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Introducing
the Temperature Modulated DSC

1. Introduction

The conventional DSC method, we measure heat flow as well as temperature, such as glass transition, crystallization, or melting, by detecting differences in heat flow to a sample and reference material by heating or cooling at a constant rate. AC calorimetry, a technique that measures the specific heat capacity of a sample by measuring the oscillated temperature of that sample while periodically-heated it, has been used extensively as a method for measuring specific heat capacity. Temperature Modulated DSC (TM-DSC) is a technique that combines periodic temperature control performed by AC calorimetry and constant rate temperature control performed by standard DSC measurement. As with AC calorimetry, this method can simultaneously obtain heat capacity component (reversing heat flow) data that corresponds to the specific heat capacity, besides information obtained from conventional DSC measurements, while heating a sample at a constant rate by repeating sinusoidal temperature control. The data equivalent to DSC curve provided from conventional DSC measurement is called the Total Heat Flow. Data of components not involved in specific heat capacity can be obtained by subtracting the Heat Capacity Component from the Total Heat Flow. This component data is called the Kinetic Component (non-reversing heat flow).

Here, we will introduce principles of TM-DSC and applications using this technique.

2. Temperature Modulated DSC

2-1 Principle

DSC measures temperature differences in the heat flow path to the sample and reference material by constant rate heating, and detects differences in heat flow (ΔQ) that flows to both the sample and reference material. TM-DSC heats samples by a temperature program that adds sinusoidal temperature control to linearly heating at constant rate. Sample temperature is raised on average at a constant rate by repeated heating and cooling of the temperature in short time period (Figure 1).
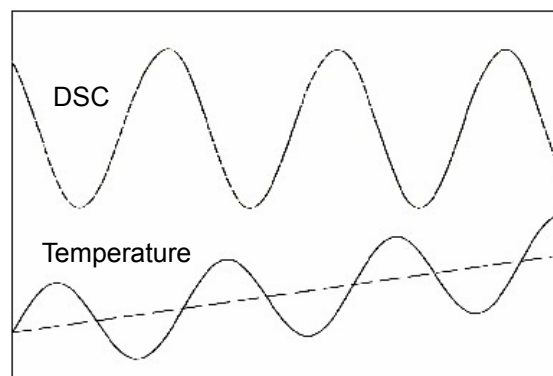
Figure 1   Temperature curve and
DSC signal for TM-DSC

Generally, the DSC signal can be expressed by the following equation.

$$dQ / dt = - Cp \cdot (dT / dt) + K(T, t) \quad \cdots \cdots \quad (1)$$

dQ / dt : DSC Total Heat Flow
dT / dt : Heating rate
Cp : Specific Heat Capasity of Sample
t : Time
T : Temperature
$K(T, t)$: Heat flow change with behavior

Equation (1) shows that the Total Heat Flow is composed of two different components, heat capacity dependent component and other phenomenon (kinetic) dependent component.

Heat flow changes that accompany the reaction mostly depend on temperature and assume that the time dependence is small. Terms of heat flow change that go with this phenomenon can be expressed as;

$$K(T, t) = K(T) \quad \cdots \cdots \quad (2)$$

If the sign of time is reversed here, the (1) equation becomes;

$$dQ / dt = - Cp \cdot (dT / dt) - K(T) \quad \cdots \cdots \quad (3)$$

When comparing equation (3) and (1), terms that depend on heat capacity have the same symbol; whereas terms that depend on the phenomenon see the signs change. Thus, the first term on the right-hand of equation (3) expresses a reversing component for the heating and cooling from the time-reversal invariance, and the second term expresses a non- reversing component.

Measurement example by TM-DSC is shown in Figure 2. The DSC curve in raw data is oscillated shape as shown in Figure 2-a. This raw data is separated into each component data by the following procedure.

