RESULTS AND DISCUSSION

Effect of Number of Predetermined Nuclei and Growth Rate

Crystallization Kinetics

Figure 11 and 12 show the effect of number of predetermined nuclei and growth rate on crystallization kinetics, respectively. Evidently, the time to reach the complete crystallization is decreased with increasing number of predetermined nuclei and growth rate. The simulation results agree very well with the results from theoretical Avrami model (Equation (4)) considering that there is no adjusting parameter. Furthermore, the simulation results are excellent agreement with simulation results from the literature (Lamberti et. al., 2004) and presented in the Figure 13. This confirms the validity of our algorithm.

We also performed the analysis of crystallization kinetics data based on the Avrami model by fitting the $\theta(t)$ function obtained for each simulation to Equation (4); the Avrami exponent n_A and the Avrami rate constant k_A were estimated by the generalized reduced gradient (GRG2) nonlinear optimization (Smith et. al., 1992). Figure 14 and 15 show the values of parameters estimated at different numbers of nuclei and growth rates, respectively. As expected, the Avrami exponent n_A is close to a theoretical value of 2, independent of number of predetermined nuclei and growth rate. The Avrami rate constant k_A is found to linearly increase with the number of predetermined nuclei, but quadratically increase with the growth rate. This again agrees well with the theory as the parameter k_A is equal to πNG^2 . One conclusion drawn from these results is that the growth rate has a stronger impact on a crystallization rate.



Figure 11Crystallization kinetics for various numbers of nuclei (a) simulated kineticsof area occupied by spherulites and (b) simulated kinetics in logarithmscale.Symbols: simulation results; Lines: theoretical results from theAvrami equation.



Figure 12Crystallization kinetics for various growth rates. (a) simulated kinetics of
area occupied by spherulites and (b) simulated kinetics in logarithm scale.
Symbols: simulation results; Lines: theoretical results from the Avrami
equation.



Figure 13 Relative crystallinity as a function of time. Dark symbols are results from simulation in this work, open symbols are results from the literature, and line are results from Avrami equation (Eq. (4)).



Figure 14 Avrami parameters estimated from simulation results obtained for various numbers of nuclei. Lines are to aid eye only.



Figure 15 Avrami parameters estimated from simulation results obtained at various growth rate. Lines are to aid eye only.

Morphological Development

Effect of Nucleation

Figure 16 shows the time evolution of number distributions of spherulite size during crystallization for three cases: (a) 50 nuclei, (b) 100 nuclei, and (c) 500 nuclei. The frequency is calculated from the number of spherulites in each range divided by the total number of spherulites.

It is found that at the beginning of crystallization process, spherulite sizes are relatively small and the distribution is relatively narrow. During the growth process, the distribution is shifted to the range of large spherulite size and broadened because some spherulites become larger with time while some stop growing upon impingement with adjacent ones. The final morphology obtained when the distribution remains unchanged with time (i.e., no more amorphous cell is available for further growth).

Considering at the same crystallization time, the distribution is shifted to the range of small spherulite size and becomes narrow as the number of predetermined nuclei increases (see Figure 17). This is because a large number of predetermined

nuclei likely fasten the impingement phenomena and increases a high level of impingement; thus, most nuclei have relatively the same small size and the deviation of spherulite size from an average value is minimized. The same reason contributes to the effect of number of predetermined nuclei on the final morphology (see Figure 17) and the average spherulite size (see Figure 18).



<u>Figure 16</u> Time evolution of distributions of spherulite size for three different numbers of nuclei: (a) 50 nuclei, (b) 100 nuclei, and (c) 500 nuclei.



Figure 17 Frequency distributions of spherulite size for three different numbers of nuclei at (a) t = 60 sec and (b) final morphology.



Figure 18 The average spherulite size as a function of time for various numbers of nuclei.

Effect of Growth Rate

Figure 19 shows the evolution of number distributions of spherulite size during crystallization at three growth rates: (a) 1 unit cell/s, (b) 3 unit cell/s, and (c) 5 unit cell/s. During the growth process, the distribution is shifted to the range of large spherulite and broadened as expected with the same reason discussed previously. The results further indicate that the spherulite size is larger and the impingement phenomena occur faster with increase in growth rate. This issue is pointed out clearly in Figure 20 when we compared the distributions at the same time.

Although the increase in growth rate speeds up the impingement phenomena, the level of impingement is likely to be the same in all cases because the number of predetermined nuclei is kept constant. This is a main reason that the final morphology and the final average spherulite size observed is independent of growth rate (see Figure 20 and 21).

