

## Generation and extinction of a crystal nucleus below the glass transition temperature

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 9187

(<http://iopscience.iop.org/0953-8984/9/43/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 10:51

Please note that [terms and conditions apply](#).

# Generation and extinction of a crystal nucleus below the glass transition temperature

Norimaru Okamoto<sup>†§</sup>, Masaharu Oguni<sup>†||</sup> and Yuko Sagawa<sup>‡</sup>

<sup>†</sup> Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152, Japan

<sup>‡</sup> Central Research Laboratories, Idemitsu Kosan Co., Ltd, 1280 Kami-izumi, Sodegaura, Chiba 299-02, Japan

Received 9 April 1997, in final form 13 August 1997

**Abstract.** The generation/extinction phenomenon of a crystal nucleus was studied for 4-dibenzylamino-2-methylbenzaldehyde-1,1-diphenylhydrazone by using a differential scanning calorimeter at 120–450 K. Glass transition and fusing temperatures were found to be  $T_g = 306.6$  K and  $T_{fus} = 422.2$  K, respectively, at the heating rate of  $2 \text{ K min}^{-1}$ . Bulk crystallization, observed in the range 390–400 K, was used to check whether the crystal nucleation did or did not proceed at low temperatures. The effective nucleus which had a radius larger than the critical value at 290 K was generated through annealing the sample for 1 h in the range 120–280 K or for 5 min at 170–270 K. The crystal nucleation process was thus found to proceed even at 120 K, lower by 186 K than the  $T_g$ . This is interpreted as indicating that the nucleation rate is controlled by the characteristic time of the  $\beta$ -molecular rearrangement process which could be much shorter than the annealing period. The crystal nucleus generated during the annealing at 220 K for 1 h was found to be extinguished by rapid heating to temperatures above 300 K. This is qualitatively understood from a classical theory.

## 1. Introduction

Molecules in liquid at low temperatures are expected to form structured clusters due to the prevalence of the enthalpic term in the expression of Gibbs energy. The issues of what structured cluster is formed and how the formation affects the static and kinetic aspects of microscopic and macroscopic properties should be pursued for clarification and control of the behaviours of supercooled liquid. The formation of a crystal embryo/nucleus is considered to be one of the processes to be investigated, since the embryo/nucleus is one such kind of structured cluster formed at low temperatures.

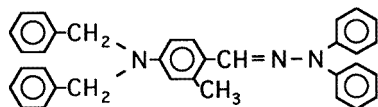
It is commonly recognized [1] that the rearrangement motions of molecules are frozen in at the glass transition temperature ( $T_g$ ). The fact that the heat capacity of glass below  $T_g$  is almost the same as that of crystal in most systems [2] is consistent with this recognition. However, we have reported that the crystal nucleation of 3,3'-dimethoxy-4,4'-bis(2,2-diphenylvinyl)biphenyl (abbreviated as DMDPVbiphenyl) proceeds even at 170 K which is lower by 175 K than  $T_g = 345$  K [3]. This means that some rearrangement motion of molecules which is indispensable for the crystal nucleation takes place at such low

<sup>§</sup> Permanent address: Central Research Laboratories, Idemitsu Kosan Co., Ltd, 1280 Kami-izumi, Sodegaura, Chiba 299-02, Japan.

<sup>||</sup> Author to whom correspondence should be addressed.

temperatures. The  $\beta$ -process of molecular rearrangement, which appears as a counterpart to the  $\alpha$ -process (relevant to the ordinary glass transition) [4], has been raised as potentially responsible for the nucleation [3,5]. If this is the case, the nucleation proceeding much below  $T_g$  should be observed in other systems as well.

In the present work, 4-dibenzylamino-2-methylbenzaldehyde-1,1-diphenylhydrazone (hereafter abbreviated as CTC191) as shown in figure 1 is taken as a candidate which might show similar crystal nucleation behaviours to those in DMDPVbiphenyl [3], and this is demonstrated to be the very case. The stability of the nucleus formed is examined as a function of temperature and time. Such a study is indispensable for the theoretical understanding of the crystal nucleation as the first step of crystallization [6,7] and of the configurational structure and rearrangement motions of molecules [8,9] in supercooled liquid.



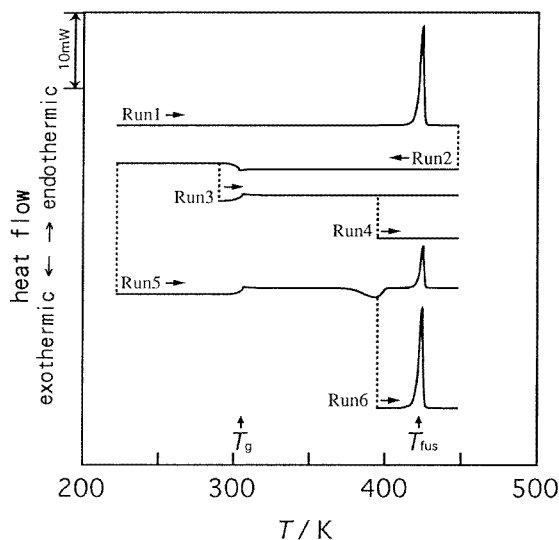
**Figure 1.** Molecular structure of 4-dibenzylamino-2-methylbenzaldehyde-1,1-diphenylhydrazone (abbreviated as CTC191).

