

Generation and extinction of crystal nuclei in an extremely non-equilibrium glassy state of salol

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

2003 J. Phys.: Condens. Matter 15 3909

(<http://iopscience.iop.org/0953-8984/15/23/306>)

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

Download details:

IP Address: 171.66.16.121

The article was downloaded on 19/05/2010 at 12:13

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

Generation and extinction of crystal nuclei in an extremely non-equilibrium glassy state of salol

Florentin Paladi¹ and Masaharu Oguni²

Department of Chemistry, Graduate School of Science and Engineering,
Tokyo Institute of Technology, O-okayama 2-12-1, Meguro-ku, Tokyo 152-8551, Japan

Received 20 February 2003, in final form 22 April 2003

Published 30 May 2003

Online at stacks.iop.org/JPhysCM/15/3909

Abstract

Strange generation and subsequent extinction of crystal nuclei were observed in the glassy state of salol (phenyl salicylate) during the course of ageing at very low constant-temperatures. The presence/absence of crystal nuclei within the glass were judged, by using a differential scanning calorimeter (DSC), from whether the crystal growth and fusion phenomena were observed in the following heating process or not. The liquid sample was cooled rapidly at 200 K min^{-1} from 333 K above the fusion temperature down to a desired ageing temperature (T_a) below the glass transition temperature ($T_g = 220 \text{ K}$), aged there for different periods (t_a), and then heated up to 213 K at 200 K min^{-1} . The DSC measurement was carried out at 10 K min^{-1} from 213 to 333 K. The ageing periods were taken in a range between 30 s and 316 min. At $T_a = 213 \text{ K}$, crystal nucleation was found to proceed for ageing longer than 100 min. No crystal nucleation was found at T_a in between 123 and 193 K. At T_a below 113 K, crystal nuclei were found immediately after the rapid cooling, then extinguished, and again generated; some nuclei formed initially, survived for longer ageing at 103 K. The generation and extinction phenomena of crystal nuclei are discussed as a general event occurring in glasses located in an extremely non-equilibrium state.

1. Introduction

It is well known that a phase transition between crystal and liquid shows a latent heat and jumps in volume and entropy [1], and therefore that fusion and crystallization can be detected by observing the accompanied absorption and evolution, respectively, of heat. It is also known that the structures of molecular aggregation are different between liquid and crystal, as the entropies and volumes are. Crystallization therefore begins with formation, within a liquid, of a small

¹ Permanent address: Department of Theoretical Physics, State University of Moldova, A Mateevici Street 60, Chisinau MD2009, Moldova.

² Author to whom any correspondence should be addressed.

region where molecules are arranged in the same way as in a crystal. This process, designated as crystal nucleation, is practically impossible to observe experimentally, for example by heat evolution, since the nucleus is generally composed of molecules of 10–1000, much less than Avogadro's number corresponding to a typical macroscopic, observable quantity. Once formed, on the other hand, the nucleus grows rather easily to bulk crystal [2–4]. The process, designated as crystal growth, proceeds on a macroscopic scale and can be easily detected by calorimetry.

In general, both processes have been recognized to proceed only in a temperature range between glass transition temperature (T_g) and fusion temperature (T_{fus}) [1–3]. This seems to be rather reasonable since the crystalline state is stable only below the T_{fus} and since the molecules can change their positions or orientations only above the T_g . However, the structure of molecular aggregation in the liquid and glassy states has not been established even as its basic model, and it has not been clarified whether the rearrangement motions of all the molecules of the system are frozen below the T_g or not. In fact, the presence of the β molecular-rearrangement process has been known for over 30 years [5, 6], indicating that some molecules can change their positions and/or orientations above the β glass transition temperature ($T_{g\beta}$). There might be a further possibility that the positions and orientations of molecules can be changed even below the $T_{g\beta}$.

