

# Investigation of heterogeneous nucleation using the induction time of crystallization: 1. Theory of induction time

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The theory of the induction time was developed which is applicable to experimental studies of the early stages of the heterogeneous crystallization of polymers which is applicable to the evaluation of the effects of the surfaces of a dispersed component. The aspects of the epitaxial and nonepitaxial nucleation on the background of the induction time theory is discussed. The model of the formation of the heterogeneous nucleus was proposed as a basis for the induction time theory. Copyright © 1996 Elsevier Science Ltd.

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## INTRODUCTION

Good performance of composite polymer systems requires that deformation be accompanied by an efficient transfer of the forces acting across the phase boundary. This condition is fulfilled if the interfacial adhesion is sufficiently high. In systems with a crystallizable polymer matrix, it is possible to affect the interfacial adhesion through the control of the crystallization process by a minority component (filler). The thin matrix layer that is in direct contact with the filler and is hence affected by its surface properties plays an important role. The structure of this layer depends both on the ability of the surface to initiate the crystallization and also on the influence of the surface as a crystallization substrate to cause lamellar ordering (epitaxy). Investigation of the morphology of this layer itself by common direct methods is not feasible and the same holds for examination of the consequences of modification of the structure of the layer by the filler surface.

Problems associated with the formation and the structure of this thin interface layer are closely linked to the theory of the heterogeneous nucleation. The theory was worked out in the past<sup>1,2</sup>, however it has not been sufficiently tested experimentally because the individual quantities or functions, with which the theory operates, are very difficult to measure. An appropriate extension of the nucleation theory into a form which would include measurable quantities would make it possible to overcome these experimental difficulties. We suggest that the theory of the induction time is an appropriate extension of the nucleation theory which is useful for this purpose. Induction time can serve as a very important tool for the study of the nucleation process, which allows a connection to be made between the theory

and experimental investigations. A low number of references on induction time<sup>3–6</sup> or its rejection<sup>7</sup> have confirmed that much work must be done to understand the nature of induction time. We have carried out some theoretical and experimental studies of the induction time<sup>8–10</sup> and the first results of the comparison of the theory with experiments seem to be promising.

## THEORY

### *Present state of the art*

Theories of the crystallization process developed earlier<sup>1,2</sup> were compared with morphological studies and with the measurements of the linear spherulite growth rate or overall rate of crystallization. Although very important, experimental confirmations of the nucleation theories are rare. The reason for this can be ascribed to the subtlety of the nuclei layers, the characterization of which represents almost unsurmountable experimental difficulties.

From the point of view of the theoretical description of nucleation, the sizes of critical nuclei are very important because they reflect quantities which are responsible for the nature and efficiency of crystal nucleation, that is the surface energy of the filler, surface nuclei energies, enthalpy and entropy of melting, and equilibrium melting temperature. Verification of nucleation theories by direct observations of nuclei is very difficult, if not impossible.

It was suggested that induction time can be used to study crystal nucleation experimentally via microscopy and X-ray diffraction<sup>3,8–11</sup>. Difficulties in the measurement of induction time consist in imperceptible macrochanges during nucleation. Recently, a new method of induction time measurement was invented<sup>8–10,12</sup> and a theory of induction time was proposed<sup>8</sup>.

From this theory it follows that induction time  $t_i$  for the nucleation of polymers reflects the size of critical

