# SOLID STATE AMORPHIZATION AND GLASS TRANSITION OF TRI-O-METHYL-$\beta$-CYCLODEXTRIN*

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Amorphous solid of tri-O-methyl-$\beta$-cyclodextrin was formed by grinding the crystalline sample with a vibrating mill at room temperature. The amorphising process was examined by X-ray powder diffraction technique and differential scanning calorimetry (DSC). The Bragg peaks disappeared and the enthalpy of crystallization became constant for the sample ground for 25 min, indicating the apparent completion of the amorphization. A glass transition of the ground amorphous solid was found by DSC. The glass transition temperature $T_g$ moved from 58°C to 79°C with grinding. The saturated $T_g$ of the ground sample was the same as that of the liquid-quenched glass. No significant difference between the ground and liquid-quenched amorphous solids was found in the X-ray diffraction patterns. Infrared spectra of both amorphous solids, however, showed a definite difference for the band at 1194 cm$^{-1}$ assigned to the rocking of the CH3 groups which are located at the molecular periphery.

Amorphous solids [1–3] are usually prepared by quenching their liquids or depositing their vapours on a cold substrate. These procedures are based on rapid removal of kinetic energies of the constituting entities. Recently, great attention has been paid to the solid state amorphization [4]. This is the process from the opposite side against the conventional procedure, i. e., supplying energy to excite the equilibrium crystal and freeze it in energized metastable amorphous state. So far many of the studies on the solid state amorphization have been done for binary alloys (Zr-transition metal [5], Ni-

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* Contribution No. 35 from the Microcalorimetry Research Centre.

Nb [6], Ni-Ti [6], Co-Y [7], etc.) and metal oxides ($3BiFeO_3$-$ZnFe_2O_4$ [8], etc.). Mechanical grinding with ball mill and irradiation by high energy electron or neutron beam are the commonly used techniques for solid state amorphization. At present the amorphization process itself and the possible structural difference between the amorphous states obtained by these techniques and the traditional ones are in the centre of interest [4]. The X-ray and neutron diffraction and EXAFS techniques have been applied to these investigations.

The amorphous solid is in non-equilibrium state, which should relax towards the equilibrium one if the atomic or molecular rearrangement can be thermally excited. This process ordinarily occurs at the glass transition region. This recovery phenomenon, referred to as structural relaxation, is substantially different from that occurring around the equilibrium state usually observed as the response to the external alternating field. The latter is called, for example, dielectric or viscoelastic relaxation. How do the physical properties of the system such as the enthalpy and volume change as a function of time in the structural relaxation? Are they coupled or independent? Which internal parameters control the relaxation rate? Many theoretical models [9, 10] have been developed to answer these questions but the accumulation of the experimental results is not sufficient enough to verify the validity of these models. Our approach is to compare the glass transitions and the enthalpy relaxation processes of the amorphous solids prepared by different methods. So far, we have measured the relaxation processes of the liquid-quenched and vapour-deposited amorphous solids [11−13], those of the liquid-quenched glasses formed by temperature-jump and pressure-jump methods [14], and those of the liquid-quenched glasses formed by rapid cooling and rapid heating methods [15]. To investigate the glass transition of the amorphous solid formed from crystal is very significant in extending the research region of the structural relaxation.

For amorphous solids originating from crystals (metals and metal oxides) so far, no glass transition has been observed as a definite jump of the heat capacity or thermal expansion coefficient. This might be due to the fact that they have small heat capacity jumps at the glass transitions and are crystallized easily above $T_g$. Recently, cyclodextrin (CD), tri-O-methyl-$\beta$-cyclodextrin (TMCD), and their inclusion compounds were found to be amorphized by mechanical grinding [16−18]. These compounds are expected to have large heat capacity jump at $T_g$ and to be stable in the undercooled liquid state above $T_g$. This is because they have many intramolecular degrees of freedom which will enhance the glass-forming ability. CD decom-

poses below the fusion temperature but TMCD can fuse at 156°. The latter compound, therefore, is a good candidate for the present research aiming at the comparison of the relaxation processes of amorphous solids prepared in various ways. We have used DSC, X-ray powder diffraction, and IR spectroscopy for the characterization of the amorphous TMCD solids prepared by a vibrating mill and liquid-quenching. The purposes of the present study were to investigate (1) the reality of existence of the glass transition in the ground sample, (2) grinding-time dependence of the thermal properties and structural change, and (3) possible difference between the ground and liquid-quenched amorphous samples.

