MATERIALS AND METHODS

Theoretical Background

Polymer Crystallization

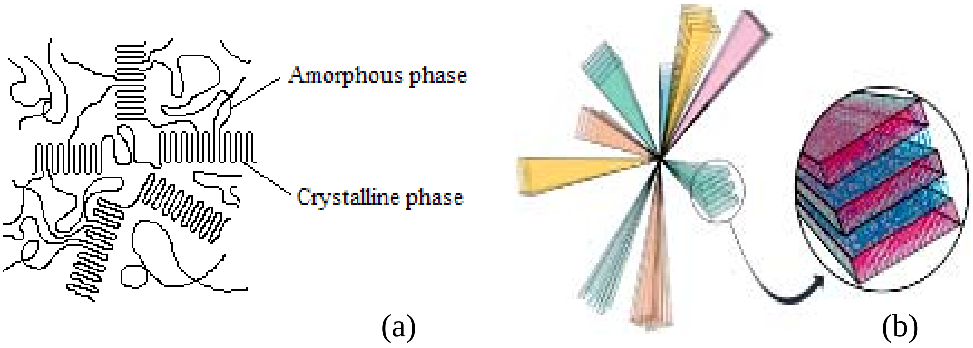
Processing of polymers relies on the shaping of molten material in either moulds or dies and the stabilization of the shape produced by crystallization (Anthony et. al., 1999). During crystallization, a microstructure develops which can control the mechanical and properties of the polymer. To produce useful materials it is essential to understand and predict this process.

Crystallization process is a process involving the regular arrangement of chain and is consequently associated with a large negative entropy change. From thermodynamic considerations alone, a crystal is in a lower free energy state than the liquid when the temperature is below the melting point for a large crystal of a very high molecular weight polymer. The necessary (but not sufficient) criterion for any spontaneous phase transformation (for a constant temperature and constant pressure process) is negative value of Gibbs free energy. The Gibbs free energy, G, is a balance between entropy, S, and the enthalpy, H

$$\Delta G = \Delta H - T\Delta \mathrm{S} \qquad (1)$$

Crystallization of polymer can be divided in to two steps. The first step is called nucleation and involves the creation of a stable nucleus from the polymer melt. As a melt is cooled there is a tendency for the molecules to move toward their lowest energy conformation, and this will favors the formation of co-operatively ordered chains and thus nuclei. The nucleation can be classified to two types by the original site where nucleation occurs. If no second surface or existing nuclei is present and the nuclei formation takes place spontaneously only due to super cooling the phenomenon is referred to as *homogeneous nuclei*. However, if any second phase is required (it may be a foreign particle or surface from the same polymer), then the nucleation is termed *heterogeneous nucleation*. Another way to classified nucleation is on the basis of time dependent at any temperature. If the nucleation is such that all nuclei start forming at approximately the same time the nucleation is referred to *athermal nucleation*. If the nucleation, on the other hand, is such that new nuclei form throughout the crystallization at particular temperature and thus different crystal sizes are obtained than the nucleation is referred to as *thermal nucleation*. It is may be implied that homogenous nucleation is often of the thermal type whereas the heterogeneous nucleation may be thermal or athermal. Two factors may obstruct the ordering required for nucleation; cooling, which reduces diffusion coefficients, and chain complication.

The second step is growth of the crystalline region by the addition of other chain segments to the nucleus. This growth is obstructing by low diffusion coefficients at low temperatures and thermal redispersion of the chains at the crystal/melt interface at high temperatures. Thus, the crystallization process is limited to a range of temperatures between the glass transition temperature, and the melting point. The alignment of polymer chains at specific distances from one another to form crystalline nuclei will be favored when intermolecular forces are strong. The greater the interaction among chains and the easier they can pack, the greater the energy change will be. Thus, symmetrical chains and strongly interacting chains are more likely to form stable crystals. When the crystals grow from individual nuclei and radiate out as illustrated in the Figure 2, the crystalline portions actually radiate out in three dimensions, forming crystallites with spherical shape structure called spherulites.



(a) (b)

Figure 2 Polymer chain arrangement in spherulite form: (a) 2-dimensions and (b) 3-dimensions.

Direct measurement of number of nuclei can be done by counting the number of spherulites appearing in a representative volume at several times during isothermal crystallization. The volumetric nucleation rate is defined as the rate of nucleus formation per unit time per unit volume. Figure 3 shows the example of measured number of spherulites per unit volume plotted against time for poly (trimethylene terephthalate). It found that, a decrease in crystallization temperature cause large number of nuclei. These is because low temperature cause high degree of undercooling (i.e. the difference between the equilibrium melting temperature (T_m^0) and crystallization temperature (T_c): $\Delta T = T_m^0 - T_c$), and the energy for transportation of molecules across the melt/solid surface is reduced.

