2002]: nucleation and crystal growth. Temperature influences nucleation rate, according to Eq. (3.22), mainly through supersaturation, \(S = S_T \exp(h/\Theta)\), and interfacial energy, \(\sigma = \sigma_0(1 - \Theta)^n\). The nucleation rate decreases near the melting temperature because of the substantial temperature dependence of interfacial energy there. Crystal growth rate, influenced by temperature mainly through the growth activation energy \(\varepsilon\) according to Eq. (3.3), increases with temperature. We are initially concerned with the effect of temperature on the time evolution of CSD. Figure 3.1 presents the temperature effects on number of macromolecules, crystal
number, crystal size, and nucleation rate at different temperatures close to the reference temperature \( T_m \). Based on experimental measurements [Xiao et al., 2002], reasonable parameter values are chosen, as listed in Table 3.1. The mass dependence of growth rate coefficient \( \lambda \) is chosen to be 0, thus the moment equations (3.5) are applied to describe nucleation and crystal growth. Considering sensitivity of crystallinity on temperature, the scaled temperature values \( \Theta \) are chosen to be 0.970, 0.972, 0.974 and 0.976. Figure 3.1.a shows the time evolution of polymer concentration, with a larger decrease speed of \( S_T \) at the lower temperature, \( \Theta = 0.97 \). Decreasing temperature speeds up nucleation, and the crystal growth rate decreases slightly because of the
lower temperature sensitivity for crystal growth. The time evolution of crystallized mass concentration, not presented in this chapter, is simply a mirror image of $S_T$ according to Eqs. (3.5) and (3.7).

The temperature effect on average crystal size is presented in Figure 3.1.b. The average crystal size increases with time by crystal growth and later does not change very much as equilibrium is approached. Increasing temperature also increases the average crystal size. According to the definition, $C_{\text{avg}} = C^{(1)}/C^{(0)}$, the decline of average crystal size results either from the increase of the number of crystals, $C^{(0)}$, or from the decrease of crystallized mass, $C^{(1)}$. As temperature drops, the nucleation rate increases according to Eq. (3.13), and more particles are generated per unit time, as given by Eq. (3.6). The crystal mass concentration, according to Eq. (3.7), grows more slowly because of the decrease of growth rate coefficient at low temperature.

The time evolution of nucleation rate (Fig. 3.1c) is caused by the decline of supersaturation due to crystallization. The nucleation rate drops quickly because of the sharp decrease of supersaturation. As the supersaturation decreases, the energy barrier for nucleation, $W^*$, tends to increase, thus the nucleation rate, according to Eq. (2.11), will decrease. The temperature effect on nucleation rate is also confirmed in Figure 3.1.c. Initially a substantial nucleation rate decrease is observed when the temperature varies from 0.970 to 0.976. Then nucleation is quenched at the end of crystallization as the supersaturation $S$ approaches unity. The characteristic Avrami plots are presented in Figure 3.1.d, and a larger crystallization rate is

Table 3.1 Parameter values in Figures (unless otherwise noted in captions).

<table>
<thead>
<tr>
<th>$C_0^{(0)}$</th>
<th>$C_0^{(1)}$</th>
<th>$S_{T0}$</th>
<th>$J_0$</th>
<th>$\lambda$</th>
<th>$w$</th>
<th>$\varepsilon$</th>
<th>$h$</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>10</td>
<td>$10^6$</td>
<td>0</td>
<td>2.0</td>
<td>1.0</td>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>
observed at lower temperature. The Avrami exponents at the four temperatures (the slopes of the characteristic Avrami plots) are around 1.95, independent of the temperature. The Avrami exponent is hardly affected by temperature near $T_m$.

![Figure 3.2 Effect of temperature dependence of interfacial energy with $\Theta = 0.97$ and other parameters given in Table 3.1.](image)

The effect of $n$, the temperature power dependence for interfacial energy, is presented in Figure 3.2. The temperature sensitivity of crystallization is strongly dependent on $n$. When $n$ is small, crystallization rate does not change much with temperature, thus large $n$ ($\approx 20$) is suggested here. According to Eqs. (2.10) and (3.2), increasing $n$ will raise the energy barrier for nucleation and thus decrease the nucleation rate. We observed a large difference in crystallization rate for a small difference in $n$, as shown in Figure 3.2. We also find that $n$ has little influence on Avrami exponents.

The investigation of the activation energy in the growth rate coefficient $k_g$ is presented in Figure 3.3. The value of $\varepsilon$ is chosen to vary from 0.1 to 3 with $\Theta = 0.97$ and other parameters given in Table 3.1. No apparent slope difference is observed in the characteristic Avrami plots;
thus, varying $\epsilon$ does not influence the value of Avrami exponents. According to Eq. (3.3), the increase of $\epsilon$ will lead to the decline of crystal growth rate coefficient, and a larger overall crystallization rate is indeed observed when $\epsilon$ is small. Despite more than one order of magnitude change in the value of $\epsilon$, however, the influence of this parameter on the time evolution of the crystallization is not as much as $n$.

The enthalpy of phase transition, $h$, is another parameter included in our distribution model for isothermal crystallization. According to experimental measurements [Ciora and Magill, 1990; Xu et al., 2002], $\Delta H$ is around 300 kJ/mol for most polymers, so that $h$ is about 100. To explore the effect of phase transition enthalpy, we chose a wide range of $h$, varying from 0.1 to 1000, in Figure 3.4. We observe no kinetics contribution from the $h$ variation because $\exp(-h/\Theta)$ in Eqs. (3.5) and (3.7) is quite small and $S_T$ is the dominant term in the equations, thus the crystallization rate does not change very much for large values of $h$.

The nucleation rate prefactor, $J_0$, according to Eq. (3.12) is related to interfacial energy, density, and polymer molecular weight; thus different nucleation rate prefactors are expected for
Figure 3.4 Effect of phase transition enthalpy $h$ with $\Theta = 0.97$ and other parameters given in Table 3.1.

different polymer systems. The investigation of the effect of nucleation prefactor is presented in Figure 3.5. As is evident from Eqs. (3.6), (3.7), and (3.8), increasing $J_0$ speeds the growth rate and the onset of nucleation, resulting in a larger number of crystals. Shorter crystallization times are therefore required to reach the final state when the nucleation rate prefactor is large, as shown in Figure 3.5. For Avrami plots, varying $J_0$ causes only a lateral shift in $\theta$. The nearly linear relationship between $\log[-\ln(1-X)]$ and $\log \theta$ allows only an order of magnitude lateral shift in $\theta$ as $J_0$ is increased by two orders of magnitude.

Denucleation, the reverse of nucleation, occurs when the crystal size is smaller than the critical crystal size. Denucleation has considerable influence on the characteristic Avrami plots, especially at the end of crystallization when denucleation dominates over nucleation. At the beginning of crystallization, most polymer crystals are larger than the critical crystal size, thus denucleation, compared with nucleation, is negligible. The critical crystal size, however, increases as the supersaturation $S$ declines when polymer deposits on the crystal, thus more
crystals become smaller than the critical size. These unstable crystals will dissolve rapidly. At the end of crystallization, denucleation and ripening become dominant because the supersaturation is close to unity, and consequently nucleation vanishes. Figure 3.6 presents the effect of denucleation by comparison of moment and numerical solutions at different nucleation rates. The dotted lines represent the characteristic Avrami plots of moment solutions, for which denucleation is not considered. The solid points are numerical solutions including denucleation, where numerical error tolerance is chosen to be 0.0001 in the calculation of $S_T$. At the beginning, the denucleation rate is small, and the moment solution agrees with the numerical solution very well. This is because the small denucleation rate delays the dominating influence of denucleation [Madras and McCoy, 2002]. As supersaturation decreases, the discrepancy between moment solution and numerical solution caused by denucleation becomes increasingly apparent. The numerically computed crystallinity reaches its asymptote while the crystallinity computed by the moment method continues to increase. The enthalpy of phase transition $h$ and interfacial energy

![Image](image_url)

Figure 3.5 Effect of nucleation rate prefactor $J_0$ with $\Theta = 0.97$ and other parameters given in Table 3.1.
also have an effect on denucleation. The critical crystal size is very small, according to Eq. (3.8), when \( S_I \) is large and \( \omega \) is small (< 0.1) or \( \theta \) is large (> 100), thus most crystals are larger than the critical size and are stable. These crystals will keep growing instead of dissolving, so denucleation is negligible.

To explore the effect of the exponent of growth and dissociation rate, \( \lambda \) is chosen to be 0, 1/3, and 2/3, representing surface independent, diffusion controlled and surface controlled deposition rates, respectively. Figure 3.7 presents the effect of \( \lambda \) at different nucleation rates, varying from \( 10^5 \) to \( 10^8 \). The dotted lines are moment solutions (\( \lambda = 0 \)). The solid lines are the numerical solutions with \( \lambda = 0, 1/3, \) and \( 2/3 \). The increase of \( \lambda \), according to Eq. (3.3), leads to the increase of crystal growth rate coefficient, thus larger crystallization rate is observed when \( \lambda = 2/3 \). Though larger crystallization rates are observed by a decrease of \( \varepsilon \) or an increase of \( J_0 \), these parameters do not have a major influence on the Avrami exponent. Therefore, compared to the influence of other parameters, the Avrami exponent is critically dependent on \( \lambda \).
Figure 3.7 The effect of $\lambda$ on the Avrami plots with $\Theta = 0.9$ at different nucleation rate prefactors: (a) $J_0 = 10^5$, (b) $J_0 = 10^6$, (c) $J_0 = 10^7$, and (d) $J_0 = 10^8$ and other parameters given in Table 3.1. The dotted lines denote the moment solutions while the solid lines represent the numerical solutions.

The validity of the distribution kinetics model is also examined by comparison with experimental data (Fig. 3.8). Since the simulation results of moment methods are based on dimensionless time $\theta = t \gamma \mu_c x_m^\lambda$, a transposition of the original experimental data, based on real time, is applied to compare with computation results. According to the definition of dimensionless time, Eq. (2.17), a horizontal transposition of $\log (\gamma \mu_c x_m^\lambda)$ units is applied to the experimental measurements to convert the experimental data into plots based on dimensionless time $\theta$. The scattered points are experimental data [Xu et al., 2002] for Poly[bis(trifluoroethoxy)phosphazene] (or PBFP) based on scaled time $\theta$ at $T = 229.8, 230.5,$
231.0, and 231.5 °C. The solid lines are the simulation results at these four temperatures. Good agreement between experimental data and simulation results is observed. The measured

Figure 3.8 The fit of distribution model to the experimental data for PBFP at four temperatures: ■ 229.8 °C, ● 231 °C, ▲ 230.5 °C, ▼ 231.5 °C, and other parameters given in Table 3.1. The dotted lines denote the moment solutions while the solid lines represent the numerical solutions.

horizontal transposition is 2.34; thus $\gamma_{\mu_e} = 218.78$ sec$^{-1}$ for the case $\lambda = 0$. This is consistent with the understanding that $\gamma_{\mu_e}$ is independent of temperature. The transposition therefore provides a value of the parameter $\gamma$. An apparent discrepancy is observed at the end of crystallization, where the experimental data slightly curves down from the model. This inconsistency is believed to result from the increasing effect of Ostwald ripening (denucleation) that cannot be incorporated in the moment equations. For the numerical solution represented by the solid line in Figure 3.8, an apparent plateau is observed at the end of crystallization, evidence of the increasing effect of denucleation. Compared with the moment solution (dotted lines), a more quantitatively realistic description is achieved by numerical solution due to the inclusion of denucleation and ripening.
The moment method provides an easy solution in modeling polymer crystallization with surface-independent crystal growth ($\lambda = 0$). When crystal growth rate is not surface-independent ($\lambda > 0$), however, the moment equations do not have a closed form, thus the numerical schemes must be applied, as shown in Eqs (3.12) and (3.13). Figure 3.9 presents the fit of distribution model to the experimental data [Xiao et al., 2002] for Poly(ethyleneterephthalate-imide) (or PET), which we suggest has a surface dependent crystal growth mechanism ($\lambda = 2/3$). By considering the denucleation effect, the numerical solution provides a more realistic prediction than the moment method at the end of crystallization. The measured horizontal transposition of experimental data is 1.30.

The value of $\lambda$ is determined by the crystal growth mechanism; surface independent ($\lambda = 0$), diffusion controlled ($\lambda = 1/3$), and surface dependent ($\lambda = 2/3$) crystal growth mechanisms were previously reported [Madras and McCoy, 2003]. These three well understood mechanisms provide good predictions to most experimental measurements. However, experiments with large
Avrami exponents ($m > 3$), which cannot be explained by these three mechanisms, are also occasionally reported [Supaphol and Spruiell, 2000; Nagarajan et al., 2000; Guo et al., 2001; Martins et al., 2003], thus it is necessary to propose a larger value ($\lambda > 2/3$). Figure 3.10 presents the fit of distribution model with $\lambda = 1$ to the experimental measurements [Guo et al., 2001] having a large Avrami exponent at three different temperatures. The points represent the experimental data of poly(ethylene oxide) (or PEO), where the measured Avrami exponent is around 4.5; the solid lines stand for the simulation results. By a horizontal transposition of 0.36 to the experimental measurements, the modeling result fits the experimental data rather well.

It is worthwhile to reemphasize why the computations represent the experimental data so well. Two features are particularly essential. First, a larger slope of the Avrami plot requires a larger exponent $\lambda$ ($0 < \lambda < 1$) in Eq. (3.3), indicating a stronger dependence of the growth and dissociation rate coefficients on cluster mass. Second, the high sensitivity of the crystallinity temperature dependence is due to the large value, $n \approx 20$, of the power in Eq. (3.2) for the interfacial energy. Finally, the placement of the crystallinity curves by transposing them on the
time axis determines the coefficient $\gamma$ in Eq. (3.3). Thus the model neatly provides a systematic approach to representing and understanding the underlying phenomena of polymer crystallization.