First, the Total Heat Flow in Figure 2-b can be obtained by performing contour integration on raw data (Figure 2-a). This data is equivalent to the DSC curve obtained by the conventional DSC measurement at constant rate heating (Figure 2-e).

Next, the heat capacity component of Figure 2-c can be obtained by performing amplitude ratio calculations of the DSC signal and temperature signal using the Fourier transform same as AC calorimetry.

$$\text{Heat capacity component} = - B \cdot \left| Cp^*(\omega) \right|$$

$$= \frac{-B}{\omega} \cdot \left| \frac{\dfrac{\widetilde{dQ}}{dt}(\omega)}{\widetilde{T}(\omega)} \right| \quad \cdots \cdots \quad (4)$$

Next, a kinetic component other than the heat capacity component in Figure 2-d can be obtained by subtracting heat capacity component (Figure 2-c) data from the Total Heat Flow (Figure 2-b).

Thus, by TM-DSC measurements, the heat capacity component and kinetic component can be obtained by a single measurement, in addition to Total Heat Flow equivalent to the DSC curve from conventional measurements at constant rate heating.

a. Raw data

Contour integration

Fourier transform

b. Total Heat Flow data

c. Heat Capacity Component data

d. Kinetic Component data (**d.** = **b.** – **c.**)

Constant heating

TM-DSC

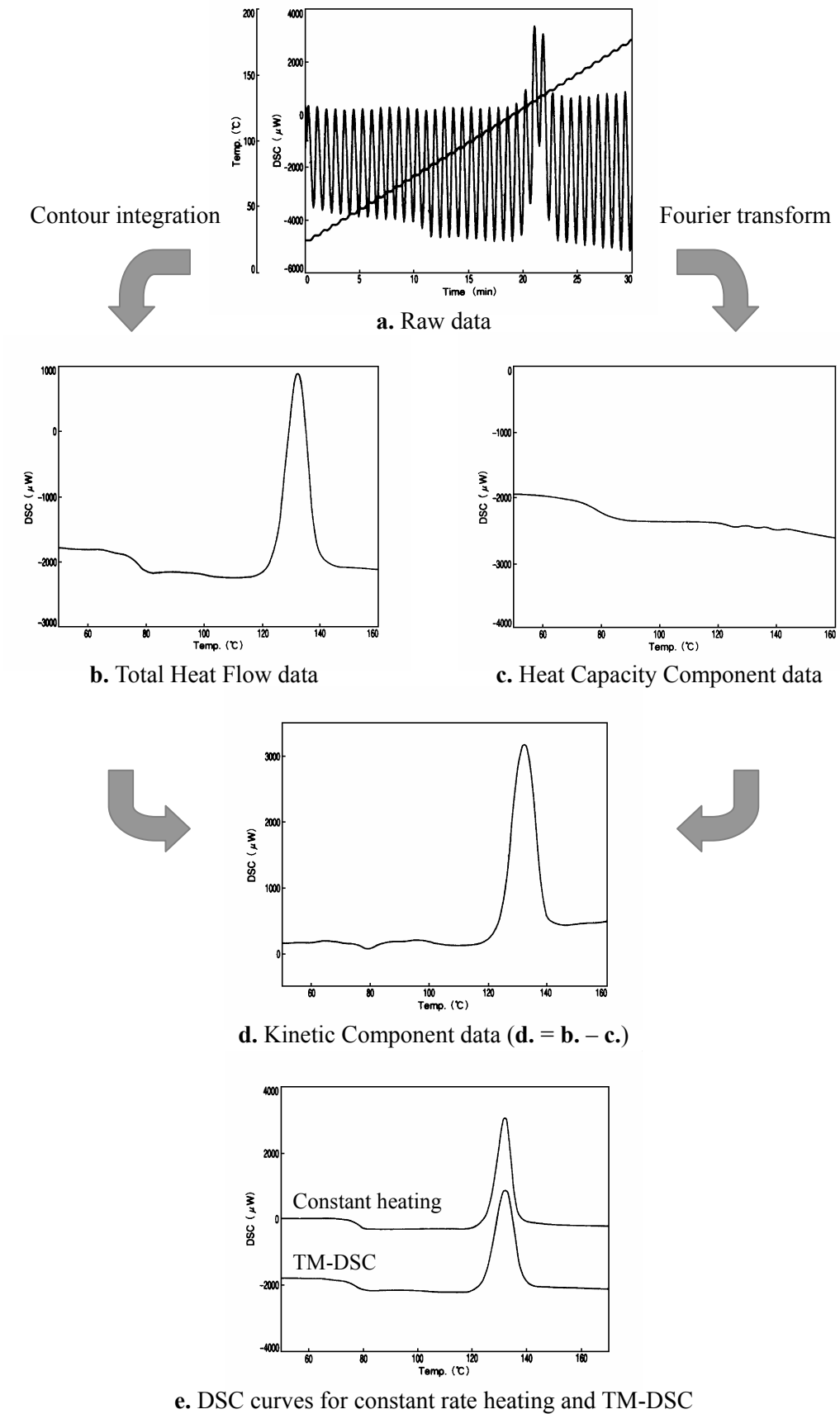**e.** DSC curves for constant rate heating and TM-DSC

