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Solid-state formation and amorphization of the inclusion compound tri-*O*-methyl-β-cyclodextrin–benzoic acid

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Abstract

Differential scanning calorimetry (DSC), X-ray powder diffraction, and IR spectroscopy of a 1:1 inclusion compound of tri-*O*-methyl-β-cyclodextrin (TMCD) and benzoic acid (BA) were carried out. About 75% of the inclusion compound was formed by shaking an equimolar physical mixture of TMCD–BA for 180 min. The X-ray diffraction pattern of the inclusion compound formed was almost the same as that of the pure TMCD crystal. The inclusion reaction was completed by grinding for 3 min with a vibrating mill. Further grinding for 40 min transformed all the inclusion crystals into an amorphous state, whose X-ray diffraction pattern is similar to that of a liquid-quenched glass. A glass transition was observed in the temperature range of 58–64°C. The grinding-time dependence of the T_g was almost the same as that of the pure TMCD, i.e. the T_g increased with grinding and approached that of the liquid-quenched glass. The amorphous TMCD–BA inclusion compound crystallized at around 80°C into a metastable phase, which has an entropy smaller than that of the stable phase. The metastable phase then underwent an irreversible transition to the stable phase at around 100°C with an endothermic effect. The stable crystalline modification fused at 174°C.

INTRODUCTION

The compound tri-*O*-methyl-β-cyclodextrin (abbreviated as TMCD hereafter) is a permethylated derivative of β-cyclodextrin (CD). These compounds are known as typical host molecules of the clathrate or inclusion compounds [1]. The TMCD or CD molecule has a tube-like molecular shape and accommodates various guest molecules in the inside space. The surface of the space is hydrophobic and its diameter is about 700 pm. For these specific properties, CD and TMCD are frequently used in the fields

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of organic chemistry and pharmacy. We are interested in these compounds, however, from the following physico-chemical points of view.

The first is the mechanism of the inclusion reaction with the guest molecules. Obviously, the inclusion phenomenon readily occurs in the solution and melt. However, Nakai et al. [2] recently found that TMCD can enclathrate benzoic acid (BA) in the solid state although this type of inclusion reaction rarely occurs in the solid state. In special cases, host–guest reactions to form complexes readily occur in the solid state, e.g. 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol and benzophenone, or 1,1-bis(*o*-hydroxyphenyl)cyclohexane and benzoquinone [3]. Nakai et al. investigated two kinds of equimolar mixture of TMCD and BA. One was a physical mixture and the other was ground with a vibrating mill at room temperature. The former underwent an inclusion reaction on heating at around 84°C and the latter during grinding at room temperature. It is interesting that the inclusion compound obtained by grinding is in an amorphous state.

Our question is whether the enclathration occurs before or after the amorphization, or simultaneously. The grinding has two effects on the materials; one is to increase the reaction surface and the other is to amorphize the material by mechanical energy, as described below. In the amorphous solid, the diffusion of the molecules can be activated and then the inclusion reaction should be enhanced. The first purpose of the present work is to clarify which of these effects dominates the solid-state enclathration in the TMCD system.

Another interest is the amorphizing process itself and the glass transition phenomenon of the amorphous solid formed. Solid-state amorphization by grinding [4] is the opposite process to conventional amorphizing procedures, such as liquid quenching and vapor deposition. The conventional procedure is based on rapid removal of the kinetic energies of the constituent entities in the disordered state, while solid state amorphization is achieved by supplying mechanical energy to destroy the equilibrium crystal and freeze it in an energized metastable amorphous state. We are interested in the glass transition and structural relaxation of this novel system. So far, solid-state amorphization has been studied for some binary alloys [5–8] and metal oxides [9]. However, no glass transition has been clearly observed because they have generally small heat-capacity jumps at T_g and crystallize easily above T_g.

Recently, our DSC and X-ray diffraction studies [10] revealed the clear existence of the glass transition in TMCD amorphized by grinding with a vibrating mill. It was very informative that the glass transition temperature shifted during the grinding. At the initial stage of the grinding, when the amorphization was just completed, the glass transition temperature was about 20°C lower than that of the liquid-quenched sample. With further grinding, the T_g gradually increased and finally approached the T_g of the liquid-quenched glass. This change in the T_g should reflect some structural changes taking place in the amorphous solids. This kind of structural change in non-crystalline solids cannot be positively detected by the experimental techniques presently available. The second purpose of the present study is to investigate this phenomenon in the TMCD–BA inclusion compound and to compare the result with that of pure TMCD.

