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# Time dependence of the complex heat capacity at the melting temperature of polyethylene crystals

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## Abstract

Time dependence of the complex heat capacity of polyethylene crystals was measured at several temperatures between 80 and 130°C using light heating modulated temperature DSC. Time dependence could be expressed as a sum of fast and slow components. The fast component had the complex value and decayed within a few minutes. On the other hand, the slow component had the real value and decreased much more slowly towards a finite value. The fast and slow components were attributed to melting and ordering of the crystal, respectively. Time dependence was significant at temperatures in the melting peak of the total heat flow (123°C and higher). However, even at the lowest temperature very small fast component was observed. This suggested that a very small amount of the crystal melted at this temperature. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Complex heat capacity; Time dependence; Melting; Polyethylene crystal; Light heating modulated temperature DSC

## 1. Introduction

Various applications of the modulated temperature differential scanning calorimetry (MTDSC) have been reported in the literatures. Those applications can be classified into four groups: (1) measurement of the equilibrium heat capacity; (2) irreversible phenomena such as chemical reaction and cold crystallisation on the heating process from the glassy state; (3) glass transition; and (4) phase transitions. The number of authors of the group (4) is less than the groups (1)–(3). One reason of this seems to be the experimental results that the heat flow separation into the reversing and non-reversing components is not successful at the phase transition temperature. The latent heat gives contribution to both the reversing and non-reversing components, although the phase transition cannot be separated into reversing and non-reversing processes. There are two reasons why the separation is not successful. The first reason is applicable to the case of sharp phase transitions observed in the low molecular weight materials. At the phase transition temperature the heat flow and/or the sample temperature notably change within the time much shorter than the modulation period. In this case the average of the observed heat flow over the modulation period is not equal to the total heat flow at the middle point of the averaging time. Since the total heat flow is necessary to calculate the reversing heat flow the separation is not successful. The second reason is applicable to polymers in which the phase transition temperature is distributed over a temperature range much wider than the amplitude of the temperature modulation. In this case the correct total heat flow can be obtained by

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averaging the observed heat flow. However, the amplitude of the cyclic heat flow (or its in-phase component) does not have the meaning of the heat flow due to the reversible phenomena in the sample. Phase transition of polymers often occurs slowly and the time necessary to finish the phase transition is comparable to the modulation period. This means that the phase transition has to be considered as the kinetic phenomenon instead of the completely reversible or non-reversible phenomenon. Mathematically we have to pay attention to the phase of the cyclic component as well as the amplitude. In other words we have to consider the complex heat capacity.

We have applied the light heating modulated temperature DSC (LMDSC) constructed in our laboratory [1–3] to the melting transition of polyethylene crystals. Frequency dependence of the apparent heat capacity was measured in the quasi-isothermal [4] and steady heating [5] conditions. In both conditions frequency dependence was observed in the frequency range from 0.01 to 1 Hz. However, the kinetic process causing the frequency dependence in the quasi-isothermal condition was considered to be different from that of the heating condition, because the relaxation times were different from each other. The observation of frequency dependence supported the idea that the phase transition has to be considered as the kinetic process. Successful estimation of the relaxation time showed usefulness of MTDSC for the studies of phase transitions.

In this work we measured time dependence of the complex heat capacity of semi-crystalline polyethylene during the quasi-isothermal condition at various temperatures between 80 and 130°C. In the work of reference [4] the experimental data between 2000 and 3000 s after starting the quasi-isothermal condition were used to study the frequency dependence, because notable time dependence was observed at the beginning of the quasi-isothermal condition. This time dependence was studied in detail in this work.

## 2. Experimental

A pellet of linear polyethylene (NIST 1475, Mw = 52,000, Mw/Mn = 2.9) was melted and pressed between polyimide films of 7.5 μm thick. The thickness of the obtained thin plate was 0.10 mm including the polyimide films. It was cut and put in an aluminium pan with an aluminium lid. The sample mass was 1.8 mg. A very small amount of grease (high vacuum silicone grease from Dow Corning) was painted on the outer side of the polyimide films to improve thermal contact between the sample and the pan/lid. Carbon was sprayed on the upper surface of the lid for light absorption. An empty pan, on which carbon was sprayed, was put on the reference side.

