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THIRTY YEARS OF THERMOANALYTICAL STUDY IN OSAKA UNIVERSITY *

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ABSTRACT

During the last three decades, we have developed various types of home-constructed DTA and calorimetric equipments which have been used in clarifying the reciprocal relationship between energy and matter associated with physical and chemical processes both qualitatively and quantitatively. Of the more than one hundred substances surveyed, some interesting results are briefly reviewed here, emphasizing the slightly different aspect of the role of DTA from that of calorimetry.

INTRODUCTION

The first DTA apparatus in Osaka University was constructed around 1950 [1] when various after-effects of World War II had almost disappeared. At that time Professor I. Nitta (deceased on January 16th, 1984) supervised the Physical Chemistry Laboratory in the Department of Chemistry. He was a great X-ray crystallographer and he always emphasized the importance of understanding a crystalline material not only from its structure but also from its properties, including the energetic aspect. Since most of the materials studied in the laboratory were molecular crystals, the apparatus was designed mainly for low temperature applications and has been used to detect solid–solid transitions and fusion [2] or to make phase diagrams of a two-component system [3]. The dehydration process of a hydrate crystal [4] was also examined by this apparatus. The laboratory is equipped with a conduction-type heat capacity calorimeter [5]. The DTA technique was used to characterize the thermal behavior of a particular material prior to the laborious and time-consuming calorimetric works. The DTA curve obtained immediately revealed the approximate purity of the sample, as well as the temperature and nature of phase transitions occasionally encountered.

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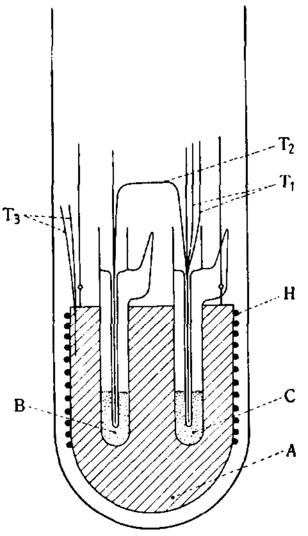

Fig. 1. Home-made DTA apparatus. (A) Copper block, (B) sample, (C) reference material, (H) heater, (T_1) thermocouple for temperature measurement, (T_2) differential thermocouple, (T_3) thermocouple for temperature control.

The DTA apparatus was simply designed, as shown in Fig. 1. The sample was put into a glass tube provided with an inner, thin-walled capillary which housed a differential thermocouple. The tube was evacuated and filled with helium as a heat exchange gas. A duplicate tube containing alumina served as the reference. Both tubes were placed in a copper block having two symmetrical, cylindrical cavities. The copper block was hung in a glass mantle connected to a vacuum line. The temperature of the reference tube was measured potentiometrically. The temperature difference was detected by a galvanometer with a lamp-scale.

This type of sample tube was suitable for keeping the specimen from contamination. Many sample tubes have been kept for a long time in this way. While examining an old specimen of $Si(OCH_3)_4$, we were astonished to find that the specimen had changed from its original liquid state to a transparent solid. Close examination of the tube showed the presence of crack in the sealing part. It turned out that slow penetration of moisture from the air had slowly hydrolyzed the substance to give rise to an $\{SiO_2\}_\infty$ polymeric material. This reaction is nowadays used to prepare silica glass.

AUTOMATION OF THE DTA APPARATUS

Since the rate of heating or cooling was usually low, say 0.5 K min^{-1}, in order to obtain thermal equilibrium as closely as possible, it was a full-day's work to obtain one DTA curve. This situation made us to aim towards

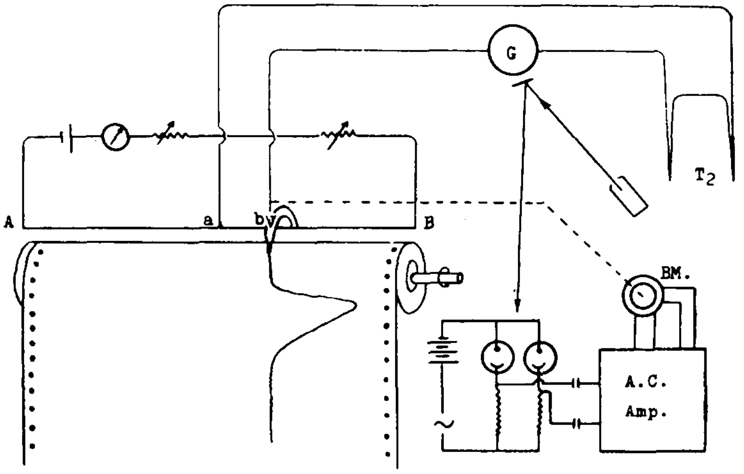

Fig. 2. Schematic diagram of automatic recording of differential signal.

automatic recording and program control for the apparatus [6]. The automatic recording part is drawn schematically in Fig. 2. Twin photo-cells received light reflected by the galvanometer for the differential thermocouple. The output of the photo-cells energized with a small a.c. voltage biased by a d.c. voltage was fed into a phase-sensitive difference amplifier, whose output was used to drive the contact point of a Lindeck potentiometer. The contact point was connected mechanically to a pen on a strip recording chart.

The heating rate of the copper block was controlled by combining another Lindeck potentiometer driven by a motor at a pre-determined constant speed with a d.c. amplifier, whose output signal was used to control the current passing through a heater wire wound around the copper block. The temperature of the copper block was registered on the recording chart at a certain EMF interval of the temperature thermocouple.