3.4 Conclusion

Based on our earlier distribution kinetics model in Chapter 2 [Yang et al., 2005a], we have investigated temperature effects in detail for 2D lamellar polymer crystallization. This model accounts for the overlapping of nucleation, crystal growth, and denucleation in polymer crystallization, processes which complicate the solidification of polymer solution or melt. Temperature affects these processes through kinetics and thermodynamics. We have suggested how our previous kinetics distribution model [Yang et al., 2005] can be modified to be applied to the investigation of isothermal crystallization. Proposing temperature dependences for interfacial energy, growth and dissociation rate coefficients, and equilibrium solubility, we studied crystallization behavior at different temperatures. This entailed the effects of growth rate activation energy, enthalpy of phase transition, nucleation rate prefactor, and the power dependence of interfacial energy on temperature. Computations (numerical solutions of the population balance equation) show that the Avrami exponent mainly depends on $\lambda$, the power dependence of growth rate on crystal mass. The characteristic Avrami plots of simulation results yielded very good fits to experimental measurements. This supports the assumed temperature dependence of interfacial energy, diffusion, growth rate coefficient, and equilibrium solubility. We also find that proposing a large $\lambda$ is the only way to predict polymer crystallization with large Avrami exponent (greater than 3). In addition, for interfacial energy a large value of the temperature power $n (\approx 20)$ is critical for explaining the temperature sensitivity of crystallization kinetics. Therefore, by appropriately choosing $\lambda$ and $n$, the cluster size distribution model is able to describe different types of polymer crystallization.
Chapter 4 Kinetics of Nonisothermal Polymer Crystallization*

4.1 Introduction

Experimental and modeling studies of polymer crystallization have often been carried out under idealized conditions of constant temperature. A polymer sample is melted at or above the equilibrium melting point, and is rapidly quenched to the temperature chosen for crystallization. In practice, however, industrial processes and some experimental studies generally proceed under dynamic and nonisothermal conditions, where the crystallization rate depends not only on the instantaneous temperature, but also on the rate of temperature change. Because the thermal history experienced by the polymer sample is critical in the determination of the final product properties, an understanding of nonisothermal crystallization is necessary. This is the motivation for extending isothermal crystallization kinetics in chapter 3 to nonisothermal conditions.

The overlapping of primary nucleation and crystal growth complicates the kinetics of polymer crystallization [Robson, 2004; Yang et al., 2005a; 2005b], ensuring that a fairly sophisticated model will be required. The first attempt to describe the kinetics of polymer crystallization was made by Evans [1945] via statistical considerations and by Avrami [Avrami, 1939; 1940; 1941] via the concept of so-called extended volume. Avrami derived the well-known expression for crystallinity as a function of time,

\[ X(t) = 1 - \exp[-V(t)] \]  \hspace{1cm} (4.1)

where V(t) is the extended volume, denoting the total volume of all domains growing from all nucleation attempts occurring at time t. For isothermal crystallization, the Avrami equation simplifies to,
where \( K \) is a rate coefficient depending on both nucleation and crystal growth rates, and \( m \) assumes the values of 1, 2, 3, or 4 depending on the nucleation type and the crystal dimensionality [Hay, 1971]. For years the kinetic analysis for polymer crystallization has involved plots based on the Avrami equation, even though it was often criticized as being oversimplified [Hay, 1971; Piorkowska, 1995; Wasiak et al., 1999]. Although the empirical basis of Eq. (4.2) allows it to describe some fundamental features of crystallization, the exponent value \( m \), determined experimentally for various polymers (mainly on the basis of DSC measurements of latent heat during crystallization), is rarely in agreement with the predicted integer numbers [Vilanova et al., 1982; Ciora and Magill, 1990; Xu et al., 2002; Xiao et al, 2002]. A number of authors [Price, 1969; Hay, 1972; Grenier and Prodhomme, 1980] also pointed out that the Avrami plot of experimental measurements, \( \log[-\ln(1-x)] \) vs \( \ln(t) \), is actually curved rather than the straight line proposed by the Avrami theory. These observations suggest that the assumptions leading to the Avrami equation are simplistic and that its foundation is inexact.

Neither Eq. (4.1) nor (4.2) can be used directly in nonisothermal crystallization unless the temperature dependence of \( V(t) \) or \( K \) is known. Nonisothermal crystallization has been modeled by applying a linear temperature change to the Avrami equation [Ozawa, 1971; Di Lorenzo, 1999; Achilias et al., 2004; Kratochvil and Sikora, 2005]. To evaluate kinetic parameters, the Tobin [1976] and Ozawa [1971] models allowed \( K \) to depend on the cooling rate. Taking into account the transient and nonisothermal effects, Ziaibicki [1996a; 1996b] proposed a new model for polymer crystallization when external variables, i.e., temperature, pressure, and stress, change in time. Generalized equations for polymer crystallization under variable external conditions were developed by introducing three temperature-dependent material functions: steady state crystallization rate, relaxation time, and isothermal nucleation. Experimental studies of
nonisothermal crystallization at cooling rates between 2 and 40 °C/min with the DSC method [Kratochvil and Sikora, 2005] showed an increase of the Avrami exponent as the cooling rate increased. The effect of cooling rate on crystallinity [Wasiak et al., 1999] indicated that the Avrami equation could not quantitatively describe nonisothermal crystallization and required an additional compensating parameter. The mathematical description of the spherulitic pattern formation in nonisothermal conditions was elaborated on the basis of the assumption of the momentary randomness of primary nucleation [Piorkowska, 1995a; 1995b; 1995c]. This probabilistic approach makes it possible to describe the formation of spherulitic structure elements in the course of nonisothermal crystallization. The temperature dependencies of the material functions are still uncertain, however, and the Avrami exponent for nonisothermal crystallization requires further investigation.

The Avrami equation with its basis in heuristic ideas is still applied to polymer crystallization, even though the controversy about the underlying mechanism has continued since the derivation of this equation. This led us to propose a new cluster distribution model for polymer crystallization kinetics by considering the similarity between crystal growth and monomer deposition on clusters [Yang et al., 2005a; 2005b]. Based on fundamental concepts of nucleation and crystal growth, the model accounts for homogeneous or heterogeneous nucleation and crystal growth for isothermal crystallization. The model proved capable of quantitatively describing experimental data for isothermal polymer crystallization. In this chapter, we will investigate nonisothermal crystallization kinetics with linear cooling rates. The temperature effect is incorporated into the model by the temperature dependencies of interfacial energy, equilibrium solubility, and growth rate coefficient. The population balance equations under different cooling rates are solved numerically to present time evolutions of crystal size distribution.
4.2 Distribution Kinetics Theory for Nonisothermal Crystallization

We hypothesize that polymer crystal growth is similar to the deposition of monomers on clusters. This deposition process by which polymer molecules of mass $x' = x_m$ are reversibly attached or dissociated from an established crystal of mass $x$ can be represented as a reaction-like process [McCoy, 1997], shown in Eq. (2.15), with $C(x)$ represents the crystal of mass $x$ and $M(x') = x_m$ is the macromolecule with a uniform molecular weight distribution, $m(x,t) = m^{(0)}(t) \delta(x - x_m)$. An activation energy is assumed to account for temperature dependence of the growth rate coefficient, $k_g(x) = k_0 \exp(-E/RT)$, in Chapter 3. The rate coefficient for growth is simply related to dissociation rate coefficient, $k_d(x) = m_{\text{eq}}^{(0)} k_g(x)$, by microscopic reversibility [Madras and McCoy, 2004]. Exponent $\lambda$ accounts for the mass dependence of the growth rate coefficient, representing surface independent, diffusion controlled, and surface dependent growth, respectively, when $\lambda$ equals 0, 1/3, and 2/3.

Temperature influences crystal growth through kinetics and thermodynamics. The activation energy for growth rate coefficient accounts for the temperature effects through kinetics, while the temperature dependence of the equilibrium solubility, Eq. (3.1), accounts for the temperature influence through thermodynamics. For a lamellar crystal with flat growth front, the Gibbs-Thomson effect vanishes, so that the difference between local equilibrium interfacial concentration $m_{\text{eq}}^{(0)}$ and solubility $m_{\infty}^{(0)}$ for a flat surface vanishes, thus $m_{\text{eq}}^{(0)} = m_{\infty}^{(0)}$.

Nucleation, the initiation of crystal nuclei, occurs simultaneously with crystal growth. By including the nucleation term, the kinetics of polymer crystallization can be described by the cluster size distribution equations [Madras and McCoy, 2002], as in Eqs. (2.16) and (2.17), with $x^*$ represents the critical crystal mass and $I$ denotes nucleation rate. For a supersaturated (metastable) system, the cluster energy of a crystal of radius $r$, reaches a maximum value, at the
critical crystal radius. According to classical nucleation theory [Oxtoby, 1992; McClurg and Flagan, 1998], the nucleation rate (mols of nuclei/vol-time) is the flux over the maximum energy barrier at the critical radius, as shown in Eqs. (2.11) and (2.12). The classical nucleation theory utilizes the sum of surface energy and formation free energy; for an equilateral lamellar crystal of characteristic length a, the total energy is represented in Eq. (2.8). The crystal interfacial energy, $\sigma$, has a temperature dependence approximated by Eq. (3.2) [Rowlinson and Widom, 1982; Yang et al., 2005b], indicating that the interfacial energy $\sigma$ vanishes at reference temperature $T_m$. The chemical potential difference ($-RT \ln S$) between the two phases is expressed in terms of supersaturation $S$, which is the ratio of bulk concentration $m^{(0)}$ over equilibrium concentration $m^{(0)}_\infty$. The maximum energy occurs at the critical crystal size, $a^* = 2\sigma_m / (\rho RT \ln S)$, which can be converted into critical crystal mass. With the definitions of dimensionless quantities in Eq. (3.4), we may write the cluster size distribution equations in dimensionless form by Eqs. (3.14) and (3.15). The initial conditions are $S_T(\theta = 0) = S_{T_0}$ and $C(\xi, \theta = 0) = 0$, where $\xi$ is defined as the number of macromolecules in the crystal. The source term $J_\delta(\xi - \xi^*)$ represents the nucleation rate of crystals having $\xi^*$ macromolecules. When ripening occurs, a sink term appears representing the denucleation of crystals smaller than the critical size.

With the definition of the jth moment, $C^{(j)} = \int_0^\infty \xi^j C(\xi, \theta) d\xi$, the dimensionless cluster size distribution equations, for the special case $\lambda = 0$, can be rewritten as moment equations, as in Eqs. (3.6) and (3.7). The zeroth moment, $C^{(0)}$, and the first moment, $C^{(1)}$, represent the time-dependent molar (number) and mass concentrations of crystal, respectively. The ratio of the two moments is the average size of the crystals, $C^{\text{avg}} = C^{(1)} / C^{(0)}$.

To use Eqs (3.5), (3.6), and (3.7) in the analysis of nonisothermal crystallization, it is assumed that the polymer sample experiences a constant cooling rate. Though we adopt a linear
decrease of temperature with time, one can easily incorporate any variation of temperature with time in the model. The relationship between crystallization time t and the crystallization temperature T is thus,

\[ T = T_i - \beta t \]  
(4.3)

where \( \beta \) is the cooling rate (°C/min). With the dimensionless quantities, \( \theta = t \gamma \mu_x x_m^{-1} \) and \( \Theta = T/T_m \), the relationship can be rewritten as,

\[ \Theta = \Theta_i - \phi \theta \]  
(4.4)

where \( \Theta_i = T_i/T_m \) is the dimensionless initial temperature and \( \phi = \beta/[\gamma \mu_x T_m x_m^{-1}] \) is the dimensionless cooling rate. Thus Eqs. (3.5), (3.6), and (3.7), for the crystallization in which a polymer sample is cooled from its melting temperature \( T_m \), can be rewritten in terms of dimensionless time \( \theta \) for nonisothermal condition,

\[
\frac{dS_T(\theta)}{d\theta} = \exp(-\varepsilon/(1-\phi \theta)) \left[ -S_T(\theta) + \exp(-h/(1-\phi \theta)) \right] C^{(0)} - J \xi^* 
(4.5)
\]
\[
\frac{dC^{(0)}(\theta)}{d\theta} = J 
(4.6)
\]
and

\[
\frac{dC^{(1)}(\theta)}{d\theta} = -\exp(-\varepsilon/(1-\phi \theta)) \left[ -S_T(\theta) + \exp(-h/(1-\phi \theta)) \right] C^{(0)} + J \xi^* 
(4.7)
\]

They can also be rewritten in terms of temperature \( \Theta \),

\[
\frac{dS_T(\Theta)}{d\Theta} = -(1/\phi) \left[ \exp(-\varepsilon/\Theta) \left[ -S_T(\Theta) + \exp(-h/\Theta) \right] C^{(0)} - J \xi^* \right] 
(4.8)
\]
\[
\frac{dC^{(0)}(\Theta)}{d\Theta} = -(1/\phi) J 
(4.9)
\]
and

\[
\frac{dC^{(1)}(\Theta)}{d\Theta} = -(1/\phi) \left[ -\exp(-\varepsilon/\Theta) \left[ -S_T(\Theta) + \exp(-h/\Theta) \right] C^{(0)} + J \xi^* \right] 
(4.10)
\]

The crystallinity \( X \) is defined as the ratio of polymer crystallized at time \( \theta \) over the total crystallized polymer mass. Thus the crystallinity time or temperature dependence can be obtained by solving the above ordinary differential moment equations with various cooling rates,
φ. By defining the temperature-independent prefactor, \( J_0 = \frac{(2\sigma_0/\pi)^{1/2}}{\rho \gamma x_m^\lambda} \), the nucleation rate can be written as Eq. (3.13).