The same LMDSC instrument with the previous works [4,5] was used. Modulation frequency was fixed to 0.1 Hz. Amplitude of the temperature modulation was smaller than 0.1 K. Temperature profile of the measurement is shown in Fig. 1. The sample was melted at 170°C and cooled to 70°C at 3 K/min. Then it was heated to the quasi-isothermal temperature at 1 K/min and time dependence was measured for 1 h. After the quasi-isothermal measurement the sample was heated to 170°C and cooled again to 70°C. This process was repeated changing the quasi-isothermal temperature. The quasi-isothermal measurement was done at 80.5, 95.2, 105.2, 115.2, 123.4, 128.4 and 130.6°C. These quasi-isothermal temperatures are shown by dashed lines in Fig. 2 with the total heat flow curve.

The complex heat capacity was calculated from only the cyclic component of the temperature difference between the sample and reference sides. The cyclic component of the sample temperature was not used, although both are used in the commercial

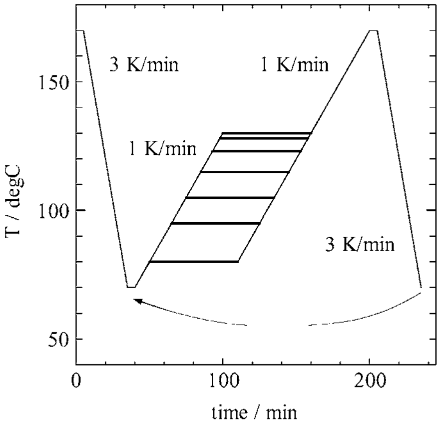

Fig. 1. Temperature profile of the experiment.

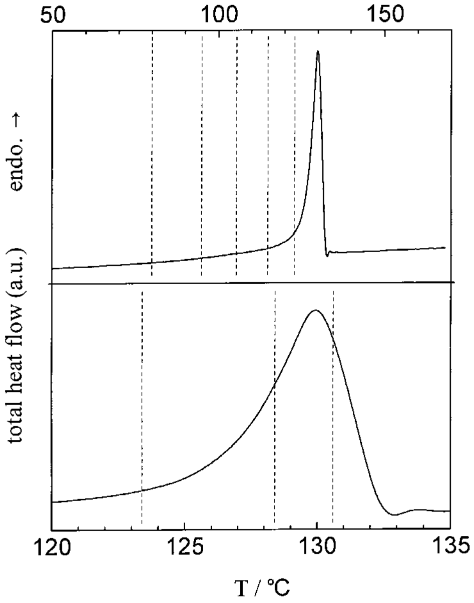

Fig. 2. Quasi-isothermal temperatures shown together with the total heat flow curves. The lower graph is extension around the melting peak of the upper one.

MTDSC instruments [6]. The next equation was used for the calculation [7,8].

$$\Delta T = \frac{\xi \Delta C}{\eta \Delta C + 1} \tag{1}$$

where $\Delta T$ and $\Delta C$ are the temperature difference and heat capacity difference between the sample and reference sides, respectively, $\xi$ and $\eta$ calibration parameters of complex values, which were determined using aluminium disks as standard samples.

