

Influence of thermal history on primary nucleation and crystal growth rates of isotactic polystyrene

Al Mamun^a, Susumu Umemoto^a, Nobuhide Ishihara^b, Norimasa Okui^{a,*}

^a Department of Organic and Polymeric Materials, Tokyo Institute of Technology, International Polymer Research Center, O-okayama, Meguro-ku, Tokyo, Japan

^b Materials Research Laboratory Idemitsu Co., Ltd., Anesaki-kaigan, Ichihara-shi, Chiba, Japan

Received 17 March 2005; accepted 8 April 2005

Available online 11 May 2006

Abstract

The influence of thermal history on primary nucleation and crystal growth rate of isotactic polystyrene (*i*-PS) was studied in a wide range of time and temperature. Samples were melted at several temperatures from 230 to 250 °C and then crystallized from those molten states and also crystallized from the glassy state. The primary nucleation rate is strongly influenced by the thermal history but the crystal growth rate is mainly governed by the crystallization temperature. Below a melt temperature of 230 °C, the nucleation density was attributed to the seed nuclei, which result from incomplete melting of the spherulites. Above 250 °C, a limited number of heterogeneous nucleation sites remain, and these sites are activated on the surface of impurities or foreign bodies in the melt. The primary nucleation is controlled heterogeneously both from the molten and the glassy states. The nucleation rate from the glassy state is faster than that from the molten state. A linear relationship between the nucleation rate and the inverse of induction time was found in each experimental condition and their slopes are related to the saturation density of the nuclei. The activation energy for the molecular transport and the primary nucleation energy were smaller than those of the crystal growth. The primary nucleation energy from the glass was lower than that from the melt. These energies are discussed in the present work.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Thermal history; Nucleation rate; Growth rate

1. Introduction

Polymer crystallization processes from the melt are made up with two main mechanisms: primary nucleation and crystal growth. Primary nucleation is the formation from the melt phase to a new three-dimensional solid phase. Primary nuclei build up sporadically at random sites in the melt (homogeneous nucleation) or on a foreign body such as an impurity particle or a polymerization catalyst acting as a nucleation center (heterogeneous nucleation). Homogeneous nucleation can be defined by spontaneous aggregation of polymer molecules to form a three-dimensional nucleus, which must reach a certain critical size below the melting point. Beyond this size, nucleation occurs sporadically. However, sporadic nucleation is not unambiguous evidence of a homogeneous process. In heterogeneous nucleation, a limited number of sites become activated instantaneously or sporadically. The number of impurities is proportional to the volume of the sample used

in an experimental setup. Therefore, when the sample is highly divided, nucleation may change from heterogeneous to homogeneous: small droplets of crystalline materials may crystallize via homogeneous nucleation when no heterogeneity is present [1,2]. The picture of such impurities is not clear, but the nucleation rate is strongly influenced by their surface energy (wetting mechanism) and their surface morphology (epitaxial mechanism). In addition, heterogeneities in polymer melt structure are also important in nucleation as they may induce a ‘memory effect’ in successive crystallizations. In such a case, most or all crystals start on heterogeneities and reappear at the same points in successive experiments.

The rates of nucleation and growth depend strongly on crystallization temperature. An unequivocal discussion on the temperature dependence requires data gathered over a sufficiently wide temperature range. The crystal growth rate is mainly affected by the crystallization temperature, but the nucleation rate is influenced by many other experimental conditions, such as the thermal history prior to crystallization. The influence of thermal history on nucleation has been studied on a small number of polymers [3–6]. Experimental data on the number of nuclei, nucleation rate and induction time are generally widely dispersed and sometimes there seems to be no

* Corresponding author. Tel./fax: +81 3 5734 2469.

E-mail address: nokui@o.cc.titech.ac.jp (N. Okui).

reproducibility in the experimental data. The dispersion of data is certainly associated with differences in experimental setup, impurities contained in the system and possible differences in the molten state. For example, the nucleation density is influenced by the temperature at which the previously crystallized sample is melted. The effect of melting condition on nucleation is often referred to as a memory effect in the melt.