### 4.3 Results and Discussion

For the unsteady-state nonisothermal polymer crystallization, our general concern is the effect of cooling rate on the cluster size distribution. Based on the relationship between temperature and time, Eq. (4.4), we investigated the cluster size distribution as a function of temperature and time, respectively, as shown in Eqs. (4.5) ~ (4.10). The choice of parameters is based on earlier work [Yang et al., 2005a; 2005b], e.g., Eq. (3.2), proposed in our previous work with suggested values of \( n \) [Yang et al., 2005b], is used to present the temperature dependence of interfacial energy. The interfacial energy parameter, \( w \), written in terms of density, is chosen to be \( w = 2 \) in our computation. The molar enthalpy of phase transition, \( h \), is usually around 100. The activation energy for growth rate, \( \varepsilon \), is typically smaller than \( h \), and a value \( \varepsilon = 1.0 \) is chosen. The homogeneous nucleation rate is very sensitive to supersaturation \( S \) and temperature, and a constant nucleation rate prefactor, \( J_0 = 10^6 \), is proposed. Assuming the polymer melt is cooled from the melting temperature, \( \Theta_i = 1 \), where the subscript \( i \) denotes the initial condition. There are no particles present initially for homogeneous nucleation, thus the initial conditions are \( S_T(\Theta = \Theta_i) = S_{T_0}, C^{(0)}(\Theta = \Theta_i) = 0, \) and \( C^{(1)}(\Theta = \Theta_i) = 0 \).

The temperature dependence of crystal size distribution is presented in Figure 4.1 at different cooling rates. The dimensionless cooling rate \( \phi \) varies from \( 10^{-4} \) to \( 6 \times 10^{-4} \). Figure 4.1.a presents the effect of cooling rate on the evolution of number of macromolecules \( S_T \), which decreases sharply as temperature drops. The effect of cooling rate on the crystal size is presented in Figure 4.1.b, where increased cooling rate diminishes the average crystal size. This can be explained by more nuclei forming as the temperature decreases at large cooling rate. The extent
of crystallization is denoted by relative crystallinity, \( X = (S_{T0} - S_T(\Theta))/(S_{T0} - e^{h(\Theta)}) \), presented in Figure 4.1.c as a function of temperature at different cooling rates. A sharp increase of crystallinity occurs after a short incubation time. According to the definition of crystallinity, \( S_T(\Theta) \) and \( X(\Theta) \) are mirror images.

According to Eqs. (4.5) ~ (4.7), the crystal size distribution can also be presented as a function of time. Figure 4.2 presents the time evolution of nonisothermal crystallization of PTT.
[poly (trimethylene terephthalate)] starting from melting temperature [Apiwanthanakorn et al., 2004], $\Theta_i = 1$. Figure 4.2.a presents the time evolution of $S_T$ at different cooling rates. We notice that the decrease of $S_T$ is delayed by increasing induction times at smaller cooling rates. The induction time prediction, not present for isothermal crystallization [Yang et al., 2005b], but occasionally reported in nonisothermal measurements [Xiao et al., 2002a; 2002b], supports the current model. The crystal average size, pictured in Figure 4.2.b for different cooling rates, increases sharply and finally reaches a constant limit. The final crystal size is also controlled by the cooling rate: a large average crystal size is caused by a small cooling rate. This can be explained by the temperature dependence of nucleation; when the cooling rate is small, nucleation and growth occur within a temperature region closer to the reference temperature where the nucleation rate is small. Time evolution of crystallinity is presented in Figure 4.2.c. The conventional Avrami plot of log $[-\ln(1-X)]$ vs $\ln(t)$ is presented in Figure 4.2.d. A constant asymptote at the end of crystallization is observed as in isothermal crystallization. The straight midportion of the Avrami plot represents nucleation and growth where denucleation and ripening are negligible. The Avrami exponent, the slope of this straight portion of Avrami plot, has little dependence on the cooling rates as the polymer sample is cooled from the melting temperature. All the crystallinity curves (Fig. 4.2.c) include the incubation time $\Delta\theta_{inc}$, defined as a time period from initial temperature, $\Theta_i$, to the onset temperature, $\Theta_{onset}$, where the polymer melt actually begins to crystallize. Thus the incubation period is formulated as $\Delta\theta_{inc} = (\Theta_i - \Theta_{onset})/\phi$ [Apiwanthanakorn et al., 2004]. We define the crystallization onset temperature, $\Theta_{onset}$, as the temperature when the crystallinity reaches 1% in the numerical modeling results. The incubation period, $\Delta t_{inc}$, is calculated by quantifying the physical properties of the polymer. Given $\Delta H = 28.8 \text{ J/g}, x_m = 5\times10^5 \text{ mol/g}, T_m = 525 \text{ K} (252 \degree\text{C}),$ by choosing $\lambda = 0, \varepsilon = 1.0, h = 100,$ and $\gamma\mu_{infty} =$
1.40×10³ mol/(s.m³) [Chung et al., 2002], the dimensionless cooling rates, φ, are converted into real cooling rates, β, according to \( \phi = \beta / \gamma T_0 \alpha m \). As found previously [Yang et al., 2005a; 2005b], polymer crystallization is insensitive to values of \( h \) and \( \varepsilon \). The dimensionless incubation time, \( \Delta t_{\text{inc}} \), determined from the moment evaluation of the kinetics model, is also converted into real cooling rates \( \Delta t_{\text{inc}} \), according to Eq. (3.4). The calculated incubation times at different cooling rates are listed in Table 4.1 for the crystallization of PTT. The equation relating \( \phi \) and \( \beta \) provides an adjustable parameter based on material properties. The relationship between increasing

Figure 4. 2 Time evolution of \( S_T \), \( C_{\text{avg}} \), crystallinity, and the conventional Avrami plot for nonisothermal crystallization of PTT at different cooling rates with \( C_0^{(0)} = 0, C_0^{(1)} = 0, S_{T0} = 10, \varepsilon = 1.0, h = 100, n = 20, w = 2.0, J_0 = 10^6, \lambda = 0 \) and \( \Theta_i = 1.0 \).
cooling rate and decreasing incubation time is presented quantitatively in Figure 4.3. Experimental measurements of incubation for PTT are also provided (Fig. 4.3) for comparison. The points represent the experimental measurements [Apiwanthanakorn et al., 2004] of incubation time for PTT, and the solid line stands for the incubation period calculated by the

Table 4.1 Calculated incubation period at different cooling rates with $\Theta_i = 1$

<table>
<thead>
<tr>
<th>Scaled cooling rate $\phi (10^{-4})$</th>
<th>Real cooling rate $\beta (^\circ\text{C/min})$</th>
<th>Scaled incubation time $\Delta \theta_{inc}$</th>
<th>Real incubation time $\Delta t_{inc}$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>633.5</td>
<td>36.3</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>356</td>
<td>20.4</td>
</tr>
<tr>
<td>3</td>
<td>4.5</td>
<td>236.5</td>
<td>13.6</td>
</tr>
<tr>
<td>5</td>
<td>7.5</td>
<td>166</td>
<td>9.5</td>
</tr>
<tr>
<td>7</td>
<td>10.5</td>
<td>103</td>
<td>5.9</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>93.5</td>
<td>5.4</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
<td>52.5</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Figure 4.3 The effect of cooling rate on incubation time for nonisothermal crystallization of PTT: (■) experimental measurements [Apiwanthanakorn et al., 2004]; (—) simulation results with $C_0^{(0)} = 0$, $C_0^{(1)} = 0$, $S_{T0} = 10$, $e = 1.0$, $h = 100$, $n = 20$, $w = 2.04$, $J_0 = 10^6$, $\lambda = 0$ and $\Theta_i = 1$. 
distribution kinetics model at different cooling rates. Good agreement is seen between model simulation and experimental results.

Usually nonisothermal crystallization experiments are conducted by decreasing the temperature from the melting point. However, as the onset temperature is below the melting temperature, our model can also represent nonisothermal crystallization starting from a temperature below melting. Figure 4.4 shows the effect of cooling rate when the initial temperature of crystallization is 0.97. Although there is no apparent Avrami exponent change in

\[ \phi = 1 \left(10^{-7}\right) \]

Figure 4.4 Avrami plots showing the effect of cooling rate for nonisothermal crystallization with $C_0^{(0)} = 0$, $C_0^{(1)} = 0$, $S_{T0} = 10$, $\varepsilon = 1.0$, $h = 100$, $n = 20$, $w = 2.0$, $J_0 = 10^6$, $\lambda = 0$ and $\Theta_i = 0.97$.

Figure 4.2.d as the crystallization temperature drops from the melting point, the slope differences for the Avrami plots in Figure 4.4 indicate considerable influence of cooling rates as the polymer sample is cooled from a temperature below melting point. This confirms that the nonisothermal crystallization is sensitively influenced by nucleation, and depends not only on the instantaneous temperature, consistent with experiments [Achilias et al., 2004].
Initial temperature is another influential parameter for nonisothermal crystallization, as shown in Figure 4.5, which presents time evolution of crystallinity for nonisothermal crystallization. Increasing with initial temperature, the incubation time reaches a maximum when the polymer melt is cooled from the melting point. The incubation periods for different initial temperature are listed in Table 4.2.

Figure 4.5 The effect of initial temperature for nonisothermal crystallization with \( C_0^{(0)} = 0, C_0^{(1)} = 0, S_{T_0} = 10, \varepsilon = 1.0, h = 100, n = 20, w = 2.0, J_0 = 10^6, \lambda = 0 \) and \( \phi = 1 \times 10^{-4} \). (a) time evolution of crystallinity \( X \); (b) the conventional Avrami plots at different initial temperatures.

Figure 4.6 presents the dependence of incubation period on initial temperature, revealing the increase in incubation time with increasing initial temperature. The initial temperature significantly influences the Avrami exponent (Fig. 4.5.b), which increases with initial temperature, as shown by the slope increase of the Avrami plots when the initial temperature increases.

The moment method provides an easy and quick solution in modeling polymer crystallization with mass independent crystal growth (\( \lambda = 0 \)). When the crystal growth rate is mass dependent (\( \lambda > 0 \)), a more general form, \( k_g(x) = \gamma x^\lambda \exp(-E/RT) \), is used to express the
Table 4.2 Calculated incubation period at different initial temperatures with $\phi = 4 \times 10^{-4}$

<table>
<thead>
<tr>
<th>Scaled temperature</th>
<th>Real temperature</th>
<th>Scaled incubation time</th>
<th>Real incubation time</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Theta_i$</td>
<td>$T(°C)$</td>
<td>$\Delta \theta_{inc}$</td>
<td>$\Delta t_{inc}$ (min)</td>
</tr>
<tr>
<td>1</td>
<td>156.6</td>
<td>520</td>
<td>11.2</td>
</tr>
<tr>
<td>0.99</td>
<td>155.0</td>
<td>420</td>
<td>9.0</td>
</tr>
<tr>
<td>0.98</td>
<td>153.5</td>
<td>220</td>
<td>4.7</td>
</tr>
<tr>
<td>0.97</td>
<td>151.9</td>
<td>130</td>
<td>2.8</td>
</tr>
<tr>
<td>0.96</td>
<td>150.3</td>
<td>104</td>
<td>2.2</td>
</tr>
<tr>
<td>0.95</td>
<td>148.8</td>
<td>65</td>
<td>1.4</td>
</tr>
<tr>
<td>0.94</td>
<td>147.2</td>
<td>30</td>
<td>0.64</td>
</tr>
</tbody>
</table>

crystal growth coefficient. The effect of $\lambda$ on the crystallization kinetics needs to be explored because it is the most important parameter influencing the Avrami exponent for isothermal crystallization [Yang et al., 2005b]. The moment equations, however, do not have a closed form for $\lambda > 0$, thus Eqs. (3.14) and (3.15) were solved at different values of $\lambda$ by a numerical procedure described in detail in our previous chapters. A comparison is made between moment

![Figure 4.6](image-url)
and numerical solution for $\lambda > 0$ (Fig. 4.7.a). Solid lines and dotted lines represent the numerical solution and the moment solution, respectively. Except for the discrepancy at the end of crystallization, caused by the increasing effect of denucleation and ripening, good agreement is confirmed at various cooling rates. Crystal resizing and ripening can be considered only with the numerical method, thus we observed a constant asymptote after the straight Avrami plot by numerical solution. This modeling result agrees with experimental observations that the Avrami e

![Avrami plots](image)

Figure 4. 7 The conventional Avrami plots with $C_0^{(0)} = 0$, $C_0^{(1)} = 0$, $S_{T0} = 10$, $\varepsilon = 1.0$, $h = 100$, $n = 20$, $w = 2.0$, $J_0 = 10^6$, $\Theta_i = 1$ when (a), the effect of cooling rate as $\lambda = 0$; (b), the effect of cooling rate $\lambda = 1/3$; (c), the effect of cooling rate $\lambda = 2/3$. (d), the effect of $\lambda$ for nonisothermal crystallization with cooling rate $\phi = 10^{-3}$. Solid lines and dotted lines represent the numerical solution and the moment solution, respectively.
plot is curved rather than a straight line [Price, 1969; Ozawa, 1971; Grenier and Prodhomme, 1980]. Figures 4.7.b and 4.7.c present the effect of cooling rates for diffusion controlled (\(\lambda = 1/3\)) and surface dependent (\(\lambda = 2/3\)) crystal growth, respectively. A large overall crystallization rate is caused when cooling rate increases, as confirmed in the moment solution. A slope increase of 2.7 in the Avrami plots is observed as cooling rate increases from \(10^{-4}\) to \(6\times10^{-4}\), in agreement with experimental studies [Achilias et al., 2004]. The effect of \(\lambda\), the exponent of growth rate coefficient, is presented in Figure 4.7.d. No apparent slope increase for the Avrami plots occurs when \(\lambda\) increases, while the overall crystallization rate rises because of the increasing dependence of growth rate coefficient on crystal mass. It is important to notice that, different from isothermal crystallization [Yang et al., 2005b], the effect of changing temperature dominates over the effect of \(\lambda\) because of the sensitivity of nucleation rate on temperature. Thus an apparent slope change in the Avrami plots is not observed for different \(\lambda\) for nonisothermal crystallization.

