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*Plenary Lecture*

# CHARACTERIZATION OF AMORPHOUS SOLID DERIVED FROM CRYSTAL

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## Abstract

Amorphous solid of tri-*O*-methyl-β-cyclodextrin was produced by grinding its crystalline sample with a rod-milling machine at room temperature. Structural and thermal characterizations of the sample during amorphizing process were done by X-ray powder diffraction and differential scanning calorimeter. The glass transition for a fully amorphized sample was found to occur at essentially the same temperature as that for a liquid-quenched glass. The heat capacities of the non-crystalline solids realized by grinding and liquid quenching and of the crystalline solid were measured by a low temperature adiabatic calorimeter. Excess enthalpies of the ground amorphous solid and liquid quenched glass over that of the hypothetical equilibrium liquid were determined calorimetrically. Similar and dissimilar thermal behavior of both non-crystalline solids were compared.

**Keywords**: amorphizing process, liquid-quenched glass, tri-*O*-methyl-β-cyclodextrin

## Introduction

There exist many glass-forming liquids composed of monomeric and polymeric molecules of organic as well as inorganic origin [1]. These liquids easily avoid their crystallizations on cooling to realize their glasses via the glass transition regions. Formation of glasses is thus a problem of by-passing the crystallizations. These traditional glasses are typical example of non-crystalline solids.

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Many non-crystalline solids were produced by various methods other than the conventional liquid cooling [2]. They are vapor condensation, chemical reaction, bombardment of high-energy particles to crystal, and so on. What kind of similar and dissimilar properties exist among these exotic non-crystalline solids. In 1968, we have successfully observed that amorphous precipitates of $As_2S_3$ produced by a chemical reaction exhibited a glass transition phenomenon which is similar in nature to that of liquid-cooled sample of orpiment (naturally occurred crystalline $As_2S_3$) [3]. Likely, amorphous magnesium acetate produced by dehydration of its tetrahydrate crystal showed a glass transition at around 469 K [4].

In recent years, we are interested in thermodynamic behavior of non-crystalline solids produced by mechanical grinding of crystalline materials. The grinding process impregnates an excess amount of energy to excite the equilibrium crystal and freeze it in an energized non-crystalline state [5]. The process is in good contrast to the liquid-quenching or vapor-deposition methods in which the energies of the constituent molecules are extracted rapidly during the vitrification process. The mechanical grinding is a novel technique for the solid state amorphization and is quite popular in the formation of amorphous alloys of binary [6] and ternary [7] systems. The method is generally referred to as mechanical alloying and the grinding procedure is done either by ball-milling or by rod-milling.

Only a few examples are known in non-metallic systems. There must exist some universal features in various kinds of non-crystalline solids. In order to compare some physico-chemical properties of these exotic and traditional non-crystalline solids, we have chosen a molecular crystal, tri-*O*-methyl-β-cyclodextrin or permethylated β-cyclodextrin (abbreviated as TMCD), and one of its inclusion compounds. These compounds were found to be good glass-formers, so that we can easily prepare their traditional glasses for mutual comparison.

## Experimental

The sample of TMCD purchased from Toshin Chemical Co. Ltd. was used without further purification. Since the product was found to contain a fraction of non-crystalline phase, the sample was annealed at around 130°C *in vacuo* over more than 24 h for complete crystallization. About 5 $cm^3$ of sample was ground by using a rod-milling machine, TI-100 Heiko Manufacturer Ltd., in dry nitrogen atmosphere. The milling operation was stopped at every 7 min and the pot was cooled with a fan in order to remove the heat arising from friction and impact between the pot and rod. A small amount of sample was taken out of the pot occasionally for thermal and structural characterizations by using DSC and X-ray diffraction methods. The corresponding liquid-quenched (LQ) sample was produced by immersing the melt sample in a closed glass ampoule into water. The estimated cooling rate was roughly $10^3$ deg·min$^{-1}$.