In many polymers, the nucleation rate is often impossible to measure: it may be too fast and too many numbers of nuclei appear instantaneously. However, it is possible to study the nucleation rate for isotactic-PS (*i*-PS) in a wide range of temperature, because of its slow crystallization rate even under high super-cooling. Also *i*-PS can easily be obtained in an amorphous state (i.e. without any detectable crystallization) by quenching below the glass transition temperature. The number of nuclei from the glass is higher than that from the melt. The number of nuclei depends also strongly on the melt temperature near (below and above) the equilibrium melting temperature [5]. Below the equilibrium melting temperature, numerous nuclei are generated instantaneously. The nuclei are called seed nuclei or induced nuclei, and are often at the root of the melt memory effect. Boon et al. have studied extensively the influence of the thermal history on nucleation of *i*-PS by dilatometry [5]. Two nucleation mechanisms have been found, for resistant and induced nuclei. The number of induced nuclei is reduced by purifying the polymer and by heating above the equilibrium melting temperature. Only resistant nuclei remain above the equilibrium melting temperature. However, the nuclei number or concentration is not determined directly, but rather is estimated from dilatometry data. In the present paper, we use a more direct approach: the number of nuclei and nucleation rate are determined by counting the number of spherulites as a function of time and temperature. The present paper also investigates the effect of the melt temperature on the nucleation and growth rates over a wide temperature range.

2. Experimental

The sample of *i*-PS ($M_w = 17,800$, $M_n = 10,600$, $M_w/M_n = 1.68$, tacticity: 96%) was supplied by Idemitsu Kosan Co., Ltd. The sample was melted between two cover glasses to form a film of a given thickness. The sample was first melted and crystallized several times in order to erase the previous thermal history. In a typical experiment, the sample was melted for 5 min at several different melt temperatures below and above the equilibrium melting temperature T_m^0 (242 °C) [7]. The DSC melting curve starts at about 210 °C and ends (tail of the curve) at 228 °C for *i*-PS crystallized for 8 h at 200 °C. Therefore, two typical melt temperatures were used: 230 °C in order to stay below T_m^0 and at 250 °C, above T_m^0 . Subsequently, the molten sample was cooled to predetermined crystallization temperatures at a 30 °C/min cooling rate ('crystallization from the molten state' procedure). Conversely, the sample was quenched to 90 °C (below the glass transition temperature) from the melt at a 130 °C/min cooling rate, kept for 5 min and then re-heated with a heating rate of 90 °C/min to the chosen crystallization temperature ('crystallization from the glassy

state' procedure). Nucleation and growth rates were measured on a temperature controlled apparatus (Linkam LK-600FTIR) under an Olympus BH-2 optical microscope (OM) equipped with a CCD camera (Pixel 600ES-CU). Linear crystal growth rates were determined by measuring spherulites radius as a function of time. The nucleation rate was measured by counting the number of spherulites that arose sporadically as a function of time and was calibrated by the measured area in the OM and the specimen's thickness.

3. Results and discussion

3.1. Effect of thermal history on nucleation rate

Fig. 1 shows the time dependence of the number of spherulites for various crystallization conditions, namely the two different melt temperatures (230 and 250 °C) and from the molten and glassy states. The time dependence of the nucleation displays first an induction time, with sporadic appearance of spherulites. Subsequently the spherulites number increases steadily, before reaching saturation for all experimental conditions. The induction time is the period needed to form a critical nucleus and is often employed as the primary nucleation rate. The crystal nuclei are difficult to observe directly by standard methods because of their very small size. Therefore, small spherulites are assumed to have started on an active individual site and they are observed after a certain induction time whereas the aggregation of polymer molecules is reversible up to the critical nucleus size. Beyond that time, an embryo with a size greater than the critical size becomes stable and the number of nuclei increases linearly with time. Therefore, the nucleation rate is determined by the slope of the number of spherulites with time. The total number of nuclei saturates at a limiting constant value before