This automated DTA system was applied to many molecular crystals. Phase transitions were newly observed at 182 and 350 K for $(CH_3)_2BrCBr(CH_3)_2$, at 175 K for $(CH_3O)_4Si$, at 275 K for $CH_3CONHCH_3$, and at 323 K for $(NH_2CHCOOH)_3 \cdot H_2SO_4$ [7]. The enthalpies of transitions for $(CH_3)_2BrCCBr(CH_3)_2$ were approximately 2.1 and 4.2 kJ mol^{-1}, respectively, indicating the highly disordered nature of the high-temperature phase. One example of the recording chart is given in Fig. 3 for the phase transition of the $Be_4O(OCOCH_3)_6$ crystal. The transition is of higher order exhibiting its heat-capacity peak at 313 K. The area under the peak corresponds to roughly 0.4 J for the 0.5 g of specimen used. Owing to the high sensitivity, some spikes due to mechanical vibration of the galvanometer appeared on the curve. Earthquakes of even less than magnitude class 1 were detected occasionally by the apparatus.

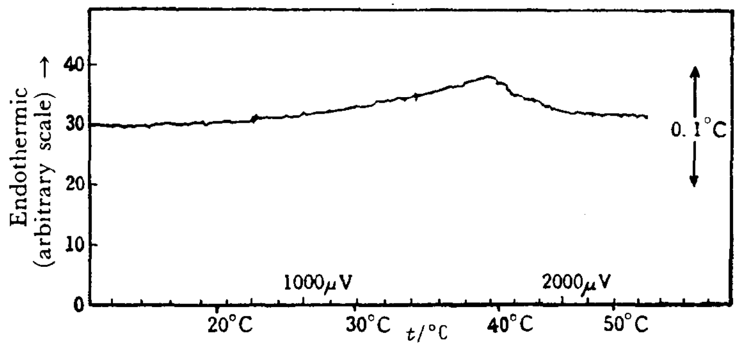

Fig. 3. DTA curve of $Be_4O(OCOCH_3)_6$.

A phase transition of resorcinol from α- to β-modification was observed at 366 K just below the melting point [8]. This transition was not detected by previous heat capacity measurements. The estimated enthalpy change associated with the transition was in good agreement with that obtained from the enthalpies of solution of both modifications [9]. As shown in Fig. 4, the liquid easily undercools to give a transparent glass through a glass transition temperature (T_g) around 250 K. It is interesting to note that a high-temperature crystallization on cooling produces the α-modification, while crystallization on heating just above T_g gives the β-modification. This example gives a good basis of the thermoanalytical method in characterizing a thermodynamic phase prior to the heat capacity measurement.

Polymeric materials were also surveyed by the apparatus. Tetron (polyethyleneterephthalate) showed a clear glass transition phenomenon which was followed by crystallization and melting on further heating. This was the first observation of the glass transition phenomenon by DTA in our laboratory. Soon afterwards we noticed a paper [10] which reported essentially the same behavior of the material. After this experiment, we mixed the chipped

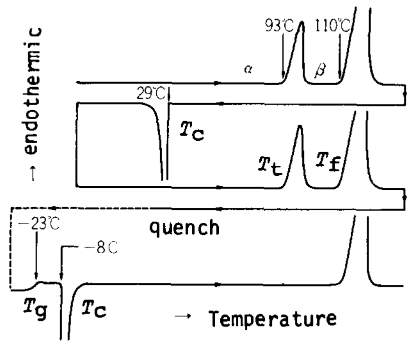

Fig. 4. DTA curve of resorcinol.

specimen with alumina as diluent to improve the thermal diffusivity. To our surprise, the melting phenomenon did not appear up to 570 K. Most probably the carbonyl groups of the Tetron were linked by –O–Al–O– bonds to give rise to a three-dimensional network polymer. This point deserves further exploration.

When we prepared to present this new development of the automated DTA apparatus at the annual meeting of the Chemical Society of Japan in 1957, we were informed that a full automatic DTA manufactured by Leeds & Northrup Co. (U.S.A.) was installed in Ōtsubo Laboratory of the Waseda University. Since that time, many commercial apparatuses started to develop in Japan. We have, however, continued to use this home-made DTA with minor changes. The galvanometric system for ΔT measurement was replaced by a commercially available d.c. microvolt amplifier. The one for T measurement was replaced by a digital voltmeter. Since then, more than one hundred substances have been investigated by the apparatus prior to heat capacity measurements.

In 1961, the Low Temperature Laboratory was built in our Faculty of Science. Liquid helium and hydrogen were supplied from the laboratory on demand. The temperature range of DTA was sometimes extended down to 20 K. At the same time, an adiabatic low-temperature calorimeter was constructed in our laboratory for the determination of the third-law entropy of a material [11].

STUDY ON DIELECTRIC LOSS BY DTA

This idea came to us when we listened to a lecture given by Professor C.P. Smyth at Osaka in 1962. As is well known, a dielectric with a polar group absorbs energy when it is placed under an a.c. electric field. The amount of absorbed energy is proportional to the dielectric loss, ϵ'', of the material, to the square of the strength, and to the frequency of the electric field. A simple calculation shows that the temperature rise due to this irreversible process can be detected easily by the conventional DTA technique, if the dielectric loss of a specimen is appreciably large at relevant frequencies. In order to test the possibility, a pair of aluminum foils as electrodes were attached to the surface of the sample glass-tube.

The ability of the apparatus was tested on a quinol–methanol clathrate compound [12]. The clathrate compounds have a common structural feature in that a host lattice constitutes a three-dimensional framework with cavities which allow guest molecules of suitable size to be accommodated, which is considered as a model system giving a "particle in a potential box". The DTA recordings obtained for the methanol–quinol clathrate compound are shown in Fig. 5. An exothermic effect due to the dielectric loss of a polar methanol molecule appears depending on the applied frequency. A sharp

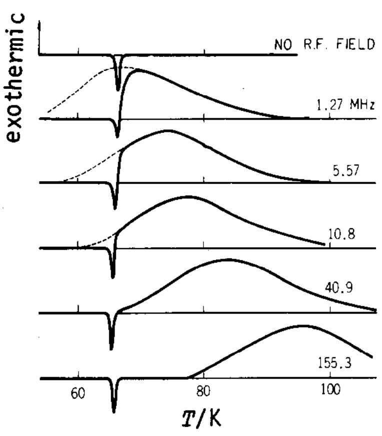

Fig. 5. DTA curves of methanol clathrate compound under a.c. electric fields.

endothermic peak always appears, which is independent of frequency. Motivated with these findings, the heat capacity of the compound was measured by an adiabatic calorimeter. It turned out that the endothermic peak is due to a phase transition arising from an order–disorder orientation of the guest molecules. It is conjectured that dipole–dipole interactions among the guest molecules is responsible for the alignment of their molecular axes in such a way that it leads to a phase transition. It is not unreasonable to assume that such a long-range force is operative among the guest molecules through the host lattice. This kind of interaction has been neglected in the classical thermodynamic treatment of clathrate formation.

