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β-Molecular Rearrangement Process, But Not an α-Process, as Governing the Homogeneous Crystal-Nucleation Rate in a Supercooled Liquid

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The time dependence of the growth rate of homogeneous-nucleation-based (HNB) crystallization in *o*-terphenyl was tracked by a temperature-jump method through microscopic observations, and HNB crystallization was found to proceed at a steady rate, specified by the tracking temperature just after the jump. Two sets of numerical computations were carried out according to a classical homogeneous nucleation theory for the temperature-jump experiment on alternative assumptions that the homogeneous nucleation process is governed by the α-molecular rearrangement process or by the β-process in the liquid. From a comparison between the experimental and calculated results, the homogeneous nucleation, and thus the crystal growth as well, were concluded to be governed by the β-rearrangement process rather than the α-process, differently from the common recognition that they are governed by the latter.

Crystallization proceeds through two processes of nucleation and the growth of crystal;[1,2] knowledge concerning nucleation as an important initial process is indispensable for understanding the whole crystallization process. No direct observation of the nucleation process, however, has been reported so far to our knowledge, and the nucleation process has been hardly understood either experimentally or theoretically.

We recently found a homogeneous-nucleation-based (HNB) crystallization in *o*-terphenyl and salol (phenyl salicylate) at very low temperatures, just above the glass transition region;[3,4] the crystallization was observed as an advance of the crystal front into the liquid phase under a microscope. This phenomenon was interpreted to occur according to the mechanism that the crystal embryos are remarkably stabilized as fine crystal particles by reduction in the interfacial energy of the embryo to the liquid due to their contact with the crystals already present, and that the HNB crystallization proceeds through a coalescence of the crystal embryos/nuclei into the crystalline phase on the liquid-crystal interface. The HNB crystallization, therefore, potentially gives an important clue to understanding the details concerning the homogeneous crystal nucleation process.

The homogeneous nucleation rate is characterized by the number of nuclei that appear per unit time per unit volume in a liquid. Turnbull and Fisher[5,6] expressed the steady-state homogeneous nucleation rate (I_V) in a liquid as

$$I_V \approx N_V \nu \exp\left(-\frac{\Delta G^*}{k_B T}\right) \qquad (1)$$

by extending the classical nucleation theory proposed by Volmer and Weber.[7] Here, N_V is the number of molecules per unit volume, since any molecule has a chance to become the central one for the formation of a critical nucleus, ν is the frequency of molecular transport across the interface between the embryo/nucleus and the liquid, ΔG^* is the Gibbs energy for the formation of an embryo/nucleus with the critical size, and k_B is Boltzmann's constant. Since this equation was proposed, the frequency (ν) has been connected with a diffusion coefficient of molecules in the liquid, and has been estimated from the viscosity of the liquid on the tacit assumption that the homogeneous nucleation rate would be governed by the α-molecular rearrangement process.[8] With the nucleation rate, the growth rate (u) due to HNB crystallization is given as a rough approximation by a relation

$$u \approx 8 I_V (r^*)^4, \qquad (2)$$

where r^* denotes the critical radius of the crystal nucleus.[3] The growth rate is thus governed not only by ΔG^*, but also by the frequency (ν). When we evaluated numerically, according to the above equations, the growth rate of HNB crystallization in *o*-terphenyl, a large discrepancy of 10 orders of magnitude was found between the observed and calculated maximum values of the rate,[3] even though the nucleation-enhancement effect, due to a reduction of the interfacial energy between the crystal embryo/nucleus and the liquid, was taken into consideration in evaluating ΔG^* in Eq. 1. The large discrepancy might thus be ascribed to an underestimation of the frequency (ν) in Eq. 1.

