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Anomalous generation and extinction of crystal nuclei in nonequilibrium supercooled liquid *o*-benzylphenol

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Crystal-nucleation phenomena of supercooled liquid *o*-benzylphenol are studied by differential scanning calorimetry (DSC). While crystallization proceeds with crystal nucleation and growth processes, only the latter process can be observed calorimetrically. Whether there exist crystal nuclei in the supercooled liquid or not was therefore judged by whether crystal growth does or does not proceed in the course of subsequent DSC measurement. The liquid sample was cooled rapidly at 200 K min^{-1} from above fusion temperature down to each desired aging temperature (T_a) below the α-glass transition temperature ($T_{g\alpha}=223$ K), and annealed there for different periods (t_a) for enhancement of crystal nucleation, if any. The sample was then heated at 200 K min^{-1} up to 213 K a little below $T_{g\alpha}$, and measured at 10 K min^{-1} to examine if the crystallization/fusion behaviors appear. It was discovered that (1) crystal nuclei are generated and increased in the number during the aging at 143 K$\leqslant T_a \leqslant$213 K; (2) they are generated immediately after the rapid cooling, then extinguished and again generated at 128 K$\leqslant T_a \leqslant$133 K; and (3) they are generated and decreased in the number but some survive at $T_a \leqslant$123 K. The generation and extinction of the crystal nuclei in a nonequilibrium state much below the $T_{g\alpha}$ are discussed based on the ordered-clusters aggregation model for a supercooled-liquid structure.

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I. INTRODUCTION

Gas, liquid, and crystal are three typical states of molecular aggregation. In the gaseous state, molecules are arranged randomly with respect to their positions and orientations. Liquid can be formed through a continuous change of state from gas by going around the liquid-gas critical point, and it is macroscopically isotropic and fluid without any long-range order in the molecular arrangement.[1] Crystal, in principle, has an ordered arrangement with respect to both positions and orientations of molecules in the long range. The arrangement of molecules is, accordingly, quite different between a liquid and a crystal. Crystallization from liquid, therefore, needs to begin with the generation of a crystal embryo/nucleus as the formation of a small region within which the molecules are arranged in the same ordered manner as in the crystal. Crystal nucleation as a microscopic process should occur through a fluctuation of the liquid structure, and is followed by crystal growth as a macroscopic crystallization process.[2,3]

We have found, in the α-glass transition regions of *o*-terphenyl,[4,5] triphenylethylene,[6] and salol,[7] a strange crystal-growth process which is separate in the temperature range from the ordinary growth process taking place in the middle between $T_{g\alpha}$ and fusion temperature (T_{fus}). The crystals formed in the two processes were the same in structure. This new growth process has been interpreted as follows: The crystal embryos, being a kind of structured clusters, are generated and extinguished ubiquitously in supercooled liquid, but the embryos, generated right above the crystalline surface and possessing the same orientation as the crystal, coalesce into the crystal and are stabilized as a process of crystal growth. This process was accordingly called homogeneous-nucleation-based crystallization.[4–7] The fact that this crystal-growth process was found in more than one substance implies the universal occurrence of generation and extinction phenomena of crystal embryos.

The stability of a crystal embryo/nucleus is ordinarily measured in reference to the Gibbs energy of real liquid.[8,9] If this is the case, the following situation can be imagined. Assume that the liquid sample is brought to an extremely nonequilibrium state, for example, by rapid cooling. The Gibbs energy of the liquid is much larger than the equilibrium value, and therefore certain ordered-structural regions such as a crystal nucleus tend to be generated as one of more stable states than liquid state. The liquid structure then relaxes toward an equilibrium structure with time. The Gibbs energy of the liquid accordingly decreases upon approaching the equilibrium value, and the crystal nucleus becomes comparatively unstable and is potentially extinguished with time. The potential occurrence of such a generation/extinction phenomenon of a crystal nucleus can also be imagined from the view that a supercooled liquid is composed of fluctuating structured clusters, since the crystal embryo and nucleus can be recognized as representatives of the clusters. If this phenomenon is found experimentally, it would provide, in some sense, evidence supporting a picture[10,11] of the cluster structure for supercooled liquid in an exaggerated way.