![Figure 4.8](image)

Figure 4.8 The fits of cluster size distribution model with \(C_{0}^{(0)} = 0, C_{0}^{(1)} = 0, S_{T0} = 10, \varepsilon = 1.0, h = 100, n = 20, w = 2.0, J_{0} = 10^{6}, \lambda = 0, \) and \(\Theta_{i} = 0.96\) to the nonisothermal crystallization measurements for PPT at cooling rate: (■) \(\beta = 40 ^\circ C/min\); (×) \(\beta = 20 ^\circ C/min\); (▲) \(\beta = 10 ^\circ C/min\); (◆) \(\beta = 5 ^\circ C/min\); (▼) \(\beta = 2.5 ^\circ C/min\); (●) \(\beta = 1 ^\circ C/min\).
To verify the application of the cluster size distribution model to nonisothermal crystallization, we fitted experimental measurements with the model. Figure 4.8 presents the comparison between simulation results of the model and experimental data [Achilias et al., 2002] for PPT [poly(propylene terephthalate)]. The solid lines represent the model fit, and the points denote the measurements at various cooling rates. A unit transposition is made on the data since our model calculation is based on dimensionless time while the experimental data is based on real time. Here a horizontal transposition of $\log_{10}(\gamma \mu_\infty \lambda x_m^3)$ units is applied to convert the experimental data into plots based on dimensionless time $\theta$ [Yang et al., 2005b]. The experimental measurements present the conventional Avrami plots at cooling rate, $\beta$, equal to 1.0, 2.5, 5, 10, 20 and 40 °C/min, respectively. Good agreement between experiment and simulation results is observed, indicating a realistic description of nonisothermal crystallization by the crystal size distribution approach.

4.4 Conclusion

The crystal size distribution kinetics approach [Yang et al., 2005a; 2005b] applied in this chapter permits an investigation of nonisothermal crystallization. Following our earlier studies on isothermal polymer crystallization [Yang et al., 2005b], we have investigated the effect of cooling rates in detail for nonisothermal crystallization with linearly decreasing crystallization temperature. The temperature dependencies of crystallinity, supersaturation, and average crystal size are presented for nonisothermal crystallization at different cooling rates. Time evolutions of crystal size distributions are also revealed at different cooling rates. The effect of initial temperature is investigated in detail. An apparent Avrami exponent increase occurs as the initial temperature increases. The effect of cooling rate, however, is counteracted by increasing initial temperature, e.g., increasing the cooling rate has little influence if the crystallization temperature begins from the melting point. The incubation period was also investigated in detail at different
cooling rates and different initial temperatures. An increasing incubation period is caused by raising the initial temperature or decreasing the cooling rate. We also investigated the effect of power dependence for growth rate coefficient $\lambda$ and did not observe the apparent Avrami exponent increase when the polymer melt is cooled from the melting point, as indicated in isothermal crystallization. The validity of the crystal size distribution model was also examined by comparison with experiment measurements. The model accurately describes the effect of cooling rate on incubation time and on Avrami plots of crystallinity vs. time. Although an analytical, closed expression cannot be derived in our approach, the model and simulation results for degree of crystallization provide a theoretical foundation for Avrami plots. Because the characteristic Avrami plot for experimental data is curved rather than straight indicates that our approach is capable of providing a more realistic prediction than the oversimplified Avrami theory.
Chapter 5  A Distribution Kinetics Approach for Crystallization of Polymer Blends

5.1 Introduction

Polymer blending is a useful and economical way to produce new materials with a variety of properties. Many high-performance thermoplastics are prepared by the crystallization of polymer blends. The polymer-polymer interactions during crystallization can alter crystal structure, thermal stability, and mechanical properties such as rigidity and toughness. Understanding how adding a polymer component affects the morphology, crystallization, and mechanical and thermal properties of the polymer blend is a significant scientific challenge. To explore the crystallization kinetics of neat polymer melt, a cluster size distribution approach for nucleation accompanied by crystal growth and Ostwald ripening has been developed in previous Chapters. Polymer nucleation and crystal growth involve the dynamics of polymer chains, including the folded chain structures. Population balance equations based on crystal size distribution and concentration of amorphous polymer segments were established. The related moment and governing differential equations were also solved numerically under isothermal and nonisothermal conditions. The approach presented a fundamental, quantitative explanation for the mechanism of nucleation and crystal growth. In this chapter, we extend this approach to the application of polymer blend crystallization. The miscibility of polymer blends complicates the kinetics and dynamics of crystallization. Understanding how the addition of one component affects the crystallization behavior of the other can potentially be used to design and develop new types of high performance polymer materials and to control product properties, e.g., microscopic structure, average size of polymer crystals, and crystal-size polydispersity.

* Portion of this chapter is from J. Yang, B. J. McCoy and G. Madras, J. phys. chem. B, 110, 15198 (2006)
Several studies have investigated the crystallization of neat polymer [Ciora and Magill, 1990; Yang et al., 2005a; 2005b; 2005c], but binary polymer blend crystallization has received less attention. Experimental investigations on the miscibility and crystallization of polymer blends have been reported occasionally [Wang et al., 2002; Yi and Goh, 2003; Su and Shih, 2005; Hsu, 2005], but only a few studies have been directed toward fundamental theoretical investigations. The understanding of how the presence of one component affects the morphology and crystallization of the other is still not clear for polymer blends. Polymer crystallization involves two phenomena: nucleation and crystal growth. The addition of a second polymer alters the crystallization kinetics of polymer solute mainly through these two steps. The temperature dependence of crystallization rates for neat (unmixed) polymers is approximately parabolic; crystallization rate is zero at $T_g$ (glass temperature) and $T_m$ (melting temperature), and the maximum rate appears between these two points. The addition of a second polymer to a semicrystalline polymer can act as a diluent, causing either a decrease in crystallinity by decreasing crystal number concentration or an increase in crystallinity by increasing chain mobility. The existence of polymer-polymer interactions also influences the deposition mechanism, causing either an increase or decrease of the crystal growth rate. For example, the spherulite radial growth rate of poly(ethyl methacrylate) was found to decrease as poly(ethylene oxide) is added as the binary component [Cimmino, 1999]. By contrast, the presence of poly(vinyl methyl ether) was found to enhance the spherulite growth rate of isotactic polystyrene [Bartczak et al., 1984]. Increases in the spherulitic growth rate and crystallinity were also found for poly(vinyl methyl ether) added as a second ingredient in isotactic polystyrene [Martuscelli et al., 1985]. The miscibility and crystallization of PES [poly(ethylene succinate)] and PVPh [poly(vinyl phenol)] blends was investigated and it was found that the growth rate of neat PES was higher than that of blended PES crystallized at the same temperature [Qiu et al., 2004],
which indicates that the addition of PVPh reduces the spherulite growth of PES in blends. The Avrami exponent was almost the same despite the blend composition and crystallization temperature.

A theoretical model was developed by Rostami [1990] to explain the slower rate of spherulite growth in thermodynamically miscible blends of semicrystalline and amorphous polymer. Harris and Robeson [1987] proposed a hypothesis to explain the enhancement of the crystallinity of a crystallizable component diluted with a miscible polymer. The interlamellar region, which contains the amorphous fraction, increased as the amorphous component is added to semicrystalline polymer. The increased amorphous fraction reduces the glass transition temperature and lends additional mobility to the crystallizable ingredient, thus allowing a higher fraction of this ingredient in the crystalline phase.

For immiscible polymer blends, crystallization occurs within a single phase domain of single component. The miscibility and crystallization of PHBV [poly(3-hydroxybutyrate-co-hydroxyvalerate)] and PCL [poly(ε−caprolactone)] blends was investigated and these two polymers were not miscible [Qiu et al., 2005]. The crystallization of the blends was studied using a two-step process: as the blend was cooled, the component with higher melting temperature crystallized first, and the lower melting component crystallized later. The crystallization rate of PHBV decreased with increase of PCL, while the crystallization rate of PCL increased with increasing PHBV fraction. The Avrami exponent for crystallization of PCL varied as the component fraction of PHBV changed, and was almost the same for crystallization of PHBV as fraction of PCL changed.

In this chapter, we focus on the crystallization kinetics of binary miscible polymer blends; crystallization of immiscible polymer blends presents no difference with neat polymer crystallization that was addressed in previous chapters. Our approach is to represent the
5.2 Distribution Kinetics Theory for Crystallization of Polymer Blends

The addition of a second polymer can act as a diluent, either decreasing crystallinity by decreasing concentration of crystallizable component and nuclei numbers, or increasing crystallinity by enhancing nucleation rate or increasing chain mobility. Five patterns of crystallinity development are identified upon addition of a crystallizable polymer additive [Long et al., 1995]: (1) the diluent does not affect the crystallization; (2) the diluent retards the crystallization rate; (3) the diluent prevents crystallization (particularly at high concentrations); (4) the diluent accelerates crystallization; (5) the diluent provides enough thermal mobility to cause crystallization of a normally non-crystalline polymer. As mentioned, the addition of a second polymer ingredient affects crystallization mainly through nucleation and crystal growth rates. We use classical nucleation theory to account for the nucleation of polymer blends. The nucleation rate, according to classical nucleation theory [Oxtoby, 1992], can be represented as the flux over the energy barrier $W^*$, as shown in Eqs. (2.10), (2.11) and (2.12). Here $m^{(0)}$ is the bulk concentration of amorphous polymer segments in the miscible polymer blend, $\sigma$ accounts for the interfacial energy of nucleus, $\delta$ represents the thickness of the crystalline lamellae, and $x_m$ is the molecular weight of polymer segments. The thickness $\delta$ of the crystalline lamellae is approximated by the length of polymer segments, which is constant for a certain polymer. The equilibrium concentration $m_{\infty}^{(0)}$, which is constant for a certain polymer blend, exclusively depends on crystallization temperature and the miscibility of the polymer blend. Thus blending influences the nucleation rate through the dilution effect on the crystallized component concentration, $m^{(0)}$. As we increase the volume fraction of the second component, the nucleation
prefactor $k_n$ decreases, so does the exponential term because of the increase of nucleation energy barrier. Nucleation vanishes when the polymer concentration, $m^{(0)}$, is equal to or less than the equilibrium concentration, $m_{\infty}^{(0)}$, because of the high energy barrier.

The addition of a second component affects crystal growth by altering the growth rate coefficient and deposition-rate driving force. As proposed in our previous studies [Yang et al., 2005a; 2005b; 2005c], crystal growth is represented by a reversible mechanism of addition and dissociation on nuclei. The polymer-polymer interaction introduced by blending may affect the deposition, and consequently alter the growth rate coefficient $k_g$. Thus the established population balance equation in our previous work can be applied to polymer blends. Reasoned thusly, the governing equations for crystallization of neat polymer and polymer blends are the same, and the mixing effects are incorporated into the evaluation of $m^{(0)}$, $m_{\infty}^{(0)}$, and growth rate coefficient $k_g(x)$. The governing equations are represented by Eqs. (2.16) and (2.17). A general expression for growth rate coefficient $k_g(x)$ is a power law dependence on crystal mass $x$, $k_g(x) = \kappa_g x^\lambda$, where the value of power exponent $\lambda$ depends on the deposition mechanism. A polymer segment that deposits on a crystal surface diffuses through the solution to react on the crystal surface; such diffusion-controlled reactions have a rate coefficient represented by [Madras and McCoy, 2002],

$$k_g = 4\pi D r_c$$  \hspace{1cm} (5.1)\

where $D$ is the diffusion coefficient. The crystal size is related to its mass $x$ by $r_c = (3x/4\pi \rho_c)^{1/3}$, in terms of crystal density $\rho_c$, which is constant at given temperature. Thus the power $\lambda = 1/3$ represents diffusion controlled crystal growth. In dilute solutions, $D$ is linearly dependent on blending fraction [Yamakawa, 1971; Cussler, 1997]. However, the polymer segment-segment interactions complicate the determination of the diffusion coefficient in polymer-polymer
mixtures. We may express the diffusion coefficient in terms of tracer-diffusion of each component $D_i^*$, degree of polymerization $N_i$, blending fraction $\phi$, and the Flory-Huggins interaction parameters $\chi$ [Flory, 1953; White, 1986; Kanetakis and Fytas, 1987; Brochard, 1983]

$$D = (D_A^* N_A \phi_B + D_B^* N_B \phi_A ) (\phi_A/N_B + \phi_B/N_A - 2 \phi_A \phi_B \chi)$$

(5.2)

with subscripts A and B representing the two polymer components. As activation energy for the growth coefficient accounts for activated diffusion, Eq (5.2) can be expanded into a polynomial in blending fraction $\phi_A = 1 - \phi_B$,

$$D = D_0 \exp(-E/RT) (1 + a_1 \phi_A + a_2 \phi_A^2 + a_3 \phi_A^3)$$

(5.3)

where $a_1$, $a_2$ and $a_3$ are constants for a certain polymer blend depending on, $D_i^*$, $N_i$, and $\chi$. The diffusion activation energy $E$ also varies as the blended polymer or its fraction changes, leading to the variation of growth rate coefficient. Substituting $r_c = (3x/4\pi\rho c)^{1/3}$ and Eq (5.2) into Eq (5.1) gives a detailed expression for growth rate coefficient,

$$k_g(x) = \gamma x^{1/3} \exp(-E/RT)(1 + a_1 \phi_A + a_2 \phi_A^2 + a_3 \phi_A^3)$$

(5.4)

with $\gamma = 4\pi D_0 (3/4\pi\rho c)^{1/3}$. The volume fraction $\phi_A$ can also be related to $m^{(0)}$, the molar concentration of component A, by,

$$m^{(0)} = \phi_A/\nu_m$$

(5.5)

where $\nu_m$ is molar volume of crystallized component A. Thus the growth rate coefficient can be represented in terms of $m^{(0)}$ as,

$$k_g(x) = \gamma x^{1/3} \exp(-E/RT)(1 + b_1 m^{(0)} + b_2 m^{(0)^2} + b_3 m^{(0)^3})$$