## 2. Experiment

CTC191 was used as purchased from Anan Co., Ltd, and the crystallization behaviour was examined by using a Perkin–Elmer differential scanning calorimeter (DSC) type 7. Nearly 10 mg of sample was loaded into an aluminium calorimeter pan. After each heating run for measurement of crystallization and fusion, the calorimeter pan with sample was changed for a new one for fear of potential decomposition of the sample during the measurement at high temperatures. Liquid nitrogen was used as a coolant and the measurements were carried out in the temperature range of 120–450 K. The purity of the sample was estimated from the analysis of fractional melting [10] to be 0.995.

## 3. Results

Figure 2 shows the heating/cooling curves of DSC obtained. The heating/cooling rates were taken to be  $2 \text{ K min}^{-1}$ . Fusion of the crystal sample was observed at  $T_{\text{fus}} = 422.2 \text{ K}$  as shown in runs 1, 5 and 6. Run 3, taken on heating from 290 K in the process of cooling run 2, showed no crystallization and fusion phenomena but only the glass transition at  $T_g = 306.6 \text{ K}$ . Even in run 4, taken after annealing for 30 min at 398 K part way through heating run 3, no sign of fusion was found. Run 5, on the other hand, heated from 220 K showed crystallization at around 390 K and fusion at 422.2 K. The effect of the fusion was, however, considerably smaller than that in run 1. Run 6 was thus taken after annealing for 30 min at the peak temperature, 398 K, of crystallization in run 5, and it showed a large peak, comparable with that in run 1, of fusion. The above results mean that the rate of crystal growth at around 398 K is rather slow so that the crystallization cannot be completed on heating the sample at  $2 \text{ K min}^{-1}$ , and also that the crystal nucleation proceeds potentially much below the  $T_g$ . Hereafter in all the heating runs the samples are annealed for 30 min at 398 K, prior to the measurements of fusion, to enhance the crystal growth if it occurs.

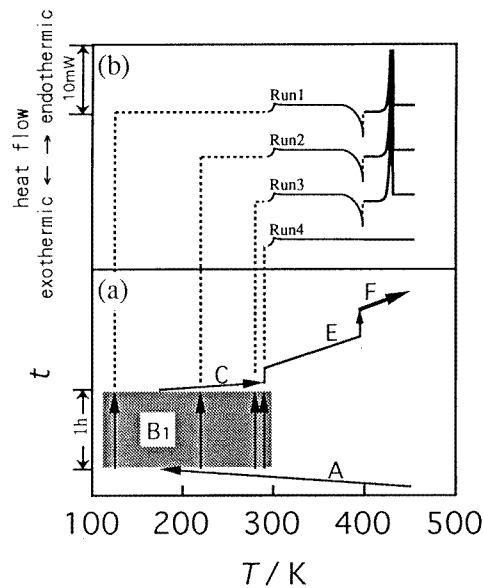


**Figure 2.** DSC curves obtained at the heating/cooling rate of  $2 \text{ K min}^{-1}$  for CTC191. Run 6 was taken after annealing for 30 min at the peak temperature, 398 K, of crystallization in run 5. Baseline shifts at 306.6 K, sharp endothermic peaks at 422.2 K, and an exothermic peak at 390–400 K are attributed to glass transition, fusion, and bulk crystallization of supercooled liquid, respectively.

Such crystallization and fusion phenomena were not observed to occur in every experiment even though the thermal treatment adapted in advance was expected to induce the crystal nucleation: this means that the nucleation starts rather accidentally and the event should be considered to be probabilistic. Hereafter, the phenomena will be stated to occur if they are observed to occur at a probability over 80%. When the phenomena are stated not to occur, however, it is meant that they have been never observed to occur for the samples.