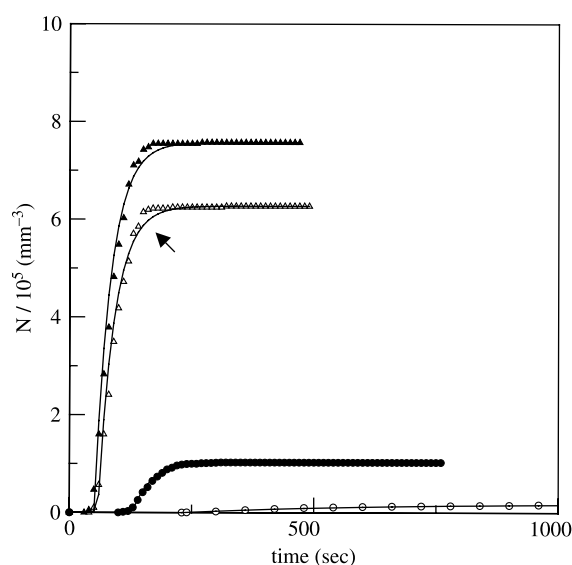


Fig. 1. Time dependencies of the number of nuclei from the melt (open symbol) and from the glass (solid symbol) at two melt temperatures of 230 °C (Δ) and 250 °C (\circ). An arrow indicates a position where the residual melt region remaining is about 90%. Solid lines are calculated from Eq. (2).

crystallization is completed (the residual melt region is about 90% at the position indicated by an arrow in Fig. 1). The limiting values are not associated with the reduction of the space available for nucleation (such as impingement of spherulites) but could be related to the number of foreign bodies and/or of surviving crystal structures in the polymer melt, as discussed in Section 3.2. This result indicates that the total nucleation sites is (pre)determined by the limited number of active sites in the polymer melt. These nucleation behaviors can be described as heterogeneous nucleation with sporadic appearance and limited total number of nuclei. The nucleation rates from the melt and the glass are much faster for melt temperature at 230 °C than for 250 °C. The saturation number of spherulites for 230 °C is also much larger than for 250 °C.

The effective nucleus number (N) in the heterogeneous nucleation with the limited number of active sites (N_s) (saturation nuclei number) is assumed to be proportional to the residual sites ($N_s - N$) with the frequency of nucleation per active site (J_0) (expending rate of active site or activating rate on predetermined sites) and thus can be expressed by the following equation.

$$\frac{dN}{dt} = J_0(N_s - N) \quad (1)$$

Here, J_0 and N_s are strongly dependent on the distribution of active sites and their thermal stability. Integration of Eq. (1) gives the following equation with the initial condition $N=0$ at $t=\tau_0$, where τ_0 is the mean time to build up a critical nucleus (induction time).

$$N = N_s[1 - \exp(-J_0(t - \tau_0))] \quad (2)$$

Fig. 2 shows the natural logarithm of the fraction of residual nucleus sites of $(N_s - N)/N_s$ based on Eq. (2) as a function of time. The residual fraction decreases linearly with time giving the rate constant of J_0 . The straight line can be applied up to

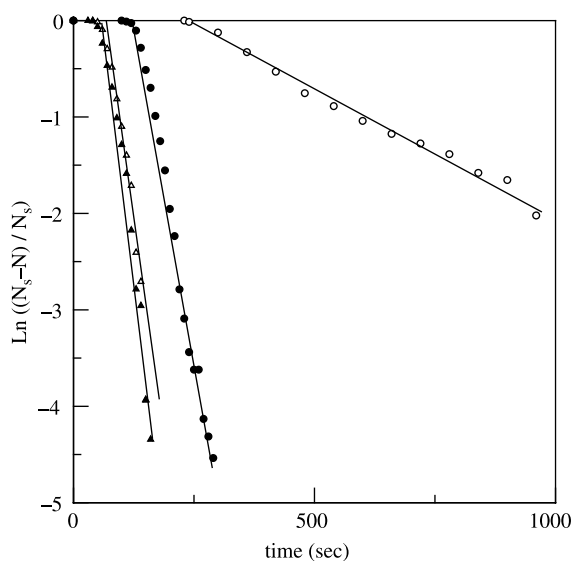


Fig. 2. Natural logarithm of the fraction of residual nucleus sites as a function of time. N_s denotes the limited number of nuclei (saturation number of nuclei). Symbols in the figure are the same in those in Fig. 1.

90% of the active sites. The solid lines in Fig. 1 are calculated with Eq. (2) based on the data of N_s and J_0 . These results clearly indicate that almost all the active sites with the limited number are controlled by the heterogeneous nucleation mechanism even from the molten state above the equilibrium melting temperature.