**Experimental**

The sample TMCD was purchased from Toshin Chemical CO., LTD. It was annealed at about 130° in vacuo for more than 24 h to be dried and crystallized completely. The latter process was found to be necessary during the course of experiment because the original sample contained a fraction of solid in amorphous state. The purity of the sample was checked by an elemental analysis and a fractional melting method with DSC. The result of the elemental analysis was as follows:

|      | C%    | H%   | O%    |
|------|-------|------|-------|
| Obs. | 52.76 | 7.94 | 39.30 |
| Calc.| 52.93 | 7.90 | 39.17 |

The purity calculated from the fractional melting was 98.2%.

The sample of about 5 cm³ (4.0 g) was ground by using a vibrating sample mill TI100 (Heiko Manufacturing, LTD.) in dry nitrogen atmosphere. The machine is unique in the sense that a single rod was used in place of many balls widely used, making it easy to take out a sample of sticky nature from the pot. The pot and the rod were made of aluminium oxide and the free space of the pot was about 10 cm³. The milling operation was stopped at every 7.5 min and the pot was cooled with fan to remove the heat arising from friction and impact between the pot and the rod. The surface temperature outside of the pot was kept below 40° during the milling. At 5, 10, 15, 25, 60, 120, 210, 300 min after starting the milling, the pot was opened and a small amount of the sample for DSC and X-ray diffraction was taken out of the pot in dry nitrogen atmosphere. The liquid-quenched sample was

prepared by immersing the TMCD melt in a closed glass tube into water with ice. The cooling rate was estimated to be about 1000 deg· min$^{-1}$.

Differential scanning calorimetric measurements were carried out in the temperature range between 30 and 180° by using Perkin-Elmer DSC 7 with aluminium sample pans. The mass of the sample was 5−9 mg and the heating rate was 3 deg·min-1. The glass transition temperature was determined as the intersection of the thermogram and the bisector of the baselines above and below $T_g$. The crystallization and melting temperatures were determined as the top and the onset of the peaks, respectively.

The X-ray powder diffraction pattern was 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. The sample of
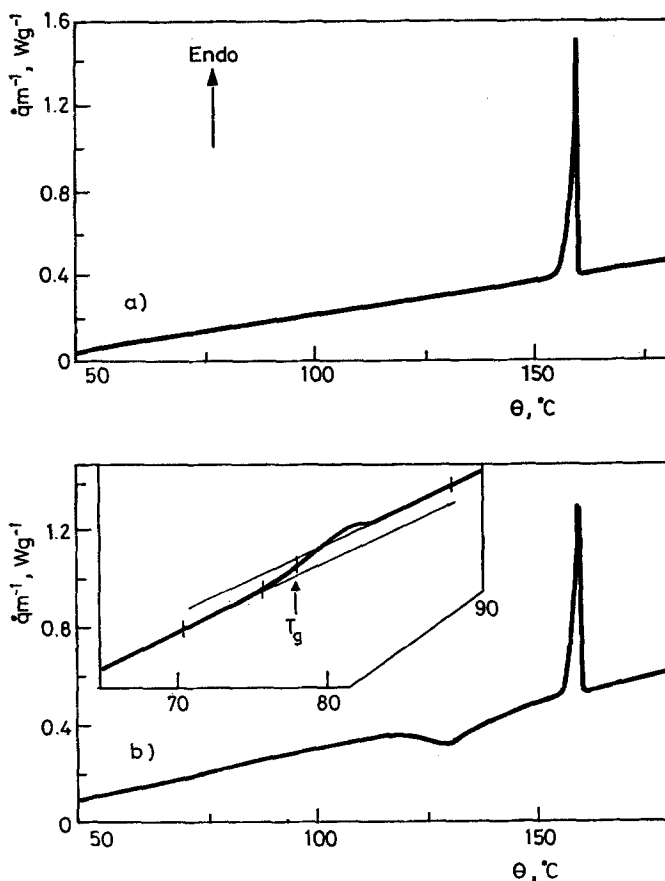


Fig. 1 DSC curves of TMCD: (a) Crystal, (b) liquid-quenched glass

0.2 mm thickness was mounted on the sample holder made of glass. The range of diffraction angle $2\alpha$ was 3–90 deg and the scanning speed was 3 deg·min$^{-1}$.