Figure 3(b) shows DSC curves obtained at the heating rate of  $2 \text{ K min}^{-1}$  for the samples annealed for 1 h at some different temperatures below 290 K. The detailed thermal treatments of the samples are shown in figure 3(a): the liquid samples were cooled in process A rapidly at  $200 \text{ K min}^{-1}$  from 450 K above the fusing temperature to desired annealing temperatures, kept there for 1 h in process B<sub>1</sub> and then heated up to 290 K at the rate of  $200 \text{ K min}^{-1}$  in process C. The annealing temperatures were taken to be 120 K, 220 K, 280 K, and 290 K for runs 1–4, respectively. Then the DSC measurement was carried out in the temperature range 290–398 K at the heating rate of  $2 \text{ K min}^{-1}$  in process E, the sample was annealed at 398 K for 30 min, and the DSC measurement was carried out again in the range 398–450 K at  $2 \text{ K min}^{-1}$  in process F. Crystallization was observed for the former three samples annealed below 280 K, but not for the last sample annealed at 290 K; in fact, even if the annealing at 290 K was adapted for 24 h, no crystallization was observed. This indicates that the crystal nucleation process proceeds in a certain temperature range only below the  $T_g$  as found in DMDPVbiphenyl.

Figure 4 shows the results of similar DSC experiments with the annealing period of 5 min instead of 1 h in figure 3. Runs 1–5 in figure 4(b) are DSC curves obtained in processes E and F above 290 K at the heating rate of  $2 \text{ K min}^{-1}$  for the samples annealed at 120 K, 170 K, 180 K, 270 K, and 280 K, respectively, in advance in process B<sub>2</sub> in figure 4(a). Processes A, C, E, and F are the same as in figure 3(a). Crystallization and fusion were observed to take



**Figure 3.** A scheme of thermal treatments (a) and DSC curves of the CTC191 samples annealed for 1 h at different low temperatures (b): process A, rapid cooling at  $200 \text{ K min}^{-1}$  from 450 K in the equilibrium liquid state to each specified annealing temperature below 290 K; B<sub>1</sub>, 1 h annealing for enhancement of crystal nucleation; C, rapid heating at  $200 \text{ K min}^{-1}$  from the annealing temperature to 290 K; E and F, DSC measurements at the heating rate of  $2 \text{ K min}^{-1}$  from 290 K. The samples were annealed for 30 min at 398 K between the processes E and F.

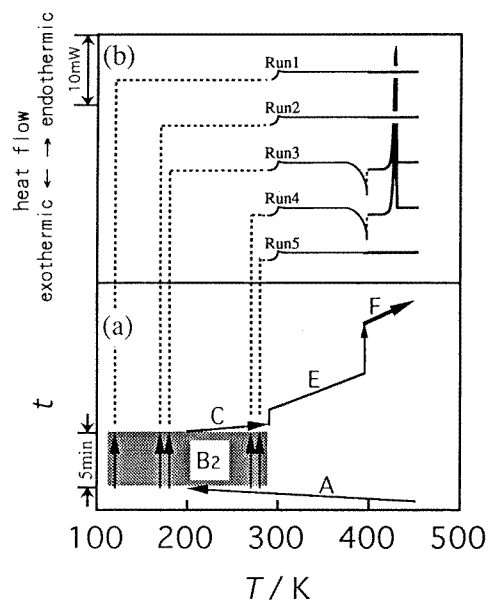
place only for the samples annealed in the range between 180 K and 270 K. The temperature range, in which the annealing caused a crystal nucleation effectively followed by a bulk crystallization, became narrower especially on the low-temperature side than in the case shown in figure 3. The fact that no crystallization and fusion phenomena were observed for the sample annealed at 120 K means not only that a large enough crystal nucleus was not generated in the course of the annealing at 120 K but also that no crystal nucleation process proceeded during the process C of rapid heating from each annealing temperature to 290 K.

In figure 5, the temperature at which the DSC measurement (process E) was started was changed. The samples were cooled rapidly at  $200 \text{ K min}^{-1}$  from 450 K to 220 K in process A, annealed there for 1 h in process B<sub>3</sub>, then heated at  $200 \text{ K min}^{-1}$  up to 290 K, 300 K, and 320 K respectively in process C, and, after being left for 2 min in process D, reheated for the DSC measurements of runs 1, 2, and 3 respectively at the rate of  $2 \text{ K min}^{-1}$  in processes E and F. Run 1 showed crystallization and fusion, but runs 2 and 3 did not. This means that some crystal nuclei were formed during annealing at 220 K as shown also in figure 3, but extinguished through heating rapidly to 300 K.

## 4. Discussion

### 4.1. Crystal nucleation proceeding much below the $\alpha$ -glass transition temperature

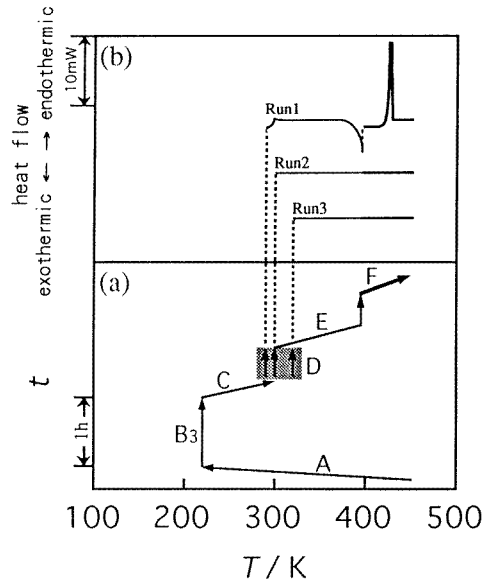
Figure 6 shows the annealing temperature–time region of crystal nucleation leading effectively to the bulk crystallization; the time as an ordinate axis is the period of