This technique was also applied to glycerol and cyclohexanol, both of which are dipolar substances [13]. As shown in Fig. 6, the dielectric loss peak, as manifested by the exothermic peak, shifts to higher temperature as the frequency of the applied field is increased. A slight endothermic shift of the baseline corresponds to the well-known glass transition of glycerol. A

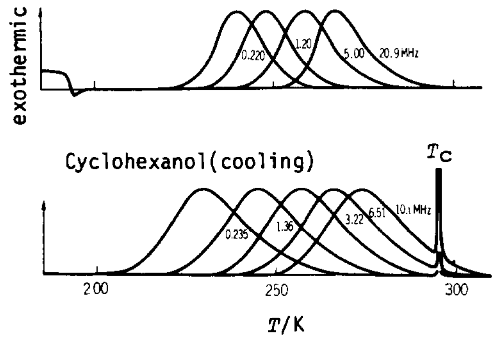

Fig. 6. DTA curves of glycerine and cyclohexanol under a.c. electric fields.

similar behavior was observed to occur in the high-temperature FCC phase of cyclohexanol. As is seen in the curve for 10.1 MHz obtained in the cooling direction, the crystallization peak is superposed on the high-temperature side of the dielectric loss peak without breaking the continuity of the latter. This indicates the highly disordered nature of the FCC phase. The high-temperature phase is easily undercooled and the dielectric loss peak appears in the temperature range 230–280 K in the frequency interval 0.2–10 MHz. A small endothermic baseline shift characteristic of the glass transition was observed to occur around 150 K on the curve. This anomaly is not shown in the figure. The meaning of the existence of the glass transition phenomenon in a crystalline material was not clarified until the precise entropy of the phase was determined by the adiabatic calorimeter [14]. The heat capacity and the corresponding entropy curve are summarized

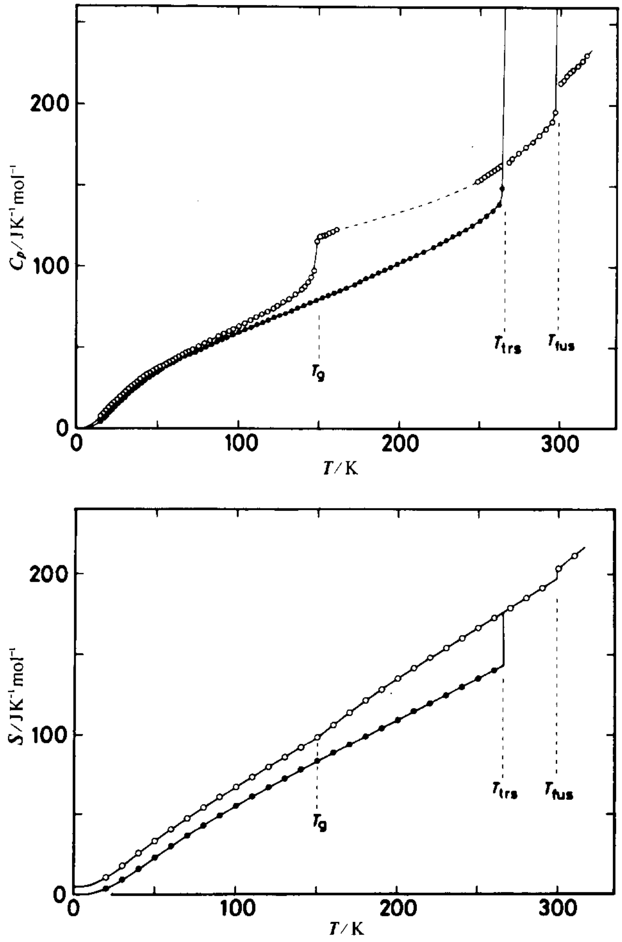

Fig. 7. Heat capacity and entropy curves of cyclohexanol.

in Fig. 7. Comparison of the calorimetric and spectroscopic entropies of cyclohexanol in the ideal gas state shows that the low-temperature phase (cr II) obeys the third law of thermodynamics. However, the loop calculation along cr II(0 K) → cr II(T_{trs}) → cr I(T_{trs}) → cr I(0 K) shows that the undercooled high-temperature phase (cr I) retains a residual entropy arising from the frozen-in orientational degrees of freedom of constituting molecules. Clear enthalpy relaxation is observed calorimetrically around 150 K. Thus the undercooled crystal of cyclohexanol resembles an ordinary glassy liquid in both its thermodynamic and relaxational behavior. One clear difference between the two glassy states is the translational invariance of the molecular arrangement existing in the glassy state of the cyclohexanol crystal. This experiment gave the first example of "glassy crystals" in which molecular centers of mass have translational invariance but molecular orientations are in a frozen-in disordered state.