Based on the two interests described above, differential scanning calorimetry (DSC), X-ray powder diffraction and IR spectroscopy were carried out for two samples of the equimolar mixture TMCD–BA; one was a fine, powdery mixture shaken in a sealed bottle, and the other was ground by a vibrating mill after shaking. The shaking- and grinding-time dependence of the inclusion reaction, structure and glass transition was carefully investigated.

EXPERIMENTAL

Sample preparation

TMCD (from Toshin Chemical Co., Ltd.) and BA (NBS standard reference material 39i) were used without further purification after drying in vacuo for 24 h at room temperature. The purity of the samples was checked by an elemental analysis and a fractional melting method using DSC. Good agreement between the observed and calculated values was obtained in the elemental analyses of both samples. TMCD: carbon %, 52.62 (obs.), 52.93 (calc.); hydrogen %, 7.96 (obs.), 7.90 (calc.), oxygen %, 39.42 (obs.), 39.17 (calc.). BA: carbon %, 68.82 (obs.), 68.85 (calc.); hydrogen %, 4.83 (obs.), 4.95 (calc.); oxygen %, 26.35 (obs.), 26.20 (calc.). Fractional melting experiments also showed very high purities for both samples (TMCD, 99.9%; BA, 100%).

Because the particle size of the BA crystal was fairly large, the crystal was ground by a mortar made of aluminum oxide to obtain a fine powder similar to the TMCD sample. Equimolar component crystals, 5.9307 g of TMCD and 0.5078 g of BA, were mixed in a sealed glass bottle and shaken for 180 min. During the process of shaking, a small amount of the sample was taken from the bottle for the DSC measurements, X-ray powder diffraction and IR spectroscopy. Then the sample was ground for 240 min using a vibrating sample mill TI-100 (Heiko Manufacturing, Ltd.). The pot and rod of the mill were made of aluminum oxide and the free space of the pot was about 10 cm^3. The volume of the powdery sample was about 8 cm^3. The milling operation was stopped every 10 min and the pot was cooled with a fan to remove the heat arising from the friction and impact between the pot and the rod. The surface temperature of the pot was kept below 40°C during the milling. During the milling, some sample was removed from the pot for the DSC and X-ray powder diffraction experiments. All the operations described above were made under dry nitrogen atmosphere because of the hygroscopic nature of the TMCD crystal.

The elemental analysis of the ground sample showed good agreement between the calculated and observed values as follows: carbon %, 53.87 (obs.), 54.18 (calc.); hydrogen %, 7.69 (obs.), 7.67 (calc.); oxygen %, 38.44 (obs.), 38.15 (calc.). This shows that the sample was not contaminated with aluminum oxide from the pot and rod during the grinding. Good purity of the sample (99.8%) was also obtained from the fractional melting experiment by DSC.

The liquid-quenched sample was prepared by rapid cooling of the melt of the TMCD–BA mixture ground for 240 min. The sample was loaded in a closed glass tube, and kept at about 200°C for 10 min before the quenching in order to make the inclusion reaction complete. The cooling rate was estimated to be about 1000°C min^{-1}.

DSC measurement

Differential scanning calorimetry (DSC) was carried out in the heating direction using a Perkin–Elmer DSC 7 with aluminum sample pans. The temperature range covered was between 30 and 200°C. The mass of the sample was 3–7 mg and the heating rate was 3°C min^{-1}. The samples measured were the TMCD–BA mixture shaken in the bottle for 45 and 180 min, those ground by the vibrating mill for 1, 3, 5, 7.5, 10, 15, 25, 40, 60, 100, 160 and 240 min, and the liquid-quenched glass. Pure TMCD and BA crystals were also measured for comparison. The glass transition temperature (T_g) was determined as the intersection of the thermogram and bisector of the baselines above and below T_g. The temperatures of the irreversible transitions (e.g. crystallization) and the fusion were determined as the top and the onset of the peaks, respectively.