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nuclei and the rate of their development<sup>8</sup>. In the case of heterogeneous nucleation, induction time can be expressed as a sum of the time necessary for the formation of the first layer on the foreign material surface (usually filler surfaces) ( $t_h$ ), and the time period ( $t_s$ ) in which further layers are formed until the growth of the critical nucleus is completed (see Appendix),

$$t_i = t_h + t_s \quad (1)$$

The time periods  $t_h$  and  $t_s$  can be expressed by the relations

$$t_h = A_1 e^{\frac{16\sigma_{b1}\sigma_{ab}\Delta\sigma(T_m^0)^2}{kT(\Delta H_m\Delta T)^2}} e^{\frac{\Delta G_\eta}{kT}} \quad (2)$$

$$t_s = A_2 \left( \frac{2\Delta\sigma T_m^0}{\Delta H_m\Delta T b_0} - 1 \right) e^{\frac{4\sigma_{b1}\sigma_{ab}b_0T_m^0}{kT\Delta H_m\Delta T}} e^{\frac{\Delta G_\eta}{kT}} \quad (3)$$

where  $A_1, A_2$  are proportionality constants,  $\sigma_{b1}$  and  $\sigma_{ab}$  are Gibbs specific surface energies of the growing nucleus,  $\Delta\sigma$  is the difference energy parameter which characterizes the surface energy of the material initiating the nucleation,  $T_m^0$  is equilibrium melting temperature,  $\Delta H_m$  is the enthalpy of crystal melting,  $\Delta T$  is undercooling,  $b_0$  is the thickness of one layer of folding chains (given by the thickness of the polymer chains), and  $\Delta G_\eta$  is the activation energy of diffusion. A detailed description of the derivation of these relations is given in the Appendix.

There is a number of quantitatively unexpressed parameters in these equations, which are very difficult to measure. A direct comparison of the theory with experimental measurements would not be possible without the quantitative evaluation of these parameters. In our previous paper an approximation method was briefly outlined, which enabled us to connect the theory and experimental results<sup>8</sup>. A detailed analysis of this method, with respect to the possibility of comparing this theory with experimental results and some further development of the induction time theory, is the objective of the present work.

#### High-temperature approximation of the induction time equation

It is known that the size of the critical nuclei increases with crystallization temperature<sup>1</sup>. For sufficiently high temperatures of crystallization, when the number of the folding segment layers is much higher than unity, the time of the formation of the first layer ( $t_h$ ) can be neglected in comparison with the time in which remaining layers are formed. In this case, equation (1) for the induction time can be simplified to:

$$t_i = A_2 \frac{2\Delta\sigma T_m^0}{\Delta H_m\Delta T b_0} e^{\frac{4\sigma_{b1}\sigma_{ab}b_0T_m^0}{kT\Delta H_m\Delta T}} e^{\frac{\Delta G_\eta}{kT}} \quad (4)$$

The equation can be rewritten into a logarithmic form

$$\ln(t_i\Delta T) = \ln \frac{C\Delta\sigma T_m^0}{\Delta H_m b_0} + \frac{4\sigma_{b1}\sigma_{ab}b_0T_m^0}{k\Delta H_m} \frac{1}{T\Delta T} \quad (5)$$

where the influence of the transport term is included in the constant  $C$ . According to equation (5), the dependence of  $\ln(t_i\Delta T)$  on  $1/T\Delta T$  is a straight line with slope

$K$ , where

$$K = \frac{4\sigma_{b1}\sigma_{ab}b_0T_m^0}{k\Delta H_m} \quad (6)$$

and with intercept  $Q$  on the axis of  $\ln(t_i\Delta T)$ :

$$Q = \ln \frac{C\Delta\sigma T_m^0}{\Delta H_m b_0} \quad (7)$$

After using the well-known relation for the equilibrium melting temperature<sup>1</sup>

$$T_m^0 = \frac{\Delta H_m}{\Delta S_m} \quad (8)$$

where  $\Delta H_m$  and  $\Delta S_m$  are the changes in enthalpy and entropy of equilibrium crystal melting per volume unit, respectively, equations (6) for the slope  $K$ , and (7) for the intercept  $Q$ , can be rewritten

$$K = \frac{4\sigma_{b1}\sigma_{ab}b_0}{\Delta S_m} \quad (9)$$

$$Q = \ln \frac{C\Delta\sigma}{\Delta S_m b_0} \quad (10)$$

The quantities  $K$  and  $Q$  can be acquired from experimental measurement of the induction time dependence on crystallization temperature.