3.2. Saturation nucleus density

A saturation nucleus density is defined as a density of the limited number of effective sites on foreign particles that have an impact on the nucleation process or as a density of the surviving crystal nuclei in the polymer melt. The surviving nuclei might be associated with a trace of crystal structure that remained even above the actual melting temperature (DSC). In other words, when the crystals are not melted completely, the scaffold of the crystals remains in the polymer melts and acts as seed nuclei. In fact, the spherulites appeared almost in the same place (commonly called the memory effect) in successive experiments when the polymer was melted (annealed) below the equilibrium melting temperature. The number of seed nuclei depends strongly on the thermal history prior to crystallization. Below the equilibrium melting temperature, many seed nuclei exist in the melt and their thermal activity will be different. Fig. 3 shows a common logarithm of the saturation nucleus density as a function of the melt temperature. Below 230 °C, the saturation density is very high and remains almost constant. At 230 °C, the spherulites are melted but their structure cannot be destroyed completely since the tail of DSC melting curve is at 228 °C. Above 230 °C, the saturation density decreases rapidly within the 230–245 °C temperature range and levels off to a constant value. The saturation densities below 230 °C are three orders of magnitude larger than those above 250 °C. These results indicate that the seed nucleus sites decrease rapidly with an increase in

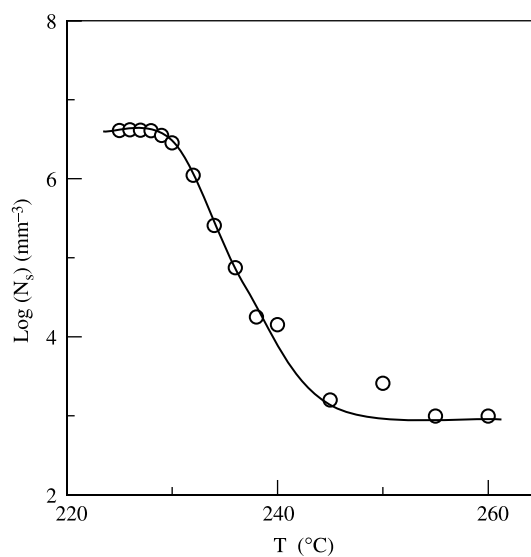


Fig. 3. Relationship between the saturated density of nuclei (N_s) and melt temperatures. Samples were crystallized at 165 °C from the melt at various melt temperatures.

the melt temperature and the seed nuclei disappear above the equilibrium melting temperature of 242 °C.

At this stage, it might be thought that DSC melting curves are reflected from the distribution of crystal size (lamellar thickness). The melting curve of *i*-PS spherulites spans about 18° (from start to end of the peak). The melting temperature range coincides with the temperature range for the transition from the high to the low saturation density of nuclei in Fig. 3. A large crystal size may require longer relaxation times and higher temperature to return to the equilibrium molten state. In other words, the thermal stability of the seed nuclei is distributed in a higher temperature range than the DSC melting curve. Above the equilibrium melting temperature, the sporadic nucleation mechanism may be confused with homogenous nucleation. However, the sporadic nature of nucleation is not unambiguous evidence in favour of a homogeneous process. Even above the equilibrium melting temperature, a saturation of the nuclei density is observed, but the actual concentrations are very low in comparison with those observed below 230 °C. The saturated nucleation density above the equilibrium melting temperature can be related to preexisting nuclei (e.g. catalyst residues, stabilizers in commercial polymers, etc.). These impurities could be still active, heterogeneous nucleation agents in the molten state even after heating above the equilibrium melting temperature. Such preexisting active sites will depend strongly on the type of polymeric material. For example, there are many active sites for primary nucleation in the *i*-PS case but the crystal growth rate is very slow. For PEO on the contrary [4], the nucleation rate is small but the crystal growth rate is fast. However, these characteristics of the active sites are not known in details.

In the other explanation for the saturation density, there is a nucleation exclusion zone [8]. The nucleation will stop and reaches a saturation density when the exclusion zone overlaps the whole substrate surface. The zone might be associated with density fluctuations around the active sites or similar density fluctuations caused by diffusion and conformational changes of polymer molecules in the molten state. Such fluctuations might be correlated with spinodal decomposition in polymeric systems [9,10]. It is interesting to note that the sequence length of helix in *i*-PS increases with a decrease in temperature, especially at the temperature just before the start of crystallization, as determined by IR measurements [11]. The nucleation density might be related to the molecular aggregation in the polymer melt. This aggregated structure can be associated with the change in the molecular conformation such as the degree of helix content or the length of helix in the melt prior to nucleation. However, the relationship between the exclusion zone and the active sites are not known in detail.