In addition to the α-process, there is a β-molecular rearrangement process reported to exist in liquids. The existence of a β-process has been predicted by Goldstein,[9] even for the liquids of rigid molecules; in fact, it has been observed in some systems. Also, in *o*-terphenyl, which is a material to be focused on in the present work, a β-glass transition due to a freezing-in of the β-process has been observed by a precise calorimetry in a temperature region much lower than the α-glass transition temperature.[10] Figure 1 shows Arrhenius plots of the relaxation times associated with the α- and β-processes. Here, the triangles represent the relaxation times from the viscosity data,[11] the squares from the dielectric measurement,[12,13] circles from the adiabatic calorimetry,[3,10] and the solid line from the ac calorimetry;[14] the filled marks are associated with the β-process, while open ones are associated with the α-process; and a dotted line represents the estimated temperature dependence of the β-relaxation time. While the α-process is considered to originate from the motion of molecules within structured clusters formed in the liquid, the β-process would originate from the motion of molecules in the gap between clusters.[10] The β-relaxation time is correspondingly much shorter than the α-relaxation time near the α-glass transition temperature. Therefore, if the frequency (ν) in Eq. 1 should correspond to that of the β-rearrangement process in the liquid, the homogeneous nucleation rate would be drastically enhanced. This possibility is quite high from the point of view that the embryo/nucleus could be recognized to be a kind of structured cluster, and that the cluster increases in size through a rearrangement of the molecules on the boundary of the cluster.

In the present work, the molecular-rearrangement process governing the homogeneous nucleation rate was investigated based on the time dependence of the crystal growth rate in *o*-terphenyl after a sudden temperature jump in the HNB crystallization temperature region. The growth rate after the jump was followed for a long time by a microscopic observation, the time dependence of the growth rate was numerically evaluated on both assumptions of the α- and β-processes as determining the above-mentioned frequency (ν) on the basis of classical nucleation theory, and the two sets of evaluated results were compared with the experimental one. The reason for this attempt is that the HNB crystallization proceeds in the glass transition temperature region in which the relaxation time are of the experimental time scale; thus, if the frequency (ν) is really governed by the α-rearrangement process, some relaxation property should appear in the time dependence of the growth rate just after a sudden temperature change in the HNB crystallization temperature region. It followed from a comparison that the nucleation rate (and thus the growth rate as well) must be governed by the β-molecular rearrangement process, not the α-process as generally recognized.

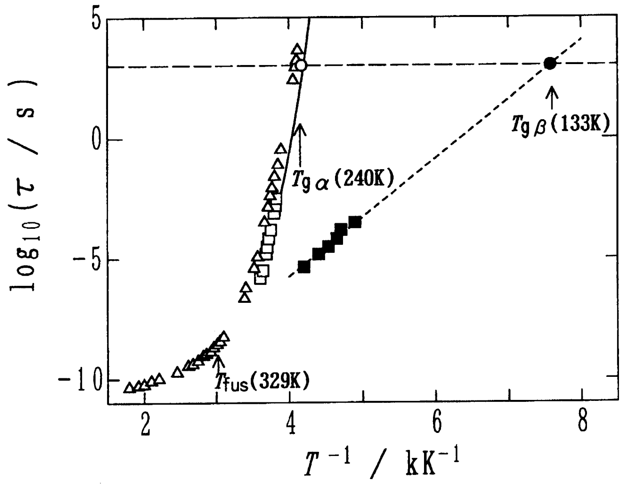

Fig. 1. Arrhenius plots of the relaxation times of liquid and glass of *o*-terphenyl: △, from viscosity measurement;[11] □, ■, from dielectric measurement;[12,13] ○, ●, from adiabatic calorimetry;[3,10] —, from ac calorimetry.[14] Open marks correspond to the α-process and filled marks to the β-process. A dotted line represents the estimated temperature dependence of the β-relaxation time.

Experimental

o-Terphenyl, purchased from Tokyo Chemical Ind. Co., was purified by recrystallization from a methanol solution three times, and then by sublimation under a vacuum at 320 K. The mole-fraction purity of the sample was determined by a fractional melting experiment to be 0.9997±0.0001, as described before.[3]

A direct observation of the crystallization process was carried out for a purified sample in the temperature range of 224 to 263 K by using an Olympus SZ1145 microscope with a calibrated filar eyepiece and a home-made variable-temperature cold stage.[3,15] The sample was melted at about 330 K between the stage and a glass cover slip under a vacuum, quenched to the glass transition temperature region, and then kept at the desired temperature, controlled within ±0.1 K. The thickness of the sample was confirmed not to affect the crystallization properties within its used range in the present experiment.