Thermal characterization of each sample was carried out by using a Perkin Elmer DSC 7 with a heating rate of 3 deg·min$^{-1}$. The glass transition temperature, the crystallization temperature, and the fusion temperature along with the associated enthalpy effects were measured as a function of the grinding time. Structural characterization was done by using a Rigaku Denki RAD-ROC X-ray diffractometer. A sample of 0.2 mm thickness was mounted on the sample holder made of glass. The range of diffraction angle 2α was 3~90 deg and the scanning speed was 3 deg·min$^{-1}$.

The molar heat capacities and the relaxation processes of the ground amorphous solid (GAS) and liquid-quenched glass (LQG) were measured by a low temperature adiabatic calorimeter with a build-in cryo-refrigerator [8]. An adiabatic calorimeter is a meter which determines the enthalpy function of a sample as a function of temperature. The heat capacity is obtained simply by taking a derivative of the enthalpy with respect to temperature. If the calorimetric temperature is constant with time, the whole system is in thermal equilibrium. If the temperature changes systematically with time, it gives a clear indication of occurrence of enthalpy relaxation of the sample from non-equilibrium to the equilibrium state. The rate of enthalpy relaxation is proportional to the change in the calorimetric temperature under an adiabatic condition. Since the adiabatic calorimeter has a very high thermal stability and temperature resolution, the calorimeter provides a sensitive way in detecting any irreversible process of sample in non-equilibrium towards the thermal equilibrium. The relevant time domain is between $10^3$ and $10^6$ s.

The calorimeter cell was made of gold-plated copper and the inner volume was 5.83 cm$^3$. A Rh-Fe resistance thermometer (27 Ω at 273 K; Oxford Instrument Ltd.) was used for the temperature measurement. The thermometer was calibrated in advance based on the temperature scales EPT-76 below 27 K and IPTS-68 above that. The imprecision of the temperature measurement was estimated to be ±0.7 mK ($T<27$ K), ±3.3 mK (27 K$<T<$300 K), and ±1 mK ($T>300$ K). The amount of sample loaded in the calorimetric cell was 3.0362 g for LQG and 2.4469 g for GAS and crystal. The crystalline sample was obtained from GAS by crystallization in the sample cell *in situ*. The heat capacity was measured by intermittent heating mode which is composed of energizing period and equilibration period.

## Results and discussion

TMCD crystal melts at 157.6°C with the associated enthalpy change of 40.6 J·g$^{-1}$. The melt is easily undercooled to form glassy state ultimately. The

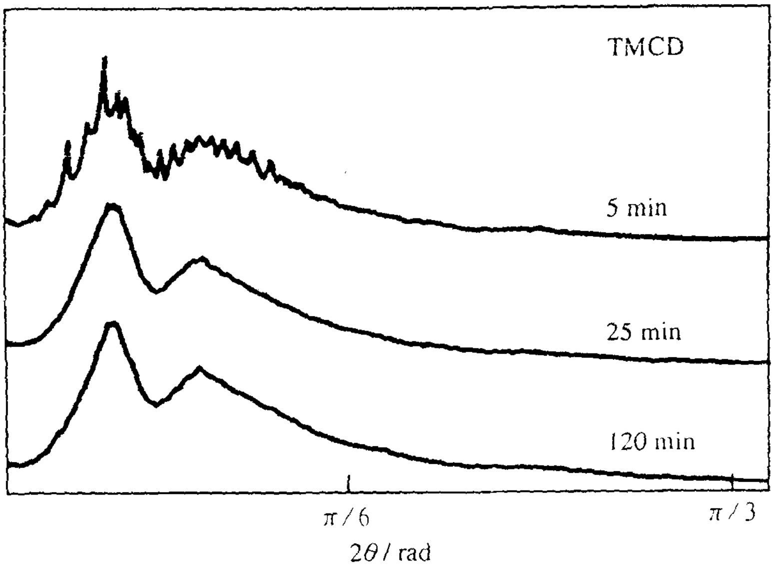

**Fig. 1** X-ray powder diffraction patterns of TMCD taken at several stages of grinding the crystalline sample

LQG sample exhibited three thermal anomalies on warming; the glass transition temperature at 77.8°C with discontinuous heat-capacity jump of 0.19 $J \cdot K^{-1} \cdot g^{-1}$, the exothermic peak due to crystallization at around 125°C, and the endothermic peak due to the fusion at 157.6°C. The glass transition temperature of liquid-quenched sample of TMCD was observed for the first time in this experiment.