*Nonepitaxial nucleation.* When the heterogeneous nucleation is nonepitaxial, the segments are organized in the close-packing arrangement. The changes of molar entropy,  $\Delta s$ , and molar Gibbs energy,  $\Delta g$ , reach their maximum values when the equilibrium crystal melts. As the structure of nuclei is not influenced by a foreign surface (e.g. of a filler), all parameters which are connected with the nuclei structure must be identical, provided nucleation conditions are the same. This means that quantities  $\sigma_{b1}, \sigma_{ab}, b_0, \Delta H_m, \Delta S_m, T_m^0$  and the number of moles of folding segments of the chain molecules per unit volume must be constant. The straight-line dependences according to equation (5) have the same slope  $K$  which characterizes the crystallizing material. The intercepts ( $Q$  values) give information about the difference energy parameters  $\Delta\sigma$  which are specified with the exception of a multiplicative constant. The comparison of these  $Q$  values enables us to quantitatively evaluate the nucleation characteristics of the materials on which crystal nucleation takes place. In particular, it is possible to classify surface treatments of a filler with respect to the crystallization behaviour of the composite material.

*Epitaxial nucleation.* The structure of epitaxially grown nuclei is different from that in nonepitaxial nuclei arrangement. The epitaxy results in changes in the molar entropy of equilibrium crystal, the number of moles of segments per unit volume, the molar Gibbs energy of the nucleus and the energies of the intermolecular and intramolecular interactions of segments in the nuclei. The number of moles of segments per unit volume is reflected in the densities of segments and foldings on the nuclei surfaces. Both the changes in the segment interactions and the changes in the surface densities of the segments and foldings have their consequences in alterations of the surfaces energies of the nuclei. Moreover,

it is to be expected that the equilibrium melting temperature of the epitaxial crystal will differ from that of the nonepitaxial one.

The molar entropy of epitaxial nucleation is unambiguously higher than that of nonepitaxial process. On the other hand, the entropy of unit volume need not be necessarily higher in epitaxial nucleation, as the segment arrangement may be less dense in the case of epitaxial nucleation. Similar considerations can be made for the Gibbs energy of volume unit and for the specific surface energies.

On the basis of previous considerations, we can state that epitaxial nucleation manifests itself by the change in the value of the quantity  $K$  (equation (6)). Quantity  $Q$  also reflects changes which are the result of epitaxial nucleation. Whereas in the case of nonepitaxy it is possible to evaluate the quality of the nucleation sites on the substrate surface using the  $Q$  values (see Nonepitaxial nucleation), in the case of epitaxy the direct comparison of  $Q$  values is irrational. This is due to the fact that those parameters that influence  $Q$  (equations (7) and (10)) are also dependent on the type of nucleation and hence on the structure of nuclei.

Evaluating constants  $K$  and  $Q$ , it can be also estimated which of the nucleation types (epitaxial, nonepitaxial) is preferred in the nucleation process. The nucleation barrier at the beginning of the process, when the first folding segment layer is being built up, can be expressed as the sum of the critical Gibbs energy for heterogeneous nucleation and activation energy of the transport<sup>8</sup>

$$E = \frac{16\sigma_{b1}\sigma_{ab}\Delta\sigma(T_m^0)^2}{k(\Delta H_m\Delta T)^2T} + \frac{\Delta G_\eta}{kT} \quad (11)$$

Using equations (6) and (7), it is possible to rewrite the condition into the form

$$E = \frac{4Ke^Q}{T(\Delta T)^2C} + \ln\left(\frac{C}{2A_2}\right) \quad (12)$$

From this equation it is apparent that the type of the nucleation will be preferred which offers the minimum value of the  $Ke^Q$  term.