Results

The homogeneous-nucleation-based (HNB) crystallization in *o*-terphenyl was observed below 250 K to begin with an accidental emergence of crystallite; it proceeded as an enlargement of the crystalline phase with an advance of the crystal front into the liquid phase, forming a fan-shaped crystal region as the ordinary crystal growth process above 255 K proceeded.[3] While the crystalline sample appeared to be an aggregate of fine crystallites, the liquid-crystal interface was smooth in the microscopic scale of 1 μm order. Since HNB crystallization was observed as an advance of the crystal front into the liquid phase, the growth rate of the crystalline phase was evaluated from the advancement length of the front in a specified period. The rates obtained in the temperature range between 224 and 263 K are plotted in Fig. 2 together with those above 254 K reported in the literature.[16] No correlation was observed between the growth rate and the thermal history of the sample as long as the sample was treated below 250 K. The growth rate increased continuously with increasing temperature from 224 to 248 K with a peak of about 0.018 $\mu\mathrm{m\,s}^{-1}$ at around 248 K, it ceased suddenly at 250 K, and further increase in the temperature brought about the occurrence of ordinary crystal growth at a rate in good agreement with the previously reported values above 254 K.[16]

In these measurements, even if the temperature of the sample under observation was suddenly changed, continuous crystal growth was observed after the temperature jump in the temperature range below 250 K. Figures 3 and 4 show

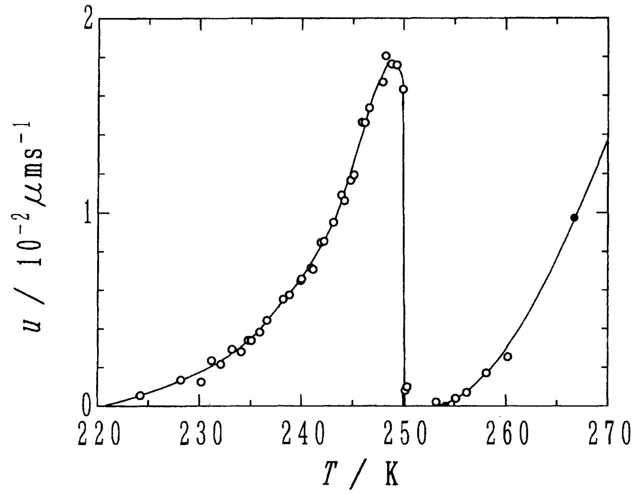

Fig. 2. Crystal growth rate vs. temperature relation in *o*-terphenyl: ○, data from the microscopic observation (our work); ●, data from literature.[16]

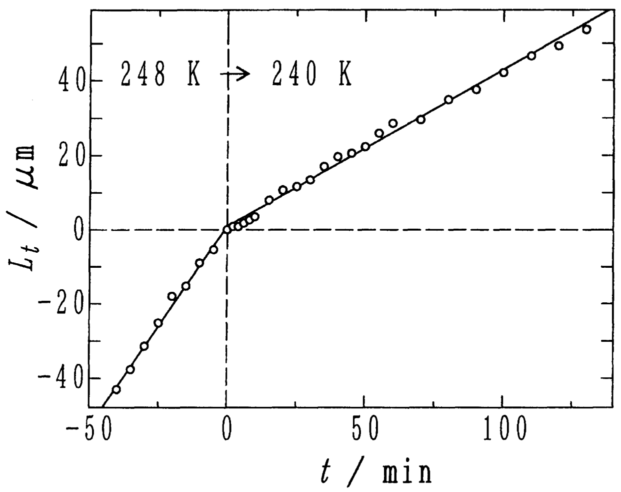

Fig. 3. Time dependence of the advance length of the crystal front in *o*-terphenyl before and after the temperature jump from 248 to 240 K. Solid straight lines represent the smooth dependences fitted to the data before and after the jump, respectively.

the time dependences of the advance length of the crystal front proceeding into the liquid phase when the temperature was jumped from 248 to 240 K and from 240 to 245 K, respectively. In the former case, the temperature started to decrease at t=0 from 248 K, and reached 240 K within 1 min; in the latter, the temperature increase was achieved within 2 min. In the both cases, the crystal front was found to advance continuously at a steady rate corresponding to the reached temperature immediately after the jump.