X-ray powder diffraction measurement

X-ray powder diffraction patterns were taken at room temperature using a diffractometer model RAD-ROC (Rigaku Denki Co., Ltd.) at the X-ray Diffraction Service of the Department of Chemistry, Faculty of Science, Osaka University. The sample, 0.2 mm thick, was mounted on the glass sample holder. The range of the diffraction angle 2α was 3–90 deg and the scanning speed was 3 deg min^{-1}. The samples measured were the TMCD–BA mixture shaken in the bottle for 45 and 180 min, those ground by the vibrating mill for 1, 3, 5, 7.5, 10, 15, 25, 40, 60 and 100 min, and the liquid-quenched sample. Pure TMCD and BA crystals were also measured for comparison.

IR spectroscopy

The IR spectra were recorded at room temperature in the wavenumber range 4000–400 cm^{-1} using an FT/IR-3 (Japan Spectroscopic Co., Ltd.). The samples measured were the TMCD–BA mixture shaken for 45 and 180 min, the sample ground for 240 min and pure BA. For the IR experiment, the shaken samples were prepared separately from those for the DSC and X-ray diffraction experiments. All the samples were physically mixed with KBr powder and shaped into disks under a pressure of about 50 MPa. The ratio of KBr to TMCD–BA was about 5:1 and that of KBr to BA was about 50:1.

RESULTS AND DISCUSSION

Formation of the inclusion compound

Figure 1 shows the DSC curves of (a) BA crystal, (b) TMCD crystal and (c) 1:1 mixture of BA and TMCD crystals shaken for 180 min. In the sample (c), the endothermic peak due to the fusion of TMCD (157°C) was shifted down to 153°C, and became smaller and broader than that of the pure sample. The peak due to the fusion of BA was split into several broad

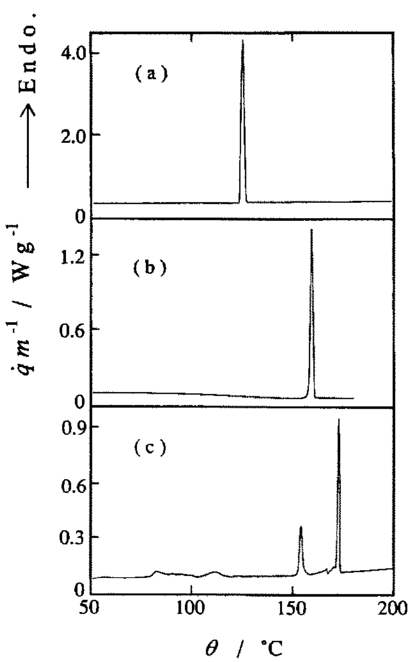

Fig. 1. DSC curves of (a) BA crystal, (b) TMCD crystal, (c) 1:1 TMCD–BA mixture shaken for 180 min.

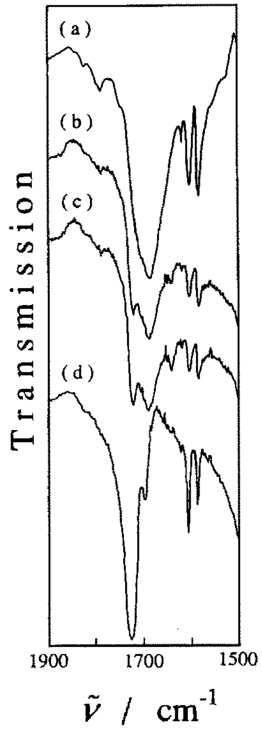

Fig. 2. IR spectra of (curve a) BA, (curve b) TMCD–BA mixture shaken for 45 min, (curve c) mixture shaken for 180 min and (curve d) mixture ground for 240 min.

ones located in the temperature range 80–120°C. It is also possible that some other thermal effects were included in these peaks. Similar results were obtained in the DSC of the mixture shaken for 45 min. The enthalpy of fusion of the TMCD decreased with shaking as follows: with t(shaking) = 45 min, $\Delta_{\text{fus}}H(\text{shaken})/\Delta_{\text{fus}}H(\text{pure}) = 0.36$; with t(shaking) = 180 min, $\Delta_{\text{fus}}H(\text{shaken})/\Delta_{\text{fus}}H(\text{pure}) = 0.25$.