From the discussions above, it is clear that number of predetermined nuclei has a significant impact on both crystallization kinetics and polymer morphology. An increase in the number of predetermined nuclei fastens a crystallization process by speeding up the impingement phenomena and increasing the level of impingement as well. A growth rate has a stronger impact on crystallization kinetics, but it only helps speed up the impingement phenomena without increasing the level of impingement. Although a growth rate influences an average spherulite size and distribution of spherulite size during the crystallization, it has no effect on a final morphology.



Figure 19 Time evolution of distributions of spherulite size for three different growth rates: (a) 1 pixel/s, (b) 3 pixels/s, and (c) 5 pixels /s.



<u>Figure 20</u> Frequency distributions of spherulite size for three different growth rates at (a) t = 14 sec and (b) final morphology.



Figure 21 The average spherulite size as a function of time for various growth rates.

Effect of Crystallization Temperature

The spherulite growth rate, nuclei density (*N*), and Avrami rate constant (k_A) as a function of crystallization temperature were shown in Figure 22. It was found that the growth rate of spherulite exhibits the typical bell-shape dependence with the crystallization temperature and maximum in the growth rate data occurs at 70°C. The effect of number of predetermine nuclei are also reported in the Figure 22 Evidently, as the crystallization temperature increases, the number of predetermined nuclei decreases. In the real situation, the change in crystallization temperature alters both concentration of predetermined nuclei and growth rate in the system simultaneously. As shows in the Figure 22 when the temperature is decreased from 90°C to 70°C, both total concentration of nuclei and growth rate are increased monotonically. When the crystallization temperature decrease from 70°C to 40°C, the number of predetermined nuclei still increases but the growth rate decreases. Depending on crystallization temperature, two scenarios can be considered: (1) both number of predetermined

nuclei and growth rate increase and (2) the number of predetermined nuclei increases while the growth rate decreases. Combined effect of both spherulite growth rate and number of predetermined nuclei are represented by the Avrami rate constant curve and reported in the same Figure.

For the first case in the crystallization range of 70°C -90°C, both number of predetermined nuclei and growth rate increase as crystallization temperature decrease; therefore, the Avrami rate constant is increased rapidly. In the crystallization temperature range of 60°C -70°C, the Avrami rate constant still increase in the same direction as the number of predetermined nuclei although growth rate decreases. Evidently, this temperature range is dominated by effect of the number of predetermined nuclei. When the crystallization temperature decrease from 60°C to 40°C the Avrami rate constant decreases in the same direction as growth rate. This represents that, at temperature range of 60°C to 40°C, the crystallization process is mainly influenced by the growth rate.



<u>Figure 22</u> The effect of crystallization temperature on growth rate of spherulite, G, Avrami rate constant, k_A , and nucleation density, N.

Crystallization Kinetics

The relative crystallinity as a function of time at various crystallization temperatures in the range of 40°C -60°C and 65°C -90°C were reported in the Figure 23 and Figure 24 respectively. During the temperature range where both number of predetermined nuclei and growth rate increase as crystallization temperature decrease, the Avrami rate constant (k_A) is also increased. Therefore, the time to reach the complete crystallization is decreased (see Figure 23). The competing effect of both growth rate and number of predetermined nuclei occur since temperature below 70°C to 40°C, this cause the Avrami rate constant (k_A) decreases with crystallization temperature decrease (Figure 24).

We also performed the analysis of crystallization kinetics data based on the Avrami model by fitting the $\theta(t)$ function obtained for each simulation to Equation (2); the Avrami exponent n_A and the Avrami rate constant k_A were estimated by the generalized reduced gradient (GRG2) nonlinear optimization (Smith and Lasdon, 1992). Figure 25 shows the values of parameters estimated at different crystallization temperatures. As expected, the Avrami exponent n_A is close to a theoretical value of 2, independent of crystallization temperature (see Figure 25(b)).



Figure 23Crystallization kinetics at various crystallization temperatures in the rangeof $65^{\circ}C \leq T_{c} \leq 85^{\circ}C$ (a) simulated kinetics of area occupied byspherulites and (b) simulated kinetics in logarithm scale.Symbols:simulation results; Lines: theoretical results from the Avrami equation.



<u>Figure 24</u> Crystallization kinetics at various crystallization temperatures in the range of $40^{\circ}C \le T_c \le 60^{\circ}C$. (a) simulated kinetics of area occupied by spherulites and (b) simulated kinetics in logarithm scale. Symbols: simulation results; Lines: theoretical results from the Avrami equation



Figure 25 Avrami parameters (a) Avrami rate constant (k_A) and (b) Avrami exponential (n_A) estimated from simulation results obtained at various crystallization temperatures. Lines are to aid eye only.