Discussion

Assuming a spherical form for the crystal embryo and nucleus, the Gibbs energy (ΔG_n) of an embryo containing n molecules can be expressed as

$$\Delta G_n = -nv_{\mathrm{m}}\Delta G_V + (36\pi)^{1/3} v_{\mathrm{m}}^{2/3} n^{2/3} \sigma, \tag{3}$$

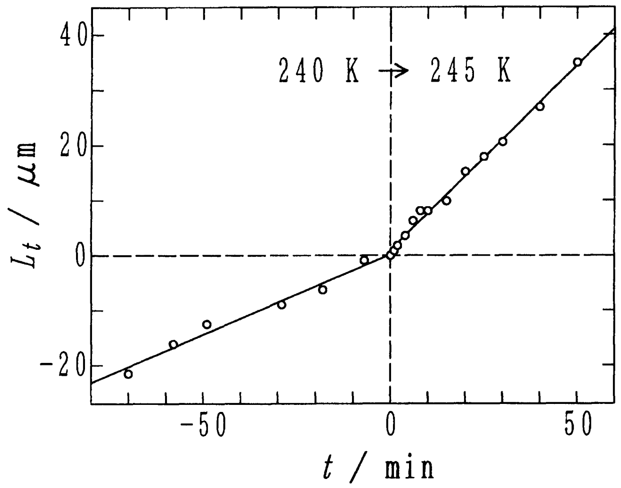

Fig. 4. Time dependence of the advance length of the crystal front in *o*-terphenyl before and after the temperature jump from 240 to 245K. Solid straight lines represent the smooth dependences fitted to the data before and after the jump, respectively.

where v_{m} is the molecular volume, ΔG_V is the difference in the Gibbs energy per unit volume between the liquid and crystalline phases, and σ is the interfacial energy per unit surface area of the embryo facing the liquid.

Embryos could be assumed to evolve in size by a series of reactions:

$$\mathrm{e}_{n-1} + \mathrm{e}_1 \underset{k_n^-}{\overset{k_{n-1}^+}{\rightleftharpoons}} \mathrm{e}_n$$

and

$$\mathrm{e}_n + \mathrm{e}_1 \underset{k_{n+1}^-}{\overset{k_n^+}{\rightleftharpoons}} \mathrm{e}_{n+1},$$

where e_n represents an embryo/nucleus containing n molecules, e_1 is a single molecule, k_n^+ is the reaction rate of taking a molecule into an embryo comprising of n molecules, and k_n^- is the rate of losing it. The time-dependent number density ($N_{n,t}$) of the embryo (e_n) is determined by solving a series of differential equations with different numbers (n) of the form

$$\frac{\mathrm{d}N_{n,t}}{\mathrm{d}t} = N_{n-1,t}k_{n-1}^+ - \left[N_{n,t}k_n^- + N_{n,t}k_n^+\right] + N_{n+1,t}k_{n+1}^-. \tag{4}$$

Figure 5 shows a schematic diagram illustrating this situation: (a) the evolving embryo/nucleus number density and the reaction for the evolution, and (b) the energy diagram illustrating the reaction. For nucleation in the liquid phase, k_n^+ and k_n^- are given by:

$$\begin{aligned} k_n^+ &= 4(n+1)^{2/3} \nu_0 \exp\left(-\frac{\Delta g_{\mathrm{a}} + \Delta g_n/2}{k_{\mathrm{B}}T}\right) \\ &= 4(n+1)^{2/3} \nu_0 \exp\left(-\frac{\Delta g_{\mathrm{a}}}{k_{\mathrm{B}}T}\right) \exp\left(-\frac{\Delta g_n}{2k_{\mathrm{B}}T}\right) \\ &= 4(n+1)^{2/3} \nu \exp\left(-\frac{\Delta g_n}{2k_{\mathrm{B}}T}\right) \end{aligned} \tag{5}$$

and

$$k_n^- = 4n^{2/3} \nu_0 \exp\left(-\frac{\Delta g_{\mathrm{a}}}{k_{\mathrm{B}}T}\right) \exp\left(\frac{\Delta g_{n-1}}{2k_{\mathrm{B}}T}\right)$$