(5.6)

with $b_1 = a_1/\nu_m$, $b_2 = a_2/\nu_m^2$ and $b_3 = a_3/\nu_m^3$. When the growth is limited by the crystal surface, the rate coefficient is proportional to the crystal surface area, $r_c^2$, so that the power exponent of growth is $\lambda = 2/3$, which represents surface controlled deposition rate coefficient. If the deposition rate is independent of crystal surface area, then the power exponent of growth is $\lambda = 0$
indicating crystal growth rate is independent of mass. With the definition of dimensionless quantities as Eq. (3.4), the population balance equations, Eqs (2.16) and (2.17) are rewritten as,

\[ \frac{dS_T(\theta)}{d\theta} = (1 + d_1S_T + d_2S_T^2 + d_3S_T^3)\exp(-\varepsilon/\Theta) \left[ -S_T(\theta) + \exp(-h/\Theta) \right]C^{(k)} - J \xi^* \]  (5.7)

and

\[ \frac{\partial C(\xi, \theta)}{\partial \theta} = (1 + d_1S_T + d_2S_T^2 + d_3S_T^3) S_T(\theta) \exp(-\varepsilon/\Theta) \left( -\xi^*C(\xi, \theta) + (\xi-1)^2C(\xi-1, \theta) \right) \\
- \xi^*\exp(- (\varepsilon+h)/\Theta)C(\xi, \theta) +(\xi+1)^2 \exp(- (\varepsilon+h)/\Theta)C(\xi+1, \theta) + J\delta(\xi-\xi^*) \]  (5.8)

with \( d_1 = b_1\mu, \ d_2 = b_2\mu^2 \) and \( d_3 = b_3\mu^3 \). The scaled nucleation rate \( J \) can be written in terms of \( S_T, \) interfacial energy \( w, \) temperature \( \Theta, \) and phase transition enthalpy \( h, \) as in Eqs. (3.12) and (3.13)

For the simple case of surface independent deposition, \( \lambda = 0, \) the moment technique can be used to rewrite the population balance equations as

\[ \frac{dS_T(\theta)}{d\theta} = (1 + d_1S_T + d_2S_T^2 + d_3S_T^3)\exp(-\varepsilon/\Theta) \left[ -S_T(\theta) + \exp(-h/\Theta) \right]C^{(0)} - J \xi^* \]  (5.9)

\[ \frac{dC^{(0)}(\theta)}{d\theta} = J \]  (5.10)

\[ \frac{dC^{(1)}(\theta)}{d\theta} = - (1 + d_1S_T + d_2S_T^2 + d_3S_T^3)\exp(-\varepsilon/\Theta)\left[ -S_T(\theta) + \exp(-h/\Theta) \right]C^{(0)} + J \xi^* \]  (5.11)

For any nonzero \( \lambda, \) the moment equations lack closure, thus a numerical technique is required to solve Eqs (5.7) and (5.8).

The number of macromolecules in the critical crystal nucleus is, \( \xi^* = \left[ w \left( 1 - \Theta \right)^3 / \Theta \left( \ln S_T + h / \Theta \right) \right]^2, \) which varies with time, because of the time dependence of the scaled number of crystallizing polymers \( S_T, \) and is strongly dependent on temperature. In terms of the initial number of polymer molecules \( S_{T0}, \) the scaled mass conservation for a closed system follows from the population balance equations, Eqs (5.9) and (5.11),

\[ C^{(1)}(\theta) + S_T(\theta) = C_0^{(1)} + S_{T0} \]  (5.12)
where $C_0^{(1)}$ is the initial cluster mass, representing heterogeneous nuclei and seeds, and is zero for homogeneous nucleation, and $S_{T0}$ is the initial number of polymer molecules. The degree of crystallinity, $X$, is defined as the ratio of the mass crystallized at time $t$ divided by the total mass crystallized,

$$X = \frac{(C^{(1)} - C_0^{(1)})}{(C_{eq}^{(1)} - C_0^{(1)})}$$

(5.13)

Substitution of the mass conservation equation, Eq (5.21), simplifies the above equation to,

$$X = \frac{(S_{T0} - S_T(\theta))}{(S_{T0} - e^{-\frac{h}{\Theta}})} \approx 1 - \frac{S_T}{S_{T0}}$$

(5.14)

The growth rate coefficient is not the only parameter subject to change under different blend fractions, though only its dependence on blend fraction is mathematically approximated in the population balance equations. Melting temperature, phase transition enthalpy, and activation energy may also change with blending fraction, e.g., the melting temperature of poly(vinylidene fluoride)[PVDF]/poly(vinyl acetate)[PVAc] blends varies from 170.7 °C to 152.4 °C as the fraction of PVAc increases from 0 to 30% [Chiu, 2002]. To keep the governing equations simple, we consider the effects of blending fraction on those parameters in computation rather than approximate them mathematically in the population balance equations.

5.3 Results and Discussion

For the crystallization of miscible polymer blends, we are concerned with the effect of blending on the kinetics of crystallization for the easily crystallizing component, i.e., the component crystallizing at the relatively higher temperature. The increase of second ingredient fraction, according to Eqs (2.10), (2.11), and (2.12), leads to decreasing nucleation rate because of the dilution of concentration $m^{(0)}$. The dilution also slows the crystal growth rate by decreasing the deposition rate and the driving force, $-S_T(\theta) + \exp(-\frac{h}{\Theta})$. Thus, by incorporating the blending effects for melting temperature $T_m$, enthalpy of fusion $\Delta H$, and activated diffusion
energy $\varepsilon$, introducing a second polymer component generally delays the crystallization by decreasing nucleation and crystal growth rates.

For the simple case of surface independent deposition, $\lambda = 0$, the governing moment Eqs (5.9) ~ (5.11) are solved by NDSolve in Mathematica to assess the effect of blending on nucleation and crystal growth rate. The moment method provides an easy and quick model for polymer crystallization with surface-independent crystal growth ($\lambda = 0$). However, a general approach is to solve the equations numerically based on methods described previously [Yang et al., 2005a; 2005b; 2005c]. The difference differential equation Eq. (5.8) is solved by Runge-Kutta technique with an adaptive time step and $C(\xi, \theta)$ is evaluated at each time step sequentially. The mass variable, $\xi$, is divided into 5000 intervals and the adaptive time, $\theta$, step varied from $10^{-5}$ to $10^{-2}$ ensuring stability and accuracy at all values of the parameters. At every time step the mass conservation (Eq. (5.12)) was verified. The numerical results are further validated by comparison with the analytical moment solutions obtained for $\lambda = 0$.

Our choice of parameters is based on earlier work [Yang et al., 2005a; 2005b; 2005c] and experimental measurements [Xiao et al., 2002]. Previous work suggested a value [Yang et al., 2005b] $n = 20$ to represent the temperature dependence of interfacial energy. The interfacial

<table>
<thead>
<tr>
<th>$\phi_0$</th>
<th>$S_{T0}$</th>
<th>$\varepsilon$</th>
<th>$h$</th>
<th>$\Theta$</th>
<th>$C_0^{(0)}$</th>
<th>$C_0^{(1)}$</th>
<th>$J_0$</th>
<th>$\lambda$</th>
<th>$w$</th>
<th>$n$</th>
<th>$d_1$</th>
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<td>$10^6$</td>
<td>0</td>
<td>2.0</td>
<td>20</td>
<td>1</td>
<td>0</td>
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<td>3.5</td>
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<td>0</td>
<td>0</td>
<td>$10^6$</td>
<td>0</td>
<td>2.0</td>
<td>20</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
energy parameter $w$, written in terms of density, is chosen to be $w = 2$. The molar enthalpy of phase transition $h$ is usually about 10. The activation energy, $\varepsilon$, for growth rate is typically smaller than $h$, and a constant nucleation rate prefactor, $J_0 = 10^6$, is proposed. The values of various parameters used in the model are summarized in Table 5.1. There are no particles present initially for homogeneous nucleation, thus the initial conditions are $S_T(\theta = 0) = S_{T0}$, $C^{(0)}(\theta = 0) = 0$, and $C^{(1)}(\theta = 0) = 0$.

![Graphs showing time evolution of supersaturation, number of crystals, average crystal size, and nucleation rate for various blending fractions.](image)

Figure 5. 1 Time evolution of (a) supersaturation, (b) number of crystals, (c) average crystal size, (d) nucleation rate for various blending fractions (parameters are listed in Table 5.1).
Figure 5.1 presents the computational results of crystallization time evolution as the fraction of second polymer component changes. The initial values of scaled solute concentrations, $S_{T0} = 10, 9, 8, \text{ and } 7$, correspond to second component fraction of 0% (neat polymer), 10%, 20%, and 30%. The parameters $d_1, d_2 \text{ and } d_3$, which depend on polymer physical properties, are chosen to equal 1.0, 0, and 0, respectively. Such a linear approximation for the diffusion coefficient $D$ may constrain applicability to a certain range of blend fraction. For a miscible blending system, crystallization is initiated only above the critical blending fraction where the two components are in equilibrium. Most of crystallization processes are initiated by cooling; and polymer-polymer solutions become supersaturated as the temperature decreases. Consequently the supersaturated component begins to nucleate only after the fraction of crystallized component in the liquid phase decreases to the equilibrium blending fraction corresponding to the crystallization temperature. Thus crystallization of miscible polymer blends occurs only within a certain range of blending fraction.

Figure 5.1.a shows the time evolution of supersaturation $S_T$. The consumption rate of free solute (in the amorphous state) decreases as the fraction of second polymer increases because the neat polymer has the largest solute consuming rate. Compared with neat polymer melt, the blended system requires more time to complete the crystallization. The time evolution of crystal number and crystal size is represented in Figure. 5.1.b and 5.1.c. The influence of the second polymer in the blend (Fig. 5.1.b) shows that the fraction increase of the second polymer dilutes the solute concentration. Meanwhile, the initial critical size $\xi_0^*$ (Eq (3.17)) is also subject to increase because the supersaturation decreases as the blending fraction increases. Figure 5.1.c presents the time evolution of the average crystal size, indicating the influence of blending fraction on crystal growth rate. The rise of the second polymer component fraction slows the crystal growth rate by decreasing the growth rate coefficient and deposition-rate driving force.
As a consequence, the smallest average crystal size at a blending fraction of the second component under 30% is observed. The influence of the second polymer in the blend shows that the fraction increase of the second polymer decreases nucleation rate, as shown in Figure 5.1.d.

The model is also used to represent the Avrami plots of the crystallinity time evolution, as shown in Figure 5.2. The evolution of crystallinity with time integrates the blending effects on both nucleation and crystal growth, and indicates the negative influence on crystallization time for the second polymer component. The variation of the blending fraction does not affect the Avrami exponent significantly. Denucleation, the reverse of nucleation, occurs when the crystal size is smaller than the critical nucleus size. Denucleation has considerable influence on the characteristic Avrami plots, especially at the end of crystallization when denucleation dominates over nucleation. At the beginning of crystallization, most polymer crystals are larger than the critical crystal size, thus denucleation, compared with nucleation, is negligible. The critical crystal size, however, increases as the supersaturation declines when polymer deposits on the crystal, thus more crystals become smaller than the critical size. These unstable crystals will dissolve rapidly. At the end of crystallization, denucleation and ripening become dominant because the supersaturation is close to unity, and consequently nucleation vanishes. Figure 5.2 presents the effect of denucleation by comparison of moment and numerical solutions. The solid lines represent the characteristic Avrami plots of moment solutions, for which denucleation is not considered. The dotted lines represent the numerical solutions that account for denucleation. At the beginning, the denucleation rate is small, and the moment solution matches the numerical solution very well because the small denucleation rate delays the dominating influence of nucleation. As supersaturation decreases, the discrepancy between moment solution and numerical solution caused by denucleation becomes increasingly apparent. The numerically
computed crystallinity reaches its asymptote whereas the crystallinity computed by the moment method continues to increase.

Figure 5.2 Avrami plot showing the time evolution of crystallinity comparing the moment solution (solid line) and the numerical solution (dotted line) with the parameters listed in Table 5.1.

Figure 5.1 presented model predictions when the diffusion coefficient D is approximated

Figure 5.3 Effect of $d_1$ on the time evolution of (a) crystallinity and (b) crystal size with $\phi_0 = 0.80$ and the parameters listed in Table 5.1.
by a linear dependence on blending fractions, $\phi_A$, and Figure 5.3 shows the time evolution of crystallinity and crystal size based on the linear approximation of diffusion coefficient by varying $d_1$ in the range of 0.1 to 10 (see Eqs (5.7) and (5.8)). It is observed that a stronger dependence of the diffusion coefficient on the blending fraction leads to faster crystallization rates. The slope of the Avrami plot (Avrami exponent) does not depend on $d_1$, as shown in Figure 5.3.a. The effect of $d_1$ on average crystal size is presented in Figure 5.3.b. According to the linear expression of the diffusion coefficient, a large value of $d_1$ leads to an increase in the diffusion coefficient resulting in a larger average crystal size, as shown in Figure 5.3.b.

We next determine the effect of a polynomial dependence of $D$ on blending fractions. The time evolution of crystallization based on linear and polynomial expressions for diffusion coefficient $D$ is shown in Figure 5.4. The polynomial expression for diffusion coefficient does not lead to a significant variation in Avrami exponent, suggesting that the linear expression is a valid approximation.

![Figure 5.4 Comparison between linear and nonlinear expression for diffusion coefficient with $C_0^{(0)} = 0$, $C_0^{(1)} = 0$, $\phi_A = 0.80$, $J_0 = 10^6$, $\lambda = 0$, and $n = 20$. The dotted line is the linear approximation for $D$ ($d_1 = 1$, $d_2 = 0$, and $d_3 = 0$) and the solid line represents the polynomial expression for $D$ with $d_1 = 1$, $d_2 = -0.02$, and $d_3 = 0.02$.](image)
The presence of the second polymer in the blend may either decrease or increase the absolute value of $T_g$ and $T_m$ of the semi-crystalline ingredient [Long et al., 1995], depending upon the difference between the isothermal crystallization temperature, $T_i$, and $(T_g + T_m)/2$. Depending on whether this difference increases or decreases with the addition of the second ingredient, the crystallization rate decreases or increases, respectively. In the proposed model, Eq. (5.11) indicates that crystal growth and crystallization rate would increase or decrease depending on whether $\Theta$ increases or decreases with blending fraction, respectively, consistent with the observed experimental data [Long et al., 1995].