The IR spectra were recorded at room temperature in the wavenumber range 400–2000 cm–1 using FT/IR-8000 (Japan Spectroscopic Co., LTD.). The sample for the IR experiment was prepared by grinding TMCD crystal for 3 h by hand with a pestle in a mortar. All the samples were mixed with KBr powder in a weight ratio of KBr:TMCD = 99:1, and shaped into disks under a pressure of 460 MPa.

## Results and discussion

### Crystal and liquid quenched glass

Figure 1 shows the DSC curves of TMCD of (a) crystal, and (b) liquid-quenched glass. The endothermic peak in Fig. 1(a) is due to the fusion of TMCD; the fusion temperature was 157.6° and the enthalpy of fusion was 40.6 kJ g–1. The step-like anomaly in Fig. 1(b), clearly shown in the inset, is due to a glass transition of TMCD, which is first found in this study. The
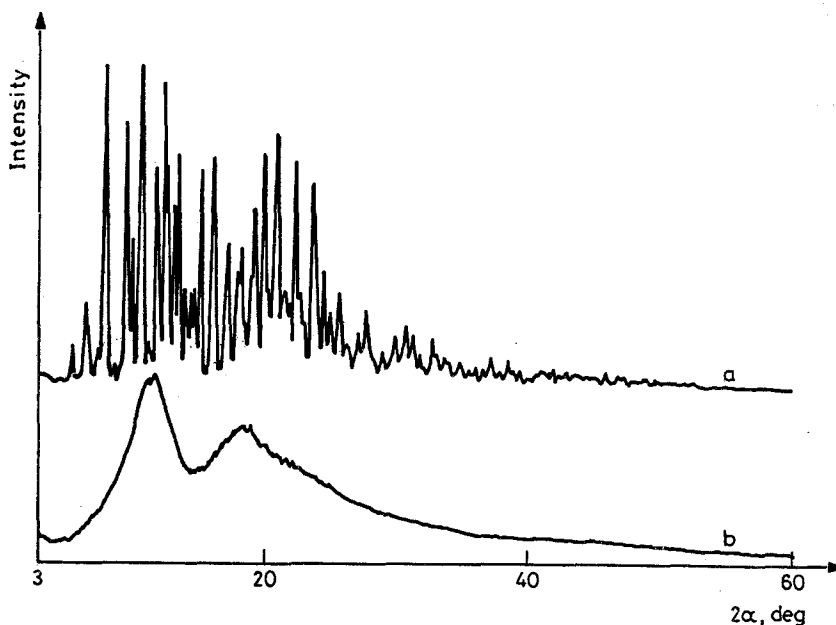


Fig. 2 X-ray powder diffraction patterns of TMCD: (a) Crystal, (b) liquid-quenched glass

glass transition temperature was 77.8° and the heat capacity jump was 0.19 $JK^{-1}$ $g^{-1}$. The subsequent broad exothermic and sharp endothermic peaks were due to crystallization and subsequent fusion, respectively.

Figure 2(*a*) and 2(*b*) show the X-ray diffraction patterns of crystal and liquid-quenched glass of TMCD, respectively. Sharp Bragg peaks were observed in Fig. 2(*a*) while halos characteristic of glasses were observed in Fig. 2(*b*). A small hump around 25 deg, looking like a shoulder of the second halo in Fig. 2(*b*), was caused by the sample holder made of glass.