#### Relationship between induction time and surface nucleation ability

Induction time, which is defined as the most probable time necessary for the critical nuclei formation, is directly associated with the nucleation ability of a filler surface (quantitatively expressed as nucleation density on the filler surface). Nucleation ability is influenced by the surface energy of a filler expressed by the difference energy parameter  $\Delta\sigma$  and by the possible changes of nuclei structure introduced by the filler surface arrangement (equations (6) and (9)). These energy and structure conditions are not the only ones determining surface density of the nuclei occurrence (nucleation density). Filler surface cannot be usually considered as homogeneous in relation to the nucleating segments, i.e.  $\Delta\sigma$  varies along the filler surface. The density of nucleation sites (the sites on the filler surface with sufficiently low  $\Delta\sigma$  parameter) is influenced by a number of factors such as corrugation of the surface, orientation of crystallites on the surface of a polycrystalline filler material and chemical structure of the filler. Induction time curves

provide no information on the density of the crystallization sites on the filler surface as they involve only the influence of surface energy and the ability of nucleation sites to modify the structure of nuclei.

The number of the critical nuclei per unit surface, which were successfully completed, can be expressed as a product of the nucleation site density and the probability of the completion of the critical nuclei. This probability can be calculated as the product of the probabilities of the completion of all critical nucleus layers. These individual probabilities are inversely proportional to the time periods which are necessary for completion of the particular layers. Thus the surface density of successfully completed nuclei (nucleation density) ( $p$ ) can be expressed as

$$p = BP \frac{1}{t_h} \left(\frac{n-1}{t_s}\right)^{(n-1)} \quad (13)$$

where  $B$  is a proportionality constant depending on measuring units,  $P$  is the density of nucleation sites and  $n$  is the number of layers in the critical nuclei. The last quantity can be expressed as<sup>8</sup>:

$$n = \frac{2\Delta\sigma T_m^0}{b_0\Delta H_m\Delta T} \quad (14)$$

Following this expression and equations (2) and (3), nucleation density is given by the equation:

$$p = BPe^{-\frac{16\sigma_{b1}\sigma_{ab}\Delta\sigma(T_m^0)^2}{kT(\Delta H_m\Delta T)^2}} e^{-\frac{\Delta G_\eta}{kT}} \left(e^{-\frac{4\sigma_{b1}\sigma_{ab}b_0T_m^0}{kT\Delta H_m\Delta T}} e^{-\frac{\Delta G_\eta}{kT}} \left(\frac{2\Delta\sigma T_m^0}{\Delta H_m\Delta T b_0} - 1\right)\right) \quad (15)$$

At high crystallization temperature the term for the transport activation energy can be regarded as a constant<sup>1</sup>. If we use equations (6) or (7) and (9) or (10) for  $K$  and  $Q$  parameters, respectively, we can transform equation (15) into a clearer expression, where those quantities are involved which can be experimentally measured

$$p = BPe^{-e^Q(K\frac{k_1}{(\Delta T)^2T} + \frac{k_2}{\Delta T}) + K_T\frac{1}{\Delta T}} \quad (16)$$

$$\text{where } k_1 = \frac{3e^{-\frac{\Delta G_\eta}{kT}}}{A_2} \text{ and } k_2 = \frac{\Delta G_\eta}{A_2 e^{\frac{\Delta G_\eta}{kT}}} \text{ are constants.}$$

To elucidate the influence of viscosity of the melt on the nucleation density we replace parameter  $Q$  in equation (16) by its definition from equations (4) and (5), and obtain

$$p = BPe^{-\frac{2\Delta\sigma T_m^0}{\Delta H_m b_0} \left(\frac{3K}{T(\Delta T)^2} + \frac{\Delta G_\eta}{kT\Delta T}\right) + \frac{K}{\Delta T}} \quad (17)$$