Figure 2 shows the IR spectra of (a) BA, (b) TMCD–BA mixture shaken for 45 min, (c) shaken for 180 min and (d) ground for 240 min. The absorption peak observed at 1688 cm^{-1} in spectrum (a) is assigned to the carbonyl stretching band of the cyclic dimer structure of the benzoic acid molecule. The spectra (b) and (c) indicate that the intensity of this peak is decreased and that of a new peak at 1724 cm^{-1} is increased, with shaking of the TMCD–BA mixture. The peak at 1724 cm^{-1} is caused by monomer benzoic acid molecule enclathrated inside the TMCD molecule [2]. In the sample (d), the inclusion reaction of TMCD and BA has almost completed. The results of the DSC and IR absorption experiments indicate that the guest BA is enclathrated in the host TMCD molecule by shaking them at room temperature. The exothermic peak at around 84°C [2], which has been ascribed to the inclusion reaction of BA and TMCD, was not

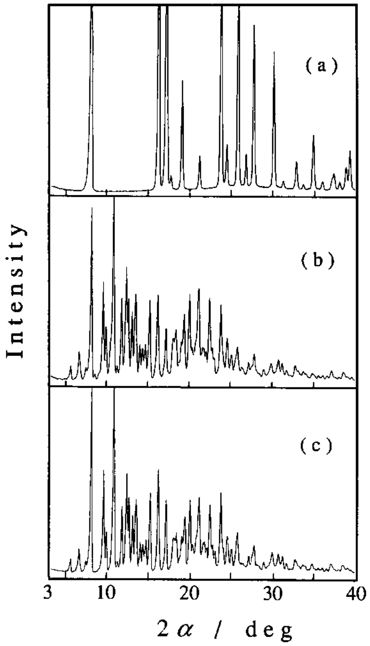

Fig. 3. X-ray diffraction patterns of (a) BA crystal, (b) TMCD crystal, (c) 1:1 TMCD–BA mixture shaken for 180 min.

observed in the present DSC experiment. This is probably because our sample was shaken for a much longer time than the reported sample and so a major part of our sample reacted at room temperature.

Figure 3 gives the X-ray diffraction patterns corresponding to the DSC curves of Fig. 1. Surprisingly, the diffraction pattern of the shaken mixture (c) is very similar to that of the pure TMCD (b). Some peaks on which strong peaks of the remaining BA overlap, are stronger than those observed in the pure TMCD. Obviously, there are no peaks associated with the crystalline phases of the TMCD–BA inclusion compound obtained by grinding (see Figs. 10(b) and 10(c), below). This result indicates a very strange and significant fact that the structure of the inclusion compound formed by the shaking is almost the same as that of pure TMCD. In other words, the enclathration of BA at room temperature does not deform, to any significant extent, the structure of the pure TMCD crystal.

As described later, the endothermic peak at 174°C in Fig. 1(c) is due to the fusion of the stable phase of the TMCD–BA inclusion compound. It is surprising that the fusion observed was not that of the metastable phase formed by the shaking, but that of the stable phase. We postulate that an irreversible transformation to the stable phase occurred during heating, as indicated by the thermal anomalies around 100 or 160°C. The exothermic effect observed around 165°C may be due to the inclusion reaction of the

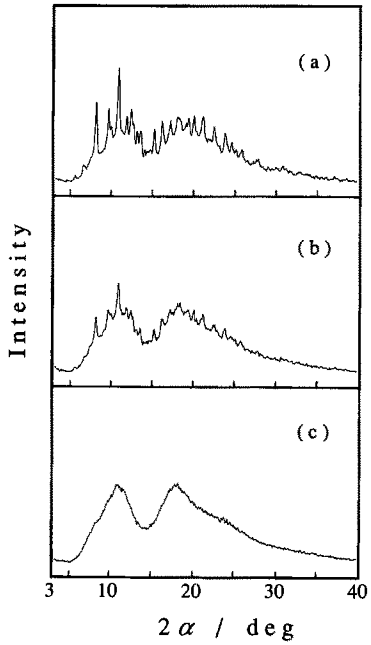

Fig. 4. X-ray powder diffraction patterns of TMCD-BA inclusion compounds ground for (a) 3 min, (b) 15 min, (c) 40 min.

remaining TMCD and BA, because the inclusion reaction usually occurs readily in the liquid state.