*Amorphization and glass transition of the ground sample*

Figure 3 shows the X-ray powder diffraction patterns for the sample ground for (*a*) 5 min, (*b*) 25 min, (*c*) 2 h. The overlapping Bragg peaks and halos were observed in Fig. 3(*a*). Their positions and relative intensities are essentially the same as those observed in the respective pure specimens, showing coexistence of the crystalline and amorphous solids. The intensity of the Bragg peaks decreased with grinding and disappeared almost completely for the 25 min sample (Fig. 3(*b*)). After 25 min, the diffraction pattern was not changed by further grinding as shown in the pattern of the 2 h sample (Fig. 3 (*c*)).
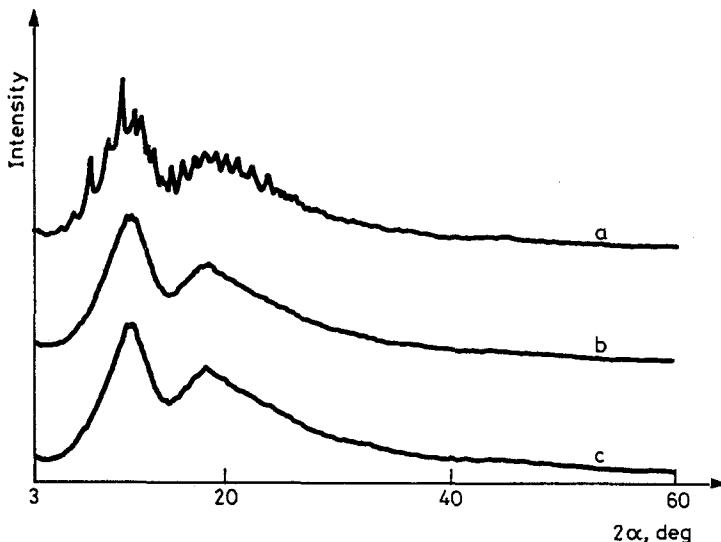


**Fig. 3** X-ray powder diffraction patterns of TMCD ground for (*a*) 5 min, (*b*) 25 min, (*c*) 2 h

Table 1 Effect of grinding time on thermal properties of TMCD derived from DSC

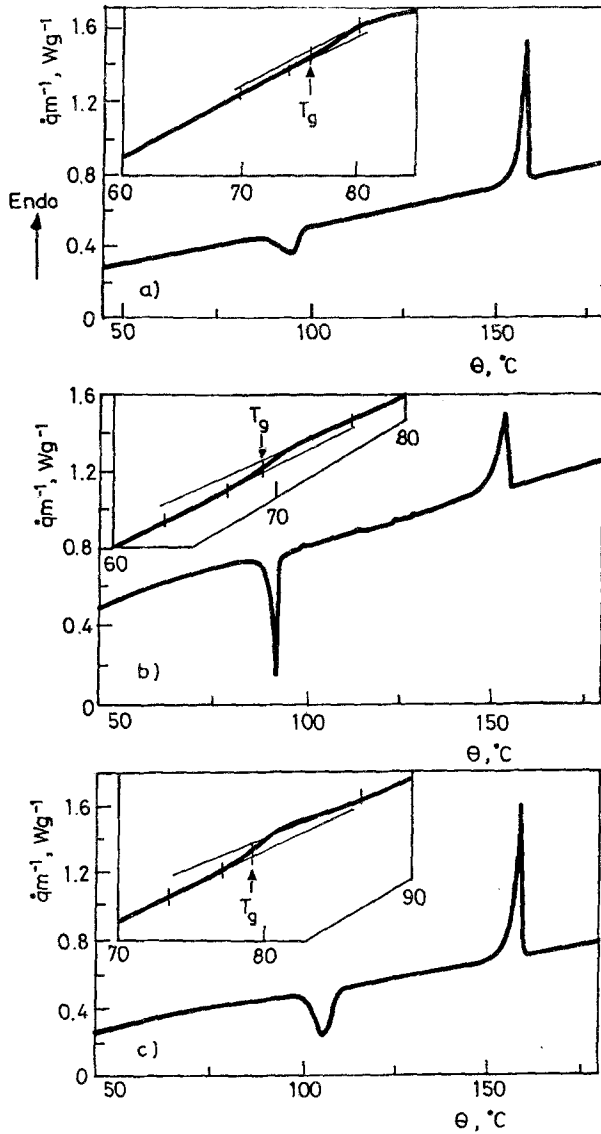| $\dfrac{t}{min}$ | $\dfrac{T_g}{°C}$ | $\dfrac{\Delta C_p}{JK^{-1}g^{-1}}$ | $\dfrac{T_{fus}}{°C}$ | $\dfrac{\Delta_{fus}H}{Jg^{-1}}$ | $\dfrac{T_{cr}}{°C}$ | $\dfrac{\Delta_{cr}H}{Jg^{-1}}$ | $\dfrac{\Delta_{cr}H(T_{fus})}{Jg^{-1}}$ | $-\dfrac{\Delta_{cr}H(T_{fus})}{\Delta_{fus}H}$ |
|---|---|---|---|---|---|---|---|---|
| 5 | 75.9 | 0.12 | 155.8 | 37.7 | 94.3 | −16.3 | −23.9 | 0.63 |
| 10 | 65.0 | 0.12 | 153.4 | 34.5 | 80.0 | −16.0 | −25.3 | 0.73 |
| 15 | 58.0 | 0.15 | 155.8 | 35.2 | 74.9 | −18.2 | −30.6 | 0.87 |
| 25 | 70.1 | 0.19 | 150.4 | 35.5 | 90.8 | −22.2 | −34.9 | 0.98 |
| 60 | 73.6 | 0.17 | 155.4 | 37.0 | 98.2 | −25.0 | −35.1 | 0.95 |
| 120 | 79.1 | 0.16 | 156.4 | 38.3 | 104.5 | −25.9 | −34.4 | 0.90 |
| 210 | 79.1 | 0.19 | 157.1 | 38.4 | 104.6 | −27.7 | −37.8 | 0.98 |
| 300 | 78.7 | 0.19 | 157.6 | 38.8 | 106.9 | −28.1 | −37.7 | 0.97 |