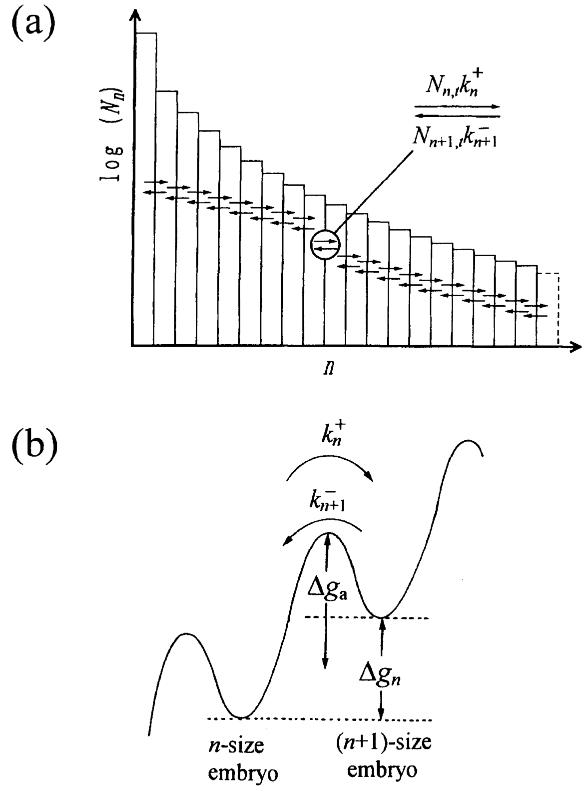

Fig. 5. Schematic diagram illustrating the situation for the evolution of embryos: (a), the evolving embryo/nucleus number density and the reaction for the evolution; (b), the energy diagram illustrating the reaction.

$$=4n^{2/3}\nu\exp\left(\frac{\Delta g_{n-1}}{2k_{\mathrm{B}}T}\right), \tag{6}$$

respectively, where $4(n+1)^{2/3}$ represents the number of molecules on the boundary of a spherical embryo containing n molecules, and ν_0 is a frequency factor; thus, ν is the frequency for a molecule on the boundary to jump across the interface onto or out of the embryo, and

$$\Delta g_n=\Delta G_{n+1}-\Delta G_n. \tag{7}$$

From Eq. 3, at any temperature below the fusing point, ΔG_n has a maximum value (ΔG^*) at some critical size,

$$n^*=\frac{32\pi}{3v_{\mathrm{m}}}\frac{\sigma^3}{\Delta G_V{}^3}. \tag{8}$$

Thus, at the critical radius of the embryo,

$$r^*=\frac{2\sigma}{\Delta G_V}; \tag{9}$$

ΔG^* is expressed by

$$\Delta G^*=\frac{16\pi\sigma^3}{3\Delta G_V{}^2}. \tag{10}$$

Embryos with n larger than n^* are the crystal nuclei, and thus the time-dependent nucleation rate ($I_{V,t}$), the growth rate in the HNB crystallization (u_t), and the advance length of the crystal front (L_t) are given by

$$I_{V,t}=N_{n^*,t}k_{n^*}^+-N_{n^*+1,t}k_{n^*+1}^-, \tag{11}$$

$$u_t\approx 8I_{V,t}(r^*)^4, \tag{12}$$

and

$$L_t=\int_0^t u_{t'}\mathrm{d}t'\approx\int_0^t 8I_{V,t'}(r^*)^4\mathrm{d}t', \tag{13}$$

respectively.