The solid-state inclusion reaction of BA and TMCD was first found by Nakai et al. [2], but they could not determine whether the inclusion reaction occurred in the crystalline state or in the amorphous state. The present study has shown that the enclathration actually occurred in the crystalline state, preserving the crystal structure of the host TMCD. It is not easy to imagine how the BA molecule diffuses in the TMCD crystal and is quickly enclathrated at room temperature. This problem deserves further investigation.

Effect of the grinding and amorphization process

Figure 4 shows the X-ray diffraction patterns of the equimolar TMCD-BA mixture ground with the vibrating mill for (a) 3 min, (b) 15 min and (c) 40 min. With grinding of the sample, the intensity of the Bragg peaks of the mixture, compare with Fig. 3(c), decreased and halos characteristic of an amorphous material appeared. The crystalline and amorphous solids coexisted in samples (a) and (b). The Bragg peaks completely disappeared after grinding the sample for 40 min (sample (c)) and the shape of the halo was not changed by further grinding.

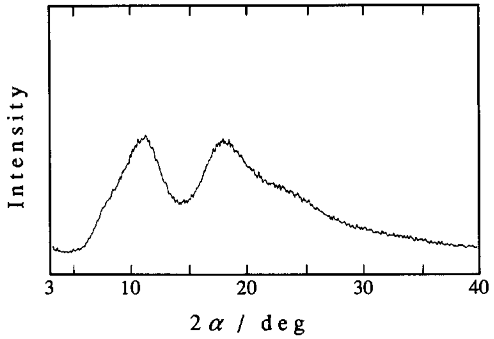

Fig. 5. X-ray powder diffraction patterns of the liquid-quenched glass of TMCD–BA inclusion compound.

Figure 5 shows the X-ray diffraction pattern of the liquid-quenched glass of the TMCD–BA inclusion compound. This halo pattern is almost the same as Fig. 4(c), indicating that the amorphous state formed by grinding is very similar to that formed by liquid-quenching. This is the same result as obtained in pure TMCD [10].

Figure 6 reproduces the DSC curves corresponding to Fig. 4. In sample (a), the endothermic peak due to the fusion of TMCD (157°C) disappeared completely, indicating that the inclusion reaction completed within 3 min of

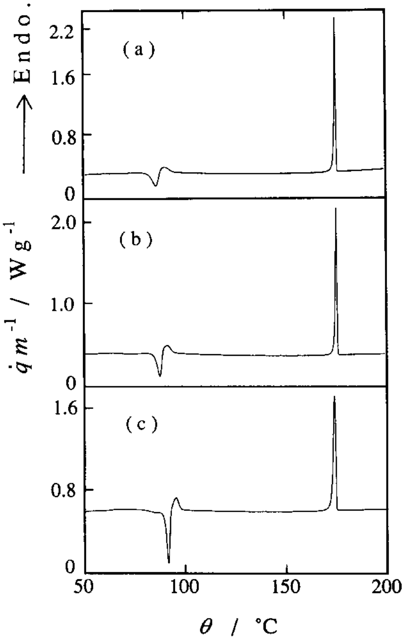

Fig. 6. DSC curves of TMCD–BA inclusion compounds ground for (a) 3 min, (b) 15 min, (c) 40 min.

grinding. In samples (b) and (c), four thermal anomalies were observed on heating: a baseline jump at about 60°C (shown clearly in Fig. 7, below), successive exothermic and endothermic peaks at around 80–90°C, and a sharp endothermic peak at 174°C. These anomalies are considered to be due to a glass transition, an irreversible crystallization to a metastable phase, an irreversible transition to the stable phase, and to the fusion, respectively.

Table 1 summarizes the thermal properties of the ground TMCD–BA inclusion compound derived from the DSC experiment. The glass transition was observed in samples ground for more than 10 min. The baseline jump for some samples could not be determined owing to the instability of the baselines. For the samples ground for less than 100 min, the crystallization and the irreversible solid–solid transition occurred too close together for their enthalpy changes to be analyzed separately. No crystallization was observed in the liquid-quenched glass (LQG), probably owing to the absence of any crystalline nuclei. The notation Cr(a) indicates the crystal obtained by heating the amorphous solid ground for 100 min up to 115°C, and Cr(b) indicates the crystal obtained by annealing the LQG at around 94°C for more than 23 h. Further discussion of the glass transition and the two crystalline modifications will be given in the following sections.