The validity of the distribution kinetics model is also examined by comparison with the experimental data of the PVDF/PVAc blend [Chiu, 2002] (Fig. 5.5), where $\Theta$ decreases with increasing blending fraction and, therefore, the crystallization rate decreases with the blending fraction. The simulation results are based on dimensionless time $\theta = t \gamma \mu \lambda $, so a transposition of the original experimental data, based on real time, is applied to compare with simulations.

According to the definition of dimensionless time, a horizontal transposition of \log(\gamma \mu \lambda ) units is applied to the experimental measurements to convert the experimental data

<table>
<thead>
<tr>
<th>PVDF/PVAc</th>
<th>$T_m/\degree C$</th>
<th>$\Delta H_m/J/g$</th>
<th>$E/J/g$</th>
<th>$\phi_A$</th>
<th>$S_0$</th>
<th>$\epsilon$</th>
<th>$h$</th>
<th>$\Theta$</th>
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<tr>
<td>100/0</td>
<td>170.7</td>
<td>64.54</td>
<td>0.96</td>
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<td>0.949</td>
</tr>
<tr>
<td>90/10</td>
<td>168.4</td>
<td>55.27</td>
<td>1.03</td>
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<td>9</td>
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<td>2.8</td>
<td>6.61</td>
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<td>40.06</td>
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<td>7</td>
<td>7.5</td>
<td>6.21</td>
<td>0.989</td>
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</table>
Figure 5.5 Model prediction of the experimental data of the PVDF/PVAc blend with different blending fractions with (a) $\lambda = 0$ and (b) $\lambda = 1/3$; (▼): PVDF/PVAc = 100/0, (▲): PVDF/PVAc = 90/10 (●): PVDF/PVAc = 80/20, (■): PVDF/PVAc = 70/30.

into plots based on dimensionless time $\theta$. The points are experimental data [Chiu, 2002] and the model parameters are listed in Table 5.2. A moment solution with surface-independent crystal growth ($\lambda = 0$) does not fit the experimental data (Fig. 5.5.a), so $\lambda = 1/3$ is chosen [Yang et al., 2005c] and the population balance equations are solved numerically. The measured horizontal transposition is unity, independent of the blend fraction or temperature. Good agreement between experimental data and simulation results (Fig. 5.5.b) with $\lambda = 1/3$ is observed indicating that the crystal growth for PVDF/PVAc blending system is diffusion dominated.

5.4 Conclusion

Based on a previous distribution kinetics approach, we have investigated the crystallization kinetics of miscible polymer blends in this chapter. This model accounts for the effects of polymer blending on nucleation and crystal growth rates. Adding a second polymer influences the crystallization mainly through thermodynamics and kinetics (equilibrium solubility and deposition mechanism). These effects are incorporated by varying the initial
values of monomer concentration and growth rate coefficient. Assuming that the deposition mechanism does not change during crystallization, we have investigated the crystallization kinetics for various blending fractions. Computation results indicate that increasing the second polymer fraction leads to the decrease of both nucleation and crystal growth rates, while the Avrami exponent does not change. The diffusion coefficient plays an important role in determining the time evolution of polymer blends because of the strong polymer-polymer interactions. A polynomial expression and a linear approximation for the diffusion coefficient on the blending fraction are compared and it is found that the linear expression is an adequate approximation. The model is used to simulate the experimental data of the time evolution of crystallinity for the blend of poly(vinylidenefluoride) [PVDF] and poly(vinyl acetate) [PVAc] at various blending fractions.
Chapter 6  Cluster Kinetics and Dynamics during Spinodal Decomposition

6.1 Introduction

Spinodal decomposition is a spontaneous, barrierless phase separation caused by conditions that force the system to become thermodynamically unstable. The process can be understood by visualizing a phase diagram with a coexistence (or binodal) curve (the solid curve in Fig. 6.1) representing separated phases in equilibrium and ending at a critical point. The binodal encloses a spinodal curve (the dashed curve in Fig. 6.1) setting the limits of metastability and hence of nucleation. The classical spinodal is the curve on the phase diagram where the critical cluster vanishes [Goldenfeld, 1992]. For metastable systems in the region between the binodal and spinodal curves, homogeneous nucleation generates stable clusters that grow by rate-limited processes. When a homogeneous fluid is brought rapidly into the unstable spinodal.

Figure 6.1  Schematic phase diagram of a binary mixture where $T_c$ is critical temperature and $\phi_B$ represents the polymer volume fraction.

region, by changing its temperature or composition, a spontaneous phase separation occurs [Cahn, 1961; 1962; Alexander et al., 1993; Seol et al., 2003]. This condensation has been experimentally studied for the vapor phase [Ruth and Hirth, 1988], binary alloys [Mainville, 1997], and polymer mixtures [Gennes, 1980]. In polymer solutions during phase separation, the polymer-rich phase becomes more viscoelastic with time, causing spinodal decomposition to produce fascinating network structures and patterns [Wang and Mashita, 2004]. Understanding the phenomenon of spinodal decomposition and its underlying mechanism is pertinent because of the intrinsic importance not only in scientific investigation but also in industrial materials manufacture.

The basic processes in condensation phase transition are nucleation, dispersed cluster growth by reversible monomer deposition, cluster aggregation (coalescence), and Ostwald ripening (coarsening). The critical nucleus size plays a crucial role in these processes, providing the criterion for nucleus formation (homogeneous nucleation) and for nucleus dissolution (denucleation). The premise of this chapter is that when the nucleation barrier is vanishingly small, unhindered cluster coalescence dominates the phase transition. According to these notions, the kinetics and dynamics of clusters necessarily underlie condensation phase transitions.

The classical models of phase transitions are developed by Becker and Doring (BD) [1935], Lifshitz and Slyozov [1961] (LS) and Wagner [1961] (W). The BD model for transitions from the metastable state was based on the formation of clusters by the addition or subtraction of monomers (with no coalescence among larger clusters). The BD equations were generalized [Penrose and Lebowitz, 1976] to allow the monomer concentrations to vary, with the key restrictive assumption that only monomers can interact with clusters. LSW theory is concerned with ripening (coarsening) of the cluster size distribution due to transfer of mass from smaller less stable clusters to larger more stable clusters, with attendant dissolution of unstable
(subcritical) clusters. Marqusee and Ross [1983] showed that the LSW solution can be represented as leading terms in an expansion of the long time solution. Further studies of these two classical models of phase transitions, the BD and LSW equations, discussed the connections between them [Laurençot and Mischler, 2002] and the different time regimes observed [Bolton and Wattis, 2002].

For coalescence and breakage, the general model proposed by Smoluchowski [1916] allows clusters of all sizes to aggregate and for a cluster to split into unequal fragments. Monette and Klein [1992] realized that coalescence of clusters is crucial to the occurrence of spinodal decomposition, the premise that we expand upon in this work. Unlike condensation from a metastable state, the proposal is that spinodal decomposition occurs when the nucleation energy barrier is negligible, allowing clusters to form and coalesce rapidly. A Smoluchowski-like population balance equation, previously applied to Ostwald ripening and shown to converge to the LSW solutions asymptotically, is applied to model spinodal decomposition [Madras and McCoy, 2002; 2003].

The Cahn-Hilliard [1958; 1959] theory of spinodal decomposition relies on defining a spinodal curve in terms of the free energy density, \( f(c) \), by \( (\frac{\partial^2 f}{\partial c^2})_T = 0 \) for \( c = c_s \). Through its basis in equilibrium thermodynamics, this definition requires a state equation that provides \( f(c) \), and is predicated on existence of equilibrium, at least locally. Concentration fluctuations are supposed to be governed by the collective diffusion coefficient, \( D = \zeta (\frac{\partial^2 c}{\partial \phi^2})_T \), where \( \zeta \) is a mobility coefficient [Binder et al., 1986]. In the unstable region, where \( (\frac{\partial^2 f}{\partial c^2})_T < 0 \), \( D \) would be negative, and spinodal decomposition is postulated to involve the amplification of small-amplitude, long-wavelength density or concentration fluctuations caused by thermal fluctuations. The Cahn-Hilliard theory thus enlists a model that is unrelated to and does not transition
smoothly from homogeneous nucleation theory, which is fundamental to understanding phase transitions from the metastable state.

Based on a generalization of liquid-state theory of uniform fluids and on the Fisk-Widom generalization of the thermodynamic theory of van der Waals and Cahn-Hilliard, a theory for the description the thermodynamics and structure of non-uniform fluids was proposed to analyze the thermodynamic stability of a single phase fluid in the spinodal region [Abraham and Barker, 1975]. Molecular dynamics was employed to investigate the time evolution of phase separation by spinodal decomposition in a simulated Lennard-Jones fluid [Abraham, 1978]. More recently, Moore et al. [2002] reported that a two-dimensional Cahn-Hilliard equation was able to model spinodal decomposition of a supersaturated Al-Ag alloy. Through mean field theories and Monte Carlo simulations of simple lattice models, Frenkel [1999] and Hu [2003] theoretically investigated the interplay of polymer crystallization and liquid-liquid demixing. This interplay results in a shift of the crystallization and liquid-liquid demixing curves in the phase diagram. A kinetic model was proposed, by incorporating the nearest-neighbor pair approximation, to investigate the kinetics of spinodal decomposition for a binary alloy system [Cheng, 1998]. The morphology of polymer crystals was dominated by the interplay of polymer crystallization and liquid-liquid demixing. Employing the simple lattice model, Hu and Frenkel [2004] concluded that the kinetic interplay of spinodal decomposition and polymer crystallization controls the final crystallite morphology. Many small crystallites are produced if crystallization is induced by the prior liquid-liquid phase separation during spinodal decomposition.

The kinetics of spinodal decomposition was experimentally studied by quenching the homogeneous liquid mixture to the unstable region inside the miscibility gap. Jones et al. [1991] experimentally investigated the segregation of a mixture of poly (ethylene-propylene) (PEP) and perdeuterated PEP (dPEP), which was preferentially wetted by d-PEP. Although these
experiments showed the formation of the condensed phase, quantitative results for the time-dependence of the domain size was not presented. By improving the experimental techniques, Krausch et al. [1993] investigated a similar system and observed that the growth of the condensed phase domain size follows the power-law dependence $R(t) \sim t^{1/3}$. Bulk phase separation, where fluid is driven by advective transport along the domain boundaries, yields faster growth of the phase domain size. Other experimental studies presented a fast mode of condensed phase growth in polymer and fluid mixtures [Wiltzius and Cumming, 1991].

In simple fluid systems, two time regimes are observed [Valls and Farrell, 1993]. At relatively early times, the time variation of the condensed phase domain size is power-law with an exponent of $0.3 \sim 0.4$; at longer times the variation becomes linear, i.e., the exponent becomes unity. The early time regime is supposed to be diffusion dominated because diffusion governs material transport in homogenous liquids. At longer times, the newly-formed condensed phase establishes density differences between the two phases and causes convection to be the driving force. By incorporating hydrodynamic effects, the phase separation can be modeled at both the microscopic and coarsed-grain levels [Puri and Frisch, 1997; Binder, 1998; Puri, 2005]. Guenoun et al. [1990] reported that domain growth parallel to the surface was slower than bulk growth and was characterized by a growth exponent of $0.5 \sim 0.7$. Bray [1994] summarized the growth law for the condensed phase in different regimes with growth exponents of $1/2$, $1$ and $2/3$ as diffusive regime, viscous and inertial hydrodynamic regimes, respectively. The analytical, numerical and experimental investigations of spinodal decomposition have been extensively reviewed [Puri and Frisch, 1997; Binder, 1998; Geoghegan and Krausch, 2003; Puri, 2005].

The objective of this study is to investigate the kinetics of phase separation during spinodal decomposition. A cluster size distribution model, previously applied to Ostwald ripening [Madras and McCoy, 2002] and polymer crystallization [Yang et al., 2005a], is used to
model these phenomena. It is shown that the model, by including aggregation, successfully simulates spinodal decomposition and exhibits the two time regions observed experimentally for the evolution of the average size of the dense phase domains.

6.2 Distribution Kinetics Model for Spinodal Decomposition

Spinodal decomposition can be conceptualized in the context of general phase transition dynamics and considered as a limiting case that occurs when the fluid is unstable. In contrast to conventional theories that are unrelated to and do not transition smoothly from homogeneous nucleation theory, it is suggested that the process smoothly connects with nucleated condensation of metastable fluids. Classical nucleation theory [Oxtoby, 1992; McClurg and Flagan, 1998] accounts for nucleation rate by means of the cluster energy $W$ as a function of cluster radius $r$ expressed in terms of temperature $T$, interfacial energy $\sigma$, the monomer molar volume $x_m/\rho$, and supersaturation $S$,

$$W(r) = 4\pi r^2 \sigma - \frac{4}{3} \pi r^3 \left(\frac{\rho}{x_m}\right) k_B T \ln S$$

(6.1)

The mass $x$ of a spherical condensate cluster is related to the cluster mass density $\rho$ and the radius $r$ by $x = \frac{4}{3}\pi r^3 \rho$. The cluster energy reaches a maximum value $W^*$ at the critical cluster radius $r^*$,

$$r^* = 2\sigma x_m/(\rho k_B T \ln S)$$

(6.2)

thus by Eq. (6.2), the energy barrier for nucleation is

$$W^* = (16/3) x_m^2 \pi \sigma^3/(\rho k_B T \ln S)^2$$

(6.3)

The critical cluster mass $x^*$ may be scaled in units of monomer mass $x_m$,

$$\xi^* = x^*/x_m = (\omega/\ln S)^3$$

(6.4)

where

$$\omega = \left(\frac{4\pi x_m^2}{3\rho^2}\right)^{1/3} 2\sigma/k_B T$$

(6.5)
is the ratio of monomer interfacial energy to thermal energy \( k_B T \) and plays a key role in controlling nucleation, growth, and ripening [Madras and McCoy, 2004]. The classical expression [McClurg and Flagan, 1998] for the nucleation rate (nuclei/vol-time) is the flux over the maximum energy barrier (at \( r = r^* \)),

\[
I = k_n \exp\left(-\frac{W^*}{k_B T}\right) \tag{6.6}
\]

with the prefactor

\[
k_n = (m(0))^2 \left(\frac{2\sigma m}{\pi}\right)^{1/2}/\rho \tag{6.7}
\]

where \( m(0) \) is the monomer concentration. The supersaturation is defined by

\[
S = \frac{m(0)}{m_{\infty}(0)} \tag{6.8}
\]

where \( m_{\infty}(0) \) is the monomer concentration in equilibrium with its plane \((r \to \infty)\) condensed phase.