Fig. 4 DSC curves of TMCD ground for (a) 5 min, (b) 25 min, (c) 2 h

Table 1 shows the effect of grinding time on the thermal properties derived from the DSC experiments for the 8 samples. Figure 4 shows the observed DSC curves of the samples ground for (a) 5 min, (b) 25 min, (c) 2 h, each corresponding to Fig. 3. 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 liquid-quenched glass. This is the first observation of the glass transition for the amorphous molecular solid obtained by grinding to the best of our knowledge.

The crystallization peak was broad and appeared at rather high temperatures in the initial stage of the grinding (see Fig. 4(a)). On further grinding, the process took place sharply at lower temperatures (Fig. 4(b)). Finally the peak became broad at higher temperatures again (Fig. 4(c)). It is interesting to note that the peak of the fusion became broad and $T_g$ became low when the crystallization peak was sharp (see Fig. 4(b)). It is difficult to explain this phenomenon from the present information but it is probably due to a complicated competition of the three conceivable effects: remaining nuclei of the crystal which help the crystallization, mobility of the molecules which is directly related to $T_g$, and increased grain boundary and lattice imperfections which smear the crystallization and fusion.

In order to compare the enthalpies of crystallization at the same temperature, the enthalpy of crystallization occurring at $T_{cr}$ was reduced to the value at the fusion point $T_{fus}$ by the following equation:

$$\Delta_{cr}H\ (T_{fus}) = \Delta_{cr}H\ (T_{cr}) - \Delta C_p\ (T_{fus} - T_{cr})$$

Here, $T_{fus}$ was fixed to be 157.6°, and $\Delta C_p$ was estimated from the heat capacity jump at $T_g$ and assumed to be constant in the temperature range between $T_{fus}$ and $T_{cr}$. The enthalpy ratio $-\Delta_{cr}H(T_{fus})/\Delta_{fus}H$ should be 1 if the amorphization and the crystallization are complete. The latter condition might be valid for every sample because the crystallization peak is fairly sharp and $T_{cr}$ is much lower than $T_{fus}$. The enthalpy ratio is plotted in Fig. 5 as a function of the grinding time. The ratio became almost constant after 25 min, which was the same as the time when the Bragg peaks disappeared in the X-ray diffraction pattern. The rather large scattering of the data and the asymptotic value slightly less than 1 are due to the assumption ($\Delta C_p$ is independent of temperature over a wide range) and the uncertainties in the estimation of $\Delta C_p$ and in the determination of peak area.