Figure 6(a) shows the size dependence of the Gibbs energy of the embryo (ΔG_n) calculated according to Eq. 3 for *o*-terphenyl at 240 and 248 K. In this calculation, the Gibbs-energy difference (ΔG_V) between the liquid and crystal was derived from precise heat-capacity data[3] and a molar volume of $V_{\mathrm{m}}=2\times10^{-4}$ m^3 mol^{-1}. An interfacial energy of $\sigma=12.6$ mJ m^{-2} was used as reported by Onorato et al.[17] Increasing temperature brought about an enlargement of both the size (n^*) and the Gibbs energy (ΔG^*) of the critical nucleus. The critical nucleus size (n^*) was determined from the calculation to be 39 and 47 at 240 and 248 K, respectively. Figure 6(b) shows the embryo number densities (N_n) in the steady state at 240 and 248 K, which were calculated according to Eq. 4 on the assumption that the number of molecules in the liquid phase is constant at $N_{1,t}=N_{\mathrm{A}}/V_{\mathrm{m}}$, where N_{A} is Avogadro's number, and with the restriction that the number density of the embryos containing more than 100 molecules is set to be zero. The above assumption is reasonable because the total number of molecules in the liquid phase is considered to be much larger than that forming embryos and nuclei, and the restriction was confirmed not to affect the embryo number density around the critical size (n^*) by comparing the results calculated in the cases with larger limiting values than 100. Figure 6(b) indicates that the embryo number density at 240 K is larger than that at 248 K as a whole, in correspondence with a smaller ΔG_n at 240 K.

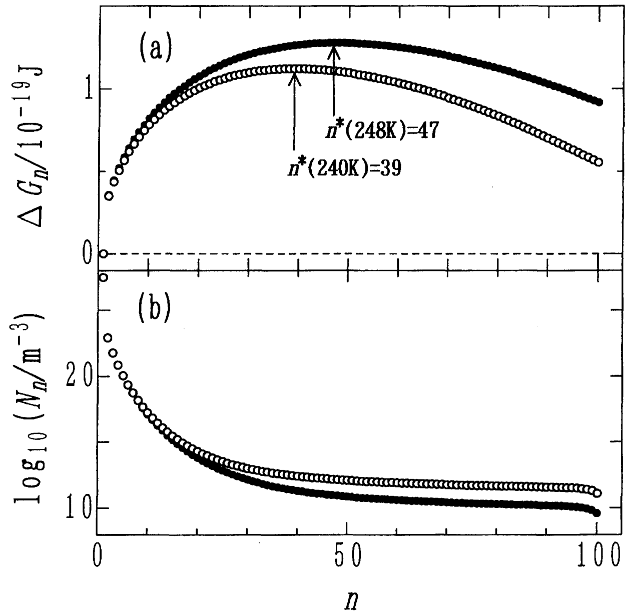

Fig. 6. Gibbs energy of a spherical crystal embryo/nucleus (a) and calculated steady-state number density of embryos/nuclei (b) in *o*-terphenyl at different temperatures: ○, at 240 K; ●, at 248 K.

Figure 7 shows the time dependence of the advance length of the crystal front (L_t) at 240 K after the temperature jump from 248 K, calculated according to Eq. 13 by using relations Eqs. 11 and 12. In this calculation, the embryo density distribution at t=0 was taken to be equal to the steady-state distribution at 248 K, and the relaxation time (τ) of 245 s at 240 K, and thus $\nu=1/(2\pi\tau)=6.5\times10^{-4}$ s^{-1}, from a.c. calorimetry[14] was used by assuming that the α-molecular rearrangement process governed the nucleation rate. From the figure, the approach to the steady growth rate definitely takes a few tens of min; namely, based on this assumption the growth rate as the advancement rate of the crystal front should exhibit a time lag after the temperature jump. Figure 8, on the other hand, shows the result simulated for the advance length after the temperature jump from 240 to 245 K using a relaxation time of 6.0 s (ν=2.6×10^{-2} s^{-1}) at 245 K by assuming the α-relaxation process. An enhancement effect, in contrast to suppression in the case of the jump from 248 to 240 K, of the advancement rate of the crystal front is found to appear for a few min immediately after the jump.