For nucleation of a metastable vapor, the number of monomers in the critical nucleus, \( \xi^* \), is typically greater than 10, and nucleation precedes cluster growth. According to Eq. (6.4), however, for sufficiently small \( \omega \) and large \( S \), the nucleus critical size is smaller than a monomer \((\xi^* < 1)\) when the solution is brought into the spinodal region by changing its temperature and composition. This unrealistic critical nucleus size indicates that, unlike nucleation of a metastable vapor, spinodal decomposition does not involve a nucleation barrier mechanism, because the monomer (molecule in the solution) is larger than the critical nucleus. According to this view, spinodal decomposition is actually condensation by cluster aggregation in the solution.

Experiments show that small microdomains or clusters rapidly appear and grow by diffusion and coalescence until they become large enough to sediment [Gupta, 1999]. The hypothesis of the present investigation is prompted by these observations. As the supersaturation increases, or (less likely) the interfacial energy decreases, the critical nucleus size \( \xi^* \) decreases. When \( \xi^* < \sim1 \), the concept of a smallest stable cluster loses its meaning, and condensation has no
nucleation barrier. At such high values of $S$, the density or concentration of the fluid is large enough that an aggregation process, similar to step polymerization, can occur. Thus, monomers combine to form dimers, dimers combine with monomers or with other dimers, the resulting trimers or tetramers combine with other clusters, and so on. By means of this cascading coalescence, in addition to diffusion-influenced monomer addition to clusters (growth), the fluid rapidly condenses. Going beyond mean field theories that are based on thermodynamic equations of state, the present model is thus based on heterogeneous cluster kinetics and dynamics. Through its dependence on supersaturation, the hypothesized process allows a smooth transition between the theories of homogeneous nucleation and spinodal decomposition. Homogeneous nucleation with reversible cluster growth has been applied previously to crystal growth in polymer crystallization [Yang et al., 2005a; 2005b; 2005c].

Since the critical cluster size is less than one molecule, the condensation, according to the pattern evolution of spinodal decomposition [Califano and Mauri, 2004], can be represented as a reversible aggregation-fragmentation process for clusters,

$$\begin{align*}
C(x) + C(x') & \xrightarrow{k_a} C(x+x') \\
& \xleftarrow{k_b} C(x')
\end{align*}$$

(6.9)

where $C(x)$ represents cluster having mass of $x$, $k_a$ stands for the aggregation rate coefficient and $k_b$ stands for fragmentation rate coefficient. We assume that monomer-cluster interactions are negligible.

The population balance equations that govern the distribution of the clusters, $c(x, t)$ is based on mass conservation for the processes represented by Eq. (6.9):

$$\begin{align*}
\frac{\partial c(x,t)}{\partial t} = & -2c(x,t) \int_{0}^{\infty} k_a(x, x') c(x',t)dx' + \int_{0}^{x} k_a(x', x-x')c(x',t)c(x-x',t)dx' \\
& -k_b(x)c(x,t) + 2 \int_{x}^{\infty} k_b(x')c(x',t)dx'
\end{align*}$$

(6.10)
Integral forms of the rate expressions in the population balance equation lead themselves to the calculation of moments, defined as integrals over $x$,

$$
c^{(n)}(t) = \int_{0}^{\infty} c(x, t)x^n \, dx. \tag{6.11}
$$

The zeroth moment, $c^{(0)}(t)$, is the time-dependent molar concentration of clusters, and the first moment, $c^{(1)}(t)$, is mass concentration (mass/volume). The average cluster mass is the ratio,

$$
c_{\text{avg}} = \frac{c^{(1)}}{c^{(0)}} \tag{6.12}
$$

In general both rate coefficients, $k_a$ and $k_b$, are functions of cluster mass, as well as temperature and other local thermodynamic state conditions. If we consider them constants, applying the moment operation implied by Eq. (6.10) yields

$$
dc^{(n)}/dt = -2k_ac^{(0)}c^{(n)} + k_a\sum_{j=0}^{\infty} \binom{n}{j} c^{(j)}c^{(n-j)} -k_bc^{(n)} + 2k_bc^{(n)}/(n+1) \tag{6.13}
$$

It follows that the cluster moment equations for $n = 0$ and 1 are

$$
dc^{(0)}/dt = k_a(k_b/k_a - c^{(0)})c^{(0)} \tag{6.14}
$$

and

$$
dc^{(1)}/dt = 0 \tag{6.15}
$$

where Eq. (6.15) is the mass balance. The initial condition is molar concentration $c_0^{(0)}$ (of monomers), which gives the constant mass concentration,

$$
c_0^{(1)} = x_mC_0^{(0)} \tag{6.16}
$$

To satisfy microscopic reversibility (detailed balance), the local equilibrium condition for Eq. (6.16) imposes,

$$
k_b/k_a = c_{\text{eq}}^{(0)} \tag{6.17}
$$

According to experimental observations, however, all the clusters finally aggregate into one continuous dense phase (or a relatively few clusters), $c_{\text{eq}}^{(0)} \approx 0$. It can be concluded that the
fragmentation rate coefficient is relatively small, $k_a >> k_b$, and fragmentation can be neglected in Eq. (6.10). We therefore focus on an irreversible aggregation model.

As mentioned, the aggregation rate coefficient is a function of the masses of combining clusters. Previous studies [Vigil and Ziff, 1989] have considered $k_a (x, x') = \kappa (xx')^a$ or $(x+x')^b$. Here, the rate coefficient is represented as a general power law form,

$$k_a (x, x') = \kappa (xx')^\mu (x+x')^\nu$$  \hspace{1cm} (6.18)

where the aggregation rate coefficient prefactor $\kappa$ and the powers $\mu$ and $\nu$ are constants.

Dimensionless quantities are scaled by the prefactor $\kappa$ and molecular weight $x_m$,

$$\xi = x/x_m, \theta = t \kappa x_m^{2\mu+\nu}, C(\xi, \theta) = c(x, t) x_m$$  \hspace{1cm} (6.19)

where $\xi$ is the number of molecules in the cluster and $C(\xi, \theta) d\xi$ represents the number of dense phase domains including molecules in the range ($\xi$, $\xi + d\xi$) at time $\theta$. Based on the dimensionless quantities, the population balance equation, Eq. (6.10), neglecting fragmentation, can be written as

$$\partial C(\xi, \theta)/\partial \theta = -2 \xi^\mu C(\xi, \theta) \int_0^\infty \xi'^\nu (\xi+\xi')^\nu C(\xi', \theta) d\xi'$$

$$+ \xi^\nu \int_0^\xi (\xi-\xi')^\mu \xi'^\mu C(\xi', \theta) C(\xi-\xi', \theta) d\xi'$$  \hspace{1cm} (6.20)

Similarly, the $n$th moment of dense phase domains can be rewritten into dimensionless form,

$$C^{(n)}(\theta) = \int_0^\infty C(\xi, \theta) \xi^n d\xi$$  \hspace{1cm} (6.21)

Applying the moment operation to Eq. (6.20) for integer values of $\nu$ yields,

$$dC^{(n)}(\theta)/d\theta = -2 \sum_{j=0}^{\nu} C(\xi)^{(n+\mu+j)} C(\mu+j) + \sum_{j=0}^{n+\nu} C(\mu+j) C((n+\mu+j-\nu)$$  \hspace{1cm} (6.22)
For \( n = 1 \), \( \frac{dC^{(1)}}{d\theta} = 0 \) for all values of \( \mu \) and \( \nu \), indicating conservation of mass, \( C^{(1)}(0) = C^{(1)}_0 \).

The simplest case, \( \mu = \nu = 0 \) (i.e., \( k_a(x, x') = \kappa \)), represents mass independence of the rate coefficient. The zeroth moment based on Eq. (6.22) is \( \frac{dC^{(0)}}{d\theta} = -C^{(0)}_0 \), which can be solved with the initial condition \( C^{(0)}(\theta = 0) = C^{(0)}_0 \) yielding \( C^{(0)} = C^{(0)}_0/(1 + C^{(0)}_0 \theta) \). Thus, for \( \mu = \nu = 0 \), the average mass of condensed phase domains can be written in analytical form,

\[
C^{\text{avg}} = C^{\text{avg}}_0 (1 + C^{(0)}_0 \theta) \quad (6.23)
\]

The case \( \mu = 0 \) and \( \nu = 1 \) (i.e., \( k_a(x, x') = \kappa (x+x') \)) represents the coagulation kernel [Ziff and McGrady, 1985; Vigil and Ziff, 1989], and is relevant to branched polymerization processes, where the biparticle interaction depends on the mass of both particles. The zeroth moment based on Eq. (6.22) is \( \frac{dC^{(0)}}{d\theta} = -2C^{(1)}C^{(0)} \), which can be solved with the initial condition \( C^{(0)}(\theta = 0) = C^{(0)}_0 \) yielding \( C^{(0)} = C^{(0)}_0 \exp(-2C^{(1)}_0 \theta) \). Thus, for \( \mu = 0 \), \( \nu = 1 \), the analytical solution is

\[
C^{\text{avg}} = C^{\text{avg}}_0 \exp(2C^{(1)}_0 \theta) \quad (6.24)
\]

The case \( \nu = 0 \) with \( \mu \) not equal to zero represents the kernel [Madras and McCoy, 2002] where the biparticle interaction has a power law dependence on the size of interacting particles. For instance, \( \nu = 0 \) with \( \mu = 1 \) represents the kernel commonly encountered when polymers react to form crosslinks and has been shown to lead to the phase transition known as gelation [Li and McCoy, 2005]. The substitution of \( \mu = 1 \) and \( \nu = 0 \) into Eq. (6.22) yields for the zeroth moment, \( \frac{dC^{(0)}}{d\theta} = -C^{(1)}_0 \), which can be solved with the initial condition \( C^{(0)}(\theta = 0) = C^{(0)}_0 \) yielding \( C^{(0)} = C^{(0)}_0 - C^{(0)}_0 \), \( C^{(0)} \theta \). Thus for \( \mu = 1 \) and \( \nu = 0 \) the corresponding analytical solution for \( C^{\text{avg}} \) is,

\[
C^{\text{avg}} = C^{\text{avg}}_0/(1 - C^{\text{avg}}_0 C^{(1)}_0 \theta) \quad (6.25)
\]

For other values of \( \mu \) and \( \nu \), analytical solutions are not possible. If the cluster size distribution follows a certain distribution function, a closure approximation [Li and McCoy, 2005] can be
used to solve the equations. However, a general approach is to solve the equations numerically based on methods described earlier [Yang et al., 2005a]. The differential equation Eq. (6.20) was solved by Runge-Kutta technique with an adaptive time step with \( C(\xi, \theta) \) evaluated at each time step sequentially. The mass variable (\( \xi \)) was divided into 5000 intervals and the adaptive time (\( \theta \)) step varied from \( 10^{-5} \) to \( 10^{-2} \). These values ensured stability and accuracy at all values of the parameters. At every time step, the mass balance (Eq. (6.15)) was verified. The numerical results were further validated by comparison with analytical moment solutions.

6.3 Results and Discussion

We investigate a range of \( \mu \) and \( \nu \) values to explore the kinetics of phase transition in spinodal decomposition. The initial conditions of the first two moments are assumed to be \( C_0^{(0)} = 1 \) and \( C_0^{(1)} = 50 \). Figures 6.2.a and 6.2.b show the effects of \( \mu \) and \( \nu \), respectively, on the time evolution of average mass of the condensed phase. The solid lines are numerical solutions, which match well with the available analytical moment solutions (represented by symbols). The

![Figure 6.2](image_url)
average mass increases sharply as \( \mu \) increases while the effect is less pronounced with increasing \( \nu \). However, in all cases, the condensed phase domains coalesce and finally evolve into one single phase, which is consistent with the pattern evolution of phase separation via spinodal decomposition [Califano and Mauri, 2004]. As in experimental observations, the increase of average mass is slow at small times but becomes rapid at larger times.

![Graphs showing time variation of average cluster size](image)

Figure 6. Time variation of the average cluster size, \( R \), for (a) systems with analytical solutions, (b) systems solved numerically (c) a plot versus \( \theta^{1/3} \) to show power law relationship at early times, (d) a linear plot to show the linear variation at long times.
Since the initial critical size of the condensed phase domain, $\xi^*$, is less than 1, $c_0^{\text{avg}}$ is the mass of a single molecule, $x_m$. For spherical dense phase domains, the average characteristic length is

$$R(\theta) = \left(\frac{3}{4} \frac{C^{\text{avg}}}{N\pi \rho} \right)^{1/3} = \alpha \left(\frac{C^{\text{avg}}(\theta)}{}\right)^{1/3} \quad (6.26)$$

where $\rho$ stands for the density of the dense phase domains and $N$ is Avogadro's number. For simulation, $\alpha$ is assumed to be of the order unity. Figure 6.3.a shows the time evolution of the average size of the dense phase domains, $R$, for the three cases having analytical solutions (based on Eqs. (6.23), (6.24) and (6.25)). The time variation of $R$ is also plotted for various values of $\mu$ and $\nu$ (Fig. 6.3.b) for the numerical solutions. The plot indicates that the time variation of the average size of the condensed phase domain has a power-law relationship with the exponent increasing gradually from $1/3$ at short times to unity at longer times. To further illustrate this, Figures 6.3.c and 6.3.d are replotted against $\theta^{1/3}$ (Fig. 6.3.c) at short times and against $\theta$ (Fig. 6.3.d) at longer times. The plots are nearly linear indicating that the model successfully predicts the two time regions observed experimentally [Valls and Farrell, 1993]. Thus this model, which includes aggregation but ignores fragmentation, is able to simulate the time evolution of the average size of the dense phase domains showing both the diffusion controlled and convection controlled regimes.