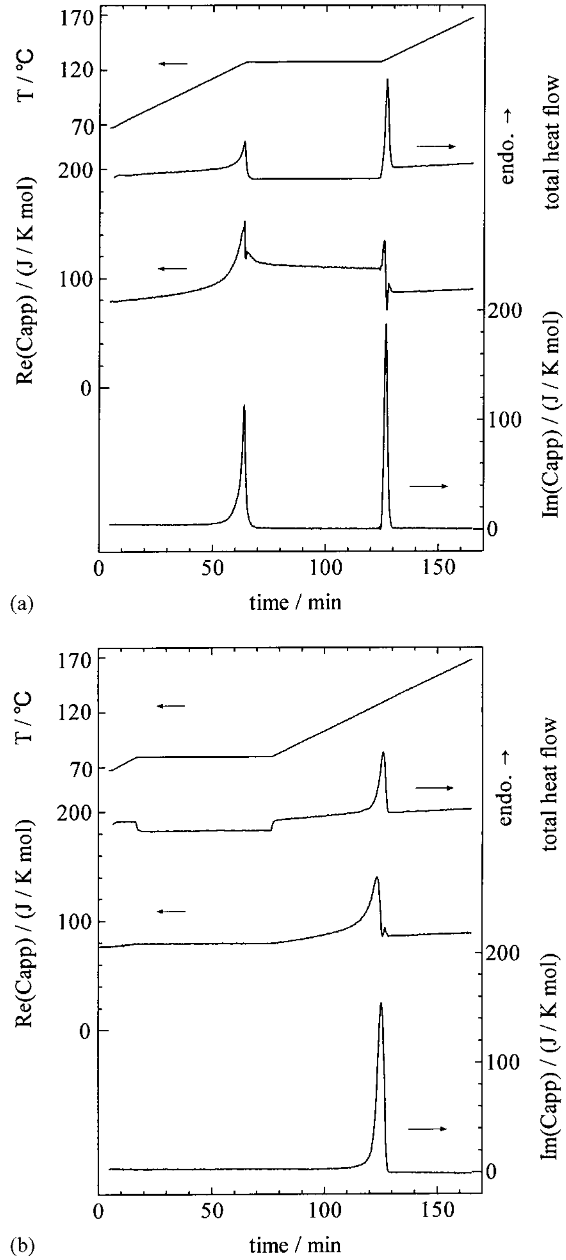

Fig. 3. Time dependence of temperature (top), total heat flow (second), real part (third) and imaginary part (bottom) of the complex heat capacity. Quasi-isothermal temperatures are: (a) 128.4°C and (b) 80.5°C.

## 3. Results

Fig. 3 shows the curves of temperature, total heat flow, real part and imaginary part of the complex heat capacity against time. The quasi-isothermal temperatures of Fig. 3(a) and (b) are 128.4 and 80.5°C, respectively. At the beginning and ending of the quasi-isothermal condition the total heat flow curves of (a) and (b) shifted suddenly. However, as known well, in many cases this shift does not mean exothermic heat flow from the sample, because the total heat flow signal changes in proportion to the underlying heating rate if the sample stays in equilibrium. Precisely, quantitative measurement is necessary to determine whether there is heat flow during the quasi-isothermal condition or the shift of the total heat flow can be attributed only to the change in the underlying heating rate. On the other hand, the beginning and ending of the quasi-isothermal condition does not cause the shift of the complex heat capacity curve if the sample stays in equilibrium. If the complex heat capacity curve shifts at the beginning and ending of the quasi-isothermal condition, it means that the state of the sample changed accompanying the change in the heating rate. In Fig. 3(b) shift of the complex heat capacity curve was very small, although it was notable in Fig. 3(a). From these results it can be said without precisely quantitative measurement that the state of the sample notably changed at the beginning of the quasi-isothermal condition at 128.4°C, but did not at 80.5°C. Besides, time dependence of the complex heat capacity can be seen during the quasi-isothermal condition at 128.4°C. This is an advantage of MTDSC in comparison with the conventional DSC.

It should be noted that the calculated complex heat capacity was not correct just at the boundary between the heating and quasi-isothermal processes. Fig. 4 shows time dependence of temperature, real and imaginary parts of the complex heat capacity around the start of the quasi-isothermal condition at 128.4°C. The real part exhibited strange behaviour at the boundary. This is due to the abrupt change in the total heat flow. As described above the total heat flow cannot be calculated correctly by averaging the data when the total heat flow changes notably in a much shorter time than the modulation period. In this work the data after the dotted line were used. The data at the beginning of the quasi-isothermal condition were omitted at other quasi-isothermal temperatures as well. Fig. 5(a) and (b) show time dependence of the real and imaginary parts of the complex heat capacity, respectively, during the quasi-isothermal condition. In Fig. 5(b) the numbers of the vertical axis show the values of the 80.5°C curve. Other curves are shifted upwards at intervals of 5 J/K mol to avoid overlapping.