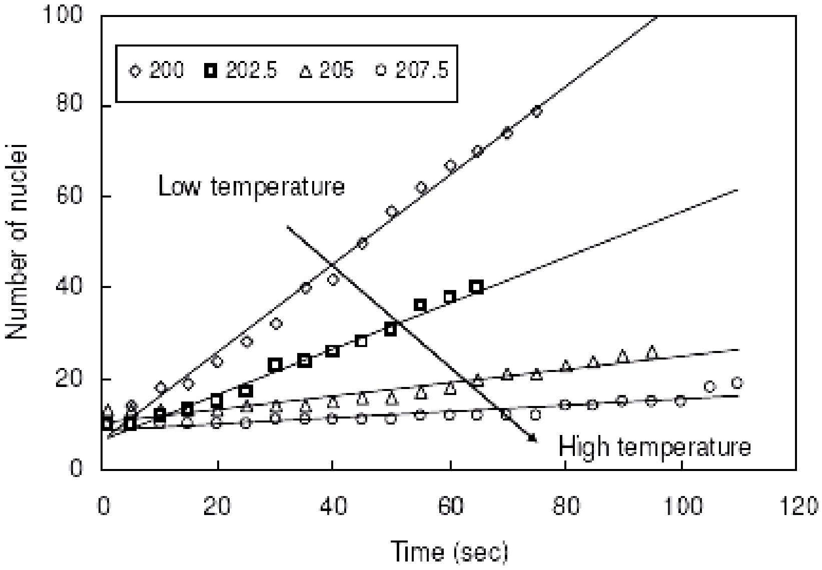


Figure 3 Number of nuclei versus time during the crystallization of poly (trimethylene terephthalate) at several crystallization temperatures.

Source: Ketdee *et. al*. (2006).

Spherulite growth measurements are normally made directly using an optical microscope. The typically reported results are the spherulites diameter plotted against time during crystallization as shown in Figure 4. The spherulites growth rate is slope of the curve in Figure 4.

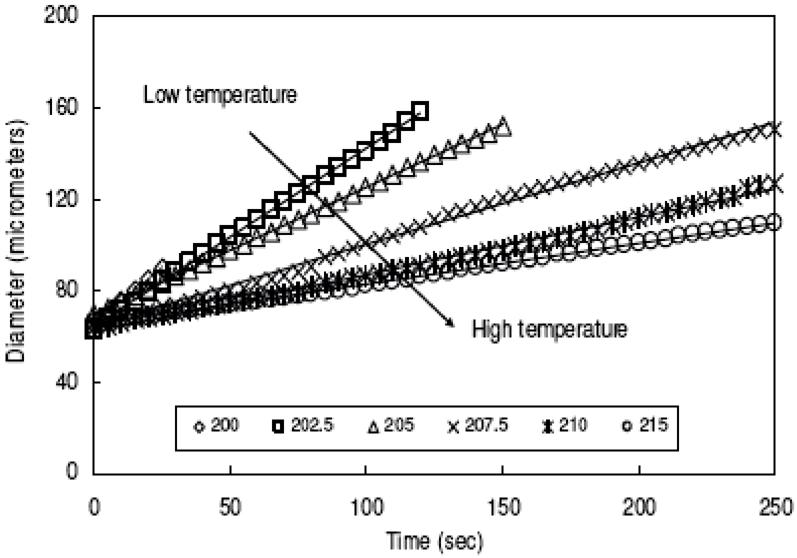


Figure 4 The spherulites size as a function of time during crystallization of poly (trimethylene terephthalate) at several crystallization temperatures. Source: Ketdee *et. al*. (2006).

The spherulites growth rate as a function of crystallization temperature can then be obtained (see Figure 5 for example).

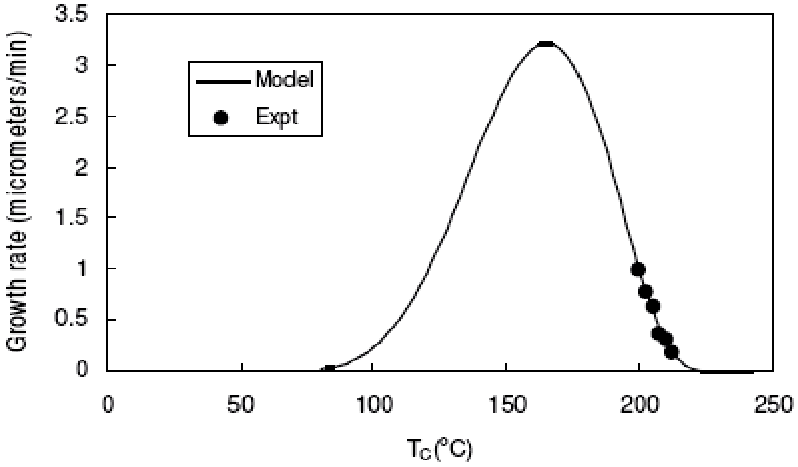


Figure 5 Spherulite growth rate at various crystallization temperatures for poly (trimethylene terephthalate). Dots are experimental results and line is Laurizen-Hoffman model.
Source: Ketdee *et. al*. (2006).