Figure 2   DSC data of Temperature Modulated measurement

2-2 Features

Because the glass transition phenomenon changes the specific heat capacity of a material before and after, the DSC signal that corresponds to that change appears in the heat capacity component. On the other hand, phenomenon (irreversible phenomenon) observed as peaks, which include enthalpy change such as thermal curing reaction, cold crystallization, vaporization, or volatilization appear in the kinetic component (table 1). TM-DSC is able to retrieve by a single measurement data not obtained by conventional methods separated into a heat capacity component and kinetic component. These can be separated when the glass transition and other irreversible phenomenon overlap. Also, when two or more measurements were required in the past because of reasons such as water evaporation or elimination of thermal history, measurement efficiency has improved because data can be obtained with a single measurement.

Table 1　Classification of DSC Measurement Phenomena

Specific Heat Component	Kinetic Component
Glass Transition	Evaporation Crystallization Curing Decomposition, etc.

A summary of the advantages of TM-DSC are listed below.
- Improved separation of proximities or overlapped transitions
- Improved detection of small transitions and secondary transitions
- Separation into a heat capacity component and kinetic component
- Specific heat capacity measurement (In particular, specific heat capacity measurement under the low heating rate.)
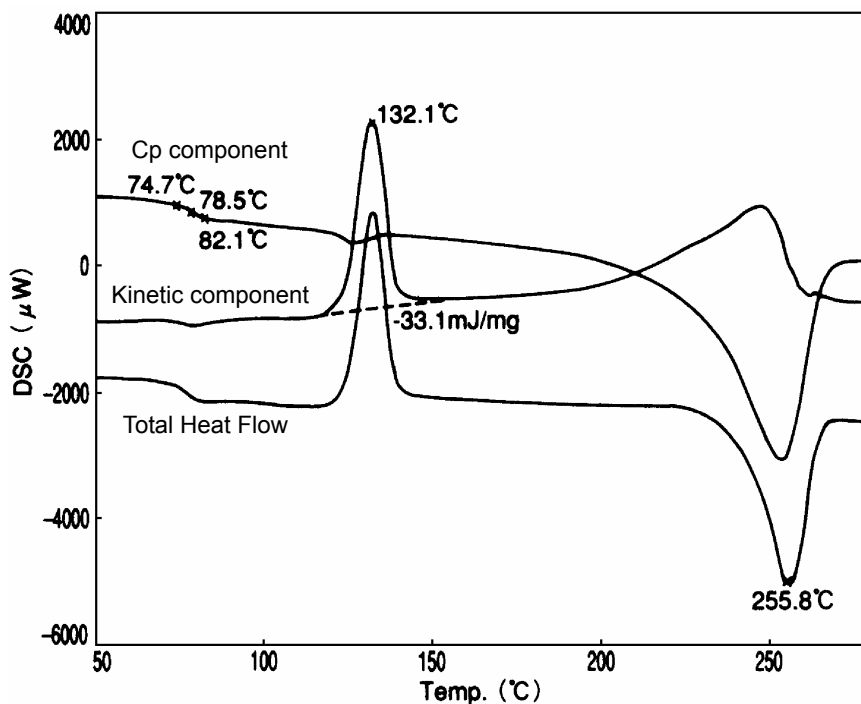