A crystal nucleus is considered to be composed of 10^2-10^3 molecules. Therefore, while the nucleus is large enough to be recognized as a structured cluster in liquid, the nucleation phenomenon is rather difficult to observe by techniques usually used for phase changes of bulk material composed of $\sim 10^{23}$ molecules. On the other hand, the crystal growth process can be observed macroscopically, for ex-

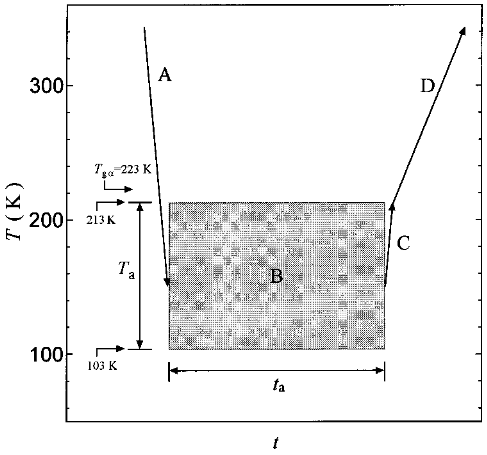

FIG. 1. Scheme of procedures taken in the present differential scanning calorimetry (DSC): *A*, rapid cooling at 200 K min^{-1} from 343 K to each specified aging temperature (T_a); B, aging at T_a; C, rapid heating at 200 K min^{-1} from T_a to 213 K; D, DSC heating measurement above 213 K at 10 K min^{-1}; t_a, aging period at T_a.

ample, by differential scanning calorimetry (DSC). However, no growth proceeds without a crystal nucleus. Therefore, the presence or absence of crystal nuclei within a supercooled liquid can be judged by whether the growth process can be observed or not.[12,13] In the present work, by making a contrivance for thermal treatment in the DSC, we examine how processes of the nonappearance, generation, extinction, or reappearance of crystal nuclei proceed during the course of aging at constant temperature after a rapid cooling.

II. EXPERIMENT

o-Benzylphenol $[C_6H_4(OH)CH_2C_6H_5]$, purchased from Tokyo Chemical Industry Co., Ltd., was purified by recrystallization from an aqueous solution and sublimation at 320 K under reduced pressure. The obtained sample was kept within a desiccator in coexistence with a dry silica gel. The sample was repurified by sublimation every half a month for fear of any vitiation. A Perkin-Elmer DSC-7 instrument was used, and 8–10 mg of the purified sample was loaded in each aluminum DSC pan. The thermal treatments taken are shown in Fig. 1: The initial, melt sample was obtained by heating the loaded crystalline sample at 200 K min^{-1} from room temperature up to 343 K, which is above the fusion temperature (325 K) of the stable crystalline phase, and by holding there for 2 min. The melt sample was cooled in process *A* rapidly at 200 K min^{-1} down to each specified aging temperature (T_a) which is below the α-glass transition temperature ($T_{g\alpha}=223$ K), held there for each desired period (t_a) in process *B*, and then heated up to 213 K (a little below $T_{g\alpha}$) at a rate of 200 K min^{-1} in process *C*. The aging temperatures were taken to be $T_a=103$, 123, 128, 133, 143, 153, 173, 193, and 213 K, and the aging periods (t_a) to be in a range from 30 s to 316 min. The DSC measurement was carried out in the temperature range 213–343 K at a heating rate of 10 K min^{-1} in process *D*.

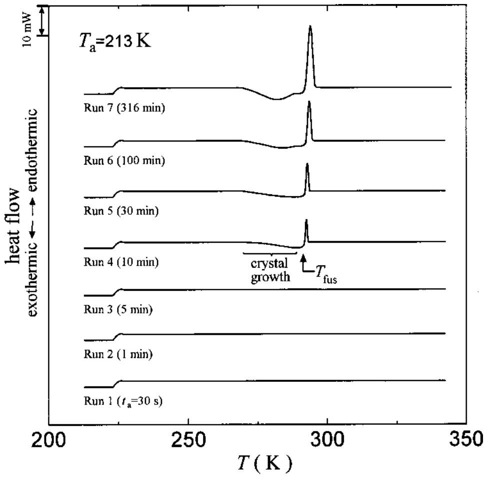

FIG. 2. DSC curves of the *o*-benzylphenol samples aged for different periods at $T_a=213$ K. The aging period (t_a) is given, as parenthesized, after run number of DSC measurement.