Glass transition

Figure 7 shows an enlarged view of the DSC curves near the glass transitions of the amorphous samples prepared by (a) grinding for 40 min and (b) liquid-quenching. The baseline jump with overshooting effect was clearly observed in both curves. Two straight lines represent the extrapolations of the baselines above and below T_g. The glass transition temperature is shown by a vertical bar on the rising part of the curve. The grinding-time dependence of T_g is shown in Fig. 8. The dashed line represents the T_g of the liquid-quenched glass. At the initial stage of the grinding, the T_g of the ground sample was about 6°C lower than the T_g of the liquid-quenched glass, and then increased up to that value with grinding. The heat capacity jump at T_g (ΔC_p) of the ground sample was also saturated to the corresponding value of the liquid-quenched glass. These distinctive features of the glass transition of the ground sample are similar to those of pure TMCD [10]. Thus it is found that all the properties of the TMCD–BA inclusion compound associated with the amorphization and glass transition are similar to those of the pure TMCD.

The saturated T_g of the TMCD–BA inclusion compound is 13°C lower than that of pure TMCD. This is an interesting effect because the intermolecular interaction of the inclusion compound is not much different from that of pure TMCD. It is not easy to explain this effect based only on

TABLE 1

Effect of grinding time on the thermal properties of TMCD–BA derived from DSC

	t (min)	T_g (°C)	ΔC_p (J K^{-1} G^{-1})	T_{fus} (°C)	$\Delta_{fus}H$ (J g^{-1})	T_{cr} (°C)	$\Delta_{cr}H$ (J g^{-1})	T_{trs} (°C)	$\Delta_{trs}H$ (J g^{-1})
	3	–	–	174.3	39.3	85.6	–	89.6	–
	5	–	–	173.6	38.7	87.0	–	90.4	–
	7.5	–	–	174.1	39.1	86.0	–	89.3	–
	10	58.2	0.24	174.3	39.4	87.2	–	90.7	–
	15	58.1	0.28	174.2	37.5	87.2	–	90.8	–
	25	57.1	–	174.3	38.7	87.1	–	90.7	–
	40	62.7	0.30	172.8	38.2	91.5	–	95.2	–
	60	62.0	–	174.0	37.6	81.1	–	90.8	–
	100	64.9	–	173.5	38.4	74.8	−18.7	97.5	7.9
	160	64.2	0.29	174.0	38.4	78.3	−18.8	101.6	11.2
	240	64.1	0.34	173.7	37.7	79.6	−19.3	102.1	12.2
Cr(a)		–	–	173.9	38.7	–	–	–	–
Cr(b)		–	–	174.2	40.1	–	–	–	–
LQG		64.5	0.28	–	–	–	–	–	–

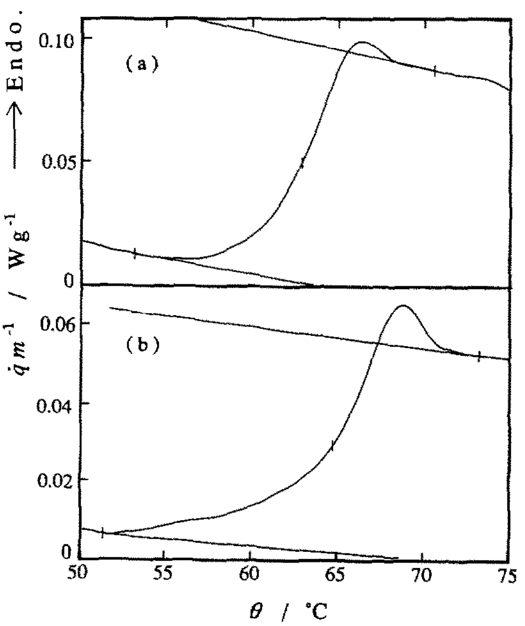

Fig. 7. Enlarged view of the DSC curves of TMCD–BA inclusion compounds near the glass transition temperature: (a) amorphous solid ground for 40 min, (b) liquid-quenched glass.

the difference in molecular weight. A systematic study is required to investigate the guest dependence on the glass transition temperature of the TMCD inclusion compounds. A DSC study of TMCD enclathrating other