X-ray diffraction pattern of the TMCD crystal is composed of many diffraction peaks. As the grinding process is started, the intensity of each Bragg peak diminished rapidly [9]. Figure 1 shows the X-ray powder diffraction patterns of the sample ground for (a) 5 min, (b) 25 min, and (c) 2 h. The overlapping Bragg reflection peaks and halos are observed in Fig. 1. Their positions and relative intensities of the Bragg component are essentially the same as those observed in pure crystal. The halo component of the pattern is the same as that of the LQG sample, indicating coexistence of the crystalline and amorphous phases. The intensities of the Bragg peaks decreased with grinding and disappeared almost completely for the 25 min sample. The diffraction pattern remained unchanged for further grinding.

Figure 2 draws typical three DSC curves of the sample ground for (a) 5 min, (b) 25 min, (c) 2 h, each corresponding to Fig. 1. The insets give the glass transition region on a magnified scale. For every sample, the glass transition, crystallization and fusion were observed systematically, as in the case of the LQG

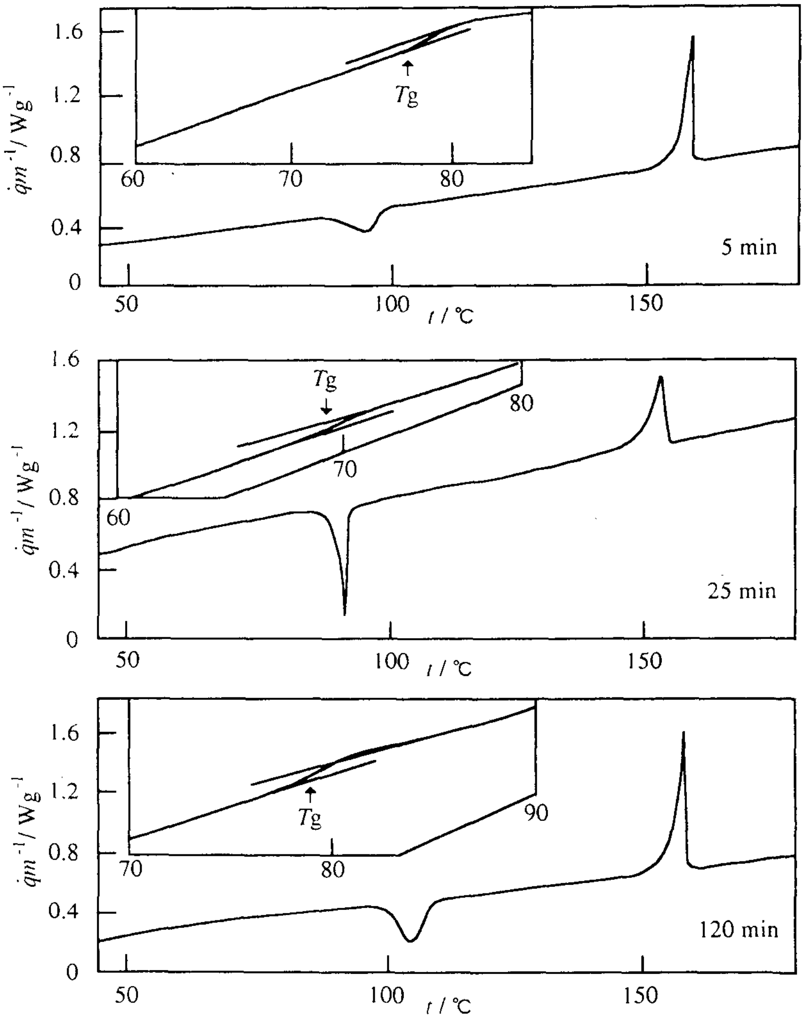

**Fig. 2** DSC curves of TMCD measured at three stages of grinding corresponding to Fig. 1

sample. Thus the ground sample behaved thermally in essentially the same manner as that of the LQ sample. The crystallization peak was broad and appeared at rather high temperatures in the initial stage of the grinding (top of Fig. 2). With further grinding, the process took place sharply at lower temperatures (middle of Fig. 2). Finally the peak became broad again at higher temperatures (bottom of Fig. 2). These changes will arise from delicate competition of the conceivable effects: remaining nuclei of the crystal, mobility of the molecules, and increased lattice imperfections due to stored strain energy.