Figure 3　TM-DSC measurement of amorphous PET

3. Measurement Examples

3-1 Amorphous polyethylene terephthalate

Figure 3 shows a measurement example of a polyethylene terephthalate (PET) of amorphous by TM-DSC. Shifting due to glass transition at 75 to 82°C, exothermic peak from cold crystallization at 132°C, and endothermic peak from melting at 256°C are observed in the Total Heat Flow. Glass transition and melting are observed in the heat capacity component; and cold crystallization and melting are observed in the kinetic component. Accordingly, phenomena measured by DSC are divided into a heat capacity component and kinetic component. Melting phenomena are shown to contain both components.

3-2 Glass transition with enthalpy relaxation

Figure 4 shows the measurement result of an epoxy resin (cured sample) as an example of glass transition with enthalpy relaxation using TM-DSC. Polymer glass transition may be included with the endothermic peak because of enthalpy relaxation due to the thermal history of the sample. The endothermic peak in the example in Figure 4 is large, resulting in the possibility of it being mistaken for a melting peak. The existence of the endothermic peak makes finding an accurate glass transition temperature difficult. Nonetheless, shifting of the DSC curve by glass transition and endothermic peak by enthalpy relaxation, as seen in Figure 4, are separate in TM-DSC measurements; and therefore, shifting by glass transition can be obtain clearly. Further, because the quantity of heat can be found from the area of the enthalpy relaxation peak separated as the kinetic component, the size of the relaxation phenomenon can be estimated.
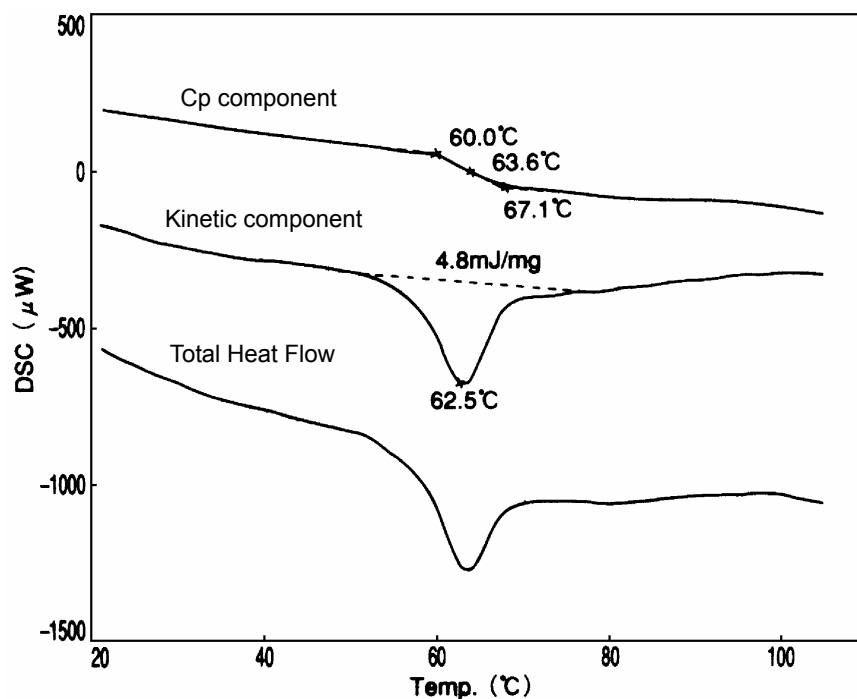