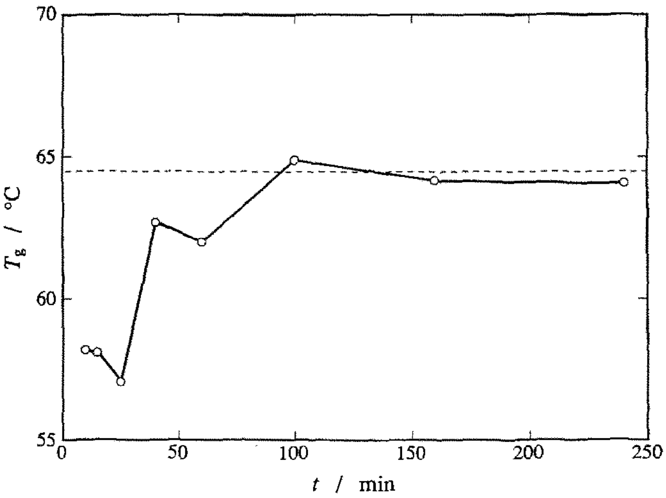

Fig. 8. Grinding-time dependence on the glass transition temperatures of TMCD–BA inclusion compounds.

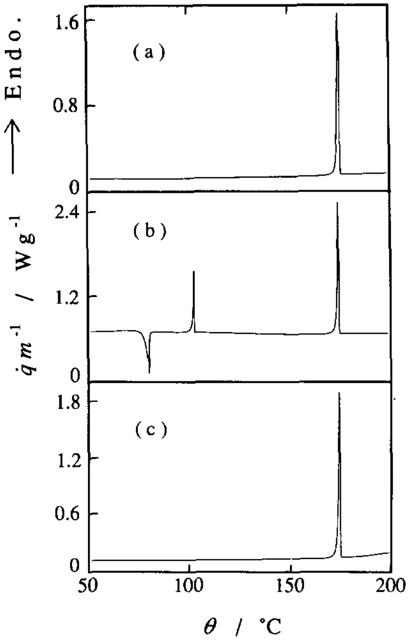

Fig. 9. DSC curves of TMCD–BA inclusion compounds: (a) crystal obtained by annealing the liquid-quenched glass, (b) amorphous solid ground for 240 min, (c) crystal obtained by heating the amorphous solid up to 115°C.

guest molecules, e.g. *p*-nitrobenzoic acid, *p*-hydroxybenzoic acid, is now in progress in our laboratory and will be published in the near future.

Crystalline phases of the inclusion compound

Figure 9 reproduces the DSC curves of the TMCD–BA inclusion compounds which completed inclusion reactions. Sample (a) is the crystal obtained by annealing the liquid-quenched sample at 94°C for 23 h (Cr(b) in Table 1). A sharp endothermic peak due to the fusion of the TMCD–BA inclusion compound was observed at 174°C. Sample (b) is the amorphous solid obtained by grinding for 240 min (the longest grinding time in this study). On heating, exothermic and endothermic peaks were observed separately at 80 and 100°C, respectively. The fusion temperature was the same as that of sample (a). Sample (c) was prepared by heating the sample ground for 100 min, which has almost the same thermal property as that ground at 240°C, up to 115°C and then cooling it down to room temperature (Cr(a) in Table 1). Only one endothermic peak due to the fusion appeared at the same temperature as those of the fusions of samples (a) and (b). The enthalpy of fusion was almost the same for the three samples (see Table 1). These DSC measurements have clarified that both exothermic and endothermic peaks were irreversible in nature and that the

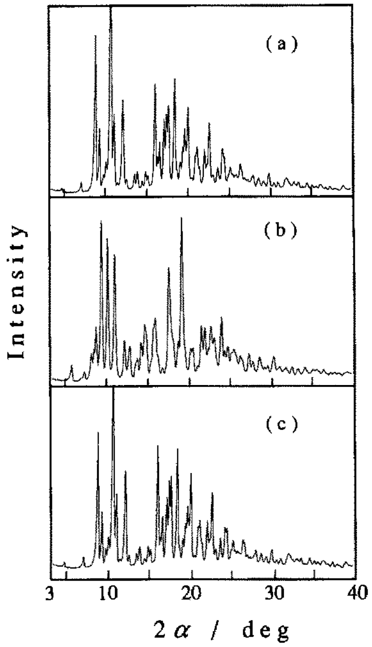

Fig. 10. X-ray powder diffraction patterns of TMCD–BA inclusion compounds: (a) crystal obtained by annealing the liquid-quenched glass, (b) crystal obtained by heating the amorphous solid up to 78°C, (c) crystal obtained by heating the amorphous solid up to 121°C.

crystalline phase just below the fusion temperature was identical for all the samples.