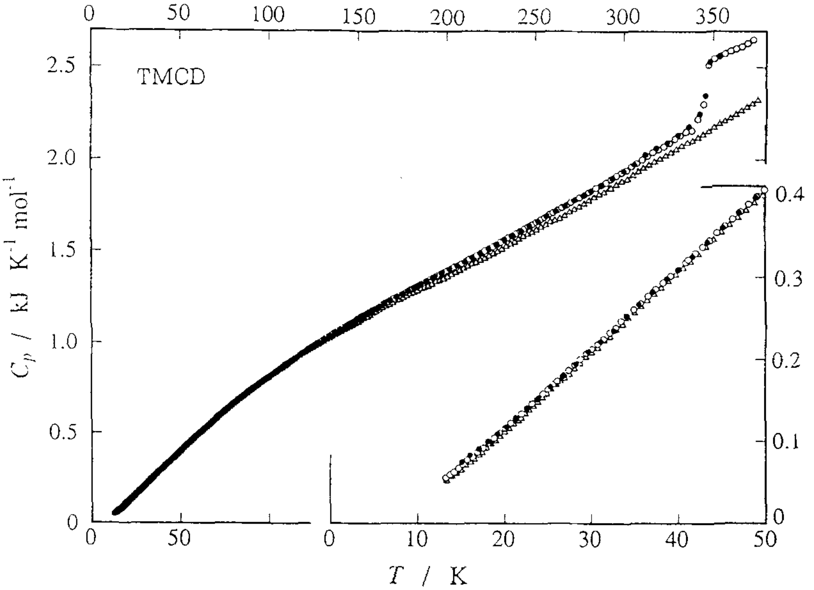

**Fig. 3** Molar heat capacities of TMCD; (o) liquid quenched glass; (•) ground amorphous solid; (Δ) crystal

One of the most peculiar phenomena in the solid-state amorphization process was the change in the glass transition temperature $T_g$ with the grinding time. At the initial stage of the grinding, $T_g$ was about 20°C lower than that of the LQG sample, and then rose with further grinding. Finally the temperature approached asymptotically the $T_g$ value of the LQG sample. The initial low value and the subsequent increase of $T_g$ was really unexpected phenomenon. Structural characterization of the intermediate state which might be a mixture of semi-crystalline and non-crystalline solids, is surely the subject of further study. Even after 25 min when the X-ray pattern shows apparently complete amorphization, some structural changes due to strain energy stored during the grinding are still going on.

The molar heat capacities obtained by the adiabatic calorimeter are given in Fig. 3 [10]. The symbols closed circle, open circle, and triangle correspond to the data for the GAS, LQG and crystalline samples, respectively. The enthalpy relaxation rate $\mathrm{d}H_c/\mathrm{d}t$ observed during each equilibration period in the temperatures below and around $T_g$ is plotted against temperature in Fig. 4. The quantity was evaluated by multiplying the spontaneous temperature drift rate $\mathrm{d}T/\mathrm{d}t$ by the heat capacity of sample including the sample cell. The temperature drift rate due to irreversible enthalpy relaxation was measured at 10 min after each energy input, when thermal equilibrium was attained in the normal region without any relaxational process. A minor effect arising from residual heat leakage was