Figure 4   TM-DSC measurement of glass transition with enthalpy relaxation

3-3 Curing reaction of Thermoset polymer

Figure 5 shows the measurement result of an epoxy resin (uncured sample), as an example of curing reaction of a thermoset resin. With Total Heat Flow, glass transition with enthalpy relaxation appears around 70°C after which immediately the exothermic peak from thermal curing reaction across a wide temperature range near 180°C is observed. The curing peak appears only in the kinetic component when separated into each component, because the thermal curing reaction of the thermoset polymer is enthalpy change. This makes possible accurate reading of the end temperature of the glass transition and the start temperature of curing reaction.
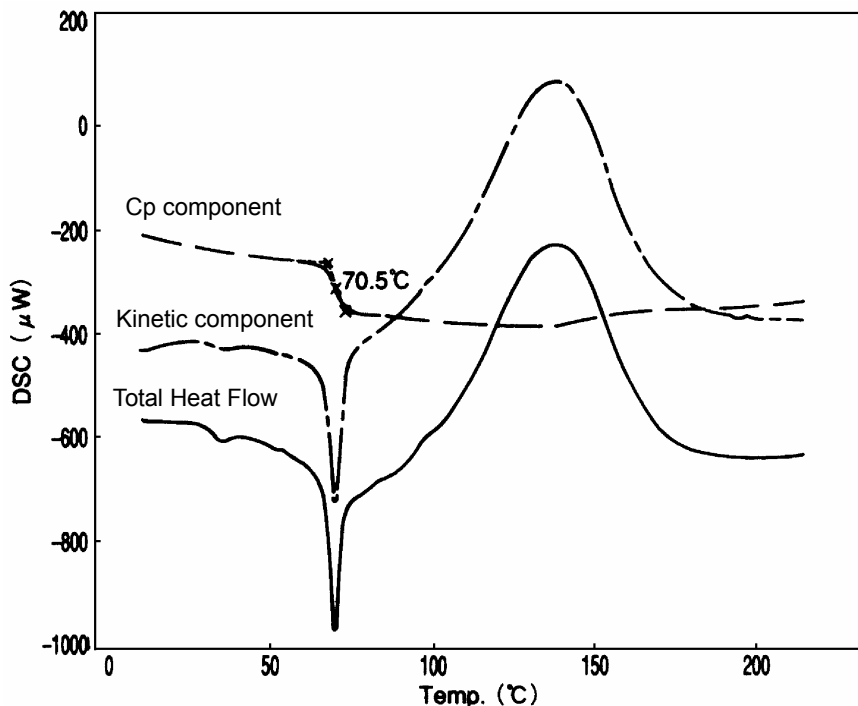

Figure 5   TM-DSC measurement of epoxy resin (uncured sample)