Figure 10 shows the X-ray diffraction patterns of the TMCD–BA compound taken after the following thermal treatments: sample (a) corresponds to the sample (a) in Fig. 9, which is the crystal obtained from the liquid-quenched sample; sample (b) was prepared by heating sample (b) in Fig. 9 up to a temperature above the exothermic peak at 80°C and then cooling it down to room temperature, so that this diffraction pattern reflects the structure of the metastable phase existing between the exothermic peak at 80°C and the endothermic peak at 100°C; sample (c) was obtained by cooling the sample (b) in Fig. 9 from a temperature above the endothermic peak at 100°C, corresponding to the phase existing just below the fusion point. The diffraction pattern of Fig. 10(c) is the same as that of Fig. 10(a) but different from that of Fig. 10(b). Thus, the present X-ray diffraction experiments have clarified that the phase existing between 80 and 100°C is a metastable one exhibiting a crystal structure different from that of the stable phase existing just below the fusion point. It is also worth noting that all the diffraction patterns drawn in Fig. 10 are different from that of Fig. 3(c). This means that the crystalline phase which is formed when BA was enclathrated in TMCD by shaking is in a different metastable

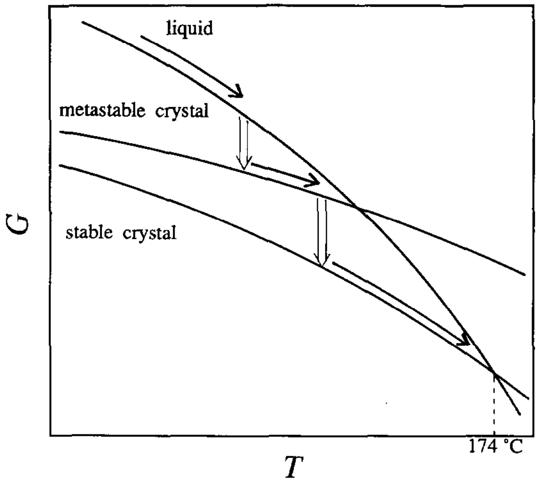

Fig. 11. Schematic diagram of Gibbs energy of TMCD–BA inclusion compound (see the text for details).

state. In total, three crystalline phases were found in the TMCD–BA inclusion compound.

From the results obtained by DSC and X-ray diffraction, we have drawn a schematic Gibbs energy curve (G curve) as a function of temperature (Fig. 11). Here, the G curve of the supercooled liquid above T_g of the ground sample was assumed to be the same as that of the liquid-quenched sample. The path followed by the amorphous sample formed by the grinding on heating is shown by the arrows. The irreversible transitions at 80 and 100°C, seen in Fig. 9(b), are shown by the thick vertical arrows in the figure. At the exothermic transition (80°C), the slope of the G curve is decreased, corresponding to the entropy decrease and the exothermic effect. At the endothermic transition (100°C), the slope is increased, corresponding to entropy increase and the endothermic effect. It is very strange and interesting that the metastable phase has a smaller entropy than the stable phase. The fusion, which is a reversible transition, is represented as the intersection of the G curves of the stable crystal and of the liquid at 174°C.

It is possible that the G curves of the metastable and stable phases intersect at low temperature. In order to examine this possibility, differential thermal analysis (DTA) was performed for both the stable and metastable phases in the temperature range from −195 to 120°C. Unfortunately, no evidence of a phase transition could be obtained over the whole temperature range. The present result indicates that the G curves of the metastable and stable crystals do not intersect above −195°C or that the transition could not be observed, owing to the supercooling and superheating effects, for a kinetic reason. A more precise study with an adiabatic calorimeter is required before a final conclusion on this problem is drawn.

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