We found previously [7], by using a differential scanning calorimeter (DSC), that the crystal nucleation of 2-benzylphenol from glass takes place immediately after cooling to very low temperatures of 103–127 K which are lower by 95–120 K than the conventional glass transition temperature ($T_{g\alpha} = 223$ K); the α -relaxation times at such low temperatures are expected to be over 10^{18} s so that the nucleation process would not proceed through the α process. It was found, in [7], that even the crystal nuclei formed tend to disappear during longer ageing at the same temperatures. The sequence of crystal nucleation/extinction phenomena is really strange and it is necessary to find another substance to show the same phenomena. In the present work, we have examined by the same DSC measurements whether the phenomena are observed in salol (phenyl salicylate) or not.

2. Experiment

Salol (2-(HO)C₆H₄CO₂C₆H₅), purchased from Tokyo Chemical Industry Co., Ltd, was purified by re-crystallization from methanol solution, followed by sublimation at 310 K under reduced pressure. The obtained sample was kept in a desiccator with dry silica gel. The sample was re-purified by sublimation every half a month to use as fresh a sample as possible. The purity of the sample was determined to be 0.9995 in the mole fraction by a calorimetric fractional-melting method of the sample refined in the same procedure [8]. Perkin-Elmer DSC type 7 was utilized for the measurements of crystallization behaviour. The purified sample of nearly 5–7 mg was loaded into an aluminium calorimeter pan and the pan was sealed tightly.

Figure 1 illustrates the procedures taken in the DSC measurement. The fusion temperature (T_{fus}) of salol is 315 K. The crystalline sample loaded was heated up to 333 K at 200 K min⁻¹ to melt, and then kept there for 2 min. The melted sample was cooled in process *A* rapidly at a rate of 200 K min⁻¹ down to a desired ageing temperature (T_a) which is below the $T_{g\alpha} = 220$ K, aged there for a desired period (t_a) in process *B*, and then heated up to 213 K, a little below the $T_{g\alpha}$, at 200 K min⁻¹ in process *C*. The DSC measurement was carried out, after having been kept at 213 K for 30 s, on heating in a temperature range 213–333 K at a rate of 10 K min⁻¹ in process *D*. In view of the fact that crystal growth never proceeds without a crystal nucleus, the presence/absence of crystal nuclei was judged from whether crystal growth and subsequent fusion do or do not take place in the process *D*. This rather roundabout way of determination

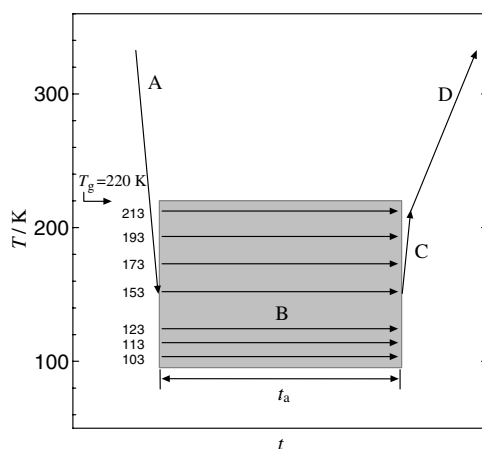


Figure 1. Scheme of the procedures taken in the present DSC: *A*, rapid cooling at 200 K min^{-1} from 333 K to each specified ageing temperature (T_a); *B*, ageing at T_a ; *C*, rapid heating at 200 K min^{-1} from T_a to 213 K; *D*, DSC heating measurement above 213 K at 10 K min^{-1} ; t_a , ageing period at T_a .

was taken because the direct observation of the presence of a crystal nucleus is practically impossible as stated above.

The above experiment was repeated more than five times for each set of T_a and t_a , because the nucleation is considered as a somewhat probabilistic event. After each heating run for the measurement of crystallization and fusion, the calorimeter pan with sample was renewed for fear of any potential decomposition of the sample during the measurement at high temperatures and any thermal hysteresis effect.