Whether crystal nuclei do or do not exist at the start of DSC measurements is judged from whether crystal growth and fusion phenomena are detected or not, respectively, on the DSC chart as described below. After each heating run of measurement in process *D*, the calorimeter pan was renewed for fear of potential decomposition of the sample during the measurement of one cooling/heating cycle. Such experiments were repeated more than five times at each set of aging temperature and period.

III. RESULTS

A. Differential scanning calorimetry

Figures 2, 3, and 4 show some typical results obtained for samples subjected to aging at $T_a=213$, 128, and 103 K, respectively. Runs 1–3 with the aging periods less than 5 min in Fig. 2 exhibit nothing but a glass transition taking place at $T_{g\alpha}=223$ K. This indicates that essentially no crystal nucleus is generated during the cooling from 343 to 213 K and the aging within 5 min at 213 K. Runs 4–7, with

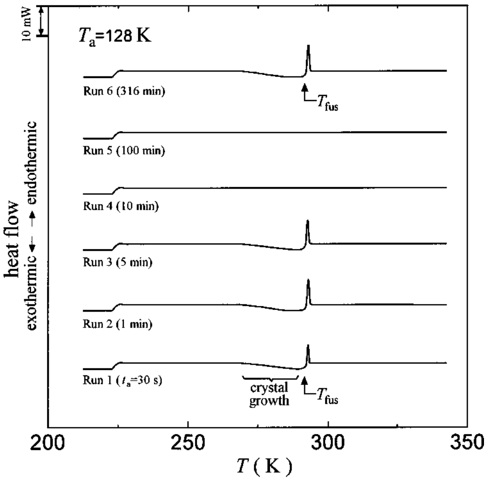

FIG. 3. DSC curves of the samples aged at $T_a=128$ K.

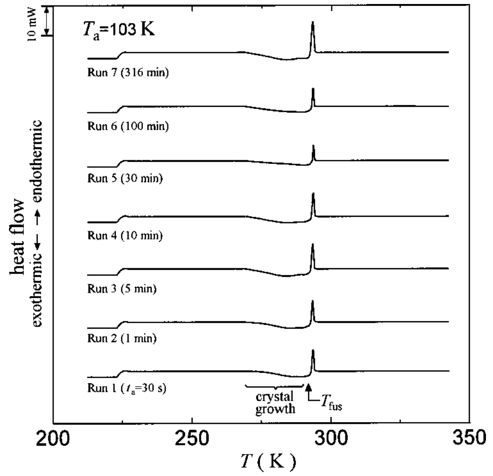

FIG. 4. Some DSC curves of the samples aged at $T_a = 103$ K. The fusion of the metastable crystalline phase appeared in all the samples.

$t_a = 10-316$ min, show a crystal growth proceeding around $T_{\mathrm{cryst}} = 280$ K and a corresponding fusion at $T_{\mathrm{fus}} = 290$ K. The crystalline phase with $T_{\mathrm{fus}} = 290$ K is metastable, since the stable phase shows $T_{\mathrm{fus}} = 325$ K. The peak area, or enthalpy, of the fusion of the formed metastable crystal increased with increasing aging period (t_a). Provided that the magnitude of the fusion enthalpy and thus the degree of progress of crystallization is proportional to the number of the crystal nuclei generated, the behavior of the crystal nucleation is consistent with the ordinary finding that the number of nuclei increases with time after some incubation time.[2,3,12,13]