Modeling of Morphology Evolution and Crystallization Kinetics

Avrami equation is an equation theoretically derived for describing the overall crystallization kinetics (i.e., the crystallinity evolution) under isothermal conditions (Avrami, 1939; Avrami, 1940). In the Avrami equation, the crystallinity, $\theta(t)$, can be written as a function of crystallization time (t) as follow:

$$\theta(t) = 1 - \exp[-k_A t^{n_A}] \in [0,1] \tag{2}$$

Where crystallinity, $\theta(t)$ is indication of amount of crystalline region in polymer with respect to amorphous content. The crystallinity has and important influence on the properties of the polymer. The k_A and n_A are the Avrami crystallization rate constant and the Avrami exponent, respectively. The k_A is simple a scaling constant which contains information on the individual rates of nucleation and linear growth. Both k_A and n_A are constant for a given polymer at a specific crystallization temperature. This generalized equation results from several models of the crystallization process that utilize combinations of the type of nucleation process with the shape of the growing entity. The use of heterogeneous nucleation or homogenous nucleation gives different time dependencies because of the time dependence of the homogeneous process. Similarly, the assumptions of a disc or a sphere as the growth entity give different power of time dependence because of the different dimensionalities of the objects. The values of the Avrami exponent and the combination of nucleation type and growth morphology are summarized for principal types in Table 1.

Table 1 Interpretation of Avrami Coefficients

Avrami Exponent	Nucleation Type	Growth Geometry	Growth Velocity
1/2	Heterogeneous	Rod	$t^{-1/2}$
1	Heterogeneous	Rod	Constant
1	Heterogeneous	Disc	$t^{-1/2}$
3/2	Heterogeneous	Sphere	$t^{-1/2}$
	Homogeneous	Rod	$t^{-1/2}$
	Heterogeneous	Disc	Constant
2	Homogeneous	Disc	$t^{-1/2}$
	Homogeneous	Rod	Constant
5/2	Homogeneous	Sphere	$t^{-1/2}$
3	Heterogeneous	Sphere	Constant
	Homogeneous	Disc	Constant
4	Homogeneous	Sphere	Constant

Source: Schultz (2001).

For our case, the spherulite growth in 2 dimensions (disc), the heterogeneous nucleation, and the constant growth rate), the parameter k_A is directly proportional to the number of predetermined nuclei N through the following equation (Schultz, 2001)

$$k_A = \pi N G^2 \tag{3}$$

Thus, Equation (1) can be rewritten as:

$$\theta(t) = 1 - \exp[-\pi N G^2 t^2] \in [0,1] \tag{4}$$

Crystallization kinetics obtained from Equation (4) has been used as the references for validation of our algorithm.

In order to investigate the crystal growth kinetics of isothermally crystallized from the melt, the Lauritzen-Hoffman equation (Supaphol *et al.*, 2001) is typically used to describe the secondary nucleation. This is then followed by formulation of a flux equation from which an equation for the rate of deposition of critical first stems, and hence, the rate of linear growth rate can be predicted. In the early version of this theory it was assumed that the crystals growth process is controlled by two competing rates, the first is deposition of critical nucleus and the second is the subsequent surface spreading process. The linear growth rate (G) of crystal is dependent on the crystallization temperature (T_c) and can be described by exponential equation of the form:

$$G = G_0 exp\left[-\frac{U^*}{R(T_c - T_\infty)} \right] exp\left[-\frac{K^G}{T_c(\Delta T) f} \right] \tag{5}$$

Where G_0 is a pre-exponential term that is not strongly dependent on temperature, U^* is the activation energy for the transportation of segments of molecules across the melt/solid surface boundary and is usually given by a universal value of 1,500 cal mol^{-1}, T_c is the crystallization temperature, T_∞ is the temperature that the molecular motion ceases (i.e., $T_\infty = T_g - 30$), R is the universal gas constant, ΔT is the degree of undercooling (i.e., $\Delta T = T_m^0 - T_c$) , and f is a factor to correct for the temperature dependence of the heat of fusion (i.e., $f = 2T_c/(T_c + T_m^0)$) and K_g is the nucleation exponent.

Referring to Eq. (5), the first exponential term, $exp\ (-U^*/R(T_c - T_\infty))$, corresponds to the diffusion of polymer molecules or segments of them from the equilibrium melt to the growth face. The second exponential term, $exp\ (-K_g/T_c(\Delta T)f)$, relates to the formation of the critical nucleus on the growth face. This term relates to the secondary nucleation rate. Intuitively, from the competing contributions of the transport and nucleation terms, one expects that there should be a maximum in the growth rate data at a temperature somewhere between the glass transition temperature and the equilibrium melting temperature, when plotted as a function of the crystallization temperature. Observation of the relationship between linear growth rate (G) and secondary nucleation rate can be examined by rearranging the logarithmic product of Eq. (5), which results in the equation:

$$\log G + \frac{U^*}{R(T_c - T_\infty)} = \log G_0 - \frac{K_g}{T_c(\Delta T)f} \tag{6}$$

In experimentally, the plot of $\log G + U^*/R\ (T_c - T_\infty)$ versus $1/Tc(\Delta T)f$ is fitted with the growth rate at various crystallization temperature obtained from experiment. The slope equals the negative value of nucleation exponent (K_g) and the intercept is the logarithm of pre-exponential term (G_0). Thus the K_g and G_0 have been determined. From the literature, the linear growth rate G of syndiotactic polypropylene (s-PP) as a function of crystallization temperature T_c was approximated from the literature base on the following equation.