3. Results

Figures 2–4 show some typical results obtained for samples subjected to ageing at $T_a = 213$, 113 and 103 K, respectively. Runs 1–5 with ageing periods less than 30 min in figure 2 exhibit nothing but a glass transition taking place at $T_{g\alpha} = 220 \text{ K}$. This indicates that essentially no crystal nucleus is generated during the cooling from 333 to 213 K and the ageing within 30 min at 213 K. Runs 6 and 7 with $t_a = 100$ and 316 min, respectively, show crystal growth proceeding around $T_{cryst} = 290 \text{ K}$ and the corresponding fusion at $T_{fus} = 300 \text{ K}$. The crystalline phase with $T_{fus} = 300 \text{ K}$ is metastable since the stable phase shows $T_{fus} = 315 \text{ K}$. The peak area, namely enthalpy, of fusion of the metastable crystal formed increased with increasing the ageing period t_a . This behaviour is consistent with the ordinary finding that the number of nuclei increases with time after some incubation time [3, 4, 9]. Intriguing, but hard to immediately explain, phenomena are found in figure 3 to occur in the state just after rapid cooling from 333 K to $T_a = 113 \text{ K}$. The sample aged for 30 s exhibits crystal growth and the corresponding fusion of the metastable crystalline phase with $T_{fus} = 300 \text{ K}$, as shown in run 1. The samples aged for 1–100 min, meanwhile, do not show crystal growth and fusion in runs 2–6. The sample aged for 316 min, however, exhibits again the crystal growth and fusion as shown in run 7. It is concluded from these results, as a matter of fact, that crystal nuclei are generated during the ageing immediately after the cooling to $T_a = 113 \text{ K}$ and then suddenly extinguished. All the samples aged at 103 K exhibit crystal growth and fusion of the metastable crystalline phase (figure 4). The peak area (enthalpy) of fusion decreases with ageing period around $t_a = 30 \text{ min}$ and then increases with longer t_a than 100 min.

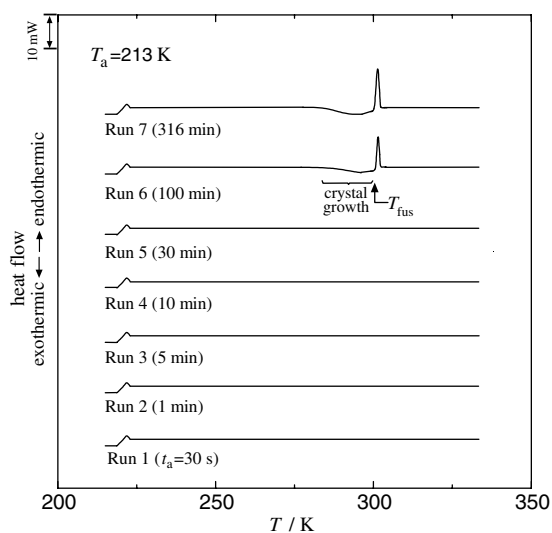


Figure 2. DSC curves of the salol samples aged for different periods at $T_a = 213$ K. The ageing period (t_a) is given, as parenthesized, after the run number of the DSC measurement.

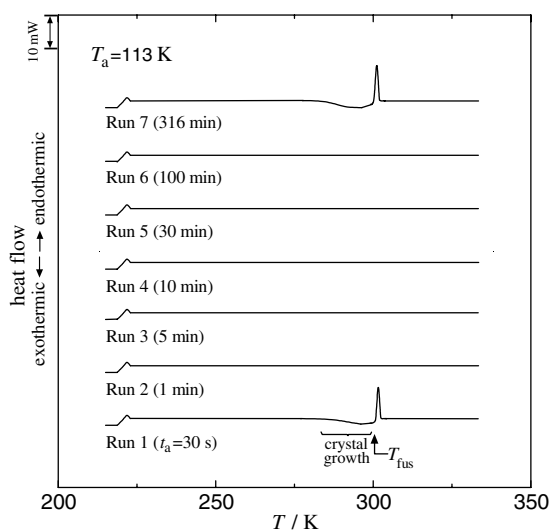


Figure 3. DSC curves of the samples aged at $T_a = 113$ K.