Intriguing, but hard to be explained immediately, phenomena are found in Fig. 3 to occur just after the rapid cooling from 343 K to $T_a = 128$ K. The samples aged for 30 s, and 1 and 5 min exhibit crystal growth and a corresponding fusion of the metastable crystalline phase with $T_{\mathrm{fus}} = 290$ K, as shown in runs 1–3. The samples aged for 10 and 100 min longer than these, meanwhile, do not show the crystal growth and fusion in runs 4 and 5. The sample aged for 316 min, however, again exhibits crystal growth and fusion, as shown in run 6. It must be concluded from these results that crystal nuclei are generated during the aging immediately after the cooling to $T_a = 128$ K, and extinguished in 10 min of the aging. The crystal growth and fusion behaviors found in run 6 would be analogous to those in runs 4–7 of Fig. 2.

Essentially all the samples aged at 103 K exhibit the crystal growth and fusion of the metastable crystalline phase, as shown in Fig. 4. The peak area (enthalpy) of the fusion decreases at around $t_a = 30$ min, and then increases at t_a longer than 100 min.

B. Gibbs energy relation between crystalline and liquid phases

In view of the thermodynamic relations that the Gibbs energy of a crystal is equal to that of a liquid at the fusion temperature, and that the change in the slope, $(\partial G/\partial T)_p$, of the Gibbs energy vs temperature associated with the fusion is equal to minus of the fusion entropy, the schematic Gibbs energy relation among the crystalline and liquid phases is given as shown by solid lines in Fig. 5. When the liquid of *o*-benzylphenol is cooled very rapidly from some high temperature such as 343 K, the configurational entropy (and thus the slope of the Gibbs energy vs temperature) remains rather high as compared with the equilibrium value of supercooled liquid at each temperature. The resulting Gibbs energy curve of the rapidly cooled liquid, being in a nonequilibrium state, is represented schematically as process *A* by a broken line with an arrow. At the aging temperature, the nonequilibrium supercooled liquid relaxes in its structure toward the equilibrium liquid, as indicated as process *B* by a dashed line with arrow. In the present case of *o*-benzylphenol, the crystal nucleation of the metastable phase proceeds simultaneously during the aging, shown as process *C* by dotted lines with arrows and by a shade in the temperature range of 103–213 K. The crystal growth (process *D*) of the metastable form was observed around 280 K macroscopically, as represented by a solid line with an arrow.

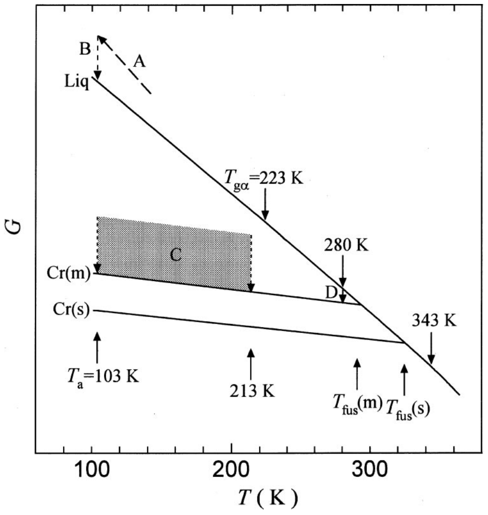

FIG. 5. Schematic Gibbs energy diagram representing the states of molecular aggregation: process *A*, rapid cooling from 343 K to each desired aging temperature (T_a); process *B*, aging at T_a; process *C*, nucleation of the metastable crystalline phase during the aging; process *D*, growth of the metastable crystalline phase in the course of the DSC measurement; Liq, liquid phase; Cr(m), metastable crystalline phase; Cr(s), stable crystalline phase. The stable crystalline phase was found as the prepared sample, and only the metastable crystalline phase was formed in the present crystallization in DSC.