Analysing equations (15), (16), and (17), it can be confirmed that nucleation density increases with the density of the nucleation sites (density of possible sites of nucleation) and decreases with increasing crystallization temperature in the range from  $\frac{T_m^0}{2}$  to  $T_m^0$  and decreases with increasing  $Q$  parameter (i.e. with increasing  $\Delta\sigma$  parameter, see equation (7)). The term including activation energy of transport  $\Delta G_\eta$  is responsible for the decrease of the nucleation ability when the melt viscosity increases, i.e. when the crystallization temperature decreases. The dependence of the nucleation density on the crystallization temperature will exhibit a maximum. The existence of the maximum is a result of the opposite

influences of the crystallization temperature on the respective terms constituting the exponent in equation (17). The term with the activation energy of transport is constant at low undercooling, however, at low crystallization temperatures (high undercooling) it strongly increases. The other exponential terms decrease with decreasing temperatures between  $T_m^0/2$  and  $T_m^0$ , in which range also the maximum occurs.

Equations (16) and (17), derived for the nucleation density, yield the results for both epitaxial and non-epitaxial nucleation. In the latter case we obtain a constant value of  $K$ , which follows from equation (5). Moreover, for various treatments of the substrate surfaces which do not change the surface density of the nucleation sites,  $P$ , it is possible to evaluate the ability of nucleation sites of the particular filler directly from the dependence of the induction time on crystallization temperature. The higher the value of the induction time, the worse the nucleation sites are from the point of view of nucleation ability.

If the surfaces which initiate nuclei of different structure are to be compared from the point of view of their nucleation abilities, the influence of the quality of nucleation sites should be estimated from equation (16). More intensive nucleation is initiated by those nucleation sites which have simultaneously low values of  $e^Q$  and  $Ke^Q$ , and high values of parameter  $K$ .

The quality of nucleation sites cannot be evaluated directly from the observation of the nucleation density. The reason lies in the fact that two contributions to the nucleation density are included in the direct microscopical observation records, i.e. the influence of the quantity of nucleating sites (density of nucleation sites) and the influence of their quality (ability to initiate nucleation). Both influences act concurrently and hence the individual effects cannot be separated.

The theoretical considerations presented in this study yield the possibility of evaluating actual systems by experimental determination of values  $K$  and  $Q$ . However, a systematic error appears when the high temperature approximation is applied. Crystallization undercooling  $\Delta T = T_m^0 - T$  depends on  $T_m^0$ , which is very difficult to measure, and the data published in literature for the same polymers vary substantially. Moreover, when the structure of nuclei is modified by the filler surface structure, changes in the equilibrium melting temperature can be expected. We have checked the importance of the uncertainty in  $T_m^0$  when evaluating the dependence of  $\ln(t_i \Delta T)$  on  $\frac{1}{T \Delta T}$ . We have found for various equilibrium melting temperatures that the dependences differ only very slightly if the equilibrium melting temperatures do not differ markedly. Therefore it can be assumed that this error is not significant.

## CONCLUSIONS

The theoretical approach to the influence of a substrate surface on crystal nucleation, presented in this study, is applicable to the evaluation of the effects caused by the surfaces of a dispersed component.

The induction time approach makes it possible to evaluate the influence of the individual qualitative parameters on the nucleation process (surface energy of nucleation sites and possible modifications of the nuclei

structure by the substrate surface) and is independent of the quantitative parameters (filler volume fraction, density of nucleation sites on the filler surface).

The high-temperature approximation of the dependence of induction time on crystallization temperature makes it possible to differentiate between epitaxial and non-epitaxial nucleation using the parameter  $K$ , regardless of the fact whether the crystal growth continues after nucleation in its unmodified form or in the changed epitaxial structure. For non-epitaxial nucleation,  $K$  parameters have the same values which are characteristic of crystallizing material. Changes in the value of this parameter indicate changes in the structure of nuclei (epitaxy). If non-epitaxial nucleation takes place, it is possible to evaluate the ability of the surfaces to initiate nucleation from the parameter  $Q$  directly, provided the value of the density of crystallization sites is the same. If the nucleation densities for epitaxial and non-epitaxial nucleation are to be compared, it is necessary to take into account the terms  $K$ ,  $Ke^Q$  and  $e^Q$ .