The presence/absence of crystal nuclei in the supercooled liquid are illustrated on the surface spanned by the ageing temperature and the ageing period in figure 5; results obtained for all the samples aged between 103 and 213 K are shown together. A dotted line around $\log(t_a/\text{min}) = 1.8$ (namely $t_a = 60$ min) separates regions 2 and 3, both corresponding to those where crystal nuclei of the metastable phase are present. The diagram shows that the nuclei of the metastable crystalline phase are generated during ageing just after the rapid cooling down to 113 K, much below the $T_{g\alpha} = 220$ K, then extinguished, and re-generated during ageing longer than 100 min. The similar tendency is also found when the ageing

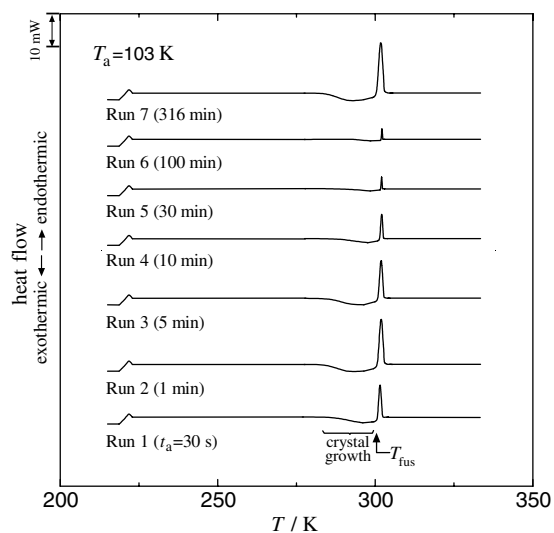


Figure 4. DSC curves of the samples aged at $T_a = 103$ K. The fusion of the metastable crystalline phase appeared in all the samples.

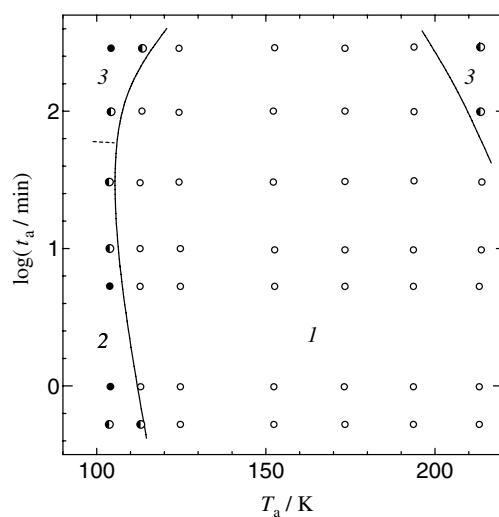


Figure 5. Presence/absence of crystal nuclei in the supercooled liquid state of salol as represented by circles and regions on the surface spanned by the ageing temperature and the (common logarithm of) ageing period. Open circle in region 1 indicates that no crystal nucleus was found. Full circle in region 2 indicates that crystal nuclei of the metastable phase were found to exist. Full circle in region 3 indicates that crystal nuclei of the metastable phase were found in the period of long ageing. Half-filled circle represents the situation that the crystal nuclei were found in some of the measurements and not in others.

temperature is decreased to 103 K. The initially generated crystal nuclei mostly disappear at around $t_a = 60$ min, as indicated by half-filled circles, but increase in number during ageing longer than 100 min. These data indicate that the crystal nuclei of the metastable phase are generated during the ageing after rapid cooling, extinguished, and then re-generated during