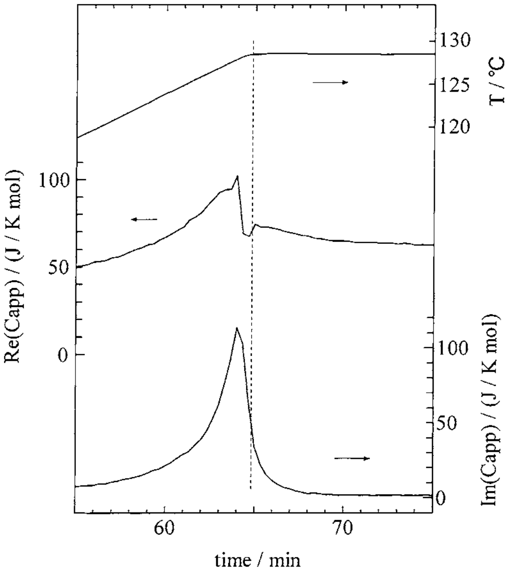

Fig. 4. Time dependence of temperature (top), real part (middle) and imaginary part (bottom) of the complex heat capacity. Data after the dotted line were used.

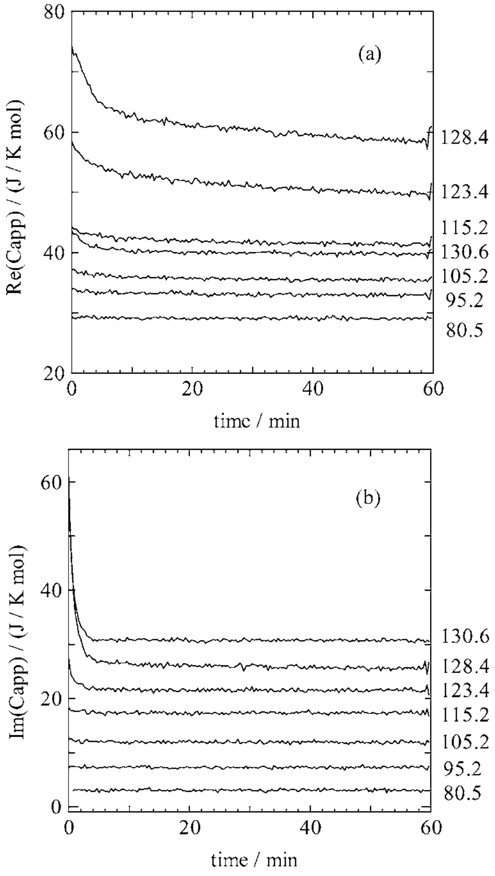

Fig. 5. Time dependence of the (a) real and (b) imaginary parts of the complex heat capacity. The quasi-isothermal temperature of each curve is shown on the right hand side of the graphs. The numbers of the vertical axis of (b) show the values of the 80.5°C curve. Other curves are shifted upwards at intervals of 5 J/K mol to avoid overlapping.