$$G(\mu(\cdot \min^{-1}) = 9.1\times10^{8} \exp\left[-\frac{754.8}{T_c - 237} - \frac{3.6\times10^{5}}{T_c(441.8 - \mathrm{T_c})f}\right] \tag{7}$$

Since the overall crystallization rate parameters (e.g., Avrami crystallization kinetics rate (k_A) and crystallization half time ($t_{0.5}^{-1}$)) relate to the subsequent crystal growth rate G and since the temperature dependent of this microscopic mechanism is well defined in the literature, the temperature dependent of overall rate parameter can be quantified and described (Supaphol *et al.*, 2001). The overall rate parameters have been taken to have similar temperature dependence to the crystal growth rate G. According to this approximation, the temperature dependence of the overall crystallization rate data (e.g., k_A and $t_{0.5}^{-1}$) can be written as:

$$\Psi(T_c) = \Psi_0 exp\left[-\frac{\Theta}{R(T_c - T_\infty)}\right] exp\left[-\frac{K^G}{T_c(\Delta T)f}\right] \tag{8}$$

Where $\Psi(T_c)$ and Ψ_0 are respective overall crystallization rate parameter (i.e., k_A and $t_{0.5}^{-1}$) and pre-exponential parameters (i.e., k_{A0} and $(t_{0.5}^{-1})_0$) respectively, Θ is a parameter related to the activation energy characterizing the molecular transport across the melt/solid interface, and K^G is a combined factor related to the secondary nucleation mechanism. Both Eq. (5) and (8) can describe the crystallization kinetics during polymer crystallization but Eq. (5) is considered crystallization kinetics only one crystal and Eq. (8) is considered overall.

Recently the isothermal melt-crystallization kinetics of syndiotactic polypropylene (s-PP) was investigated by using differential scanning calorimetry (DSC) and reported in Sapphol (Supaphol *et al.*, 2001). The overall crystallization kinetics was determined by directly fitting the experimental data to the Avrami model and crystallization half-time using a non-linear multi-variable regression program and obtains relationship between the overall crystallization kinetics and crystallization temperature. From this relationship and according to Eq. (8), temperature dependence of the overall rate function $\Psi(T_c)$ can be quantified by directly fitting the respective overall crystallization rate parameter which in this case is Avrami crystallization rate k_A and crystallization half-time $t_{0.5}^{-1}$ collected at various crystallization temperatures in the range of 40°C to 90°C to one of the equations using the same non-linear multi-variable regression program. The unknown parameters that are provided by the program are $\Psi(T_c)$, Θ and K^G. The result of the best fits according to Eq. (8) can be written as:

$$k_A(\min^{-n}) = 7.08\times10^{26}\exp\left[-\frac{1807.096}{T_c - 237}\right]\exp\left[-\frac{1.39\times10^6}{T_c(441.8 - \mathrm{T_C})f}\right] \tag{9}$$

$$t_{0.5}^{-1}(min^{-n}) = 4.82\times10^9\exp\left[-\frac{654.8}{\mathrm{T_c} - 237}\right]\exp\left[-\frac{4.98\times10^5}{\mathrm{T_c}(441.8 - \mathrm{T_C})\mathrm{f}}\right] \tag{10}$$

The number of predetermined nuclei *N* can be calculated directly from Eq.(3),(7) and (9). The calculated growth rate and number of predetermined nuclei obtained at each temperature were used in our simulation for investigating the effect of crystallization temperature on crystallization kinetics and morphological development for s-PP. Furthermore the overall crystallization kinetics (i.e., k_A and $t_{0.5}^{-1}$) obtained from Eq. (9) and (10) were used to validation our algorithm in case of effect of crystallization temperature on crystallization kinetics and morphology development.

Algorithm for studying effect of number of predetermined nuclei and growth rate

The crystallization process of semi-crystalline polymers was simulated and the morphological development was monitored from the early state of nucleation to the complete crystallization. Figure 6 shows the simplified algorithm used for our stochastic simulation.

In the algorithm, we consider the graphical simulation of polymer crystallization in a square rectangular with an active area of 800x800 pixels. Each pixel size is assumed to be equal to 0.2 micrometers. Initially, all 640,000 pixels are considered as an amorphous area before the crystallization occurs. At the initial time (t_0 = 0), the heterogeneous nucleation process occurs. The pre-determined number of predetermined nuclei per active area (*N*) appears instantaneously and randomly within a square lattice. Each nucleus is assumed to occupy one unit cell and the occupied unit cell is changed from an amorphous unit cell to a crystalline unit cell. The position of each nucleus is recorded by the program.