**Figure 4.** A scheme of thermal treatments (a) and DSC curves of the CTC191 samples annealed for 5 min at different low temperatures (b). The treatments are essentially the same as in figure 3, but the period of the annealing process B<sub>2</sub> taken below 290 K is 5 min instead of 1 h in figure 3.

annealing the sample, and the abscissa is the temperature of the annealing. There the DSC measurement starting at 290 K at the heating rate of  $2 \text{ K min}^{-1}$  was utilized to determine whether the crystal growth and fusion did or did not occur based on the presence or absence, respectively, of crystal nuclei at the starting temperature of 290 K, as described above. Some nuclei large enough for the crystals to grow during heating above 290 K are potentially generated when the sample has been annealed for 1 h at any temperature in between 120 K and 160 K, while they cannot be when the sample has been annealed only for 5 min there. Similarly, the nuclei can be generated by annealing the sample at 280 K for 1 h, but not by annealing it for 5 min. By annealing the sample above 290 K even for 24 h, the effective crystal nucleation does not proceed. When the annealing is adapted at temperatures in between 170 K and 270 K even for 5 min, some nuclei large enough for the crystals to grow above 290 K are potentially generated.

The most fascinating fact is that, while the glass transition takes place at  $T_g = 306.6 \text{ K}$ , the crystal nucleation process proceeds even at 120 K which is lower by 186 K than the  $T_g$ . The rearrangement motion of molecules which causes a crystal nucleation would be of a rather large scale leading to change in the position and/or orientation of the whole molecule and therefore of a scale similar to the  $\alpha$ -rearrangement motion connected to the glass transition. Thus the recognition common so far [1, 11] that the rearrangement motions of molecules are frozen in at  $T_g$  is not correct, and the phenomenon that the crystal nucleation takes place much below  $T_g$  is concluded to be observed not merely in DMDPVbiphenyl [3] but commonly at least in other organic compounds.



**Figure 5.** A scheme of thermal treatments (a) and DSC curves with different starting temperatures of measurement (b): process A, rapid cooling at  $200 \text{ K min}^{-1}$  from 450 K in the equilibrium liquid state to 220 K; B<sub>3</sub>, 1 h annealing for enhancement of crystal nucleation; C, rapid heating at  $200 \text{ K min}^{-1}$  from 220 K to 290 K, 300 K, and 320 K for DSC runs 1, 2, and 3 respectively in (b); D, 2 min stabilization of instrument before DSC measurements; E and F, DSC measurements at the heating rate of  $2 \text{ K min}^{-1}$ . The samples were annealed for 30 min at 398 K between the processes E and F.

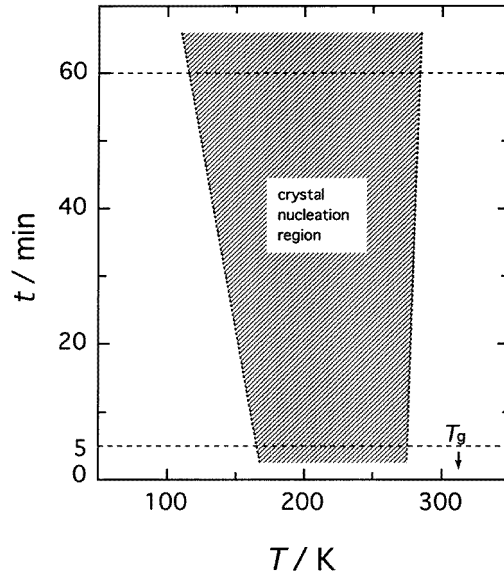
#### 4.2. Understanding of the generation and extinction of crystal nucleus on the basis of the Gibbs energy for formation of the nucleus

Below the fusion temperature, crystals are more stable than liquids, but the generation of a crystal embryo/nucleus and its growth to a large crystalline particle are not straightforward. The crystalline aggregate of molecules becomes more stable than the liquid only in the situation where the molecular interaction in the long range contributes effectively to the Gibbs energy of the aggregate; the short-range interaction sometimes favours the liquid aggregate more than the crystalline one. The Gibbs energy for formation of the crystal nucleus is classically expressed by the following equation assuming a spherical form for the crystal embryo/nucleus [6, 12]:

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma \quad (1)$$

where  $r$  is the radius of the embryo/nucleus,  $\Delta G_v (= G_v(\text{liq}) - G_v(\text{cryst}))$  is the difference in the Gibbs energy between liquid and crystalline phases per unit volume, and  $\sigma$  is the interfacial energy per area of the embryo facing the liquid. The  $\Delta G$  has the maximum value ( $\Delta G^*$ ) at some critical radius ( $r^*$ ); according to the critical condition of  $d\Delta G/dr = 0$  at  $r = r^*$ ,

$$r^* = \frac{2\sigma}{\Delta G_v} \quad (2)$$



**Figure 6.** The annealing temperature–time region in which some nuclei large enough for the crystals to grow during heating at  $2 \text{ K min}^{-1}$  above  $290 \text{ K}$  are generated for CTC191:  $T_g$ , ordinary glass transition temperature. The crystal nucleation process is concluded to proceed even at  $120 \text{ K}$ , which is lower by  $186 \text{ K}$  than the  $T_g$ .

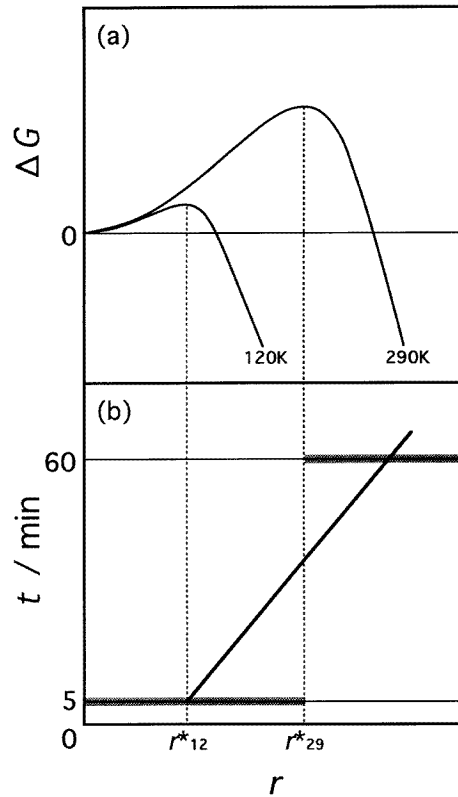
and

$$\Delta G^* = \frac{16\pi\sigma^3}{3\Delta G_v^2}. \quad (3)$$

Assuming that the  $\sigma$  is constant, both the  $r^*$  and  $\Delta G^*$  increase with increasing temperature since  $\Delta G_v$  becomes small with increasing temperature reaching a value of zero at  $T_{\text{fus}}$ . The Gibbs energy curves are schematically drawn in figure 7(a) as functions of radius ( $r$ ) of the embryo/nucleus, where  $r_{12}^*$  and  $r_{29}^*$  denote the critical sizes of nucleus at  $120 \text{ K}$  and  $290 \text{ K}$ , respectively. When the liquid is kept at  $120 \text{ K}$  after cooling down at  $t = 0$  rapidly from  $450 \text{ K}$ , the crystal embryo/nucleus grows with time. A straight line in figure 7(b) represents the expected time dependence (as a trend) of the radius of embryo/nucleus generated at  $120 \text{ K}$ . In view of the fact that no crystal nucleation occurs in the course of annealing even for  $24 \text{ h}$  at  $290 \text{ K}$  and of the subsequent heating at  $2 \text{ K min}^{-1}$  above  $290 \text{ K}$ , it is concluded that the annealing for  $60 \text{ min}$  at  $120 \text{ K}$  induces crystal nuclei with radii larger than  $r_{29}^*$  but that the annealing for  $5 \text{ min}$  does not. It is not clear whether the annealing for  $5 \text{ min}$  has or has not induced nuclei with radii larger than  $r_{12}^*$ .

A dotted line and a solid line in figure 8(b) represent schematically the time dependence of the radius of embryo/nucleus generated when the liquid was annealed at  $270 \text{ K}$  and  $280 \text{ K}$ , respectively. When the liquid was annealed at  $290 \text{ K}$  even for  $24 \text{ h}$ , no nucleation was caused: this means that the generation of a nucleus with radius larger than  $r_{29}^*$  takes a much longer time than  $24 \text{ h}$  and the frequency of generation is negligibly small. Nucleation was observed in the course of annealing at  $270 \text{ K}$  for even  $5 \text{ min}$ : this means that the nucleus developed during annealing for  $5 \text{ min}$  at  $270 \text{ K}$  already has a radius larger than  $r_{29}^*$ . In the meantime, the annealing for  $60 \text{ min}$  and  $5 \text{ min}$  at  $280 \text{ K}$  did and did not cause, respectively, successful nucleation, as shown in figures 3 and 4: this means that the radius