3.3. Temperature dependence of nucleation rate

Nucleation rate is the number of nuclei formed per unit volume and time. In our experiments, the unit volume is considered to be the initial volume observed under the optical microscope, which helps to determine a nominal nucleation rate.

In practice, the volume of non-crystalline material decreases as crystallization proceeds, and a real nucleation rate must be corrected by the actual residual volume. It was found that the temperature dependence of the nominal nucleation rate was almost identical to the real nucleation rate. Both rates coincide well within experimental error since the residual melt region is always large enough. However, the real nucleation rate will differ from the nominal nucleation rate when the residual melt region decreases.

Sporadic nucleation is often expressed by the following equation proposed by Turnbull and Fisher [12]

$$I = I_0 \exp \left[-\frac{\Delta E_1}{RT} - \frac{\Delta F_1}{RT} \right] \quad (3)$$

where I_0 is assumed to be a constant without temperature dependence, but strongly dependent on molecular weight [13]. ΔE_1 is the activation energy for the molecular transport process. ΔF_1 is the work required to form a nucleus of critical size. ΔE_1 and ΔF_1 have opposite temperature dependencies, thereby bringing about a maximum in I_{\max} . Here, ΔF_1 is commonly expressed as $\Delta F_1 = K_1 T_m^{02} / (T_m^0 - T)^2$ and K_1 is expressed as $K_1 = n_1 \sigma_{e1} \sigma_{s1}^2 / \Delta H_m^2$, where n_1 is a mode of nucleation, ΔH_m is the heat of fusion and σ_{e1} and σ_{s1} are the end- and the lateral-surface free energies, respectively. ΔT is the degree of super-cooling ($T_m^0 - T$), where T_m^0 is the equilibrium melting temperature and T is the crystallization temperature. An application to the nucleation rate based on Eq. (3) implies that the molecular transport term is very important in the lower temperature ranges. The transport term can be expressed in terms of either an Arrhenius type equation ($\Delta E_1/RT$) or WLF type ($\Delta Q_1/R(T - T_0)$) where ΔQ_1 and T_0 are adjustable parameters. Both expressions could be fitted very well with experimental data [13].

Fig. 4 shows the temperature dependence of the nucleation rates from the molten and glassy states for two different melt

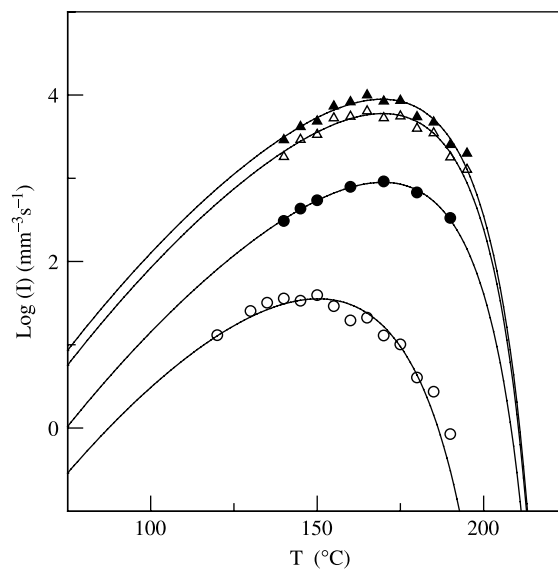


Fig. 4. Temperature dependence of the primary nucleation rate from the melt and from the glass at two melt temperatures. Symbols in the figure are the same as in Fig. 1. Solid lines result from the best fitting procedure for Eq. (3).

temperatures. The temperature dependence curve of the nucleation rate shows a bell shape for both crystallization from the melt and the glass. The nucleation rate from the glassy state is slightly higher than that from the molten state for the 230 °C melt temperature. The maximum nucleation rates from the molten and the glassy states are located at almost the same temperature. However, for samples heated at 250 °C, the nucleation rate from the glass is much higher than that from the melt. The maximum nucleation temperatures from the glassy states at 250 and 230 °C are nearly the same. The maximum nucleation temperature from the molten state at 250 °C is about 20 °C lower than that from the glassy state. That is, the nucleation on the seed nuclei discussed above gives rise to the same maximum nucleation temperature. On the other hand, the nucleation on the foreign bodies occurs at a larger super-cooling, much like a homogenous nucleation.