GLASSY STATE OF MESOPHASES

Disorder prevails in various states of aggregation of molecules: isotropic liquid, isotropic crystal (orientationally disordered crystal), anisotropic liquid (liquid crystal). The disordered states are drawn schematically in Fig. 8 along with the anisotropic crystal. Discovery of the glassy crystalline state of cyclohexanol strongly suggests that the glass transition observed hitherto exclusively in liquids is merely a single example of a more widespread condition in which a disordered system cannot maintain equilibrium with respect to some degrees of freedom during cooling. In fact, many examples of these frozen-in disordered states have been observed in our laboratory [15]. A few DTA curves of the glassy crystals are drawn in Fig. 9 [16]. These

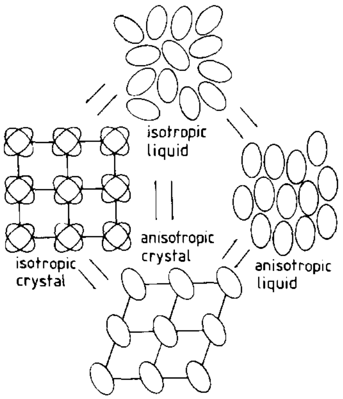

Fig. 8. Schematic diagram of various mesophases, isotropic crystal and aniostropic liquid.

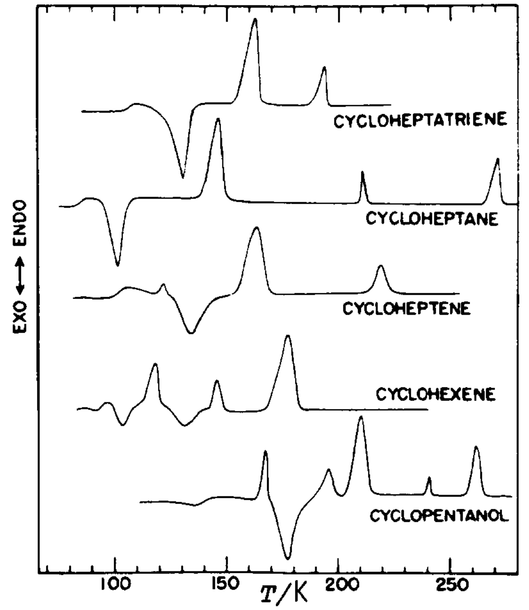

Fig. 9. DTA curves of several glassy crystals.

are cases in which the orientationally disordered high-temperature phase is easily undercooled and goes over ultimately to a glassy state. On heating the glassy crystal, irreversible recrystallization takes place either in a single process or in multiple processes in a complicated way. For example, cyclopentanol and cyclohexene transform irreversibly and indirectly to the most stable phase by passing through a series of intermediate metastable phases. This phenomenon may be an example of Ostwald's step rule. These experiments show the usefulness of DTA in characterizing the physical purity of respective phases.

The case of ethanol is interesting in that it shows two glass transition phenomena for differently disordered phases [17]. Both the glassy liquid and glassy crystals of ethanol were realized by controlling the cooling rate. The DTA results are summarized in Fig. 10, along with their Gibbs energy relationships. Since the first measurement of heat capacity, ethanol had been accepted as one of the typical glass-forming materials [18–20]. This description is true in some ways but is based on an erroneous explanation. The principal problem with the existing experiments is the cooling rate employed. Our remeasurement shows that an extremely rapid cooling of liquid (more than 50 K min^{-1}) is necessary in order to obtain the glassy liquid. If the cooling rate is moderate, as normally used in low-temperature calorimetry, say 2 K min^{-1}, metastable crystal II is formed first which goes over to glassy crystal II through another glass transition phenomenon. The residual entropy of the glassy crystal, 22.8 J K^{-1} mol^{-1}, is less than that of the glassy

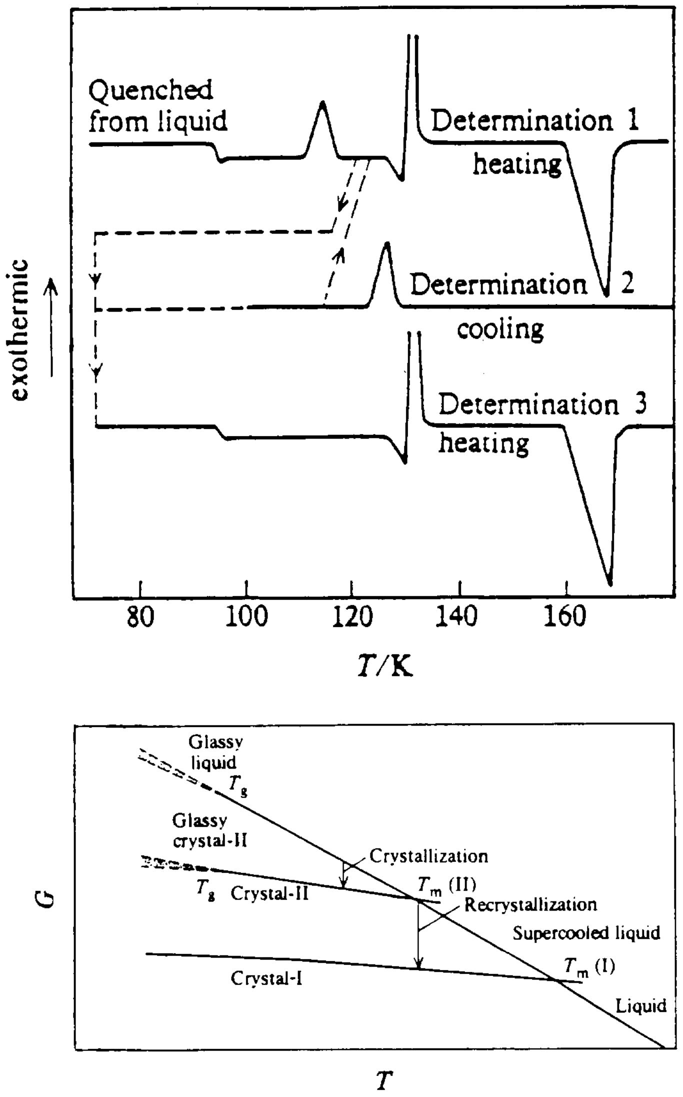

Fig. 10. DTA curves of ethanol and Gibbs energy relationship among various phases.

liquid, 35.3 J K^{-1} mol^{-1}, reflecting the smaller scale of the relevant disorder. Accurate heat capacity measurement showed that the "glassy liquid" heat capacity values of these previous workers correspond to those of our "glassy crystal II". The true heat capacity for the undercooled liquid is much higher in magnitude than that for their values and can be connected smoothly with the stable liquid above the m.p.