C. Presence or absence of crystal nuclei as functions of aging temperature and aging period

The presence or absence of crystal nuclei in a supercooled liquid is illustrated in Fig. 6 by circles and as regions on the surface spanned by the aging temperature and the (common logarithm of) aging period. Results obtained for all samples aged between 103 and 213 K are shown together. Open circles within region 1, enclosed by a solid line, represent

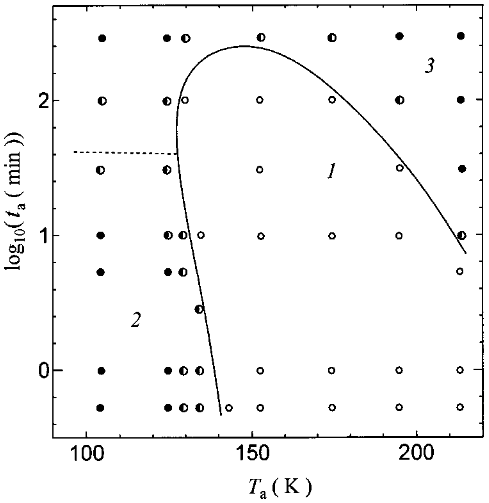

FIG. 6. Presence or absence of crystal nuclei in the supercooled liquid state of *o*-benzylphenol as represented on an aging temperature-period surface: The open circle in region 1 indicates that no crystal nucleus was found. The closed circle in region 2 indicates that crystal nuclei of the metastable phase were found to exist at the initial stage of aging by DSC. The closed circle in region 3 indicates that the crystal nuclei of the metastable phase were found in a period of long aging. The half-filled circle represents the situation that the crystal nuclei were found in some of the measurements and not in the others.

states where crystal nuclei were absent. Filled circles represent states where crystal nuclei of the metastable phase were found to exist. Half-filled circles, located mainly between the open and filled circles, indicate that the presence of the crystal nuclei was confirmed in some experiments but not in others. Regions 2 and 3, both corresponding to regions where crystal nuclei of the metastable phase are present, are separated by a dotted line, surrounded by half-filled circles, around $\log_{10}(t_a\,(\mathrm{min}))=1.6$ (namely, $t_a=40$ min). It is concluded from the diagram that, when the liquid sample is cooled rapidly to temperatures 128–133 K, much below $T_{g\alpha}=223$ K, the nuclei of the metastable crystalline phase are generated during aging just after the rapid cooling, extinguished within 10 min of the aging, and regenerated during a longer aging than 100 min. A similar tendency is also found when the aging temperature is decreased below 128 K. The crystal nuclei generated immediately after the rapid cooling mostly disappear at around $t_a=40$ min, as indicated by the presence of half-filled circles, but increases in the number during longer aging.

D. Effect of anomalous crystal nucleation on the apparent incubation time for the ordinary crystal nucleation proceeding in the range of long aging

An interesting fact, relevant to the generation, extinction, and regeneration of crystal nuclei during the aging, is found with respect to the enthalpy of fusion at 290 K of metastable crystals, as shown in Fig. 7 as a function of the aging period (t_a). The aging temperatures in Figs. 7(a)–7(e) are 213, 193, 128, 123, and 103 K, respectively, from the top through the bottom portions. The enthalpy found at around 1 min in Figs. 7(c)–7(e) decreases and disappears at around 10 min. It appears again at around 60 min. The former effect at around 1 min must originate from a remarkable structural fluctuation that takes place at the initial stage of nonequilibrium irreversible relaxation process. The latter effect is due to the ordinary crystal nucleation which has been found so far in some materials.[2,3,12,13] The apparent incubation time (t_i) for the latter nucleation exhibits a peculiar aging-period dependence: The common logarithms of the time (in min unit) are around 0.7, 1.6, 2.3, 1.9, and 1.8 at $T_a=213$, 193, 128, 123, and 103 K, respectively. It increases with decreasing aging temperature in the range 128–213 K or in the range 153–213 K according to the solid line separating regions 1 and 3 in Fig. 6. This increase is understood as reasonable due to the elongation of the relaxation time of the molecular rearrangement with decreasing temperature. What is peculiar is that the apparent incubation time decreases below 128 K. The peculiar dependence definitely originates from the event of crystal nucleation found around $t_a=1$ min below 128 K. As