Fig. 5 shows the relationship between the nucleation rate and the inverse of the induction time. A linear relationship is found for each experimental condition. The slopes for the glassy state from 230 °C and the slope for the molten state from 250 °C are the biggest and the smallest, respectively. That is, the nucleation rates are different at the same induction time and depend strongly on the number of preexisting sites in the melt. The slope can be associated with the nuclei density according to its dimension (mm^{-3}). Fig. 6 shows the relationship between the slope in Fig. 5 and the saturation nucleation density for each nucleation condition. The results indicate that the saturation density is proportional to the products of the induction time and the nucleation rate. During the induction time, only a limited number of nucleation sites are activated. In the steady state of the nucleation process, after the induction time, the nucleation occurs on the limited number of activated sites and their sites are eaten up completely much before the crystallization is completed.

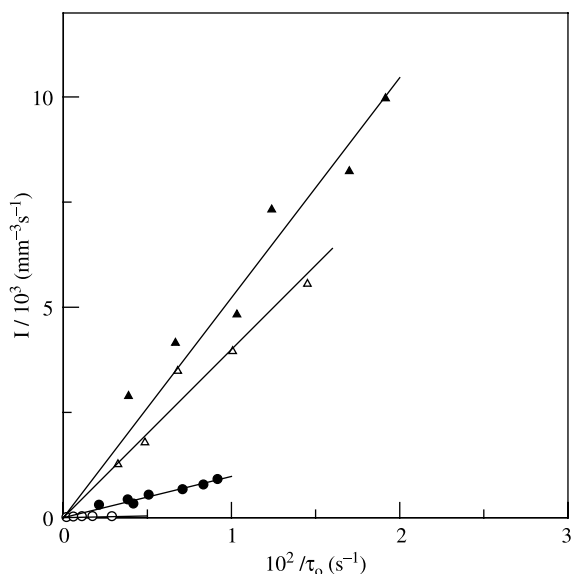


Fig. 5. Relationship between the nucleation rate (I) and the inverse of induction time (τ_0) for various nucleation conditions. Same symbols as in Fig. 1.

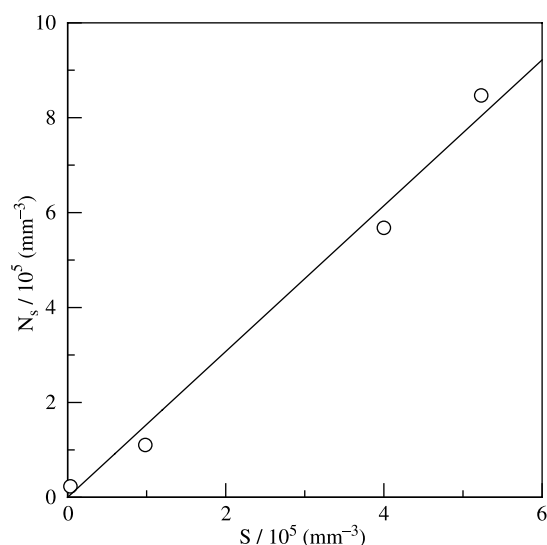


Fig. 6. Plots of the saturation density (N_s) against the slope (S) in Fig. 5.

3.4. Crystal growth rate from the molten and glassy states

Fig. 7 shows the temperature dependence of the crystal growth rate from the melt for two different melt temperatures (230 and 250 °C). The crystal growth rate shows a bell shaped temperature dependence at both melt temperatures. Their bell shaped curves are almost identical. These results are consistent with almost all crystal growth behaviors reported in polymeric materials. Crystal growth data are often analyzed with a classical crystallization theory, which is secondary nucleation controlled, proposed by Lauritzen and Hoffman [7]; it is given by Eq. (4)

$$G = G_0 \exp \left[-\frac{\Delta E_2}{RT} - \frac{\Delta F_2}{RT} \right] \quad (4)$$

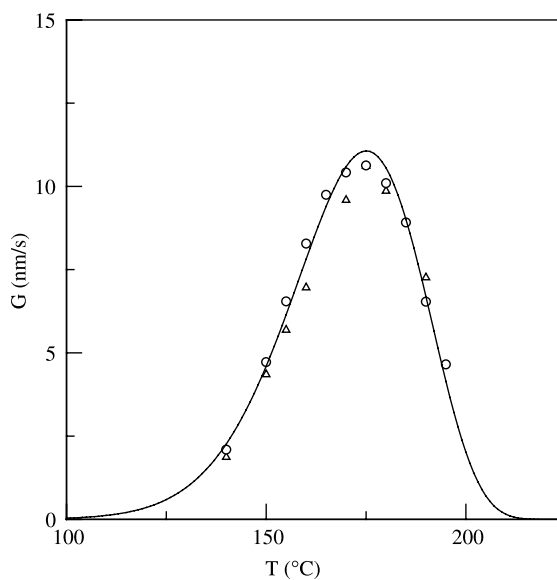


Fig. 7. Temperature dependence of the crystal growth rate from the melt at two melt temperatures of 230 °C (Δ) and 250 °C (\circ). Solid line represents the best fitting for Eq. (4).