3-4 Immiscible polymer blend

Figure 6 shows measurement result of a PET and PC (polycarbonate) polymer blend as an example of measuring an immiscible polymer blend. Around 110 to 130°C of Total Heat Flow, cold crystallization of PET and PC glass transition overlap. In such cases, accurate analysis of both PET cold crystallization and PC glass transition is difficult. However, separating data into each component shows the glass transition of PC into the heat capacity component and PET cold crystallization into the kinetic component. Thus, it is possible to be read the glass transition of PC at 114 to 123°C.
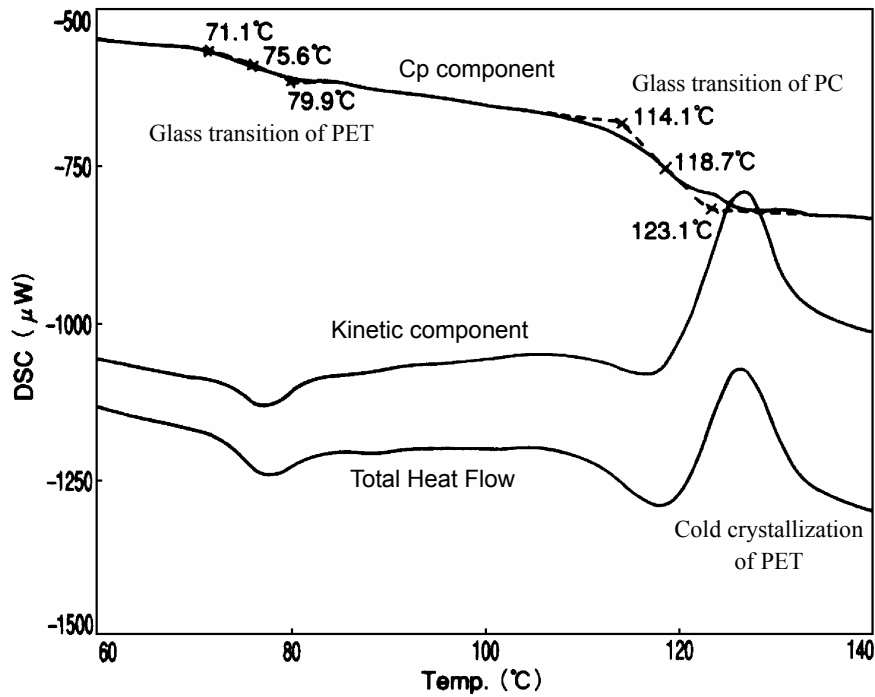
Figure 6   TM-DSC measurement of PET and PC polymer blend
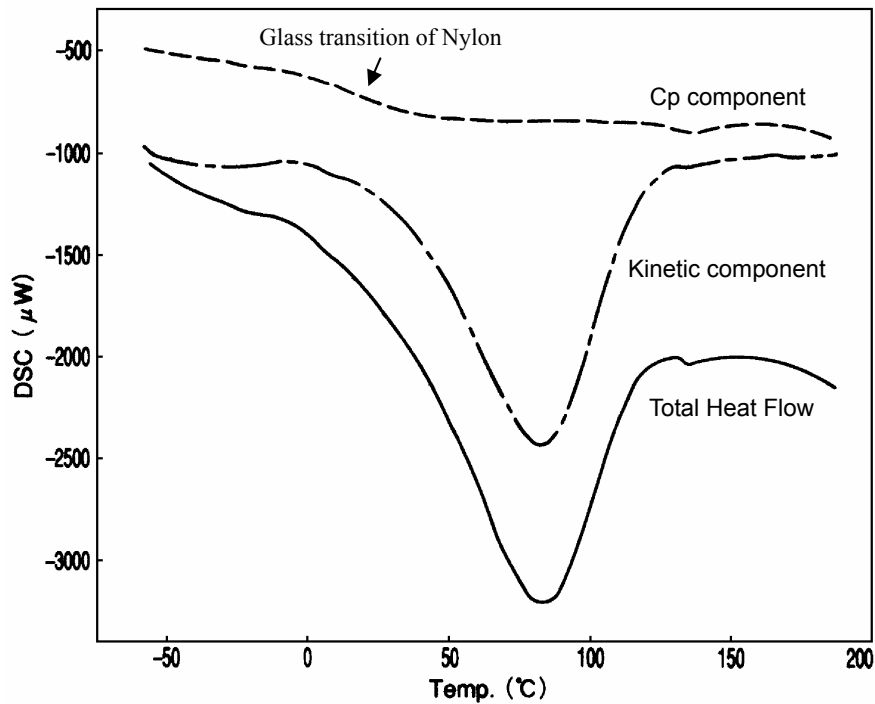