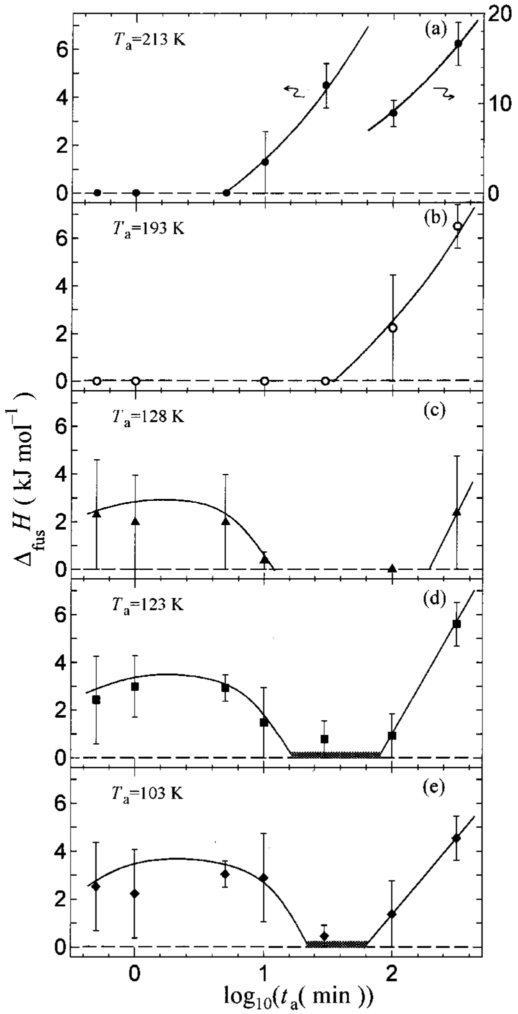

FIG. 7. Aging-period dependence of the enthalpy of fusion of the metastable crystals: (a) samples aged at $T_a=213$ K, (b) at $T_a=193$ K, (c) at $T_a=128$ K, (d) at $T_a=123$ K, and (e) at $T_a=103$ K. The gray zone represents a situation in which the presence or absence of crystal nuclei are ambiguous due to randomness in the nonequilibrium process.

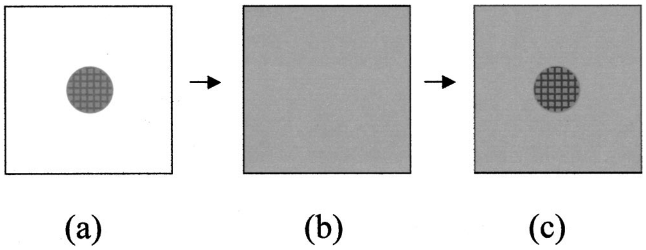

FIG. 8. Schematic diagram illustrating potential processes for generation and extinction phenomena of a crystal nucleus in the course of the irreversible structural relaxation of a nonequilibrium liquid. The encircled part stands for a crystal nucleus, and the other part for a liquid region composed of corresponding clusters. The darkness represents the degree of order in the molecular arrangements, so that the liquid molecules should be ordered from (a) to (b), and the crystal nucleus in (c) is considered to possess more ordered arrangement of molecules than that in (a).

seen more clearly in Figs. 7(d) and 7(e) at $T_a = 123$ and 103 K, respectively, it seems that some of the crystal nuclei generated around $t_a = 1$ min survive so as to work as embryos or nuclei in the ordinary nucleation process at longer times. The critical aging-period region for the disappearance or survival is indicated with a shade around $t_a = 40$ min in Figs. 7(d) and 7(e).

IV. DISCUSSION

The above results indicate that an anomalous, but expected (see Sec. I) crystal nucleation certainly occurs immediately after cooling to very low temperatures, and that the nuclei formed are then extinguished through a structural fluctuation and an irreversible relaxation of liquid in the course of aging. One might suspect that the nucleation occurred in the course of cooling. However, the nucleation must occur in a range below 143 K, since the crystal nuclei are considered to be absent for samples aged for 30 s above 143 K, as seen in Fig. 6. Thus it is reasonable to conclude that nucleation occurs in the very initial stage of aging (namely, of nonequilibrium, irreversible relaxation of liquid structure) at the temperatures below 143 K. The fact that the nucleation occurred only at such low temperatures indicates that the process is enhanced in the glassy state extremely far from equilibrium, and having a large Gibbs energy that refers to the equilibrium value of a supercooled liquid.