These results of the simulation are completely discrepant from those experimentally observed (see Figs. 3 and 4). Thus, there exists a possibility that the approach of the distribution of embryos to that in the steady state is governed by a β-molecular rearrangement process in the liquid; the β-relaxation times at 240 and 245 K are estimated from Fig. 1 to be 4×10^{-6} s and 3×10^{-6} s, respectively. Figures 9 and 10 show the time dependences of the advance length of the crys-

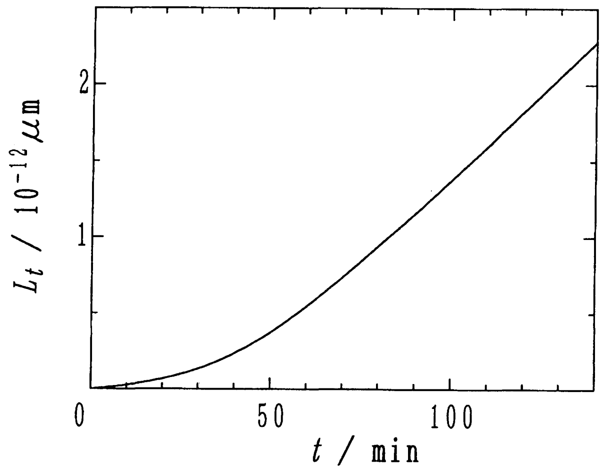

Fig. 7. Time dependence of the advance length of the crystal front in o-terphenyl calculated at 240 K after a temperature jump from 248 K with assuming the α-relaxation process to govern the growth rate of embryo/nucleus.

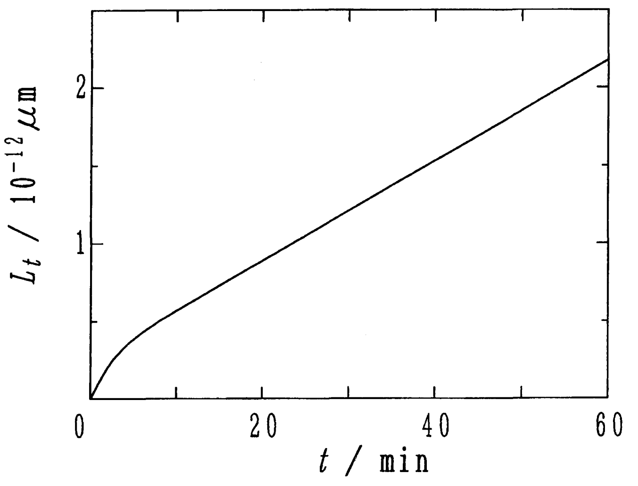

Fig. 8. Time dependence of the advance length of the crystal front in o-terphenyl calculated at 245 K after a temperature jump from 240 K with assuming the α-relaxation process to govern the growth rate of embryo/nucleus.

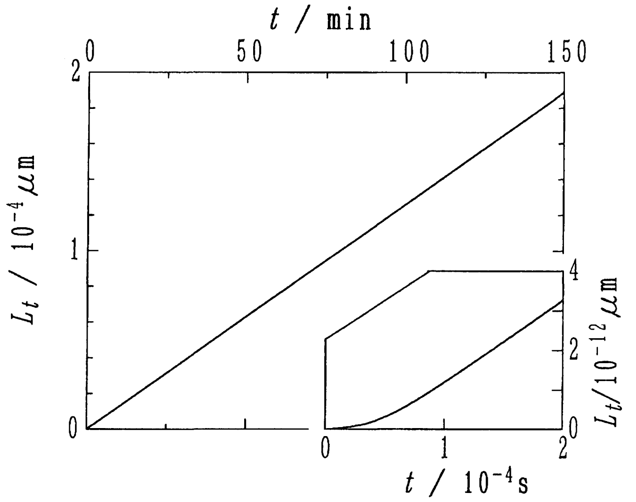

Fig. 9. Time dependence of the advance length of the crystal front in o-terphenyl calculated at 240 K after a temperature jump from 248 K with assuming the β-relaxation process to govern the growth rate of embryo/nucleus. Insert shows the dependence immediately after the jump on an enlarged scale.