where G_0 is a constant strongly dependent on molecular weight [14] and (E_2 is the activation energy for the transport process at the interface between the melt and the crystal surface. (F_2 is the work required to form a secondary nucleus of critical size, commonly expressed as $\Delta F_2 = K_2 T_m^0 / (T_m^0 - T)$. K_2 is a secondary nucleation parameter as given by $K_2 = n_2 \sigma_e \sigma_s / \Delta H_m$. Again, the molecular transport term can be expressed in terms of either Arrhenius or WLF equations [14,15]. The solid line in Fig. 7 is calculated by the best fit based on Eq. (4) where the molecular transport term is assumed to have an Arrhenius form. It is clear that the Arrhenius expression can fit the data quite well. These results indicate that the temperature dependence of the crystal growth rate is independent of the melt temperature.

3.5. Comparison between nucleation and growth parameters

According to Figs. 4 and 7, the maximum crystal growth temperature is slightly higher (about 5°) than the maximum nucleation temperature from the molten and the glassy states at the melt temperature of 230 °C and from the glassy state at 250 °C. On the hand, the maximum crystal growth rates occur at a much higher temperature (about 25°) than the maximum of nucleation rate from the molten state at 250 °C. These temperature differences can be related to the differences in the parameter for the nucleation and crystal growth rates. These maximum temperatures are represented with the ratio of the activation energy for the molecular transport (ΔE) to the nucleation parameter of K [16,17]. Table 1 shows the nucleation and growth parameters, which are estimated by the best fit with the theories of nucleation and growth rates as given by Eqs. (3) and (4). The activation energy of the molecular transport in the crystal growth is estimated to be about 41–42 kcal/mol, which is close to the activation energy of the viscosity in the super-cooled melt between the melting temperature and the glass transition temperature (46 kcal/mol) [18]. The activation energies of the viscosity in the melt and in the glass are about 30 and 69 kcal/mol, respectively [18]. The activation energy of the molecular transport in the primary nucleation is about 29–30 kcal/mol, which is almost the same value to that of the viscosity in the melt. The mechanism relating to the molecular transport term in the nucleation and growth is not clear in its details. However, the molecular transport in the primary nucleation might be considered as the molecular aggregation/association with the intermolecular and intra-molecular diffusion among polymer molecules.

Table 1
Estimated values for the activation energy of molecular transport term (ΔE), the nucleation factor (K) and the maximum temperatures (T_{max}) for nucleation rates from the melt (I_m) from the glass (I_g) and growth rates (G) at two melt temperatures

	230 °C			250 °C		
	G	I_m	I_g	G	I_m	I_g
ΔE (kcal/mol)	42	30	30	41	29	29
K (cal/mol)	950	53	53	940	112	51
T_{max} (°C)	176	170	170	176	150	170

On the other hand, the molecular transport energy in the crystal growth can be associated with the molecular diffusion of the ad-molecules on the crystal growth surface [14]. The activation energy for the ad-molecules on the crystal surface must be larger than that for the molecular diffusion in the melt.

The primary nucleation parameter of K_1 is about 51–53 cal/mol for the nucleation from the glassy state both at 230 and 250 °C and from the molten state at 230 °C. The comparatively small values of K_1 can be associated with the nucleation on the preexisting seed nuclei, which result from the insufficient melting of the lamellae in the spherulites. In fact, under these nucleation conditions, almost the same order of the limited number of nuclei is found and the spherulites reappear at the same locations. On the other hand, K_1 from the melt at 250 °C is 112 cal/mol, which can be associated with the nucleation on foreign particles acting as a nucleation agent in the melt. The nucleation energy on the seed nucleus sites must evidently be smaller than that on the surface of these foreign particles.