Typical results of DTA experiments on anisotropic liquids are summarized in Fig. 11 for a series of homologues, *N*-*p*-alkoxybenzylidene-*p*′-butylanilines [21]. Glassy states of nematic (MBBA) and smectic liquid

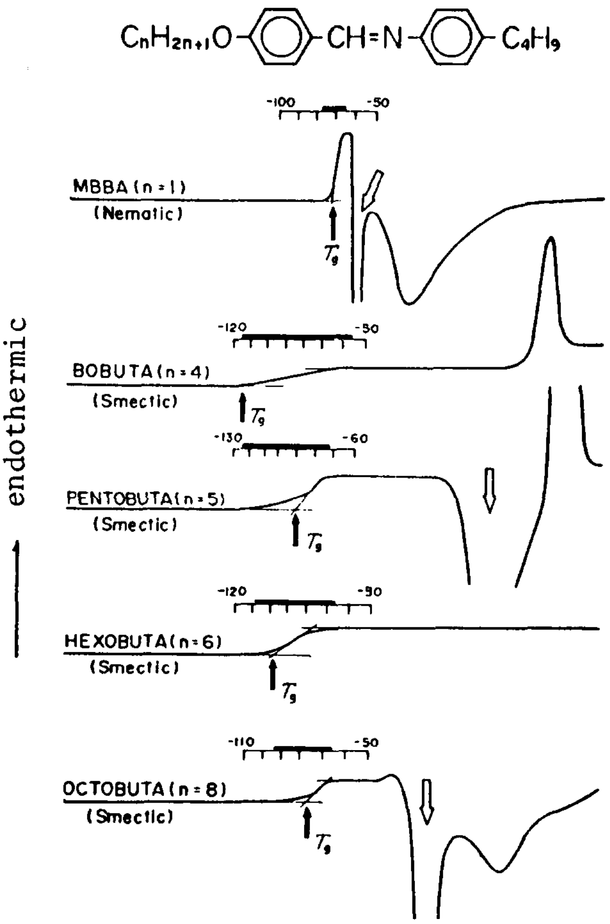

Fig. 11. DTA curves of several glassy liquid-crystals.

crystals are obtained by bypassing their ordering transition, as in the case of the orientationally disordered crystal. One of the characteristic features concerning the glassy smectic states is that glass transition takes place over an unusually wide temperature range compared with those in glassy liquids and glassy crystals. The thick horizontal bar drawn in the figure indicates the approximate temperature interval in which glass transition occurs. This implies that the relaxation process in a glassy smectic is not of simple nature. Precise heat-capacity measurements of PENTOBUTA(50 · 4) and HEXOBUTA(60 · 4) actually showed that both of the glass transitions occur in at least two steps [22,23]. This is drawn in Fig. 12 for the latter smectic. Loop calculation of the entropy along the two thermodynamic paths shows that the glassy smectic HEXOBUTA has a residual entropy of 7.51 J K^{-1} mol^{-1}. It can be concluded from these experimental findings that any disordered system can in principle be cooled down in two ways: either

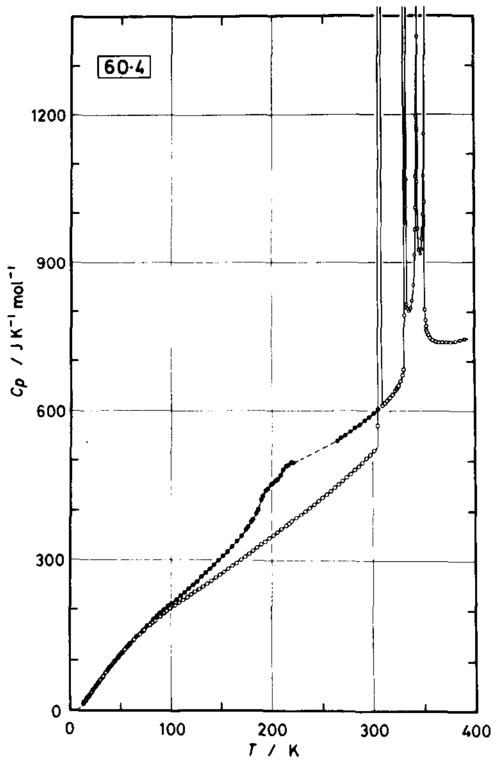

Fig. 12. Heat capacity of HEXOBUTA(*p*-*n*-hexyloxybenzylidene-*p*′-butylaniline).

discontinuously to an ordered phase through a first-order phase transition or continuously to a glassy state through a glass transition. It is observed that the residual entropy is retained in the latter case in a conjugational way and is considered to be a reflection of the ergodic to non-ergodic transition of the system. Thus the residual entropy and glass transition are considered to be useful in thermal characterization of the glassy state [24].

CHARACTERIZATION OF NON-CRYSTALLINE SOLIDS

A glassy liquid was considered as a typical material of the non-crystalline solids and prepared traditionally by the rapid cooling of a liquid from above the m.p. Glass formation is thus a matter of bypassing of the crystallization process [25]. In recent years numerous ways have been developed of bypassing of the crystallization other than quenching of a liquid: vapor deposition, chemical reaction, solution method, dehydration of hydrate crystal, etc. These non-crystalline solids have common features characteristic of a glassy liquid in that they lack three-dimensional periodicity and devitrify on heating. In order to answer an important question raised by Secrist and

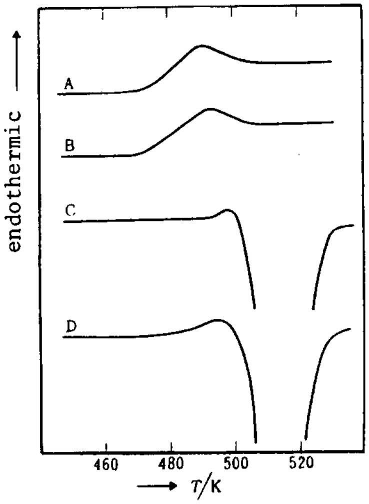

Fig. 13. DTA curves of non-crystalline As_2S_3 and Sb_2S_3 solids obtained by various methods. (A) Precipitated As_2S_3, (B) melt-quenched As_2S_3, (C) precipitated Sb_2S_3, (D) sublimed Sb_2S_3.