After the nucleation process, the crystallization time (*t*) is increased with a time step of Δt for each iteration (i.e., $t_{i+1} = t_i + \Delta t$) until reaching the final time (t_f) or the complete crystallization. During the growth process, the radius of the spherulite can be computed from the product of the growth rate *G* (unit cell/time step) and crystallization time, i.e. $r = G*t$. If an amorphous unit cell falls within the range of radius, *r*, of spherulite *j*, it is changed to a crystalline unit cell and considered to be occupied by spherulite *j*. In the case that an amorphous unit cell falls within the range of radius, *r*, of several spherulites, it is assumed to be occupied by the spherulite that has the shortest distance from the center of spherulite to that cell.

The detailed morphology (crystallinity, average spherulite size, and distribution of spherulite size) was recorded at each crystallization time. In this program, the crystallinity is defined as a ratio between the total number of crystalline pixels (or occupied cells) and total number of pixels. The average spherulite size can be calculated from the total number of crystalline pixels divided by the total number of spherulite per active area (*N*). This procedure is repeated until reaching final time (t_f) or the complete crystallization (i.e., no amorphous unit cell available for further growth).

Figure 7 shows the illustration of morphological development obtained from the program. Figure 7 (a) shows polymer morphology at t = 0 sec when heterogeneous nucleation occurs. Up until t = 20 sec, each spherulite grows individually without the impingement. Several impingement lines occur as time increases (see Figure 7 (c)) until reaching the final morphology (see Figure 7 (d)). Table 2 shows the input data of simulation in this work.

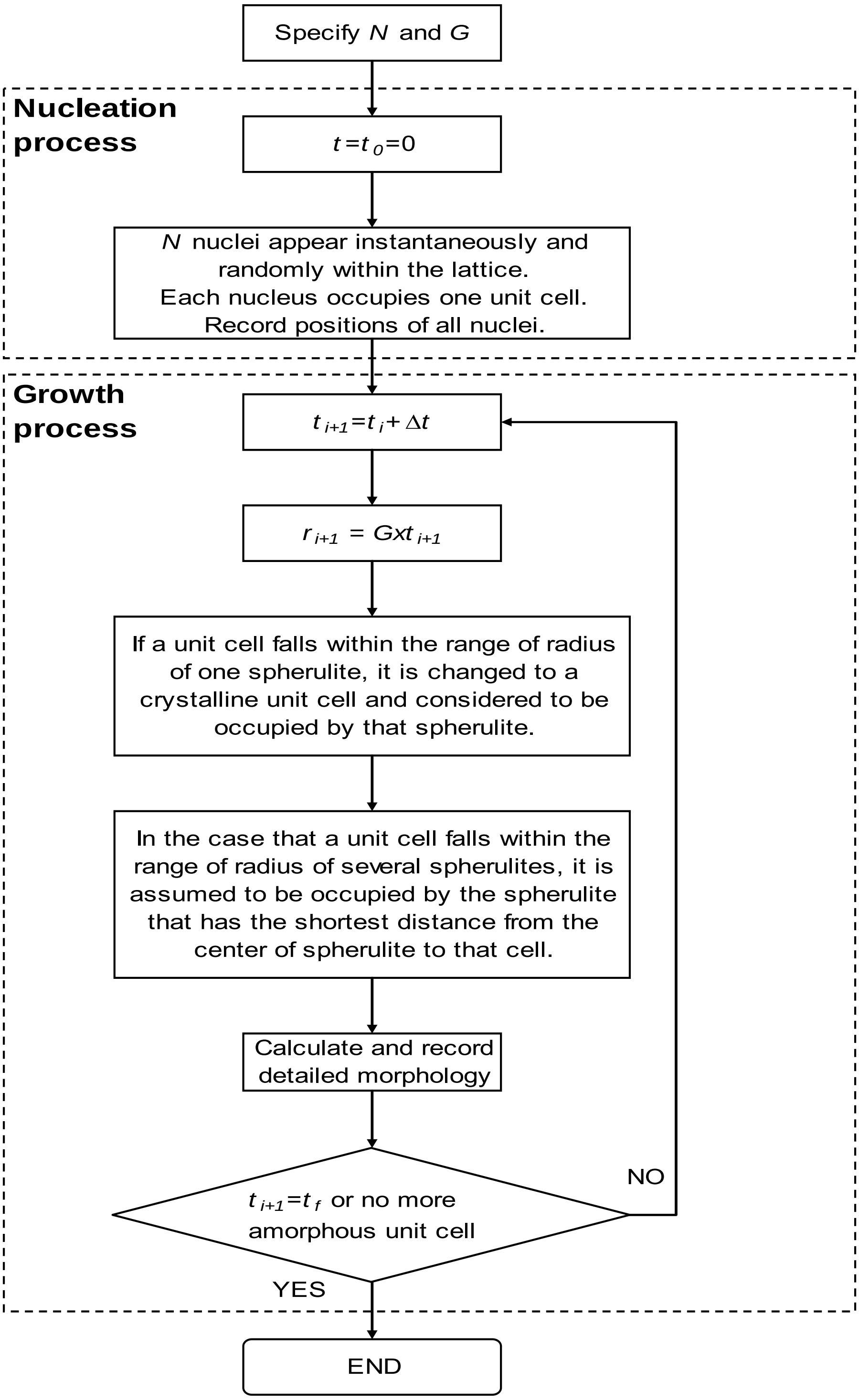
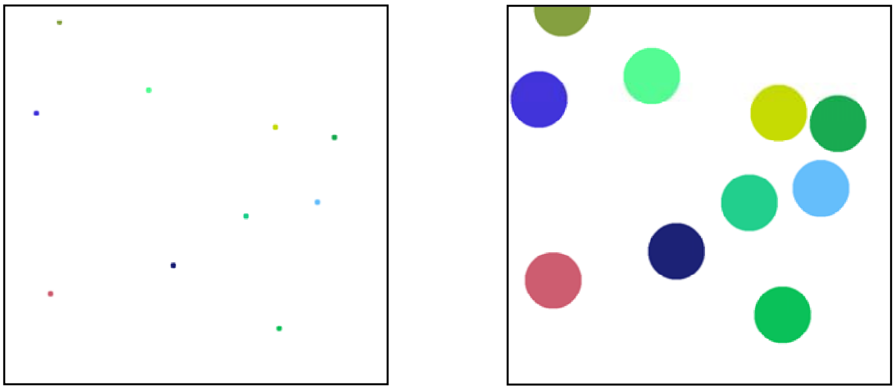
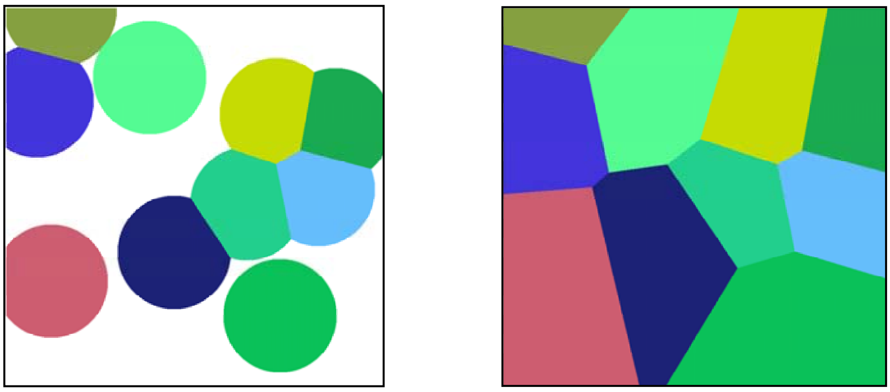