Figure 7   TM-DSC measurement of nylon fiber

3-5 Vaporization with volatilization system

Figure 7 shows measurement results of nylon fiber (nylon 6) as an example of measuring phenomenon with vaporization. Nylon easily absorbs moisture because the Amide Group, which is a Hydrophilic Function Group, is included in the molecule. During heating up nylon, vaporization occurs in the measurement. An endothermic peak from vaporization over a wide temperature range is observed by the Total Heat Flow in Figure 7. Since the glass transition of nylon overlaps this endothermic peak, the glass transition from this data cannot be observed. However, the glass transition can be clearly observed in the separated Heat Capacity Component from around 0 to 40°C. Vaporization is a kinetic phenomenon; therefore, the endothermic peak from this does not appear in the Heat Capacity Component. Thus, measurement of the glass transition of sample that includes water or solvent can be measured by TM-DSC.

3-6 Crystal Polymorphism

Due to the existence of a metastable phase of crystals in pharmaceuticals, there are many materials in which crystal polymorphism is observed by DSC. Figure 8 shows a measurement example of a pharmaceutical having crystal polymorphism. A broad endothermic peak from 40 to 80°C is observed in Total Heat Flow. This peak cannot be observed in the Heat Capacity component; therefore, from this, vaporization of trace moisture or volatilization of residual solvent is estimated. Further, endothermic and exothermic peaks at around 130°C and endothermic peak at 167°C are observed. Endothermic and exothermic action near 130°C express the fusion of the metastable phase continuing transitions to stable crystals, and the endothermic peak at 167°C is considered as a fusion of stable crystals. The endothermic peak is observed and exothermic peak is not observed by the Heat Capacity component; therefore, the endothermic phenomenon that can be seen in the Total Heat Flow is melting, and the exothermic phenomenon is thought to capture crystallization, which corroborates investigations mentioned earlier.
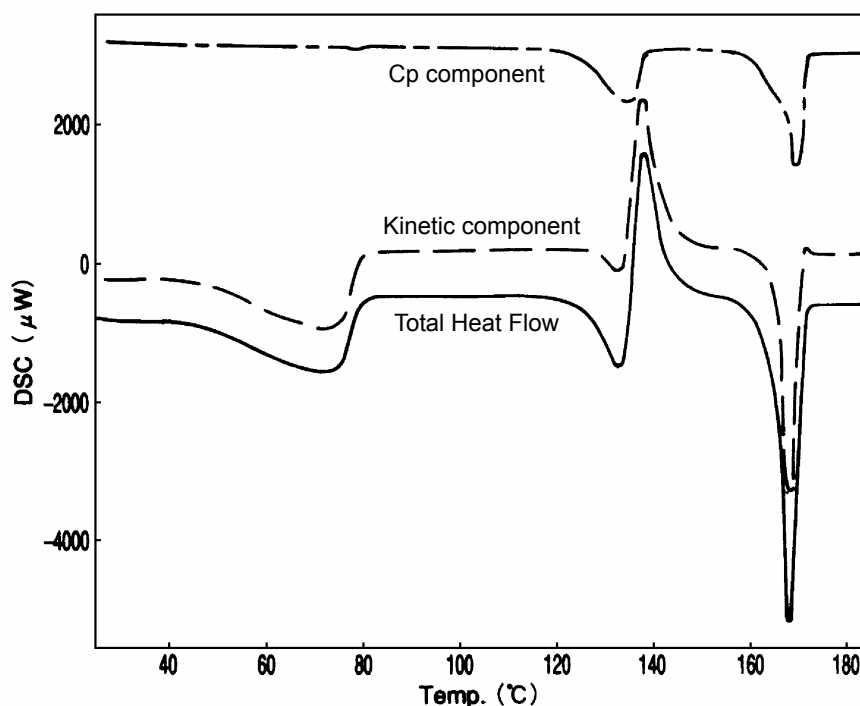

Figure 8　TM-DSC measurement of crystal polymorphism