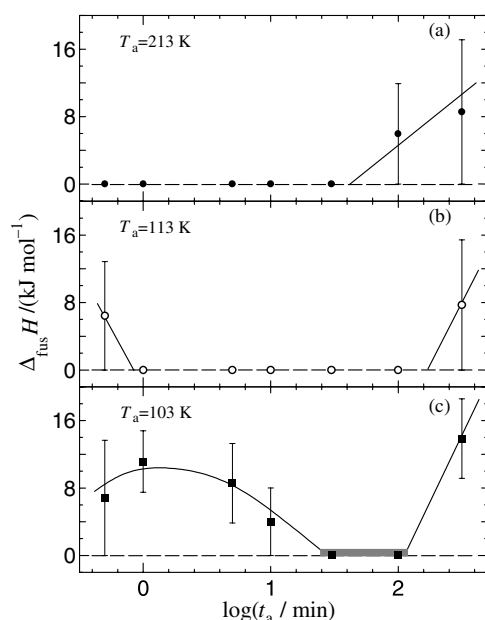


Figure 6. Ageing-period dependence of the enthalpy of fusion of the metastable crystals: (a) samples aged at $T_a = 213$ K; (b) at $T_a = 113$ K and (c) at $T_a = 103$ K. Grey zone represents the situation that the presence/absence of crystal nuclei are ambiguous due to randomness in the non-equilibrium process.

the course of ageing of a non-equilibrium supercooled liquid of salol in a very low ageing-temperature region.

Figure 6 shows the enthalpy of fusion at 300 K of the metastable crystalline phase as a function of ageing-period (t_a). The ageing temperatures in figures 6(a) to (c) are 213, 113 and 103 K, respectively, from the top to the bottom portions. The presence and disappearance of the enthalpy of fusion within about 10 min in figure 6(c) must originate from a remarkable structural fluctuation that is expected to take place at the very initial stage of the non-equilibrium, irreversible relaxation process. Its appearance again at around 100 min is due to ordinary crystal nucleation that has been found so far in some materials [3, 4, 9], although 103 K is too low as referred to the temperature range in which the nucleation process has been expected to proceed. The apparent incubation time for the latter nucleation is around 40, 160, and 100 min at $T_a = 213$, 113 and 103 K, respectively. It increases with decreasing the ageing temperature in the range 193–213 K according to the trend of the full curve separating regions 1 and 3 in figure 5. This increase is understood as reasonable due to the elongation of the relaxation time of molecular rearrangement with decreasing temperature, but the decrease of the apparent incubation time below 113 K should be definitely explained by crystal nucleation found at around $t_a = 1$ min in the ageing temperature range. It seems that some of those crystal nuclei survive so as to work as the embryos/nuclei in the ordinary nucleation process at longer times. The critical ageing-period region for the disappearance/survival is indicated with shading around $t_a = 60$ min in figure 6(c).

4. Discussion

The most fascinating fact is that crystal nucleation certainly occurs immediately after the cooling to very low temperatures and the nuclei formed are then extinguished in the course of

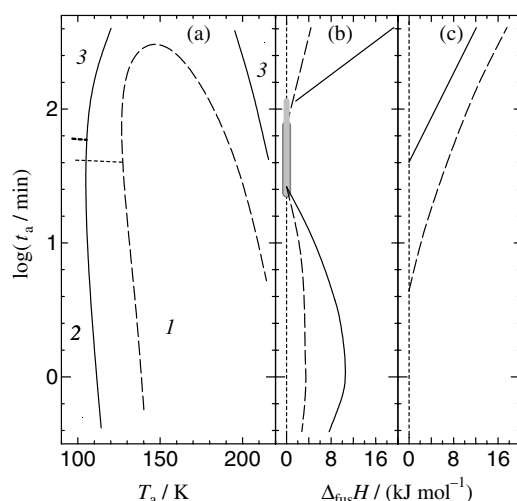


Figure 7. Comparison between the results obtained in salol and 2-benzylphenol: (a) presence/absence of crystal nuclei in the supercooled liquid state as represented by regions on the surface spanned by the ageing temperature and the (common logarithm of) ageing period; (b) and (c) dependence of the enthalpy of fusion for the samples aged at $T_a = 103$ and 213 K respectively. Full curves in (a)–(c) and thick dotted line in (a) represent the results of salol, and broken curves in (a)–(c) and thin dotted line in (a) those of 2-benzylphenol. Regions 1, 2 and 3 indicate that no crystal nucleus was found, crystal nuclei were found to exist, and crystal nuclei were found in the period of long ageing, respectively. Grey zones in (b) represent the situations that the presence/absence of crystal nuclei are ambiguous due to randomness in the non-equilibrium process but that, if any, the nuclei are small in number.