The secondary nucleation parameter (K_2) is about 940–950 cal/mol, which is much larger than that of the primary nucleation (K_1). This might be caused by the difference in surface energy between the primary and the secondary nucleation and the ratio of the lateral surface energy to the heat of fusion. The ratio of K_2/K_1 is given by the ratios of $(n_2/n_1)(\sigma_e/\sigma_{e1})(\sigma_{s2}/\sigma_{s1})(\Delta H_m/\sigma_{s1})$. In polymer crystallization mechanism, the ratio of (n_2/n_1) may be of the order of 1/8 and the ratio of $(\Delta H_m/\sigma_{s1})$ is larger than 10 [7]. Therefore, the product of the surface energies of $\sigma_e \sigma_s$ in the primary nucleation must be smaller than that in the secondary nucleation of the crystal growth. The ratio of $(\sigma_{s2}/\sigma_{s1})$ can be larger than unity, because the lateral surface energy in the primary nucleation will be reduced on the surface of the nucleation agent. However, the difference in the fold surface energy (σ_e) between the primary and secondary nucleation is not known. Detailed studies on these surface energies are clearly needed.

4. Conclusion

The influence of thermal history on the primary nucleation and the crystal growth rate was studied for *i*-PS in a wide range of time and temperature. Samples were melted at several temperatures from 230 to 250 °C and then crystallized from those molten states and also crystallized from the glassy state. The primary nucleation rate is strongly influenced by the thermal history prior to crystallization but the crystal growth rate is mainly governed by crystallization temperature. For all the experiments, the nucleation process started with an induction time; subsequently the number of the nuclei increased steadily before reaching a saturation level. The saturation nucleus density remained very high when melting was below 230 °C, and decreased by more than three orders of magnitude when melting ranged from 230 to 250 °C. The nucleation density below 230 °C was attributed to the seed nuclei, which were originated from the insufficient melting of lamellae in the spherulites. Above 250 °C, there was still

the limited number of the heterogeneous nucleus sites and the nucleation sites were activated on these heterogeneous impurities surface. The primary nucleation was heterogeneous in nature both from the molten and the glassy states. The nucleation rate from the glassy state was faster than that from the molten state. A linear relationship between the nucleation rate and the inverse of the induction time was found for all experimental conditions and their slopes were related to the saturation density of nuclei. The activation energy for the molecular transport and the nucleation energy in the primary nucleation were smaller than those in the crystal growth.

References

- [1] Cormia RL, Price FP, Turnbull D. *J Chem Phys* 1962;37:1333.
- [2] Massa MV, Dalnoki-Veress K. *PMSE Prepr* 2004;91:847.
- [3] Sharples A. *Polymer* 1962;3:250.
- [4] Banks W, Sharples A. *Die Makromol Chem* 1963;67:42.
- [5] Boon J, Challa G, van Krevelen DW. *J Polym Sci, A-2* 1968;6:1835.
- [6] Yamazaki S, Hikosaka M, Toda A, Wataoka I, Gu F. *Polymer* 2002;43:6585.
- [7] Hoffman JD, Davis GT, Lauritzen Jr JI. *Treaties on solid state chemistry*. New York: Plenum Press; 1976.
- [8] Markov I. *Crystal growth for beginners*. Singapore: World Scientific; 1998 p. 128.
- [9] Imai M, Mori T, Mizukami T, Kaji K, Kanaya T. *Polymer* 1992;33:4457.
- [10] Olmsted PD, Poon WCK, McLeish TCB, Terill NJ, Ryan AJ. *Phys Rev Lett* 1998;81:373.
- [11] Matsuba G, Kaji K, Nishide K, Kanaya T, Imai M. *Polym J* 1999;31:722.
- [12] Turnbull D, Fisher JC. *J Chem Phys* 1949;17:71.
- [13] Umemoto S, Hayashi R, Kawano R, Kikutani T, Okui N. *J Macromol Sci* 2003;B-42:421.
- [14] Umemoto S, Kobayashi N, Okui N. *J Macromol Sci* 2002;B-41:923.
- [15] Umemoto S, Okui N. *Polymer* 2002;43:1423.
- [16] Okui N. *Polym J* 1987;19:1309.
- [17] Okui N. *J Mater Sci* 1990;25:1623.
- [18] Boyer RF. In: Keinath SE, Miller RL, Rieke JK, editors. *Order in the amorphous state of polymers*. New York: Plenum Press; 1987. p. 135.