## 4. Discussion

It can be seen from Fig. 5 that both the real and imaginary parts of the complex heat capacity decreased with time during the first few minutes. After the few minutes the imaginary part was almost constant although the real part decreased more. Therefore the apparent heat capacity could be expressed as sum of two components called fast and slow components below. The complex value showed that the fast component was related to a kinetic phenomenon. In the previous works we found two types of kinetic phenomena in the same material; one was observed in the quasi-isothermal condition [4] and the other was observed in the heating process [5]. As described in the first section the frequency dependence during the quasi-isothermal condition was observed between 2000 and 3000 s after starting of the quasi-isothermal condition. Since the fast component decayed in a few minutes the kinetic process of the fast component was considered to be different from that of the frequency dependence in the quasi-isothermal condition. The frequency dependence observed in the heating process was attributed to the melting of the crystals. Toda et al. studied the melting of polyethylene and poly(ethylene terephthalate) crystals in the heating only mode using a commercial MTDSC instrument [9,10]. They observed frequency dependence and proposed a kinetic model. According to their model melting rate, defined by time derivative of the amount of the crystal to be melted, from the superheated state was modulated by the temperature modulation. Toda et al. assumed that the average amount of the crystal to be melted was constant. This assumption is based on an idea that decrease and increase in the average amount of the crystal to be melted are balanced with each other. Decrease occurs along with progress of melting. Increase occurs because as the temperature increases more and more crystals get into the superheated state from the stable crystalline state. However, the increase did not occur in this work because of the quasi-isothermal condition. Consequently, we can explain the origin of the fast component as follows. The complex value of the fast component can be attributed to the melting kinetics proposed by Toda et al. Decay of the fast component can be explained by decrease of the amount of the crystal to be melted as melting progresses.

The real value of the slow component showed that the slow component gave the thermodynamic heat capacity at each moment. This suggested that the time dependence of the slow component reflected gradual change in the crystalline state. It is known well that ordering of the crystal occurs at temperatures close to the melting point. Highly ordered crystals can have smaller heat capacity than poorly ordered crystals because of more tightly packing of the molecules. Another process that occurs at temperatures close to the melting point is lamellar thickening. Generally speaking, it is not easy to judge whether the heat capacity increases or decreases as the lamellar become thicker because the specific heat capacity of the crystal is not always smaller than that of the molten state. But in the present case the specific heat capacity of the crystal was larger than the molten state as can be seen in Fig. 3. If the lamellar thickening was the dominant process for the heat capacity change the heat capacity of the sample would have increased with time. Therefore we attributed the slow component to the ordering of the crystals.

The fast component was separated from the observed complex heat capacity by subtracting the slow component. The slow component was assumed to be linear to time and fitting was made using the data after 20 min. At high temperatures the slow component has a little curvature, but 1 h of measurement was

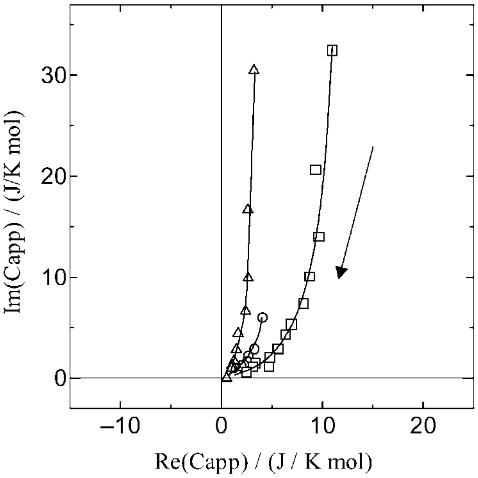

Fig. 6. The fast component plotted in the complex plane. The quasi-isothermal temperature is 123.4°C (circle); 128.4°C (square) and 130.6°C (triangle). The arrow shows the direction of increasing time.

too short to determine the correct shape of the curve. Linear assumption of the slow component does not affect seriously the fast component, because the curvature of the slow component is much smaller than that of the fast component. Fig. 6 shows the fast component of 123.4, 128.4 and 130.6°C plotted in the complex plane. The traces of the fast component were not straight lines. This means that the fast component was not proportional to the amount of crystals undergoing the melting at each moment. There can be two reasons for the curved trace; one is non-linearity between the temperature modulation