Mackenzie [26], "Is it plausible to call these non-crystalline solids glass?", it is important and necessary to characterize these non-crystalline solids from a thermodynamic point of view. Crystal or non-crystalline solids are a division of the structural aspect of materials. While the glassy state is considered from the thermodynamic aspect with respect to its non-equilibrium nature. The terms glass and non-crystalline solid have been used without unambiguous recognition in many cases in the literature.

It is well known that As_2S_3 (or Sb_2S_3) powder precipitated by reaction of As^{3+} (or Sb^{3+}) ions in aqueous solution with H_2S is a non-crystalline solid. DTA curves of these precipitates clearly exhibit the glass transition phenomenon, as shown in Fig. 13 [27]. Curve A obtained for precipitated As_2S_3 closely resembles curve B obtained from the melt by quenching. Curve C for precipitated Sb_2S_3 is essentially the same as curve D obtained by sublimation, which is also known to produce the non-crystalline solid Sb_2S_3. The observed T_g for the latter is somewhat lower than that of the precipitate. This result suggests that the two kinds of non-crystalline solids produced under different conditions are not always in an identical non-equilibrium state.

A glass transition was observed in magnesium acetate anhydride produced by dehydration of the corresponding tetrahydrate crystal under vacuum [28]. The anhydride is known to give only a broad band in the low-angle range of its X-ray diffraction pattern. This non-crystalline solid crystallizes at about 530 K, just above the glass transition region, as shown in Fig. 14. The shape and temperature of the endothermic anomaly strongly depend on the heating rate. An activation plot of the type developed by

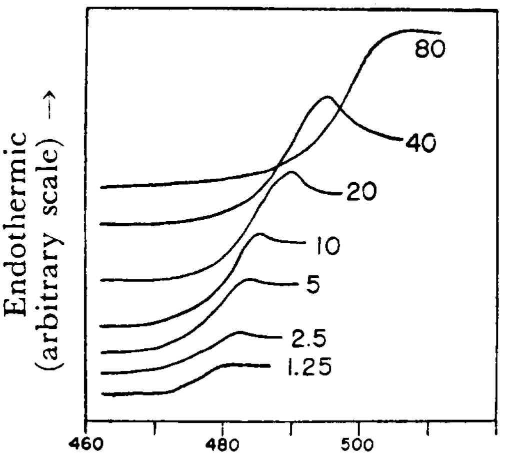

Fig. 14. DTA curves of non-crystalline $Mg(COOCH_3)_2$ solid obtained by dehydration under vacuum. The numbers in the figure stand for the heating rate in K min^{-1}.

McMillan [29] gives 550 kJ mol^{-1} as the apparent enthalpy of activation governing the relaxation process.

Vapor deposition is a powerful method of producing a non-crystalline solid [30]. The method can rapidly extract the thermal energy of molecules in a highly disordered vapor state to give rise to a non-crystalline aggregate on a cold substrate. The method yields the non-crystalline solid in molecule-by-molecule fashion without passing the liquid regime in which dangerous crystallization might take place, and was therefore widely applicable in preparing non-crystalline solids which had not been obtained by the melt-quench method. For the thermodynamic characterization of a specimen in situ, we have developed a vapor-condensation DTA apparatus with cold substrate. This is drawn schematically in Fig. 15 [31]. Liquid hydrogen was used as the refrigerant, and organic vapor was deposited onto one end of the copper plate which constituted one element of the copper–constantan thermocouple. The sampling tube was made of a copper capillary with a delicate temperature controller. Glassy states composed of pseudospherical molecules like CCl_4, $CHCl_3$ and propene were produced by this method [32]. In the case of non-crystalline propene, the value of T_g is essentially the same with that of melt-quenched specimen. Figure 16 gives the DTA curve of the latter which records the lowest value of T_g (55 K) among the liquids that have been examined.

In spite of the similar T_g values obtained under different conditions, it is natural to expect that short-range correlations among the molecules in these non-crystalline solids differ depending on the preparation condition. It is worthwhile to characterize glassy states of one and the same substance with different routes from structural as well as energetic aspects. Very recently we

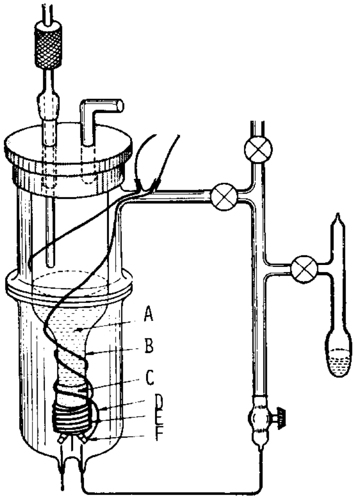

Fig. 15. Simple DTA apparatus for a vapor-deposited specimen. (A) Liquid hydrogen, (B) Dewar, (C) Kovar seal, (D) thermocouple, (E) heater, (F) sample pan.

developed a low-temperature adiabatic calorimeter for a vapor-deposited specimen and applied it to glassy butylonitrile. It turned out that the non-crystalline butylonitrile deposited on a substrate at 40 K exceeded by 1.1 kJ mol^{-1} in energy that of a liquid-quenched specimen. The deposited specimen was found to start to relax towards equilibrium enthalpy from an unexpectedly low temperature and exhibited the same T_g as the latter specimen. Detailed comparison of the relaxation processes deserves further study and the experiments are in progress [33].