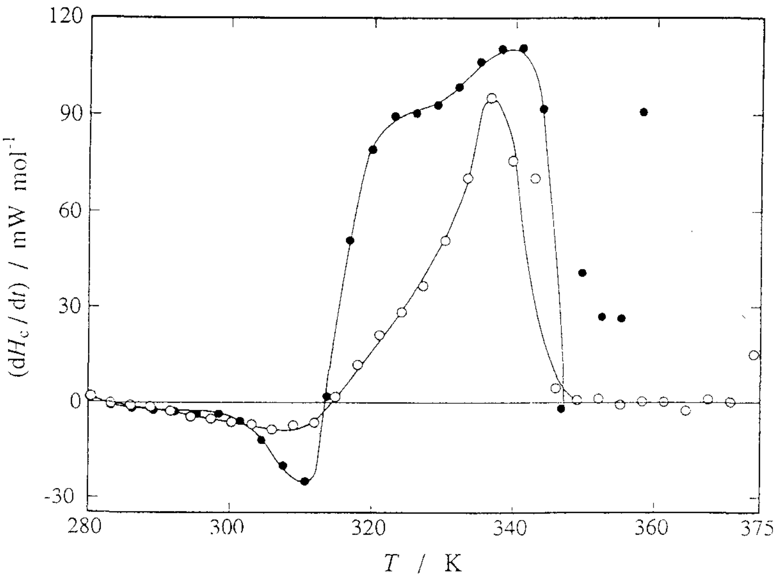

**Fig. 4** Rate of enthalpy relaxation in (○) liquid quenched and (●) ground amorphous TMCD solids

corrected for in determining the quantity d$T$/d$t$. This natural drift rate was of the order of several mK·h$^{-1}$ in most of the temperature range and was determined from the experimental data for the crystalline sample which did not exhibit any irreversible phenomenon.

A large heat-capacity jump amounting to 0.3 kJ·K$^{-1}$·mol$^{-1}$ due to the glass transition appeared at 345 K for the GAS sample. Slight endothermic followed by large exothermic temperature drifts were observed around this temperature range. The heat capacity value of the LQG sample was similar in magnitude to that of the GAS sample in the whole temperature range including the glass transition. However, the temperature dependence of the irreversible exothermic effect of the GAS sample was quite different from that of the LQG sample. A large and almost constant exothermic temperature drifts were observed in the temperature range between 310 and 345 K. This behavior is significantly different from the temperature drifts usually observed around $T_g$ of LQG. Another significant difference between the LQG and GAS samples was their crystallization behavior. A large exothermic effect arising from the crystallization occurred just above $T_g$ in the GAS sample. This facile crystallization might be associate with crystalline nuclei slightly left in the GAS sample.

The heat capacity of crystalline phase was measured with a fully crystallized sample produced by annealing the GAS sample at 360 K for one day. There was no thermal anomaly over the whole temperature region. The heat capacities of

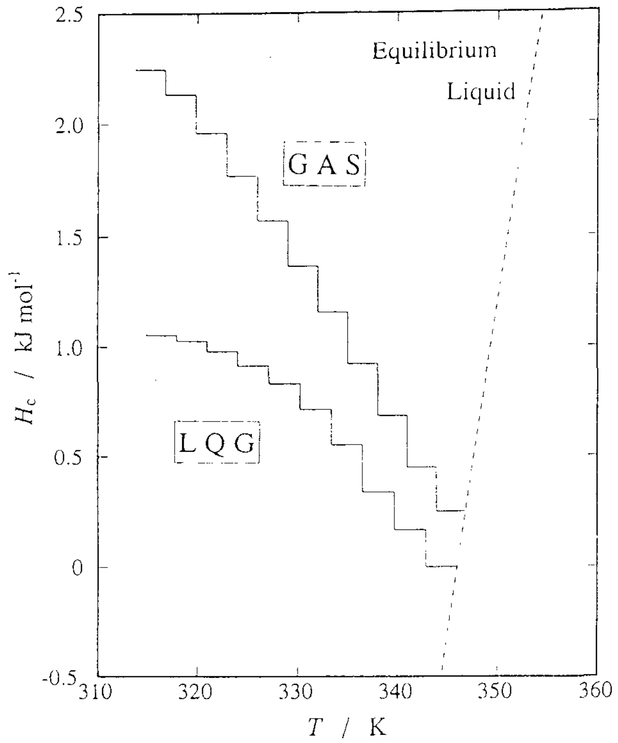

**Fig. 5** Excess configurational enthalpy of liquid quenched glass (LQG) and ground amorphous solid (GAS) over the hypothetical equilibrium liquid

the crystal were 2~3% smaller in magnitude than those of the LQG and GAS samples, as frequently observed in the glass-forming materials.