ageing. The nucleation must have occurred during the ageing in the range below 123 K, not in the course of cooling to 123 K, because the crystal nuclei are absent for samples aged for 30 s at 123 K and above temperatures, as seen in figure 5. Considering that the crystal nuclei were found to exist in some experiments but not in others repeated with the same procedures, as indicated by error bars in figure 6, the nucleation might have a heterogeneous origin; for example, the presence of the surface of a DSC pan might have helped the nucleation. If anomalous nucleation is the case, however, it is still hard to understand why the nucleation occurs only at such low temperatures and why the crystal nuclei once formed, then disappear. The realization of such generation and extinction phenomena of crystal nuclei essentially reflects the effect of the real structure and its irreversible relaxation of the glass on the stability of the nucleus.

It is valuable here to see the similarity and difference between the results obtained for salol and 2-benzylphenol [7]. Salol is the compound in which the $-\text{CH}_2-$ group connecting two phenyl rings in 2-benzylphenol was replaced by a $-\text{C}(\text{O})\text{O}-$ group, while one hydroxyl group is attached on one of the phenyl rings in the *ortho*-position for both compounds in common. The results, only as their tendencies, are given in figure 7: figure 7(a) represents the comparison corresponding to the results of figures 5, 7(b) and (c) to those of figures 6(c) and (a), respectively, and the full and broken curves represent the results of salol and 2-benzylphenol, respectively. First, it should be stressed that the tendencies are quite similar between the two compounds. Second, in passing, differences in a quantitative respect are found in two points between the two. One is that region 1 in figure 7(a) is wider in salol than in 2-benzylphenol. This indicates that the formation of crystal embryos/nuclei is more difficult in the former compound. The difference is, of course, related to that in the molecular structures: the two

phenyl rings in 2-benzylphenol are connected by two single bonds through one carbon atom, and those in salol are by three single bonds through two, carbon and oxygen, atoms resulting in the potential occurrence of a larger number of accessible conformations and therefore a more difficult situation for the formation of the crystal embryos/nuclei than in 2-benzylphenol. The other point of the difference is that the enthalpy of fusion in figure 7(b) is rather smaller in 2-benzylphenol than in salol while a larger number of crystal nuclei are expected to exist in the former rather than in the latter compound. This might be related to the difference in the crystal-growth rate as well as the nucleation rate between the two, although the thorough interpretation is not easy at present.

A crystal nucleus is a small region possessing an ordered arrangement of 10–1000 molecules and formed within the liquid and glass. The nucleus thus can be recognized as a kind of cluster with ordered structure. Considering that the crystal nuclei are generated and extinguished, many other clusters with different structures are expected naturally to exist within the glass as well. This idea leads to a ‘cluster structure model’ for supercooled liquids and glasses [10, 11]. Based on this model, the present results of the generation and extinction of crystal nuclei would be understood, as follows, as a competitive phenomenon with respect to the stabilities of crystal nuclei and liquid clusters: immediately after the cooling from a high temperature, molecules within some of the liquid clusters would be arranged in a comparatively disordered way. The Gibbs energy of the crystal nucleus suddenly formed with a somewhat incomplete crystal structure in the arrangement of molecules, is potentially lower at that moment than those of the clusters surrounding the nucleus. During the ageing, meanwhile, the molecules primarily on the interface of the reasonably stable liquid clusters rearrange to stabilize the clusters. Then the nucleus appears to become unstable as referred to the more stabilized liquid clusters and to disappear. At the same time the molecular arrangement within the liquid clusters remains frozen at a certain stage depending on the ageing temperature being much below the glass transition point [12], and a new more stable crystal nucleus with molecules arranged more neatly has a chance to be formed during long ageing since the crystalline state is naturally more stable below the fusion point than the liquid state. When the ageing temperature is too low, as it is taken to be around 103 K, the arrangement of molecules within the liquid clusters is frozen in at a lower degree of order, resulting in their lower stability [12]. Some crystal nuclei then develop through rearrangement of molecules surrounding the initially generated nuclei [11, 13, 14]. Thus, the initially generated 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.