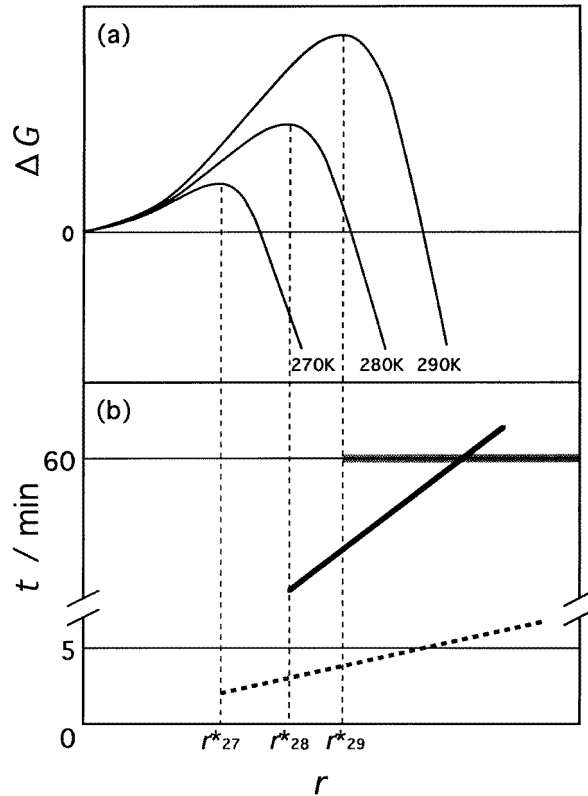


**Figure 7.** The Gibbs energy for formation of the crystal embryo/nucleus of a spherical form with its radius ( $r$ ) (a) and the expected time dependence of the radius during the annealing at 120 K (b). The annealing period of 1 h is long enough for the crystalline aggregate to be generated with the radius larger than critical radius ( $r_{29}^*$ ) at 290 K but that of 5 min is too short. It is not clear whether the crystalline aggregate larger than  $r_{12}^*$  is or is not generated during the annealing for 5 min.

of crystal nucleus generated by the annealing for 60 min at 280 K is larger than  $r_{29}^*$  but that the radius generated by the annealing for 5 min is smaller.

Figure 9(b) shows schematically the time dependence, found experimentally in figure 5, of the radius of embryo/nucleus in the course of annealing at 220 K: the radius of crystal embryo/nucleus at 220 K reaches the critical value  $r_{22}^*$  at  $t_{22}^*$ , becomes larger than  $r_{29}^*$  at 1 h, but is still smaller at 1 h than  $r_{30}^*$  as well as  $r_{32}^*$ . The crystal nucleus generated by the annealing at 220 K for 1 h thus disappears above 300 K, while the nucleus survives at 290 K as it was at 220 K.

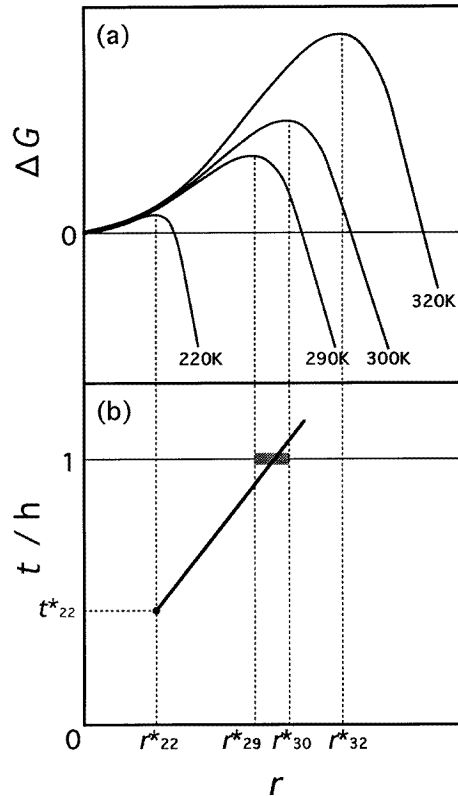
All the present results are thus understood qualitatively within the classical picture [6, 12] for the formation of the crystal nucleus. Whether the Gibbs energy ( $\Delta G$ ) for the formation of crystal nucleus is or is not expressed strictly by equation (1) is not clear at the present, but the  $\Delta G$  as a function of the radius ( $r$ ) of the nucleus would show essentially the same dependence as given in figures 7–9: the critical radius ( $r^*$ ) certainly increases with increasing temperature, and the crystal embryo/nucleus with a radius smaller than the  $r^*$  disappears with time elapse. Temperature dependence of the  $r^*$  and the incubation time ( $t^*$ ) is attractive and desired to clarify the crystallization process further.



**Figure 8.** The Gibbs energy for formation of the crystal embryo/nucleus of a spherical form with its radius ( $r$ ) (a) and the expected time dependence of the radius during the annealing at 270 K, 280 K and 290 K (b); dashed line, the dependence at 270 K; thick solid line, the dependence at 280 K. The annealing at 290 K, even if it had been adapted for 24 h, caused no generation of crystalline aggregate with radius larger than  $r_{29}^*$ .