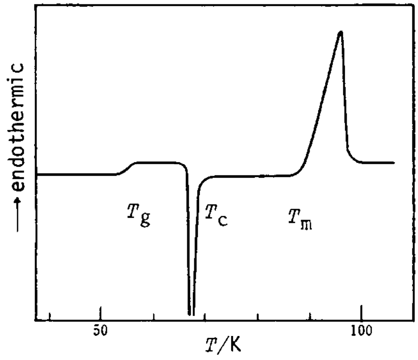

Fig. 16. DTA curve of propene.

One topic in this field is a polymerization problem of vinyl acetate (VAc) in the glassy state [34]. The calorimetric investigation of VAc was undertaken by Barkalov et al. who found that liquid VAc can easily be undercooled to give a glass-like form at 77 K [35]. This glassy form irreversibly crystallizes around 150 K and the crystal melts at 180 K. They constructed a calorimeter with a built-in electron beam source for irradiation in situ. From measurements of the enthalpies of crystallization and fusion of the irradiated and unirradiated VAc specimens, they concluded that polymerization actually proceeded in the glassy state solely during the irradiation. They did not mention, however, any T_g data. This conclusion seems to require a revision of our concept of the glassy state that molecules in the glassy state are firmly immobilized in our human time-scale.

Our DTA measurements of the irradiated and unirradiated VAc specimens are drawn in Fig. 17. The sample tube, irradiated with an electron beam from a Van de Graaff accelerator at 77 K, was put in the copper block precooled to 77 K. All the specimens except No. 1 were irradiated with a dose intensity of 5 Mrad min^{-1} and the total dose was in the range between 1 (No. 2) and 60 Mrad (No. 7). Numbers in parentheses in the figure show polymer yield determined after the DTA experiment. An endothermic baseline shift of around 125 K is due to the glass transition. An exothermic peak occurring just above T_g appears in all of the irradiated specimens and the peak area increases with the polymer yield.

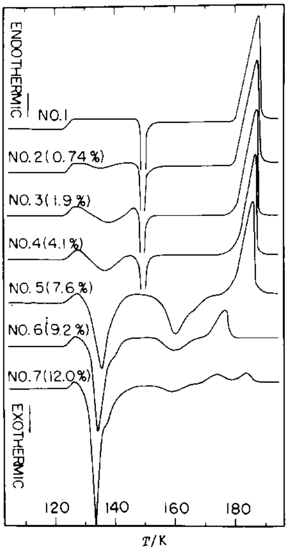

Fig. 17. DTA curves of vinyl acetate irradiated and unirradiated with electron beams.

The enthalpy change estimated from the exothermic peak area, (96 ± 13) kJ mol^{-1}, agrees well with the literature value for the enthalpy of polymerization. Moreover, when the glassy VAc was irradiated (No. 7), crushed into pieces at 77 K, and dissolved in acetone at room temperature as quickly as possible, the acetone solution was found to contain a very small amount of polymer, less than 0.1%. All these experimental observations clearly indicate that VAc does not polymerize appreciably during irradiation, but does polymerize in the undercooled liquid state just above T_g. The frozen-in arrangement of the molecules in the glassy state will melt around T_g and this dynamic change allows rearrangement and diffusion of molecules which is necessary for the polymerization reaction to take place at an appreciable rate. Sometimes the DTA study surpasses calorimetric investigation.

The case of PCl_5 provides an interesting example of a disproportionation reaction in the solid state [36]. Its trigonal bipyramidal molecule exists in the gaseous and liquid states, whereas its stable modification in the solid state is tetragonal and the crystal is composed of two distinct ionic species, PCl_4^+ and PCl_6^-. A metastable modification composed of the molecular unit PCl_5 can be obtained by vacuum sublimation onto a cold substrate. The DTA curve of the molecular modification is given in Fig. 18, which exhibits a sharp endothermic peak centering around 180 K superposed by a broad exothermic peak ranging between 165 and 215 K. Above this temperature range, NQR signals coming from the crystal correspond to that of the ionic modification. Therefore the exothermic process can be interpreted as the disproportionation reaction $2PCl_5 \rightarrow PCl_4^+ + PCl_6^-$ in the solid state. The sharp endothermic peak is considered to be due to a transition occurring in the molecular modification.

The thermoanalytical technique was applied to various classes of inclusion compound [37]. Here, we describe simply our recent observation of the decomposition processes of β-cyclodextrin inclusion complexes [38]. DTA heating curves of several inclusion complexes taken at a rate of 5 K min^{-1}

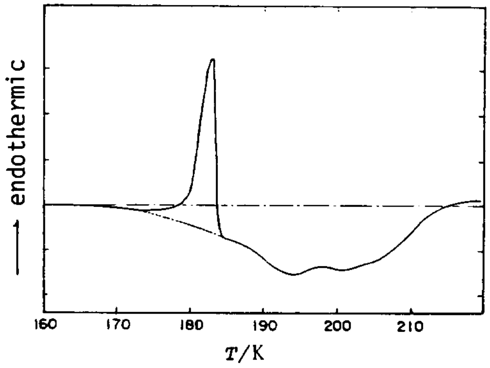

Fig. 18. DTA curve of PCl_5 crystal.

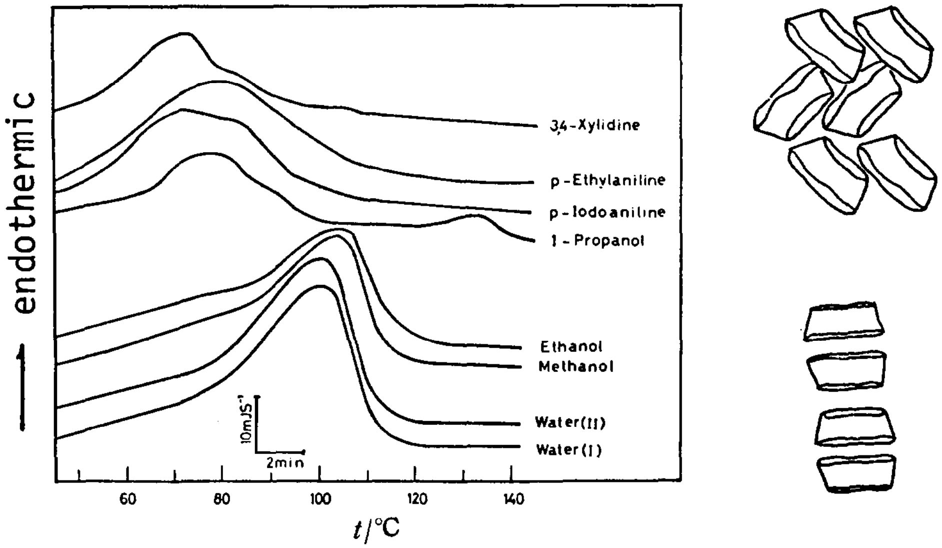

Fig. 19. DTA curves of various cyclodextrin inclusion compounds.