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## APPENDIX

Model of the growth of the critical heterogeneous nucleus for the evaluation of induction time.

The induction time in our theory is understood as the most probable time period of the critical nucleus formation<sup>8</sup>. It is obvious that this time period increases with the increasing size of the critical nuclei and decreases with the increasing rate of the nucleus growth. The sizes of the critical heterogeneous nucleus  $a_h^*$ ,  $l_h^*$  and  $b_h^*$  are given by the frequently cited relationships<sup>1</sup> and depend on the surface energies of the nucleus, difference energy parameter<sup>3,8</sup>  $\Delta\sigma$ , enthalpy of the nucleus melting,  $\Delta H_m$ , equilibrium melting temperature,  $T_m^0$  and on the undercooling,  $\Delta T$ .

The probability of joining a chain segment to the growing nucleus is proportional to the number of segments the energy of which is high enough to allow overcoming the nucleation barrier. The rate of the nucleus growth is controlled by the segments with a sufficiently high energy to enable nucleation; the influence of the viscosity of the melt is discussed in detail in ref. 8.

It follows from the nucleation theory that those segments are capable of the nucleation, the energy of which is higher than or equal to the value of the nucleation barrier<sup>1</sup>. The value of the change of the Gibbs energy for the critical size of the nuclei<sup>8</sup> ( $\Delta G^*$ ,  $\Delta G_h^*$ ,  $\Delta G_s^*$ ) is assumed to be the nucleation barrier. As this point is important for our considerations, it will be discussed here.

It follows from the definition of the Gibbs energy that, for isothermal and isobaric processes, the decrease in the Gibbs energy is the part of the overall energy of the system which is consumed to compensate for the work of the external forces. In the first stage of nucleation, the joining of the nucleating segments is accompanied by an increase in the Gibbs energy ( $\Delta G$  is positive until a stable nucleus is formed). This means that to be capable of nucleation, joining segments must possess a certain energy which is equal to the change in the Gibbs energy. As the change in the Gibbs energy is not constant in the course of the nucleation process<sup>1</sup>, the minimum energy which the nucleating segments must possess changes during the nucleation process. It is very complicated to express the nucleation barrier at every step of the nucleation process; nevertheless, the maximum of these nucleation barrier values is considered as the nucleation barrier for all the steps of the nucleation (it is the value for the critical nucleus).

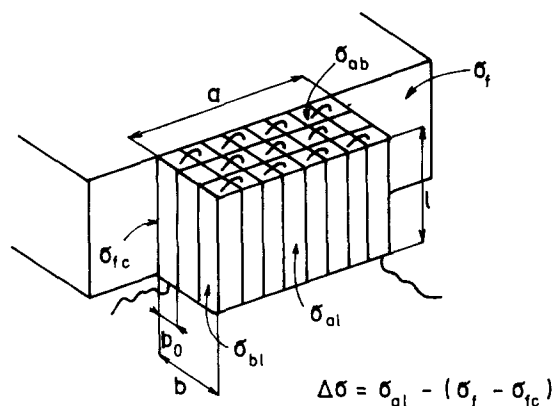
In our considerations of the time of development of a critical nucleus (induction time), the above simplification of the nucleation barrier is inappropriate as the rate of the growth of the nucleus depends in every step of the nucleation on the nucleation barrier ( $\Delta G$ ). To simplify the very complicated time-dependence of the values of the nucleation barrier during the nucleation process, we suggested the following model of the heterogeneous nucleation. The basic equation for the change in the Gibbs energy when the nuclei are heterogeneous is

$$\Delta G = abl\Delta G_v + 2ab\sigma_{ab} + 2bl\sigma_{bl} + al\Delta\sigma \quad (\text{A1})$$