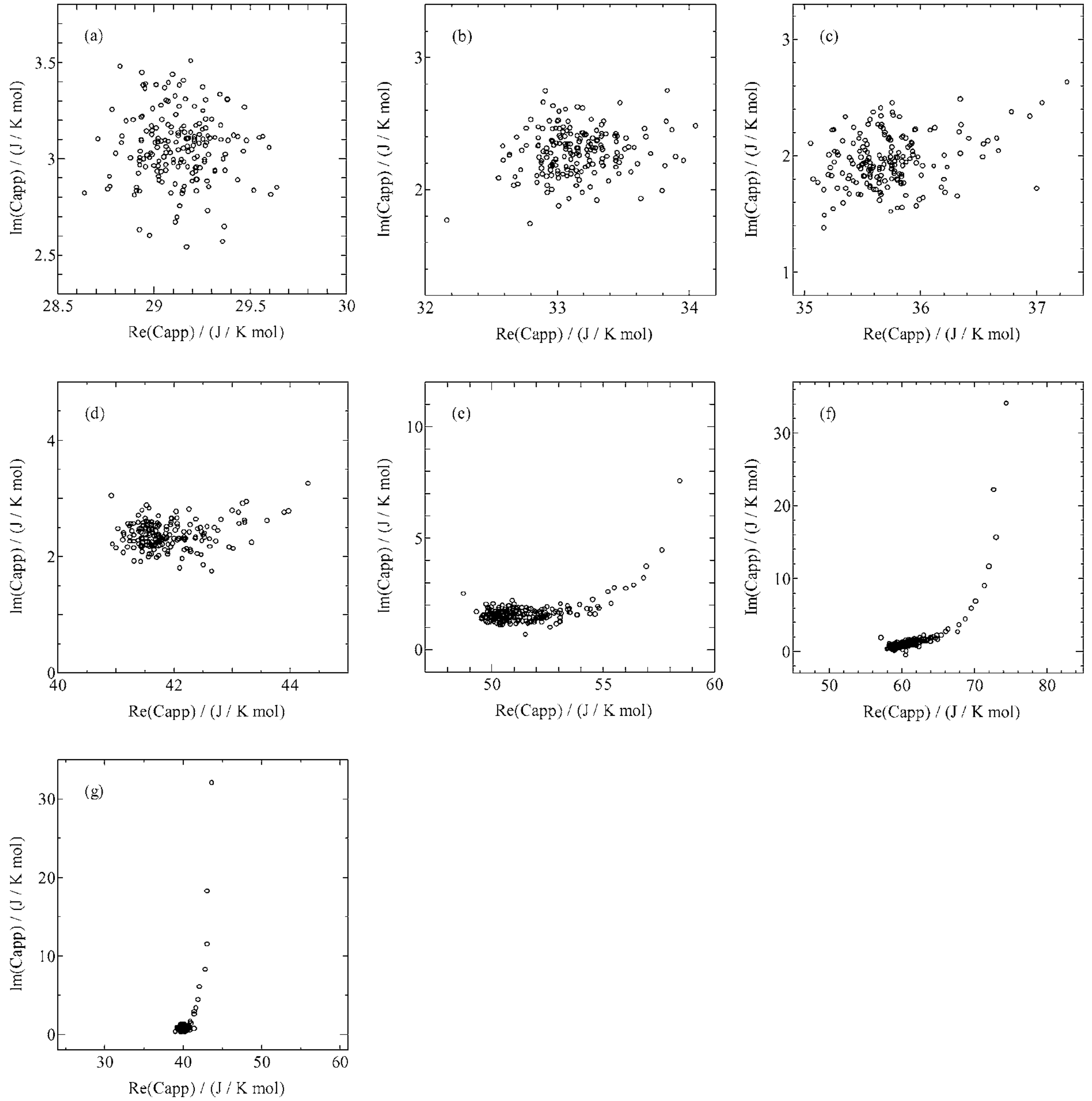

Fig. 7. The complex heat capacity during the quasi-isothermal condition plotted in the complex plane. The quasi-isothermal temperature is (a) 80.5°C; (b) 95.2°C; (c) 105.2°C; (d) 115.2°C; (e) 123.4°C; (f) 128.4°C and (g) 130.6°C. The graph areas are not identical with each other.