The grinding-time dependence of $T_g$ is shown in Fig. 6. The dashed line represents $T_g$ of the liquid-quenched glass. At the initial stage of the grinding, $T_g$ is about 20° lower than that of the liquid-quenched glass, and then rises with grinding and finally approaches asymptotically about the same temperature as $T_g$ of the liquid-quenched sample. The initial decrease and the subsequent increase of the $T_g$ value are really an unexpected observation. Structural characterization of this intermediate stage, which might be a

mixture of semi-crystalline and non-crystalline solids, is surely the subject of further study. It is worth noting that the elevation of $T_g$ is observed even after 25 min when an X-ray study shows apparently complete amorphization. This indicates that some structural change caused by grinding is still going on even after 25 min though it is not detected by X-ray technique.
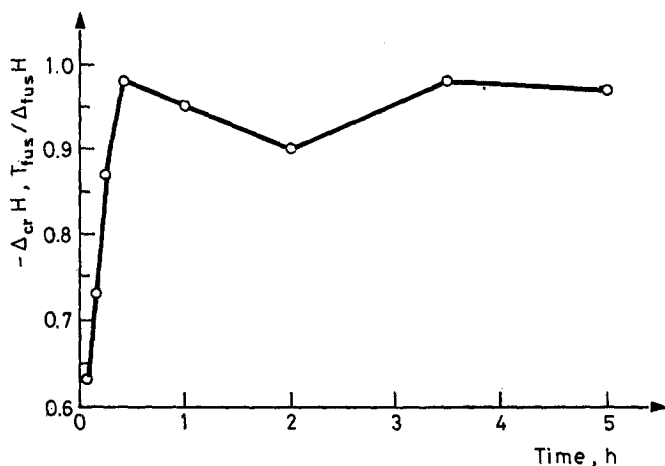
Fig. 5 Dependence of grinding time on the enthalpy ratio $-\Delta_{cr}H(T_{fus})/\Delta_{fus}H$ of TMCD (see text for the details)
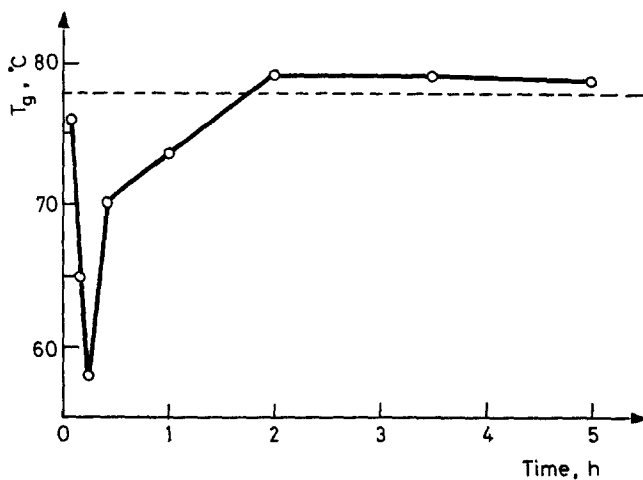
Fig. 6 Dependence of grinding time on the glass transition temperature of TMCD

*Comparison between liquid- quenched glass and ground amorphous solid*

Comparing the X-ray diffraction patterns (Fig. 2(*b*) and Fig. 3(*c*)) and the DSC curves (Fig. 1(*b*) and Fig. 4(*c*)), no significant differences can be found between the liquid-quenched glass and ground amorphous solid. To obtain more microscopic information, vibrational spectra were measured for both samples. Figure 7 shows the infrared spectra of (*a*) the crystal, (*b*) the amorphous solid ground for 3 h with a pestle in a mortar, and (*c*) the liquid-quenched glass. The amorphous solid obtained by the process (*b*) corresponds to the sample ground with vibrating mill for more than 2 h as judged from the similarity of the DSC curves. The spectra (*b*) and (*c*) have better developed peaks than (*a*) especially in the range 1200−1000 cm−1. It is considered that the field around each vibrating group of TMCD in the crystalline state is varying and anisotropic and so the absorption peaks are split into many peaks looking like the fewer, broad and ill-shaped peaks. Spectrum (*a*) contains more peaks than (*b*) and (*c*) in the low-frequency region where the internal vibrations are affected more or less by the lattice
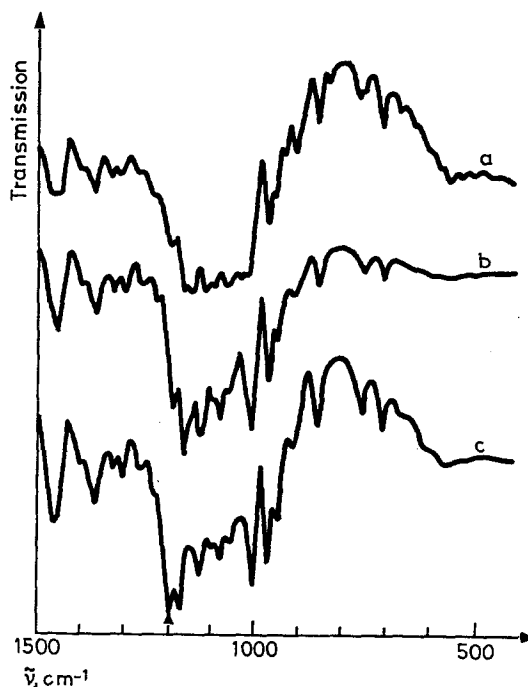