where  $\Delta G_v$  is the change in the Gibbs energy of crystallization of a unit volume in an infinite crystal,  $\sigma_{ab}$  and  $\sigma_{bl}$  are specific surface energies of the growing nucleus,  $\Delta\sigma$  is the difference energy parameter, and  $a$ ,  $b$  and  $l$  are dimensions of the growing nucleus<sup>1,8</sup> (Figure A1). According to the definition, the change in the Gibbs energy is highest when the nucleus is critical (dimensions are<sup>1</sup>  $a_h^* = -4\sigma_{bl}/\Delta G_v$ ,  $b_h^* = -2\Delta\sigma/\Delta G_v$ ,  $l_h^* = -4\sigma_{ab}/\Delta G_v$ ). The critical value of the change in Gibbs energy for heterogeneous nucleation is<sup>1</sup>

$$\Delta G_h^* = 16\sigma_{bl}\sigma_{ab}\Delta\sigma(T_m^0)^2 \frac{1}{(\Delta H_m)^2(\Delta T)^2} \quad (\text{A2})$$

where  $\Delta H_m$  is the enthalpy of crystal melting and  $T_m^0$  is the equilibrium melting temperature.



**Figure A1** Growth of a heterogeneous crystallization nucleus.  $a$ ,  $b$ ,  $l$  nucleus dimensions,  $b_0$  thickness of one stacking layer,  $\sigma_{al}$ ,  $\sigma_{bl}$ ,  $\sigma_{ab}$  specific surface energies of the nucleus growing from the melt,  $\sigma_f$  specific surface energy of the foreign substance in polymer melt,  $\sigma_{fc}$  specific Gibbs energy of the foreign substance–crystal interface

If the nucleation process involves at its beginning the formation of the complete first layer with the dimensions  $a_h^*$ ,  $l_h^*$  and  $b_0$  ( $b_0$  is the thickness of the single layer), then it can be deduced from the basic equation (equation (A1)) for the change in the Gibbs energy of the first layer  $\Delta G_{b_0}$  that the maximum value is reached for that complete layer. This value is identical with  $\Delta G_h^*$  of the heterogeneous critical nucleus (equation (A2)). It is therefore possible to assume that the nucleation barrier for the first layer is given by the term for  $\Delta G_h^*$  in equation (A2).

The value  $\Delta G_h^*$  is significant for the evaluation of the time necessary for the formation of the first layer of the heterogeneous nucleus. From the Boltzmann energy distribution, it can be derived that the number  $N_h$  of the segments which are capable of nucleating in the first layer is proportional to the term

$$N_h \sim e^{-\frac{\Delta G_h^*}{kT}} \quad (\text{A3})$$

The inverse ratio  $1/N_h$  can be considered as proportional to the time,  $t_h$ , of the formation of this first layer. If we also take into account the activation energy of the diffusion (the total activation energy is the sum of these two activation energies), the duration of the formation of the first layer is given by equation (2).

For the growth of the second and each of the following layers, the equation for the change in the Gibbs energy for every layer is a modification of the equation for secondary nucleation

$$\Delta G_{b_0i} = ab_0l_h^*\Delta G_v + 2ab_0\sigma_{ab} + 2b_0l_h^*\sigma_{bl} \quad (\text{A4})$$

where  $i = 2 \dots n$ ;  $n$  is the number of the critical nucleus layers. We suppose here that the stem length of the folded-chain nucleus has to be equal to  $l_h^*$  (the dimension of the final heterogeneous critical nucleus). For the dimension  $a$  there is no precondition except not to exceed the critical dimension of the heterogeneous nucleus  $a_h^*$ . The multiple nucleation in every layer is possible to reach the critical heterogeneous dimension and we will demonstrate later that this multiple nucleation is necessary for a successful nucleation.