and the change in the melting rate and the other is change in the melting kinetics as the melting progresses. Time dependence of the fast component will give important information about the melting kinetics, but it is difficult to explain the shape of the trace at present. Since the linearity was not established the relaxation time could not be determined correctly. But the relaxation time roughly estimated by eye fitting of the time dependence of $A\exp(-t/B)$ to the imaginary part was 45 s. Toda et al. estimated the ''characteristic time'' as a little less than 10 s at 128°C [9], which is smaller than our ''relaxation time''. However, the smaller value is reasonable, because the ''characteristic time'' is a representative time for all crystals to be melted while the ''relaxation time'' is determined by very slow melting rate of the crystal having the melting point just below the quasi-isothermal temperature.

It can be seen from Fig. 5 that the imaginary part was not zero after the fast component decayed. This seemed to be artificial. The imaginary part observed in reference [4] was notable at frequencies lower than 0.1 Hz, and the relaxation strength had a peak at a temperature in the endothermic peak of the total heat flow. The values of the imaginary part after decay of the fast component did not exhibit large value at temperatures in the endothermic peak of the total heat flow. Evaluation of the calibration parameters in Eq. (1) was considered to be insufficient, because the thermal resistance between the measured sample and the aluminium pan/lid could be different from that between the standard samples and the pan/lid.

Fig. 7 shows the same data with Fig. 5 plotted in the complex plane. In this plot existence of the fast component can be seen more easily. The fast component of 123.4, 128.4 and 130.6°C shown in Fig. 6 can be seen in Fig. 7(e–g) as well. In Fig. 7(b–d) distribution of the data points is extended to the right direction. This extension shows existence of the fast component. In these figures change in the imaginary part of the complex heat capacity is small and to distinguish the fast component from the slow component might seem to be difficult. However, a rather small number of data points in the extended area mean that the change in the complex heat capacity at the beginning of the quasi-isothermal condition occurred quickly. Therefore, it can be said that the fast component existed at 95.2, 105.2 and 115.2°C. It is difficult to see the extension of the distribution of the data points in Fig. 7(a). However, results of shift average over 3 min (Fig. 8) shows a very short extension. Existence of the fast component suggested that a very small amount of the crystal melted even at 80.5°C.

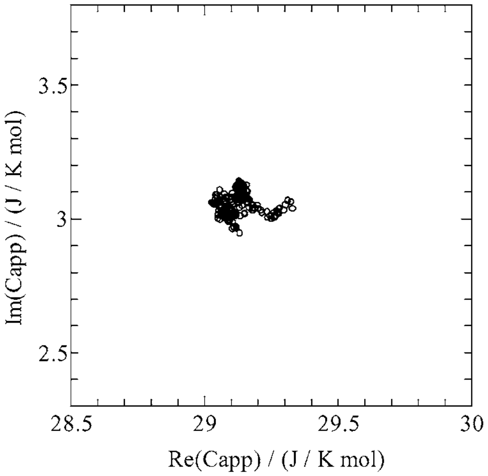

Fig. 8. Results of shift average of Fig. 7(a) over 3 min.

Melting at such low temperatures has already been known and is explained in terms of surface melting [11]. According to the reference [11] the surface melting is *reversible* in the meaning that when temperature increases some portion of the crystal close to the surface area melts and the same part crystallises when temperature decreases to the initial point. The *reversible* nature might seem to be inconsistent with our results that the fast component had complex value and it decayed with time. However, it should be noted that the *reversible* nature is not inconsistent with the fact that the process of the surface melting was a kinetic process with delay to the temperature change. It is not unusual that a material changes from state A to state B gradually after a temperature jump then come back to state A after cooling down to the starting temperature.

## 5. Conclusion

Time dependence of the complex heat capacity was measured. It was shown that the time dependence gave useful information about kinetics of the melting and the ordering of the crystal. Although the separation into the reversible and non-reversible components is not successful MTDSC can be a useful technique to study the phase transitions. To measure the complex heat capacity is essentially important for study of the phase transitions.

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