It is interesting to consider that the appearance and disappearance phenomena of the clusters occurred at very low temperatures as compared with the α glass transition temperature $T_{g\alpha}$. This fact indicates that some molecules can change their arrangement even at such low temperatures and that the supercooled liquids and glasses have the structure providing such a distribution of relaxation times of molecular rearrangements. Based on the ‘cluster structure model’ [10, 11], such a kinetic aspect of the present results is understood as follows: the glasses are pictured to have a statically heterogeneous structure composed somehow of ordered clusters and the interfacial parts (of the clusters) with somewhat disordered arrangement. In view of the fact that almost all the molecules effectively stop their rearrangement motions below $T_{g\alpha}$, it is considered that the molecules located in between the clusters would be more mobile having shorter relaxation times than those within the clusters [10, 11] and rearrange to grow the already present or new ordered clusters. The molecules located initially in the interface and included within the clusters through this rearrangement are, however, expected to stop their rearrangement and stay there at the following moment [12]. These processes would be repeated resulting in the present strange phenomena of crystal nucleation and extinction.

Similar behaviours of crystallization have been reported in molecular dynamics simulations of the freezing of copper [15] and of NaCl clusters, as well as of deeply supercooled clusters of SeF₆ [16, 17]; there crystals are formed at or near the surface of the clusters.

5. Conclusion

The generation and extinction of crystal nuclei in the extremely non-equilibrium state of a supercooled liquid of salol was discovered at very low temperatures much below $T_{g\alpha}$. This is the second substance next to 2-benzylphenol [7]. More examples of substances to show the phenomena are desired so as to indicate their universality, as a matter of course. The present discovery is, however, important in that it provides a suggestion that supercooled liquids and glasses are aggregations of somehow ordered clusters and thus have statically heterogeneous structures. The discovery is also important in that some unexpected ordering processes are indicated to proceed in the extremely non-equilibrium state. This should be stressed for understanding both the non-equilibrium irreversible and relaxation processes and the states realized through the processes [12, 18]. The liquid structures realized there would not be quite the same as those realized under equilibrium at any temperature.

Acknowledgment

FP is grateful to The Japan Society for the Promotion of Science (JSPS) for their financial support during his stay in Tokyo Institute of Technology, Japan.

References

- [1] Rao C N R and Rao K J 1978 *Phase Transitions in Solids* (New York: McGraw-Hill)
- [2] Owen A E 1985 *Amorphous Solids and the Liquid State* (New York: Plenum)
- [3] Uhlmann D R 1969 *Materials Science Research* vol 4 (New York: Plenum)
- [4] Kelton K F 1991 *Solid State Phys.* **45** 75
- [5] Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 3272
- [6] Johari G P 1987 *Lect. Notes Phys.* **227** 90
- [7] Paladi F and Oguni M 2002 *Phys. Rev. B* **65** 144202
- [8] Hanaya M, Hikima T, Hatase M and Oguni M 2002 *J. Chem. Thermodyn.* **34** 1173
- [9] Okamoto N, Oguni M and Sagawa Y 1997 *J. Phys.: Condens. Matter* **9** 9187
- [10] Fujimori H and Oguni M 1995 *Solid State Commun.* **94** 157
- [11] Oguni M 1997 *J. Non-Cryst. Solids* **210** 171
- [12] Hikawa H, Oguni M and Suga H 1988 *J. Non-Cryst. Solids* **101** 90
- [13] Hikima T, Hanaya M and Oguni M 1995 *Phys. Rev. B* **52** 3900
- [14] Hikima T, Hanaya M and Oguni M 1996 *Bull. Chem. Soc. Japan* **69** 1863
- [15] Valkealahti S and Manninen M 1997 *J. Phys.: Condens. Matter* **9** 4041
- [16] Chushak Y G and Bartell L S 1999 *J. Phys. Chem. B* **103** 11196
- [17] Chushak Y G and Bartell L S 2000 *J. Phys. Chem. A* **104** 9328
- [18] Fujimori H, Fujita H and Oguni M 1995 *Bull. Chem. Soc. Japan* **68** 447