6.4 Conclusion

Understanding the mechanism of spinodal decomposition is crucial in developing a valid model for the phase transition kinetics within the spinodal curve. Unlike condensation from a metastable state, we hypothesize that when the classical energy barrier for nucleation is negligible, single molecules aggregate and phase separate rapidly. In the present work, the detailed quantitative description of the phase separation is obtained by cluster size distribution
kinetics. Focusing on the aggregation mechanism, we have established and solved a generalized population balance equation. For specific integer values of the mass exponents, $\mu$ and $\nu$, analytical solutions are obtained. The population balance equation with varying values of $\mu$ and $\nu$ was solved numerically. The solutions were successful in demonstrating that the average size of the dense phase domains increase as a power law with an exponent of $1/3$ at shorter times and linearly at longer times.
Chapter 7 Conclusion

The extent of crystallization and the morphology formed are critical for the determination of the resulting physical properties of polymer products, thus influence their end-use values. Almost all the crystallized polymers are partly crystalline and partly amorphous. This specific semi-crystalline structure allows the adjustment of polymer products physical properties according to the application requirements. For example, polymer products friability can be increased by decreasing the extent of crystallization. Morphology also plays a critical role in determining the physical properties of polymer products. The spherulitic structure formed during polymer crystallization has significant effects influencing many properties: impact and tensile properties, kinetics of thermal degradation and gas sorption [Piorkowska, 1995]. For example, the increase of amorphous region provides better elasticity for the polymer products at the sacrifice of impact properties, while the increase of crystalline region results in the increase of friability at the expense of elasticity. Even the organization patterns of the crystalline regions have significant effects on the final product properties. Most used methods characterizing the spherulitic pattern include quantitative microscopy and imagine analysis. The crystallinity, denoting the extent of crystallization, is usually experimentally measured by differential scanning calorimetry (DSC) and wide angle x-ray scattering (WAXS). The size and shape of a spherulite are determined by its nucleation time, the position of neighboring centers, and their nucleation times and also by the process of growth. Thus a cluster distribution kinetics approach incorporating the nucleation and crystal growth mechanism has been developed to explore the fundamental characteristics of polymer crystallization in our studies.
The cluster distribution model presented fundamental investigations on the mechanisms of nucleation, crystal growth and Ostwald ripening, the three overlapping steps involved in polymer crystallization. The increase of nucleation rate enhances the crystallization rates by providing more seeds for nucleation per unit time, and consequently results in the decrease of average crystal size. The influence of nucleation rates on average crystal size plays a critical role in improving the fineness of crystalline products in pharmaceutical industry. Small impurity particles are often introduced to promote heterogeneous nucleation as this help to enhance the crystallization rates by providing more sites for nucleation. In practice, some examples for inorganic nucleating agents are talcum, barium sulfate (BaSO$_4$), and calcium carbonate (CaCO$_3$); whereas, most used organic nucleating agent is polypropylene [Charoenphol and Supaphol, 2005].

Three deposition mechanisms are proposed in our studies: surface independent, diffusion controlled and surface dependent crystal growth mechanism. Surface dependent crystal growth presents largest crystallization rate, followed by diffusion controlled crystal growth. The surface independent deposition mechanism has the smallest crystallization rate. The Ostwald ripening is crystal resizing and coarsing process which is caused by denucleation. The effect of denucleation becomes increasingly significant at the end of crystallization, as the results of supersaturation loss. The dissolution of unstable clusters leads to the decreases of crystallization rate, and results in an apparent deviation from the Avrami transition theory at the end of crystallization. The Gibbs-Thomson effect and nucleation mechanism account for the different crystallization kinetics behaviors between 3-dimensional (sphere) crystal growth and 2-dimensional (lamella) crystal growth. Our research indicates that the 3-dimensional crystal growth has a larger crystallization rate and a smaller Avrami exponent because the nucleation rate for the formation of spherical cluster is larger than the lamellar crystal.
Proposing temperature dependence for interfacial energy, growth and dissociation rate coefficients, and equilibrium solubility, we studied crystallization behavior at different temperature. According the classic nucleation theory, the nucleation rate is approximately parabolic between the glass transition temperatures $T_g$ and melting temperature $T_m$. Nucleation ceases at the glass transition temperature and melting temperature, thus a maximum nucleation rate is expected between these two points. Therefore, the increase of nucleation rate is expected as temperature decreases when the crystallization temperature is close the melting point. On the contrary, the crystal growth rate coefficient, according to the Arrhenius equation, increases with crystallization temperature, and consequently a temperature increase during the crystallization process leads to an increase of average crystal size. Therefore temperature is critical in controlling the average size of crystals in the industry crystallization process because of the strong temperature dependence of nucleation and crystal growth rate. The studies of activation energy indicates that the crystal growth rate decreases as the activation energy increases, while the crystallinity time evolution indicates that the variation of activation energy has little influence on the Avrami exponent. The kinetics contribution from the variation of phase transition enthalpy is quite small and consequently has no significant contributions to the time evolution of crystallinity. The temperature dependence of interfacial energy is critical for explaining the temperature sensitivity of crystallization kinetics. A large value of temperature power $n$ ($\approx 20$) is necessary to account for the sensitive temperature dependence for the crystallization kinetics of most polymers. Large value of $n$ indicates more sensitive temperature dependence. The Avrami transition theory assumes that Avrami exponent ranges among 1, 2, 3, and 4 [Avrami, 1941], depending on the nature of nucleation, crystal growth rate and microscopic structure of crystals, however, experiment measurements indicate that the Avrami exponent is not necessarily an integer number, and large values of Avrami exponent (greater than
4) are also reported occasionally. The cluster distribution model, with the crystal growth rates power $\lambda$ varying from 0 to unity, shows significant consistency with experimental measurements for a wide range of polymers. Therefore, by appropriately choosing $\lambda$ and $n$, the cluster distribution model is able to describe different types of polymer crystallization.

Most experimental research on polymer crystallization is carried under idealized conditions of constant temperature. In practice, however, industrial crystallization processes and some experimental studies take place under nonisothermal conditions, where the crystallization rate depends not only on the instantaneous temperature, but also the rate of temperature change. The thermal history experienced by the polymer sample is critical in the determination of the final product properties. Long chain molecule has the ability of “memorizing” historic external conditions it experienced [Keller, 1957]. The memory concerning the details of spherulitic structure is attributed to the differences in the number of nuclei that occurs during crystallization, which in turn, is affected by the thermal history of the sample. Memory effects during the process of thermal restructuring of the polymer crystal play an important role in the formation of structure in real cases of industrial process, where the crystallization occurs during fast cooling of the molten polymer. Thus, assuming linear temperature decrease, the cluster distribution model is redeveloped to explore the crystallization kinetics for nonisothermal crystallization. Our investigation indicates that polymers take shorter time to crystallize as cooling rates increases. Further investigation of the non-isothermal behavior revealed that the apparent incubation period is found to decrease exponentially as cooling rates. The initial temperature also has significant influences on the crystallization behavior for nonisothermal crystallization. Our study indicates that the crystallization rate is found to decrease as the initial temperature increases. Further investigation reveals that the crystallization is delayed for a longer time for larger initial temperatures, indicated by the increase of incubation period. This explains the fact that some of
the desired properties of the final product, such as specific morphology patterns of the spherulite, can be gained by the crystallization process after holding the polymer melt at initial temperature for a short time. The increase of initial temperature is also found to result in the increase of Avrami exponent.

Polymer blending is most useful and economical method to produce new material with a variety of desirable properties, such as impact properties, thermal stability and friability. Many desired properties are acquired through the crystallization of polymer blends. Proposing blending effects on crystal growth mechanism and nucleation rate, we established a cluster distribution model to explore the kinetics behaviors for the crystallization of miscible binary polymer blend. Our investigation indicates that the crystal growth is most likely diffusion controlled because of the increases of viscosity and chain entanglement introduced by polymer-polymer interactions. The addition of a second polymer component also results in the variation of glass transition temperature and melting temperature, thus the variation of nucleation rate. Computation results reveal that increasing the second polymer fraction leads to the decrease of average crystallization rate because of the loss of supersaturation.

The cluster distribution model is also extended to investigate phase separation kinetics within the spinodal region. Unlike condensation from a metastable state, the nucleation energy barrier is negligible and the critical size of the nucleus is unrealistically small, thus single molecules simply aggregate and results in rapid phase separation. Proposing general expressions for the aggregation rate coefficient, the distribution kinetics model is able to demonstrate the two time regimes during phase domain growth. The average size of phase domains increases as a power law with an exponent of 1/3 at early phase separation time, while a linear dependence is observed at longer times.
The validity of the distribution kinetics model is also examined by comparison with experiment measurements. The agreements with experiment measurements are confirmed and indicate that the cluster distribution model provides a reliable and accurate approximation for polymer crystallization kinetics. Our work also provides correspondence with the Avrami transition theory by examining the detailed, fundamental features of nucleation mechanism and crystal growth. The comparison with general experimental observations suggests the cluster distribution model is a more realistic approximation than Avrami equation. The investigation of model parameters offers a quantitative way to determine Avrami parameters, which can only be determined empirically by Avrami transition theory. The understanding of polymer crystallization mechanisms also indicates practical applications in industry crystallization process. The average crystal size can be manipulated by appropriately varying the crystallization temperature. For example, the temperature where the maximum nucleation rate is expected is important in the pharmaceutical crystallization process to produce fine pharmaceutical crystals. Thus most of crystalline pharmaceutical products are prepared at low temperature by rapidly cooling the polymer melt down to the crystallization temperature. The rapid cooling is able to inhibit the crystal growth to gain the desired average crystal size. The mechanical properties of polymers can also be manipulated through the extent of crystallization. As the crystallization temperature decreases from the melting temperature, $T_m$, to the point where the maximum nucleation rate is expected, the extent of crystallization increases, thus the friability of the polymer products increases. For industrial nonisothermal polymer crystallization processes, the crystallization temperature is usually programmed to decrease with time to gain the desired spherulic morphology. Scientifically, the understanding of chain folding mechanism provides insights for protein folding process, where similar finely ordered structure is also observed, and indicates the possible research openings in the field of protein science.
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Appendix A: Nomenclature

x: mass of cluster
X: degree of crystallization
ξ: number of monomer inside a cluster
x*: critical mass of cluster
ξ*: critical size of cluster
c(x): number of cluster having mass of x (mole/volume)
m(xm): number of monomer having mass of xm (mole/volume)
c(0): number of clusters having mass in the range of 0 and ∞ (mole/volume)
m(0): number of monomer having mass in the range of 0 and ∞ (mole/volume)
m_{eq}(0): local equilibrium concentration of monomer (mole/volume)
m_{∞}(0): equilibrium concentration of monomer at flat surface (mole/volume)
μ_{∞}: equilibrium concentration of monomer at high temperature (mole/volume)
c(1): mass of clusters (weight/volume)
c(avg): average weight of clusters (weight/mole)
S: supersaturation
S_{T}: scaled supersaturation
C(0): scaled number of clusters
C(1): scaled mass of clusters
a: width of lamellar crystal
m: Avrami exponent
D: diffusion coefficient (cm² s⁻¹)

n: power exponent of surface tension on temperature

r: radius of spherical cluster (c(x))

T: absolute temperature (°C)

T_g: glass temperature (°C)

T_i: initial temperature (°C)

T_m: melting temperature (°C)

W: total energy of a cluster (J)

E: growth activation energy (J/g)

ε: scaled activation energy

ΔH: molar energy of phase transition of crystallization (J/mole)

h: scaled phase transition enthalpy

R: gas constant

k_B: Boltzmann constant

k_g: growth rate coefficient (s⁻¹)

k_d: dissociation rate coefficient (s⁻¹)

γ: growth rate coefficient prefactor

λ: power dependence on cluster mass of growth rate coefficient

χ: Flory-Huggins interaction parameter

k_n: prefactor of nucleation rate

I: nucleation rate (mole l⁻¹ s⁻¹)

J: scaled nucleation rate

J₀: prefactor of dimensionless nucleation rate
δ: thickness of lamella

θ: dimensionless time

β: cooling rate (°C/s))

ϕ: dimensionless cooling rate

ϕ_i: volume fraction of component i in polymer blend

N_i: degree of polymerization of component i in polymer blend

Δt_{inc}: incubation time (s)

Δθ_{inc}: scaled incubation time (s)

σ: surface tension

ρ: density

δ: thickness of laminar crystal

Θ: scaled temperature

Θ_i: initial crystallization temperature

Θ_{onset}: crystallization onset temperature

Ω: Gibbs-Thomson factor

Ω_a: Average Gibbs-Thomson factor
Appendix B: Permission Letters

American Chemical Society

Publications Division
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VIA FAX: 225-578-1476
DATE: September 28, 2006
TO: Jiao Yang, Department of Chemical Engineering
Louisiana State University, Baton Rouge, LA

FROM: C. Arlen Courtney, Copyright Associate

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Sincerely Yours

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Vita

Jiao Yang was born in Hubei Province, People’s Republic of China, on January 14, 1977. He received his primary and secondary education there and graduated from high school. In 1995, Mr. Yang came to Shanghai for his advanced education at East China University of Science and Technology where he obtained the degrees of Bachelor of Science in 1999 and Master of Science in 2002. Shortly afterwards, Jiao came to Baton Rouge, Louisiana, where he enrolled as a doctoral student in the department of Chemical Engineering at Louisiana State University. In the past four years he worked as a research assistant under the direction of Dr. Benjamin J. McCoy and Dr. Martin A. Hjortso.