Configurational enthalpy relevant to the irreversible relaxation can be determined by subtracting the part of heat capacity due to vibrational degrees of freedom of liquid from the total heat capacity. Figure 5 draws the temperature dependence of the configurational enthalpy $H_c$ for various states of TMCD. The horizontal segments of the step-like lines represent the Joule heating and the vertical ones represent the amount of $H_c$ relaxed towards the equilibrium value that occurred during each equilibration period. The origin of $H_c$ was taken arbitrarily to the temperature at which the LQG sample reached the equilibrium state during the heat capacity measurement. It was found that the GAS sample initially produced had about twice larger configurational enthalpy than the LQG sample and relaxed towards the equilibrium state much faster than the LQG on warming.

This temperature dependence of the enthalpy relaxation for the GAS sample is similar to that observed in vapor-deposited (VD) amorphous sample [11, 12].

**Table 1** Glass transition temperature $T_g$ of non-crystalline solid

| Substance | $T_g$ / K | Method | Substance | $T_g$ / K | Method |
|---|---|---|---|---|---|
| propane | 46 | VC | butyronitrile | 97 | LQ |
| (propane)$_x$(propene)$_{1-x}$ | 46~55 | VC | | 97 | VC |
| propene | 55 | LQ | methanol | 103 | VC |
| | 55 | VC | vinyl acetate | 123 | LQ |
| (propene)$_x$(1-butene)$_{1-x}$ | 55~60 | VC | isopropylbenzene | 126 | LQ |
| 1-butene | 60 | VC | $H_2O$ | 135 | VC |
| | 60 | LQ | *m*-cresol | 200 | LQ |
| (propene)$_x$(1-pentene)$_{1-x}$ | 55~72 | VC | resorcinol | 250 | LQ |
| (butane)$_x$(1-butene)$_{1-x}$ | 60~62 | VC | phenolphtalene | ~362 | GC |
| (1-butene)$_x$(1-pentene)$_{1-x}$ | 60~72 | VC | | 362 | LQ |
| 1-pentene | 72 | VC | tri-*O*-methyl- | 352 | LQ |
| $CCl_4$ | 60 | VC | β-cyclodextrin | 352 | GC |
| isopentane | 65 | LQ | benzoic acid: tri-O- | 337 | LQ |
| $CHCl_3$ | 79 | VC | methyl-β-cyclodextrin | 337 | GC |
| 3-methylpentane (0.1 MPa) | 77 | LQ | magnesium acetate | 469 | DH |
| (108 MPa) | 85 | LQ | $As_2S_3$ | 477 | CR |
| (198 MPa) | 92 | LQ | | 477 | LQ |
| ethanol | 90 | LQ | $Sb_2S_3$ | ~489 | VC |
| cyclohexene | 92 | LQ | polytetrahydrofuran | 185 | LQ |
| dichloromethane | 93 | VC | polyoxacyclobutane | 193 | LQ |
| 1-propanol (0.1 MPa) | 97 | LQ | polyoctamethyleneoxide | 255 | LQ |
| (108 MPa) | 104 | LQ | | | |
| (198 MPa) | 109 | LQ | | | |

LQ: Liquid quenching; VC: Vapor condensation; CR: Chemical reaction; GC: Grinding of crystal; DH: Dehydration.