Figure 6 Simplified algorithm for our stochastic simulation

(Effect of number of predetermined nuclei and growth rate)



(a) t = 0 sec (b) t = 20 sec



(c) t = 40 sec (d) Final morphology

Figure 7 Examples of polymer morphology obtained from the stochastic simulation (N = 10 and G = 3 unit cell/sec) at different crystallization times: (a) t = 0 sec, (b) t = 20 sec, (c) t = 40 sec, and (d) final morphology.

Table 2 Values of parameters for study the effect of number of predetermined nuclei and growth rate.

Run ID	Number of predetermined nuc per active area (N)	Growth rate (G), unit cell/time step
N50_G1	50	1
N100_G1	100	1
N200_G1	200	1
N300_G1	300	1
N400_G1	400	1
N500_G1	500	1
N600_G1	600	1
N800_G1	800	1
N1000_G1	1,000	1
N100_G2	100	2
N100_G3	100	3
N100_G4	100	4
N100_G5	100	5
N100_G6	100	6
N100_G7	100	7
N100_G8	100	8
N100_G9	100	9
N100_G10	100	10

*The parameter $\Delta t = 2$, $t_0 = 0$, and $t_f = 100$ were hold constants for all runs.

Algorithm for studying effect of crystallization temperature

The crystallization process of semi-crystalline polymers was simulated and the morphological development was monitored from the early state of nucleation to the complete crystallization. Algorithm is very similar to previous algorithm with the only difference that both number of predetermined nuclei and growth rate need to be calculated using Eq. (3), (7) and (9) for the range of crystallization temperature between 40^{o}C and 90^{o}C. Figure 8 shows the simplified algorithm used for our stochastic simulation. Figure 9 shows concept for calculating growth rate and number of predetermined nuclei by using Eq. (3), (7) and (9).

Figure 9 shows the illustration of morphological development obtained from the program for the crystallization temperature of 85^{o}C. Figure 9 (a) shows polymer morphology at t = 0 sec when heterogeneous nucleation occurs. Up until t = 20 sec, each spherulite grows individually without the impingement. Several impingement lines occur as time increases (see Figure 9 (c)) until reaching the final morphology (see Figure 9 (d)). Table 3 shows the input data of simulation in this work for studying the effect of crystallization temperature.

Note that as positions of nuclei are chosen randomly for each run, a simulation using the same input data usually gives different results for different runs. By performing independency test on a number of predetermined nuclei and lattice sizes, it was found that the average data from a minimum of 10 runs and 5,000 runs are necessary to obtain reliable information on crystallization kinetics and distribution of spherulite size, respectively. The lattice size of 800x800 pixels used in this work was found to be sufficient for obtaining reliable distribution of spherulite size because the boundary effect becomes negligible (see Appendix A for more details).