#### 4.3. Rate-determining process of crystallization

The crystal nucleation process was found above to proceed even much below the ordinary glass transition temperature ( $T_{g\alpha}$ ). This phenomenon cannot be elucidated by the common recognition of the rate-determining process of crystallization [1, 11]; both the crystal nucleation and the crystal growth rates are interpreted to be correlated with viscosity, i.e. the relaxation time of the  $\alpha$ -process, of the liquid, and then the relaxation time at 120 K in the present substance is too long for the nucleation process to be observed. The present observation would be understood reasonably from the picture proposed recently: the 'cluster structure model' for the structure of supercooled liquids [4, 13] and the 'intra-cluster rearrangement model' for the  $\alpha$ -process [9, 14]. Some structured clusters of molecules are formed at low temperatures and develop with decreasing temperature, as illustrated in figure 10 where the left portion represents the situation at lower temperature than the right portion. Then the  $\alpha$ - and  $\beta$ -rearrangement processes of molecules should appear as a set: the  $\alpha$ -process is assigned as the rearrangement motion of molecules within the cluster and is frozen in at  $T_{g\alpha}$ . The  $\beta$ -process is, on the other hand, assigned as the rearrangement motion of molecules in the gap between the clusters and is frozen in at the  $\beta$ -glass transition

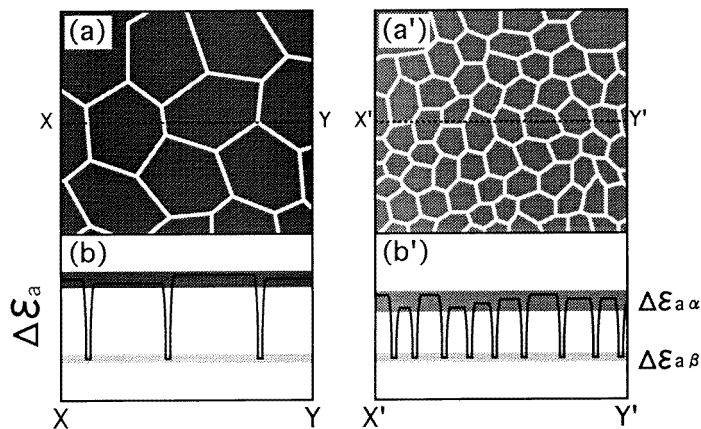


**Figure 9.** The Gibbs energy for formation of the crystal embryo/nucleus of a spherical form with its radius ( $r$ ) (a) and the expected time dependence of the radius during the annealing at 220 K (b).

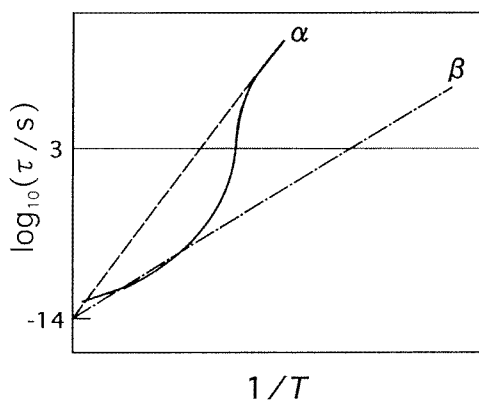
temperature ( $T_{g\beta}$ ). The relaxation times for the two processes are expressed commonly as an Arrhenius equation,

$$\tau = \tau_0 \exp\left(\frac{\Delta\varepsilon_a}{kT}\right) \quad (4)$$

where  $\tau_0$  is constant, being around  $10^{-14}$  s [4]. The relaxation time at some temperature is thus determined essentially by the activation energy ( $\Delta\varepsilon_a$ ), and the activation energy ( $\Delta\varepsilon_{a\alpha}$ ) for the  $\alpha$ -process increases with increase in the cluster size and in the degree of ordering of molecules within the cluster at lower temperatures as shown in figure 10 [9]. The temperature dependence of relaxation times for the two processes is thus schematically given as depicted in figure 11 [9]; the relaxation time for the  $\beta$ -process is generally much shorter below the  $\alpha$ -glass transition temperature ( $T_{g\alpha}$ ) than that for the  $\alpha$ -process, since the activation energy ( $\Delta\varepsilon_{a\beta}$ ) for the  $\beta$ -process is mostly constant and smaller than  $\Delta\varepsilon_{a\alpha}$ . The crystal embryo/nucleus can be recognized as a kind of structured cluster, and the growth of the embryo to a nucleus and of the nucleus to a large crystalline particle is caused by the rearrangement of molecules on the boundary of the embryo and nucleus. Then considering that the relaxation time of  $\beta$ -rearrangement process, which is short enough even much below the  $T_{g\alpha}$  in comparison with the experimental time scale of minutes, determines the rate of crystal nucleation, it is well explained that the crystal nucleation may proceed at