are summarized in Fig. 19, along with their structural packing modes of β-cyclodextrin molecules as determined by X-ray structural analysis [39,40]. It is interesting to note that the endothermic peaks due to release of guest molecules and hydrate water are divided quite clearly into two groups. The inclusion complexes whose endothermic peaks appear around 70°C have a packing mode of monomeric cage type. On the other hand, those of dimeric channel type exhibit decomposition peaks centering around 100°C. This simple experiment illustrates not only the value of DTA in the characterization of synthetic materials but also the value of themodynamic data in understanding the interaction between distinct molecular species in the inclusion compound.

APPEARANCE OF METASTABLE MODIFICATIONS

Metastable modifications appear widely in organic as well as inorganic compounds. Full clarification of the condition of appearance of these metastable modifications is very important, because ignorance of this factor can cause confusion in the description of static and dynamic properties of the material. An example was already given in the case of resorcinol which has two crystal modifications depending on the preparation conditions. Another example is crystalline ferrocene, $Fe(C_5H_5)_2$, which exhibits the well-known transition around 164 K with a subsidiary one at 169 K [41]. The phase transition is believed to be due to order–disorder of the cyclopentadienyl rings of the ferrocene molecules. There were some controversial

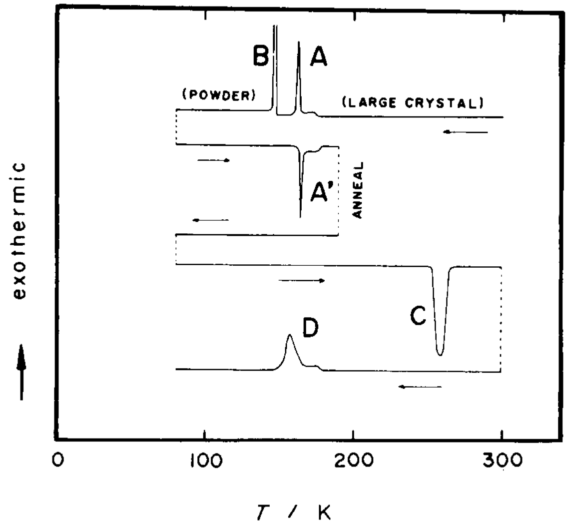

Fig. 20. DTA curves of ferrocene crystal.

discussions on the crystal structure of the low-temperature phase. In the course of our remeasurement by DTA, we found, rather accidentally, a new low-temperature phase which can exist stably below 240 K [42]. The well-known transition was found to be that taking place in the undercooled, metastable high-temperature phase.

The results of our DTA experiments are reproduced in Fig. 20. When a single crystal is cooled from room temperature, the phase transition is observed at 164 K (peak A) and after that the crystal undergoes violent disintegration into a powder with an exothermic peak (B). On heating the powdered specimen, the phase transition is recovered at the same tempera-

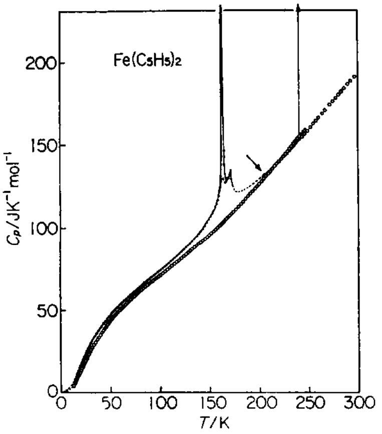

Fig. 21. Heat capacity of ferrocene crystal.

ture. However, the specimen shows a gradual exothermic effect just above the transition temperature. After annealing the specimen around 190 K for 24 h, the phase transition disappears completely and a new phase transition is observed around 250 K (peak C). This new phase transition is easily superheated and conversely the high-temperature phase is easily undercooled. The molar heat capacities of the stable and metastable phases are drawn in Fig. 21 [43]. The equilibrium temperature between the two phases was determined calorimetrically to be 242 K, which took ten days. From the standard thermodynamic calculation, it turns out that the enthalpy of the metastable phase exceeds by 2.61 kJ mol^{-1} that of the stable phase at 0 K. Loop calculation reveals that both of the modifications obey the third law of thermodynamics. In spite of this new finding, however, we are not convinced that we can insist on the new phase being the most stable form of crystalline ferrocene below 240 K. In this sense, stability is merely a relative concept based on our limited observations.

CONCLUDING REMARKS

DTA is a unique technique in that it detects a change in intensive property of a material. This is in contrast to most of the analytical techniques in which extensive properties, like volume (dilatometry), enthalpy (calorimetry), mass (gravimetry), are detected as a function of another variable. This means that the technique does not require expensive instruments. It can be constructed easily by ourselves, easily repaired, easily operated and give rapid, overall features of thermal anomalies associated with phase transition, glass transition, crystallization and chemical reaction that might occur in a specimen. Without such preliminary examination, calorimetric study sometimes leads to erroneous conclusions. Once entering into a wood, we cannot see the whole view of it for the trees. Too much emphasis cannot be placed on the usefulness of the DTA method, especially in the early stages of investigation. Qualitative and quantitative studies constitute two aspects of the key to clarifying the nature of substances.

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