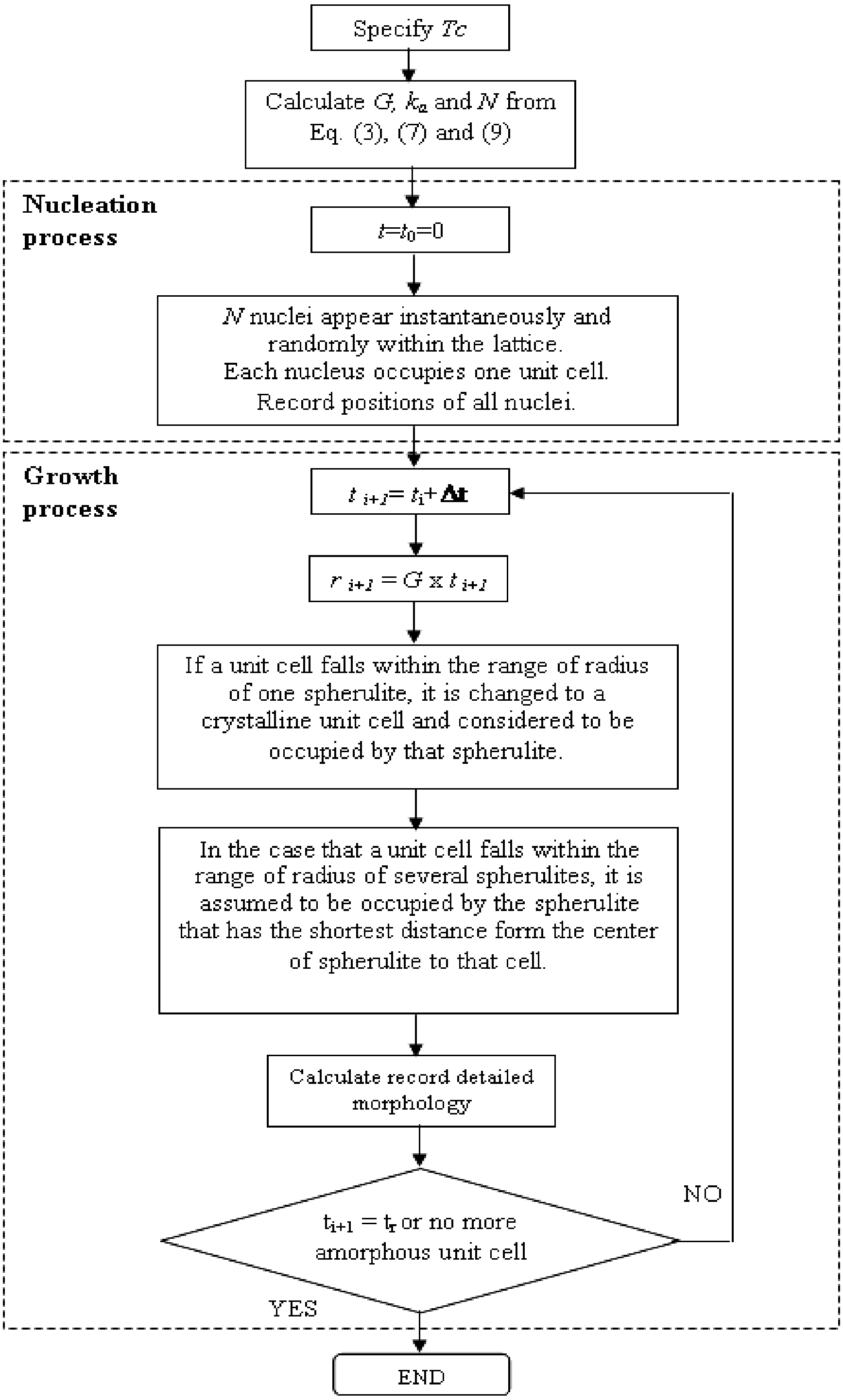


Figure 8 Simplified algorithm for our stochastic simulation
(Effect of crystallization temperature)