In the VD sample with highly excess $H_c$, a large enthalpy relaxation rate observed in the temperatures far below $T_g$ was explained by the entropy theory proposed by Adam and Gibbs [13]. The theory asserts that the relaxation time $\tau$ for the structural change is determined by the configurational entropy $S_c$ as well as the temperature $T$ through the following equation.

$$\tau = A \exp(B/TS_c),$$

where $A$ and $B$ are the constants characteristic of each substance. The GAS sample could have larger $S_c$ and hence shorter relaxation time $\tau$ than the LQG solid in the temperatures below $T_g$.

Another explanation for the unusually large enthalpy relaxation at low temperatures observed in the GAS sample is the possible existence of wide distribution of the relaxation times. The relaxation that takes place in the temperature region much lower than $T_g$ would be induced by the component with short relaxation time. It should be useful to compare the relaxation phenomena of GAS samples produced under different conditions changing the grinding temperature in order to clarify the predominant factor which plays a key role in the dynamics of the enthalpy relaxation process.

In this way, non-crystalline solids can be prepared by many means. One kind of them is produced from their disordered phases like liquid or vapor. The other kind is from ordered crystal, in good contrast to the former. The method of amorphization of crystal by mechanical grinding carried out below $T_g$ is similar in some sense to the amorphization of ice at 77 K by pressurization of sample beyond the hypothetical melting curve [14, 15]. In this case, the glass transition temperature of amorphous ice was reported to be 135 K [16]. All the non-crystalline solids prepared by exotic methods exhibit the glass transition phenomena which occur at essentially the same temperatures with those of the traditional LQ method. Some of our experimental findings are summarized in Table 1. The excess configurational enthalpy each non-crystalline solid prossesses, however, differ significantly depending on the preparation condition. The most powerful method is the vapor deposition in which the kinetic energies of the constituent molecules are extracted efficiently during a short period of condensation of vapor onto a cold substrate. The lower the substrate temperature, the higher the configurational enthalpy. The hierarchy of the non-crystalline solids with respect to their thermodynamic quantities can be controlled to some extents by the experimental conditions. The almost continuous hierarchical nature of frozen-in disordered phases is in good contrast to the discontinuous nature of various modifications (polymorphism) of crystalline phases.

In the case of grinding of crystalline substance, a non-crystalline solid is considered to form when strain energy stored by plastic deformation exceeds a critical value [17]. We also succeeded to produce non-crystalline solid of binary molecular system, TMCD and benzoic acid [18], which is known to form a 1:1 clathrate compound. It is interesting to observe that solid-state enclathration occurs at room temperature only by mechanical shaking of an equimolar mixture of them. After that, the clathrate compound can be amorphized by mechanical grinding, as in the case of pure TMCD.

Not only have the surprizing discovery about solid-state amorphization by mechanical grinding of crystal opened up a new way of preparing amorphous molecular solid, but also their importance lies in the gain of new insights into the nature of relaxations that any non-equilibrium amorphous states of matter exhibit.

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**Zusammenfassung** — Mittels Mahlen einer kristallinen Probe in einer Stabmühle bei Raumtemperatur wurde aus Tri-*O*-methyl-β-cyclodextrin ein amorpher Feststoff hergestellt. Mit Hilfe von Röntgen-Pulverdiffraktion und DSC wurde die Probe während des Amorphisierungsprozesses strukturell und thermisch charakterisiert. Man fand, daß die Glasumwandlung für eine voll amorphisierte Probe im wesentlichen bei der gleichen Temperatur stattfindet wie für ein flüssigkeitsabgeschrecktes Glas. Die Wärmekapazitäten der durch Mahlen und Flüssigkeitsabschrecken erhaltenen nichtkristallinen Feststoffe als auch der kristallinen Feststoffe wurden mittels eines Tieftemperatur-Adiabatikkalorimeters gemessen. Die Überschußenthalpien der gemahlenen amorphen Feststoffe und der flüssigkeitsabgeschreckten Gläser oberhalb derer für die hypothetische Gleichgewichtsflüssigkeit wurden kalorimetrisch bestimmt. Ähnliches und abweichendes thermisches Verhalten von beiden nichtkristallinen Feststoffen wurden verglichen.