Fig. 7 Infrared spectra of TMCD: (*a*) Crystal, (*b*) amorphous solid ground for 3 h with a pestle in a mortar, (*c*) liquid-quenched glass

modes. Comparing spectra (b) and (c), a definite difference can be found in the peak at 1194 cm$^{-1}$. This is the absorption due to the rocking mode of CH$_3$ groups [19]. It is likely that some intermolecular configurations are different between the two amorphous states because the CH$_3$ groups are located at the most outside part of the TMCD molecule. These observations led us to draw the following picture. Excess energy implanted by the grinding work is stored partly as the conformational energy of the molecule. The conformational change in the molecule induces a configurational change in a molecular assembly. The structural relaxation time controlled by configurational entropy of the system [20] affects directly the glass transition temperature. This can happen even after the apparent completion of amorphization as proved by the X-ray diffraction pattern which reflects only the three-dimensional periodic character of the molecular arrangement.

In the previous calorimetric measurement of the liquid-quenched and vapor-deposited amorphous solids [7—9], the glass transition temperatures were the same for both solids while the exothermic enthalpy relaxation occurring far below $T_g$ was observed only in the vapour-deposited sample. We may call this initial exothermic process the low-temperature relaxation. The observation has proved the effectiveness of introduction of excess energy in the vapour-deposition process over that of the liquid-quenching. In the same sense, the amorphization caused by grinding the crystal should be accompanied by increases of Gibbs free energy, entropy, and enthalpy [21]. Some exothermic effect corresponding to the low-temperature relaxation of the excess enthalpy might be observed below $T_g$, but actually nothing was observed in the present DSC experiment. The excess energy introduced by the present grinding will be too small to be detected by the DSC experiment. More precise studies using an adiabatic calorimeter is required. Detailed X-ray and neutron diffraction studies are also desired to compare directly the intermolecular configurations through the analysis of their radial distribution functions.

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**Zusammenfassung** — Amorphes festes Tri-O-methyl-ß-cyclodextrin wurde bei Raumtemperatur durch Mahlen einer kristallinen Probe in einer Vibrationsmühle hergestellt. Der Amorphisierungsprozeß wurde mittels Röntgenpulverdiffraktion und DSC verfolgt. Die Braggschen Peaks verschwanden und die Kristallisierungsenthalpie nahm nach einem Mahldauer von 25 min einen konstanten Wert an, was auf die augenscheinliche Beendigung des Amorphisierungsprozesses hinweist. Mittels DSC wurde ein Glasumwandlungspunkt des gemahlenen amorphen Feststoffes gefunden. Die Glasumwandlungstemperatur $T_g$ stieg durch das Mahlen von 58°C auf 79°C. Der Sättigungswert $T_g$ der gemahlenen Probe war der gleiche wie für flüssigkeitsabgeschrecktes Glas. In den Röntgendiffraktogrammen konnte zwischen den gemahlenen und den flüssigkeitsabgeschreckten amorphen Feststoffen keinen Unterschied feststellen. Die IR-Spektren von beiden amorphen Feststoffen zeigen einen signifikanten Unterschied für die Bande bei 1194 cm$^{-1}$, der Nickschwingung der CH$_3$-Gruppen am Molekülrand.