In our model we suppose that the stem length  $l$  of the second and all the following layers of the heterogeneous

nucleus is the same and equal to  $l_h^*$ . Then the maximum of  $\Delta G_{b_{0i}}$  (equation (A4)) is reached if  $a = a_s^* = -2\sigma_{bl}/\Delta G_v$  and it corresponds to  $\Delta G_s^*$

$$\Delta G_s^* = 4\sigma_{bl}\sigma_{ab}b_0T_m^0 \frac{1}{\Delta H_m \Delta T} \quad (\text{A5})$$

We suggest that the nucleation barrier for the second and each of the following layers be equal to the maximum value  $\Delta G_{b_{0i}} = \Delta G_s^*$  when those layers are formed, i.e. to the nucleation barrier value for the secondary nucleation.

The number of all layers in a heterogeneous critical nucleus is  $b_h^*/b_0$ . The time,  $t_s$ , necessary for the formation of all but the first layer of the critical nucleus (the number of these layers is  $b_h^*/b_0 - 1$ ) can be expressed using a procedure similar to the expression of the time  $t_h$ : the number of segments capable of nucleating involves the corresponding change in the Gibbs energy, and the inverse relation is considered as the corresponding part of the induction time (cf. equation (3)).

It is useful, though not necessary for the final value of induction time, to elucidate whether it is reasonable to assume that the growth of the nucleus proceeds layer after layer, i.e. that every following layer begins to grow after the previous layer has been completed. It follows from the analysis of equation (A1) that, if the first layer with dimension  $l_h^*$  is formed,  $\Delta G$  increases with increasing  $a$  and the maximum value is reached for  $a = a_h^*$ . Additional joining of other layers would not be accompanied by any change in  $\Delta G$ . The consequence is that there would be no driving force for joining the following layer and hence no possibility of the formation of the stable nucleus and following spontaneous growth of the crystal, as the necessary condition for the spontaneous growth is  $\Delta G < 0$ . Therefore it is clear that, before the first layer is completed, the second layer must start nucleating. Multiple nucleation for the second and all the next layers makes it possible that when the particular layer is being completed  $\Delta G_{b_{0i}}$  need not be zero. Then the total change in the Gibbs energy  $\Delta G$  for the whole growing nucleus results in the nucleus growth until a stable nucleus is reached.

Assuming that the particular layer of the nucleus arises

from several independent parts, the time period for the completion of the layer would be shorter than in the case of successive layer formation from one site. In either of the situations, the rate of the layer formation is proportional to the number of segments with energy which is higher than the nucleation barrier ( $\Delta G_s^* + \Delta G_\eta$ ). The proportionality constant  $A_2$  (equation (3)) reflects the mechanism of the layer formation.

## NOMENCLATURE

$a, b, l$	dimensions of a growing nucleus
$a_h^*, b_h^*, l_h^*$	dimensions of the critical heterogeneous nucleus
$a_s^*, l_s^*$	dimensions of the critical secondary nucleus
$b_0$	the thickness of one nucleus layer
$\sigma_{ab}, \sigma_{bl}$	specific surface energies of the heterogeneous nucleus
$\Delta\sigma$	difference energy parameter
$\Delta G$	total change in the Gibbs energy
$\Delta G^*$	change in the Gibbs energy of the critical nucleus
$\Delta G_h^*$	change in the Gibbs energy of the critical heterogeneous nucleus
$\Delta G_s^*$	change in the Gibbs energy of the critical secondary nucleus
$\Delta G_{b_{0i}}$	change in the Gibbs energy of one layer of a nucleus
$\Delta G_v$	change in the Gibbs energy of crystallization of a unit volume in an infinite crystal
$\Delta G_\eta$	activation energy of diffusion
$\Delta S_m$	change in entropy of equilibrium crystal melting
$\Delta H_m$	enthalpy of crystal melting
$T_m^0$	equilibrium melting temperature
$\Delta T$	undercooling ( $T_m^0 - T$ )
$T$	crystallization temperature
$t_i$	induction time
$t_h$	time of the formation of the first layer of the heterogeneous nucleus
$t_s$	time of the formation of the second and the following layers until the critical nucleus is completed