**Figure 10.** Cluster structure of supercooled liquid (a and a') and the activation energy for the rearrangement motion of molecules (b and b') along the segments XY and X'Y' in (a) and (a') respectively:  $\Delta \epsilon_{a\alpha}$ , the activation energy for the  $\alpha$ -rearrangement motion of molecules within structurally correlated region (cluster);  $\Delta \epsilon_{a\beta}$ , the activation energy for the  $\beta$ -rearrangement motion of molecules in the gap between the clusters. The left portion (a and b) shows the situation at lower temperature than the right portion (a' and b'). The degree of ordering of molecules is shown by the darkness of the cluster region, and the  $\Delta \epsilon_{a\alpha}$  increases with increasing degree of ordering. A crystal embryo/nucleus can be recognized as a kind of structured cluster.



**Figure 11.** Schematic temperature dependence of the relaxation times for the  $\alpha$ - and  $\beta$ -molecular rearrangement processes: solid line, the dependence for the  $\alpha$ -process; dot and broken line, the dependence for the  $\beta$ -process; broken line, the dependence expected for the ideal glass [9].

low temperatures below the  $T_{g\alpha}$  but above the  $T_{g\beta}$ . In view of the fact that the structured cluster tends to be formed as the temperature is lowered, the nucleation phenomenon would be observed rather at such low temperatures. Where the  $T_{g\beta}$  is located for the compound CTC191 has not been determined yet. The determination is desired for investigating whether the present results can really be understood by the above picture or not.

## 5. Conclusion

Crystal nucleation proceeding at the temperatures much below the  $\alpha$ -glass transition temperature ( $T_{g\alpha}$ ) was found in the organic compound CTC191 in addition to DMDPVbiphenyl [3]: the lowest temperature found is 120 K, lower by 186 K than the  $T_{g\alpha}$ . This strongly indicates that the molecular rearrangement motion which controls the rate of nucleation is the  $\beta$ -process and not the  $\alpha$ -process commonly recognized [1, 11] so far. Considering that the crystal nucleation is recognized as formation of a kind of structurally correlated region (cluster) in supercooled liquid, the result also indicates that the growth rate of a cluster is controlled by the characteristic time of the rearrangement motion of molecules in the gap between clusters and thus supports the picture proposed before [9, 14]: 'cluster structure model' for the structure of supercooled liquid and 'intra-cluster rearrangement model' for the  $\alpha$ -process. In order to develop further the understanding of the nucleation process and to control the crystallization rate through designing the structure of glass and supercooled liquid, it is indispensable to determine the radius ( $r^*$ ) of critical nucleus and the incubation time ( $t^*$ ) quantitatively as functions of temperature in future. The present study opened a possibility to work on the subject below  $T_{g\alpha}$  completely separately from the process of crystal growth.

## References

- [1] Uhlmann D R 1969 *Materials Science Research* vol 4 (New York: Plenum)
- [2] Suga H and Seki S 1974 *J. Non-Cryst. Solids* **16** 171  
Suga H and Seki S 1980 *Faraday Discuss.* **69** 221
- [3] Okamoto N and Oguni M 1996 *Solid State Commun.* **99** 53
- [4] Fujimori H and Oguni M 1995 *Solid State Commun.* **94** 157
- [5] Hikima T, Hanaya M and Oguni M 1996 *Bull. Chem. Soc. Japan* **69** 1863
- [6] Rao C N R and Rao K J 1978 *Phase Transitions in Solids* (New York: McGraw-Hill)
- [7] Owen A E 1985 *Amorphous Solids and the Liquid State* (New York: Plenum)
- [8] Ngai K L, Riande E and Wright G B (ed) 1994 *Proc. 2nd Int. Discuss. Meeting on Relaxations in Complex Systems (Alicante, 1993)* *J. Non-Cryst. Solids* **172-174**
- [9] Oguni M 1997 *J. Non-Cryst. Solids* **210** 171
- [10] Tunnicliff D D and Stone H 1955 *Anal. Chem.* **27** 73
- [11] Gutzow I and Dobreva A 1996 *Ber. Bunsenges. Phys. Chem.* **100** 1415
- [12] Volmer W and Weber A 1926 *Z Phys. Chem.* **119** 277
- [13] Fujimori H, Fujita H and Oguni M 1995 *Bull. Chem. Soc. Japan* **68** 447  
Mizukami M, Fujimori H and Oguni M 1995 *J. Phys.: Condens. Matter* **7** 6747
- [14] Oguni M 1996 *Kobunshi Ronbunshu (Japan. J. Polym. Sci. Technol.)* **53** 636