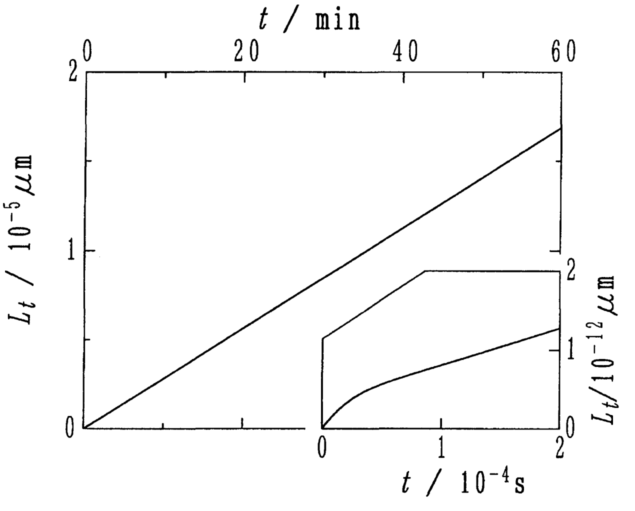

Fig. 10. Time dependence of the advance length of the crystal front in o-terphenyl calculated at 245 K after a temperature jump from 240 K with assuming the β-relaxation process to govern the growth rate of embryo/nucleus. Insert shows the dependence immediately after the jump on an enlarged scale.

tal front, calculated by using the respective frequencies (ν) corresponding to the β-process, after the temperature jumps from 248 to 240 K and from 240 to 245 K, respectively. In these cases, although the suppression or enhancement in the advancement rate of the crystal front was found as well, these effects disappeared within 10^{-4} s in both cases after the temperature jump and therefore are not observable on an experimental time scale of longer than seconds, as indicated from the figures. In view of the facts that the microscopic observation showed a continuous advancement of the crystal front at the steady rate expected at the tracking temperature just after the temperature jump, and that the β-relaxation process is considered to be associated with the motion of molecules in the gap between clusters, such as embryos, the above results strongly suggest that the β-rearrangement process, but not the α-rearrangement process, governs the homogeneous nucleation rate.

This consideration is also quite reasonable with respect to the rate of the HNB crystallization. The maximum value of the HNB crystallization in *o*-terphenyl was calculated to be ca. 10^{-12} μm s^{-1} by assuming that the α-process governed the nucleation rate, and by taking into consideration the nucleation enhancement effect on the crystal front.[3] The value is much smaller, by 10 orders of magnitude, than the experimentally observed one, ca. 10^{-2} μm s^{-1}, as mentioned above. In the HNB crystallization temperature region, the relaxation time (τ) of the β-process is shorter by 8 orders of magnitude than that of the α-process, as shown in Fig. 1; thus, taking the β-process, instead of α-process, as governing the nucleation rate causes the nucleation rate (I_V) to increase by 8 orders of magnitude through an increase in ν in Eq. 1. This increase causes an increase in the growth rate of the HNB crystallization through Eq. 2; in fact, the maximum growth rate is estimated to be ca. 10^{-4} μm s^{-1}, which comes fairly close to the experimentally observed value.

Concluding Remarks

A remarkable fact was confirmed by the present temperature-jump experiment concerning the rate of homogeneous-nucleation-based (HNB) crystallization: While it has been commonly recognized that an α-molecular rearrangement process governs the homogeneous nucleation process, in fact the β-process governs it. The β-relaxation process originates from the motion of molecules in the gap between clusters, while the α-relaxation process originates from the motion of molecules within clusters. Considering that the embryo/nucleus develops in size through a rearrangement of molecules on the boundary of embryo/nucleus, this finding is quite reasonable. In view of the fact that the crystal-growth process proceeds by taking molecules on the crystal surface into the crystalline phase in a molecule-by-molecule fashion, as well as the nucleation process, the growth process should also be governed by the β-process.

The homogeneous crystal-nucleation rate has so far been considered based on classical nucleation theory, and analyzed on the assumption that the rate is governed by the α-rearrangement process using the viscosity data of the liquid; from the analyses, especially the temperature and size dependence of the interfacial energy (σ) has been argued. However, our present result indicates that those estimations and discussions should be carefully reconsidered from the viewpoint that the homogeneous nucleation process is governed by the β-rearrangement process.

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