During the use of experimental inputs data for the Lauritzen-Hoffman (Eq. (7) and (9)) scaling procedure described earlier allows us to compare the simulation results directly with experimental observation in term of overall crystallization kinetics that are Avrami rate constant (k_A) and crystallization half-time ($t_{0.5}$ -¹). Method for this comparison can be described by the Figure 26 and the results are reported in Figure 27 - 28 and Table 4. The simulation results are in a good agreement with the data reported from experiments for isothermal crystallization of s-PP.



Figure 26 Method for validation of algorithm developed in this work with reported experimental data.



Figure 27 Comparison between Avrami rate constants obtained from simulation and Avrami rate constants reported earlier from experiment (Supaphol, 2001).



<u>Figure 28</u> Comparison between crystallization half-time obtained from simulation and crystallization half-time reported earlier from experiment of Sapphol (Sapphol *et al.*, 2001).

Table 4 Com	parison betwee	en simulation a	and experimenta	l results

Crystallizatio	Avrami rate constant, k_A		Crystallization half-time, $t_{0.5}^{-1}$			
n temperature,	Experimen	Simulati	r^2	Experimen	Simulati	r^2
T_c (°C)	t	on		t	on	
40	0.0294	0.0347	0.0000	0.2969	0.2033	0.0088
45	0.0696	0.0803	0.0001	0.4066	0.3121	0.0089
50	0.1257	0.1354	0.0001	0.5053	0.4242	0.0066
55	0.1768	0.1953	0.0003	0.5736	0.4941	0.0063
60	0.1954	0.2290	0.0011	0.5971	0.5223	0.0056
65	0.1704	0.1954	0.0006	0.5706	0.4818	0.0079
70	0.1167	0.1406	0.0006	0.5000	0.4043	0.0092
75	0.0622	0.0751	0.0002	0.4004	0.2865	0.0130
80	0.0254	0.0429	0.0003	0.2911	0.1812	0.0121
85	0.0077	0.0112	0.0000	0.1905	0.1096	0.0065
90	0.0017	0.0026	0.0000	0.1108	0.0492	0.0038

Morphological Development

Figure 25 shows the time evolution of distributions of spherulite size during crystallization for six cases: (a) 40° C, (b) 50° C nuclei, (c) 60° C, (d) 70° C (e) 80° C and (f) 90° C. The frequency is calculated from the number of spherulites in each range divided by the total number of spherulites.

It is found that at the beginning of crystallization process, spherulite sizes are relatively small and the distribution is relatively narrow. During the growth process, the distribution is shifted to the range of large spherulite size and broadened because some spherulites become larger with time while some stop growing upon impingement with adjacent ones. The final morphology obtained when the distribution remains unchanged with time (i.e., no more amorphous cell is available for further growth).

Considering at the same time, the distribution is broadened and spherulite sizes are small when the crystallization temperature decreases from 70°C to 40°C because of both growth rate and number of predetermined nuclei increase. At the crystallization temperature 80 and 90, the distribution become narrow and spherulite sizes are small because of at high temperature the number of predetermined nuclei is decrease and growth is slow.

Notice that at the crystallization temperature of 80°C and 90°C, the peak of the size distribution is at the largest spherulite size, which is distinctively different from other cases. This is because at high temperature, relatively low concentration of nuclei is formed and growth rate is minimal. Therefore, at small crystallization time, most spherulite does not impinge. The most probable size is the largest possible one.

Considering the final morphology, it was found that as crystallization temperature decreases, the distribution is shifted to the range of low crystallization temperature and becomes narrow (see Figure 26). This is because a large number of predetermined nuclei induced by decrease in crystallization temperature likely fastens the impingement phenomena and increases a high level of impingement.

Although the decrease in crystallization temperature influence both number of predetermined nuclei and growth rate, the level of impingement only depends on number of predetermined nuclei. This is a main reason that the final morphology and the final average spherulite size observed is increased when crystallization temperature decreases (see Figure 27 and 28).



<u>Figure 29</u> Time evolution of distributions of spherulite size for different crystallization temperatures: (a) $T_c=40^{\circ}C$, (b) $T_c=50^{\circ}C$, (c) $T_c=60^{\circ}C$, (d) $T_c=70^{\circ}C$, (e) $T_c=80^{\circ}C$ and (f) $T_c=90^{\circ}C$.



Figure 29 (Cont'd).



Figure 30 Final distributions of spherulite size at various crystallization temperatures



Figure 31 Evolution of spherulite size at various crystallization temperatures.



Figure 32 Effect of crystallization temperature on final average spherulites size.