In view of the result that crystal nuclei were found to exist in some experiments but not in others, even under the same conditions, there is a possibility that the nuclei were formed heterogeneously, for example, on the surface of the DSC pan. If this is the case, however, it is hard to understand the present results based only on the heterogeneity. The point of the present observation is that the realization of the generation and then extinction phenomena of a crystal nucleus essentially reflects the effect of the real structure and its relaxation of the liquid and glass on the stability of the nucleus.

The crystal nucleus can be recognized as a representative of structured clusters. Naturally, other kinds of structured clusters must appear and disappear with time, so that a liquid could be looked upon as an aggregate of clusters with a diversity of structures. The generation, extinction, and regeneration processes of crystal nucleus are schematically illustrated in Figs. 8(a)–8(c) in the order of the elapse of the aging time. Immediately after cooling from a high temperature, molecules within the clusters characteristic of liquid are arranged rather in the disordered way, and gradually becomes ordered with time, as represented by a change in the background darkness from white in Fig. 8(a) to light gray in Fig. 8(b). Meanwhile, the crystal nucleus formed would possess many aggregation faults of molecules. This is due to the fact that the Gibbs energy of the glass, as regards the stability of the crystal nucleus, is much larger than that of an equilibrium liquid, as described above; therefore, any crystal nucleus with some faults tends to remain as a comparatively stable state of a molecular aggregation. As the molecular arrangement within the liquid clusters becomes more ordered, the nucleus appears to become unstable as regards the liquid clusters present, and tends to disappear, as shown in the process from Fig. 8(a) to Fig. 8(b). But the molecular arrangement within the liquid clusters is frozen in at a certain stage depending on the aging temperature much below the glass transition point,[14] as shown by the lack of a change in the darkness of the gray in the process from Fig. 8(b) to Fig. 8(c). Then, a crystal nucleus with fewer aggregation faults of molecules than the previous one [Fig. 8(a)] is formed at a certain statistical rate with aging. As the aging temperature decreases to a lower temperature such as 123 K, the molecular arrangement within the liquid clusters (which are not drawn explicitly) is frozen in at lower degree of order, resulting in lower stability of the liquid clusters.[14] Some crystal nuclei, such as those shown in Fig. 8(a), then develop to those in Fig. 8(c) through a rearrangement of molecules surrounding the initially generated nuclei.[4,11,13] Thus clusters generated as crystal nuclei tend to survive or decay according to whether they are more stable or less stable, respectively, than the liquid clusters at each moment.

V. CONCLUSION

The peculiar generation and extinction of crystal nuclei were discovered in an extremely nonequilibrium state of supercooled liquid at low temperatures much below $T_{g\alpha}$. This discovery is important in two respects. First, it provides a kind of evidence that supercooled liquid is an aggregation of somehow ordered clusters. The reason for this, as described above, is that a crystal embryo or nucleus is just a representative of structured clusters. The observation of the extinction as well as generation of the nucleus could be strong evidence of the presence of a diversity of ordered clusters. The occurrence of such structural fluctuations in a temperature range much below $T_{g\alpha}$ also indicates that the β process might be indispensable for the progress of crystal nucleation,[10,11,15] and further that a supercooled liquid would have a heterogeneous structure composed of regions of molecules giving rise to the α and β processes, respectively.[10,11]

Second, the discovery explores quite a different method of crystallization of any liquid which is hard to crystallize, since to date it has been commonly recognized that the only way to crystallization is to wait for a long time at some temperatures. Considering that the crystal nucleation is just one extreme event in the fluctuation of a clustered structure, for example, another liquid phase with a different structure from the ordinary one would also be potentially nucleated in a similar procedure, and then there is a possibility to find a liquid-liquid phase transition in reality. The appearance of two amorphous phases in Y_2O_3-Al_2O_3 and potentially in pure H_2O systems[16–18] would be intimately related to this event.

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