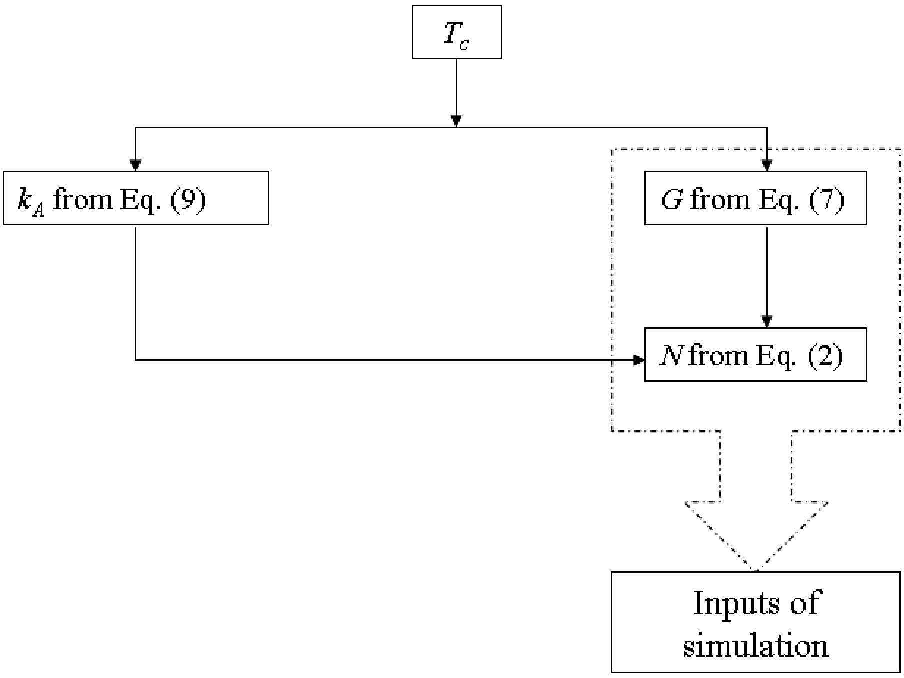
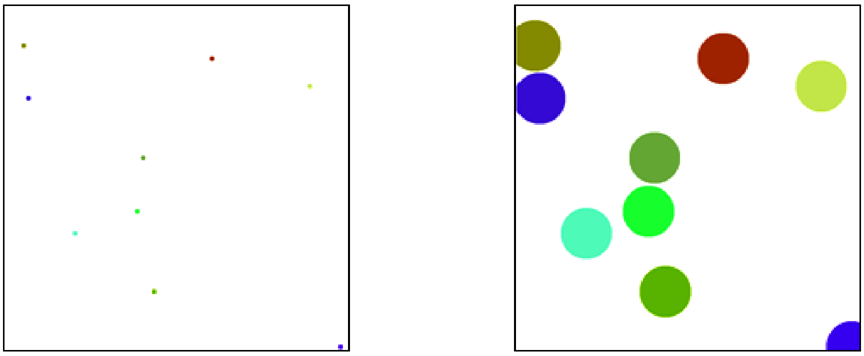
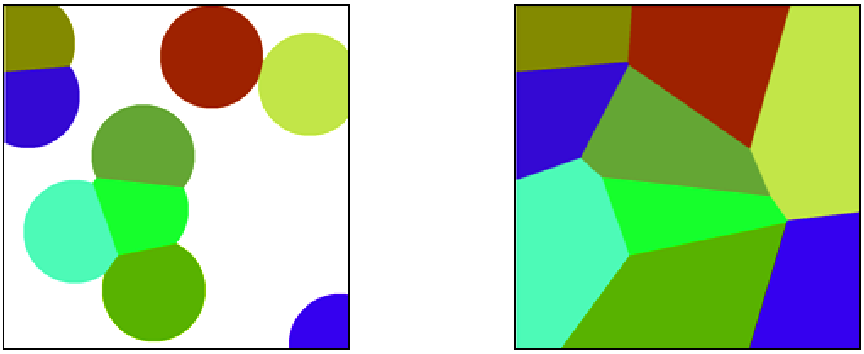


Figure 9 Calculation steps for estimating growth rate (G) and number of predetermined nuclei (N) by using experimental results for s-PP.



(a) $t = 0$ sec

(b) $t = 20$ sec



(c) $t = 40$ sec

(d) $t =$ Final morphology

Figure 10 Examples of polymer morphology obtained from the stochastic simulation (T_c =85°C) at different crystallization times:
(a) t = 0 sec, (b) t = 20 sec, (c) t = 40 sec, and (d) final morphology.

Table 3 Values of parameters for study the effect of crystallization temperature.

Run ID	Crystallization temperature, T_c(°C)	Growth rate, $G(\mu\text{m}/\text{min})$	Total number of predetermined nuclei, N (nuclei/μm^2)	Avrami kinetics rate, $k_A(\text{min}^{-n})$
Tc_40	40	0.93	0.0108	0.0294
Tc_45	45	1.47	0.0102	0.0696
Tc_50	50	2.11	0.0090	0.1257
Tc_55	55	2.76	0.0074	0.1768
Tc_60	60	3.34	0.0056	0.1954
Tc_65	65	3.74	0.0039	0.1704
Tc_70	70	3.88	0.0025	0.1167
Tc_75	75	3.72	0.0014	0.0622
Tc_80	80	3.30	0.0007	0.0254
Tc_85	85	2.68	0.0003	0.0077
Tc_90	90	1.99	0.0001	0.0017

*The parameters Δt = 2, t_0 = 0, and t_f = 100 were hold constants for all runs.
*1 μm^2 = 25 pixels^2

Assumptions of the algorithm

However, the program developed in this work can not describe the crystallization kinetics and morphological development during polymer crystallization in all polymeric systems. The program can be utilized in the system under the following assumptions:

- The crystallite is in the form of spherulites.
- The nucleation type is assumed to be heterogeneous nucleation.
- Polymer can achieve 100% crystallinity.
- Random distribution of nuclei.

- Hold well for primary crystallization
- For studying effect of crystallization temperature, the data of syndiotactic polypropylene has been used. Therefore, the results in this case apply only for syndiotactic polypropylene.